Raman Spectroscopic Study and Dynamic Properties of Chalcogenide Glasses and Liquids

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# Table of Contents

0: **OBJECTIVES OF THE PRESENT WORK** ........................................................................................................... i

1: **FUNDAMENTALS OF GLASSY STATE**

   1.1 Introductory remarks ........................................................................................................................................ 1

   1.2 Principles of amorphous materials .................................................................................................................. 2
       1.2.1 Crystalline vs. non-crystalline solids ........................................................................................................... 2
       1.2.2 Glasses ......................................................................................................................................................... 3
       1.2.3 Glass formation ........................................................................................................................................... 4
       1.2.4 Glass forming ability ................................................................................................................................. 7

   1.3 Preparation of amorphous materials ............................................................................................................... 8
       1.3.1 Melt quenching ........................................................................................................................................... 8
       1.3.2 Vapor deposition ......................................................................................................................................... 8
           1.3.2.1 Thermal evaporation ......................................................................................................................... 9
           1.3.2.2 Sputtering .......................................................................................................................................... 11
           1.3.2.3 Chemical vapor deposition ............................................................................................................ 11
       1.3.3 Pulsed Laser Deposition ......................................................................................................................... 12
       1.3.4 Sol-Gel process ......................................................................................................................................... 14
       1.3.5 Other preparation methods .................................................................................................................... 15

   1.4 Phase separation and liquid immiscibility ...................................................................................................... 16
       1.4.1 Thermodynamic of mixing ....................................................................................................................... 18
       1.4.2 Mechanisms of phase separation ........................................................................................................... 22

References of Chapter 1: ........................................................................................................................................ 27
2: Type and degree of disorder. Structural organization and defects in covalent glassy materials

2.1 Types of disorder in a solid

2.2 Chemical ordering in covalent systems
   2.2.1 Random covalent network model
   2.2.2 Chemically-ordered network model

2.3 Topological disorder
   2.3.1 Short-range order
   2.3.2 Medium-range order
      2.3.2.1 Short-range medium-range order
      2.3.2.2 Intermediate-range medium-range order
      2.3.2.3 Long-range medium-range order
      2.3.2.4 First sharp diffraction peak

2.4 Glass forming theories
   2.4.1 Zachariassen random network theory
   2.4.2 Phillip’s topological disorder
   2.4.3 Valence-force-field model

2.5 Ideal glass and defects in a glassy state
   2.5.1 Ideal glass
   2.5.2 Coordination defects
   2.5.3 Wrong bonds
   2.5.4 Density of defects
   2.5.5 Negative-U defects
3: PHOTOINDUCED PHENOMENA IN NON-CRYSTALLINE CHALCOGENIDES

3.1 Introductory remarks......................................................................................................59

3.2 Transient and metastable photoinduced phenomena..................................................60

3.3 Reversible photostructural changes.............................................................................62
   3.3.1 Photodarkening and photobleaching.................................................................62
   3.3.2 Photo-induced anisotropy..................................................................................63

3.4 Photoinduced volume change.......................................................................................64

3.5 Photo-induced fluidity................................................................................................65

3.6 Microscopic nature of photo-structural changes.........................................................66

3.7 Photoinduced change in the Phase State.....................................................................69
   3.7.1 Photo-crystallization............................................................................................69
   3.7.2 Photo-amorphization...........................................................................................70
   3.7.3 Photo-melting.......................................................................................................72

3.8 Applications of amorphous chalcogenide materials..................................................72
   3.8.1 Lithography.......................................................................................................72
   3.8.2 Ovonic devices..................................................................................................76
   3.8.3 Fiber optics........................................................................................................77

References of Chapter 3: ..................................................................................................80

4: TECHNIQUES AND PHENOMENA FOR PROBING THE STRUCTURE AND THERMAL PROPERTIES OF GLASSES

4.1 Raman scattering .........................................................................................................85
   4.1.1 Scattering phenomena.........................................................................................85
   4.1.2 Origin of molecular spectra.................................................................................87
   4.1.3 Introduction to group theory................................................................................93
   4.1.4 Symmetry of normal vibrations and selection rules............................................98
   4.1.5 Depolarization of Raman lines..........................................................................102
4.2 Differential scanning calorimetry

4.3 Scanning Electron Microscope

4.4 X-ray Diffraction

4.5 EXAFS

4.6 Neutron Diffraction

4.7 Reverse Monte Carlo simulation

References of Chapter 4: 

5: EXPERIMENTAL PART

5.1 Sample preparation

5.1.1 Sb$_x$Se$_{100-x}$ glassy system

5.1.2 As$_x$Se$_{100-x}$ glasses

5.1.3 As$_x$Te$_{100-x}$ glassy system

5.1.4 Ge$_x$S$_{100-x}$

5.1.5 (GeS$_{1.5}$)$_{100-x}$ (AgI)$_x$

5.1.6 Quasi-binary systems

5.1.7 As$_{33}$S$_{67}$ – butylamine solutions

5.1.7.1 Bulk As$_{33}$S$_{67}$ glasses

5.1.7.2 Spin-coated As$_{33}$S$_{67}$ amorphous films

5.1.7.3 As$_{33}$S$_{67}$ – butylamine solutions for DLS study

5.2 Raman scattering

5.2.1 Experimental details

5.2.3 Analysis

5.3 Thermal studies by conventional DSC
5.3.1 Sb$_x$Se$_{100-x}$ system

5.3.2 As$_x$Te$_{100-x}$ system

5.3.3 Temperature-Modulated DSC

5.4 X-ray Diffraction

5.4.1 Sb$_x$Se$_{100-x}$ system

5.4.2 As$_x$Te$_{100-x}$ system

5.5 Extended X-ray Absorption Fine Structure

5.6 Neutron diffraction

5.7 Scanning Electron Microscopy

5.8 RMC Modeling of As$_x$Te$_{100-x}$ system

5.9 Far-IR spectroscopy

5.10 Optical Absorption

5.11 Dynamic light scattering

5.12 Atomic force microscopy

References of Chapter 5: 

6: STRUCTURAL AND THERMAL STUDIES OF Sb$_x$Se$_{100-x}$ BINARY GLASSY SYSTEM

6.1 Literature survey

6.2 Results

6.2.1 Raman scattering

6.2.2 Thermal studies
6.2.3 X-ray Diffraction measurements ................................................................. 153

6.3 Analysis of the Results and Discussion .......................................................... 153

6.3.1 Structural study by off-resonance Raman spectroscopy ................................ 153

6.3.1.1 On the structure of elemental Se .......................................................... 153

6.3.1.2 Structural details of Sb-Se glasses ......................................................... 159

6.3.2 Study of thermal properties using DSC ....................................................... 163

6.4 Conclusions ...................................................................................................... 166

References of Chapter 6: ....................................................................................... 168

7: STRUCTURAL ASPECTS OF THE AS$_x$SE$_{100-x}$ GLASSY SYSTEM: A RAMAN STUDY

7.1 Brief Literature survey .................................................................................... 171

7.2 Results ............................................................................................................. 178

7.3 Analysis of the Results and Discussion .......................................................... 183

7.3.1 Analysing Raman spectra as superposition of Se chains and AsSe$_3$ pyramids
network structures ................................................................................................. 183

7.3.2 On the existence of the quasi-tetrahedral S=AsSe$_3$ unit ............................. 189

7.3.3 On the existence of Se$_8$ rings in the structure of As-Se glasses ................. 193

7.3.4 Quantitative analysis of Raman spectra ...................................................... 196

7.4 Concluding Remarks ....................................................................................... 205

References of Chapter 7: ....................................................................................... 208

8. STRUCTURE OF AS$_x$TE$_{100-x}$ (20 ≤ x ≤ 60) GLASSES INVESTIGATED WITH EXAFS, X-RAY AND
NEUTRON DIFFRACTION AND REVERSE MONTE CARLO SIMULATION.

8.1 Literature survey ............................................................................................. 211

8.2 Results ............................................................................................................. 213
8.2.1 Unconstrained simulations.................................................................213
8.2.2 Constrained simulations.................................................................214
8.3 Discussion.........................................................................................215
  8.3.1 Assessment of RMC results..........................................................219
  8.3.2 Structural details vs. Physical properties.......................................221
8.4 Conclusions.......................................................................................226

References of Chapter 8: ........................................................................228

9: STRUCTURAL STUDY OF GeₓS₁₀₀₋ₓ, (x_Ge: 33.3, 34, 35, 40) GLASSES BY RAMAN SCATTERING
  9.1 Brief Literature survey.......................................................................231
  9.2 Results.................................................................................................237
  9.3 Analysis of Raman spectra and Discussion..........................................239
    9.3.1 Spectral details of the stoichiometric glass GeS₂..............................241
    9.3.2 Spectral details of the Ge-rich binary Ge-S glass............................245
  9.4 Concluding Remarks..........................................................................252

References of Chapter 9: .........................................................................255

10: STRUCTURAL ASPECTS OF THE (GeS₁.₅)₁₀₀₋ₓ (AgI)ₓ GLASSY SYSTEM: STRUCTURAL RAMAN AND IR STUDIES.
  10.1 Literature survey..............................................................................257
  10.2 Results...............................................................................................260
    10.2.1 Raman scattering results of (GeS₁.₅)₁₀₀₋ₓ (AgI)ₓ glasses...............260
    10.2.2 IR..............................................................................................260
  10.3 Discussion.......................................................................................261
  10.4 Concluding Remarks........................................................................267
11: STRUCTURAL AND THERMAL STUDY OF THE PHASE SEPARATED \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) AND \((\text{As}_2\text{S}_3)_{100-x}\text{Ag}_x\) GLASSES USING RAMAN SCATTERING, XRD, DSC, AND SEM

11.1 Brief Literature survey

11.2 Phase separation in \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) glasses

11.2.1 Results

11.2.1.1 X-ray Diffraction measurements of \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) glasses

11.2.1.2 Raman scattering study of \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) glasses

11.2.1.3 Thermal study of \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) glasses

11.2.1.4 Morphological features of \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) glasses studied by Scanning Electron Microscopy

11.2.2 Analysis of the results and Discussion

11.3 Phase separation in \((\text{As}_2\text{S}_3)_{100-x}\text{Ag}_x\) glasses

11.3.1 Results

11.3.2 Discussion

11.4 Concluding Remarks

References of Chapter 11:

12: EFFECT OF CLUSTER SIZE OF CHALCOGENIDE GLASS NANOCOLLOIDAL SOLUTIONS ON THE SURFACE MORPHOLOGY OF SPIN-COATED AMORPHOUS FILMS

12.1 Literature survey

12.2 Results and Discussion

12.4 Conclusion remarks

References of Chapter 12:

13: CONCLUSIONS

LIST OF PUBLICATIONS
SUMMARY

Chalcogenide glasses offer unique opportunities for basic science and technological applications. The physical properties of such network-forming glasses, including the glass-forming tendency, are intimately connected to global connectivity of their backbones. Being amorphous semiconductors, chalcogenide glasses exhibit a variety of photo-induced phenomena when irradiated with proper light and therefore find a wide range of technological applications (optical data storage, telecommunications, IR optics, etc).

Photo-induced structural changes at the atomic level are the basis the photo-induced effects. As research in this field is strongly driven by the needs of high-tech industry, physical properties related to the applications are more systematically investigated than the atomic structure, which is ultimately related to the macroscopic properties. This may be the reason why the microscopic origin of fascinating physical phenomena is still not completely understood. A shortcoming of not having yet established microstructure-properties relations in chalcogenide glasses is the lack of a strategic design of new materials for specific applications.

The present study is a systematic investigation of properties for various families of ChGs using experimental techniques that probe structure (near infrared Raman scattering, x-ray and neutron diffraction, EXAFS), dynamics (IR-Photon correlation spectroscopy), thermal properties (differential scanning calorimetry) and glass morphology (scanning electron microscopy). Particular emphasis is given on binary and pseudo-ternary ChGs, which are the basis of more complex multi-component glasses, such as As-Se, Sb-Se, As-Te, Ge-S, Ge-S-AgI, As-Se-AgI, As-Se-Ag, As-S-AgI, As-S-Ag etc. over a wide glass composition range. The binary systems are known for their significant optical properties while the Ag-doped glasses belong to the class of superionic conductors. Although some of these glass-forming systems have been extensively studied in the literature, several details concerning the atomic arrangement are still not fully understood, partly due to that some of these glasses are phase separated at the microscale; a fact that is usually overlooked in related studies. In the present study, using high-resolution off-resonant Raman conditions and a more elaborate analysis of the Raman spectra, in conjunction with thermal and morphological data, we have been able to obtain a better understanding of atomic structure and to advance structure-properties relations for both the homogeneous and phase separated glasses.
На родителите ми
Кирил и Славка
и на сестра ми Лилия
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Chalcogenide glasses are a special class of amorphous solids containing “chalcogen” element sulfur (S), selenium (Se), or tellurium (Te). By alloying of chalcogen element with other elements generally from group V (Sb, As) or group IV (Ge, Si) a variety of stable non-crystalline materials can be prepared in bulk, fiber, and thin film forms using melt-quenching, vacuum deposition, and other less common techniques. This offers unique opportunities for basic science and technological applications.

Being amorphous semiconductors, chalcogenide glasses exhibit a variety of photo-induced phenomena when irradiated with light having a photon energy
comparable with that of the bandgap of the material. The photo-induced effects include changes in structural, mechanical, chemical, optical, electrical, etc. properties.

As research in this field is strongly driven by the needs of high-tech industry, physical properties related to the applications are more systematically investigated than the atomic structure, which is ultimately related to the macroscopic properties. This may be the reason why the microscopic origin of fascinating physical phenomena is still not completely understood. The aim of the present work is to study and identify structural unit organization at an atomic level and to evaluate the changes that appear when doping with chalcogenide glassy matrix with coinage and halogen elements.

In the present work we undertake a systematic investigation of various families of chalcogenide glasses using different kinds of experimental techniques that probe structure, dynamics, thermal properties, and glass morphology. Structural studies of some bulk glasses are largely absent and some others are not emphatically and clear, thus driving our scientific interests in elucidation their structure. Furthermore, a lot is known about the physical properties of superionic materials containing noble metals, and almost nothing concerning their structural arrangement and distribution of the ions in the glassy matrix. This has been the motivation to undertake a detailed Raman spectroscopic study of these structural glasses over a wide composition range. The experimental findings concerning these glasses are consistent with the phase separation that takes place in bulk, melt-quenched superionic chalcogenide materials, providing the opportunity for their high conductivity.

- In chapter 1, fundamentals of the glassy state and glass formation are presented, along with the most widely used methods for preparation of amorphous materials. This chapter contains also information concerning thermodynamic aspects of solid mixtures, their liquid immiscibility and, as a result of this, different types of phase separation.
Chapter 2 contains information about structure, defects and different types of disorder that appear in the solid materials and a more detailed description about degrees of topological disorder. Chemical ordering in covalent glasses has been explained by presenting of the two widely used models. The most popular theories concerning the glass formation also appear here.

Some prominent photo-induced effects, i.e. changes of various properties induced by illumination with light having a photon energy comparable with that of the bandgap of the material, are presented in Chapter 3. These changes include photodarkening, photoinduced volume change, as well as, photoinduced changes in the phase state. The chapter ends with some of the most important applications based on the above structural changes of the chalcogenide glassy materials.

In chapter 4 the principles of the techniques and related phenomena used in the present work are represented. Raman scattering is presented in more detail. Other experimental techniques in the course of the present work include Differential Scanning Calorimetry, Scanning Electron Microscope, X-ray and Neutron diffraction.

Chapter 5 contains detailed information regarding sample preparation of the amorphous solids and solutions of all glassy systems presented in the Ph.D. work. Experimental details about techniques used to study the materials appear also in this chapter.

In chapter 6 structural details of the off-resonance Raman spectroscopy study of \( \text{Sb}_x\text{Se}_{100-x} \) (0 ≤ \( x_{\text{As}} \) ≤ 30 %) glasses along with elucidation of the structure of elemental selenium are presented. Results from the thermal properties study of these glassy materials also appear within this chapter.

Chapter 7 presents results of Raman scattering study of the structural arrangement of \( \text{As}_x\text{Se}_{100-x} \) (0 ≤ \( x_{\text{As}} \) ≤ 40 %) glasses. Different structural models, discrepancies, and important investigations that emerge from this
study are discussed in detail. Preliminary results of *ab initio* calculations of the structure and vibrational modes of small cagelike clusters of As-Se molecules are also discussed in conjunction with the experimental data.

- A systematic and detailed investigation of the structure of As$_x$Te$_{100-x}$ glasses ($20 \leq x \leq 60 \%$) is presented in Chapter 8. The work has been undertaken using a combination of structure-probing techniques including high energy X-ray diffraction, neutron diffraction, and EXAFS measurements at the As and Te K-edges. The experimental datasets were modeled simultaneously with reverse Monte-Carlo simulation technique.

- Detailed structural investigation on the binary Ge$_x$S$_{100-x}$ ($33 \leq x_{Ge} \leq 40 \%$) glassy system is represented in chapter 9. The structural study has been undertaken with the aid of off-resonance Raman spectroscopy. Structural changes in the Ge-rich glasses are presented in respect to the stoichiometric Ge$_{33.3}$S$_{66.7}$ composition.

- A structural investigation of bulk Ge-rich Ge–S–AgI chalcohalide glasses is reported in chapter 10. A vibrational spectroscopic study of the quaternary system (AgI)$_x$ (GeS$_{1.5}$)$_{100-x}$ ($0 \leq x_{AgI} \leq 20$) has been undertaken using infrared spectroscopy and Fourier transform Raman scattering. It was found that the AgI does not act as a real modifier that would depolymerize appreciably the Ge–S network structure.

- In chapter 11 investigations on (As$_{0.4}$S$_{0.6}$)$_{100-x}$(AgI)$_x$ and (As$_{0.4}$S$_{0.6}$)$_{100-x}$(Ag)$_x$ glasses are presented. The amorphous structure has been confirmed with the X-ray diffraction for both glassy systems. Structural aspects were deduced from the Raman scattering spectra. Morphological features together with the concentration profiles of the elements were revealed with the aid of Scanning Electron Microscopy. For the I-containing system thermal study was employed by using Differential Scanning Calorimetry.

- Chapter 12 gives an answer of the question concerning the correlation between grain size of surface morphology of as-deposited spin-coated
As$_{33}$S$_{67}$ chalcogenide thin films and cluster size of the glass in butylamine solutions. In order to do that, optical absorption spectroscopy and dynamic light scattering were employed to study optical properties and cluster size distributions in the solutions at various glass concentrations. Atomic force microscopy is used to study the surface morphology of the surface of as-deposited and thermally stabilized spin-coated films. Dynamic light scattering revealed a concentration dependence of cluster size in solution. Spectral-dependence dynamic light scattering studies showed an interesting athermal photo-aggregation effect in the liquid state.

➢ Chapter 13 outlines the main conclusions extracted during the structural and thermal studies of the amorphous solids and liquids.
Chapter 1

Fundamentals of the glassy state

1.1 Introductory remarks

As independent objects, glassware perhaps existed roughly five to six thousand years ago. The technology of the glass window exploiting the property of transparency had developed around the birth of Christ and was developed to new heights of artistry by the Christian Church during the Middle Ages. Luster or shine, and in particular its durability when exposed to the elements of nature, were probably the most significant properties of glass recognized by early civilization. Glazed stone beads from Egypt date back 12000 B.C. several of the artifacts unearthed from the tombs of the pharaohs exhibit excellent glass inlay work in a variety of colors. The word glass is derived from a late-Latin term *glæsum*, used to refer to a lustrous and transparent material. Another word often used to refer to glassy substances is *vitreous*, originating from the Latin word *vitrum* [Varshneya 1994].
Amorphous chalcogenides, often also referred to as chalcogenide glasses, are not new. Small statues made from As$_2$S$_3$ glass have been known since the time of ancient Egypt [Kolobov 2001]. What is a new is the discovery in 1954 by Goryunova and Kolomiets that these glasses possess semiconductor properties [Goryunova 1955, Goryunova 1956]. This discovery opened a new field in semiconductor physics, namely, amorphous semiconductors [Kolobov 2001].

Chalcogenide glasses are produced by alloying together a “chalcogen” element (S, Se or Te) with other elements, generally from group V (Sb, As) or group IV (Ge, Si) to form covalently bonded solids. A variety of stable non-crystalline materials can be prepared in bulk, fiber, and thin film forms using melt-quenching, vacuum deposition, and other less common techniques. Chalcogenide glasses are amorphous semiconductors with bandgap energies in the range 1–3 eV. Being amorphous semiconductors, chalcogenide glasses exhibit a variety of photo-induced phenomena when irradiated with proper light and therefore find a wide range of technological applications (optical data storage, telecommunications, IR optics, etc). Photo-induced structural changes at the atomic level are the basis of the photo-induced effects. As research in this field is strongly driven by the needs of high-tech industry, physical properties related to the applications are more systematically investigated than the atomic structure, which is ultimately related to the macroscopic properties. This may be the reason why the microscopic origin of fascinating physical phenomena is still not completely understood. A shortcoming of not having yet established microstructure-properties relations in chalcogenide glasses is the lack of a strategic design of new materials for specific applications [Popescu 2008].

1.2. Principles of amorphous materials

1.2.1 Crystalline vs. non-crystalline solids

There are two possible solid states that might occur during cooling a liquid; either a polycrystalline or an amorphous state. The two solids result from the two quite different scenarios:
¬ Crystalline state: The liquid → crystal transition is marked by an abrupt contraction to the volume of the crystalline solid. In a quenching experiment carried out at sufficiently low cooling rate, this is usually the route taken to arrive at the solid state.

¬ Amorphous state: is the other possible solid state characterized by lack of infinite periodicity [Zallen 1983].

The fundamental difference between crystals and glasses is in the basic nature of their microscopic, atomic-scale structure (Figure 1.1). In crystals, as is shown in Fig. 1.1(a), the equilibrium positions of the atoms form a translationally periodic array. The atomic positions exhibit long-range order. In amorphous solids (Fig. 1.1(b)), long-range order is absent; the array of equilibrium atomic positions is strongly disordered. For crystals, the atomic-scale structure is securely known at the outset from the results of diffraction experiments, and it provides the basis for the analysis of such properties as electronic and vibrational excitations. For amorphous solids, the atomic-scale structure is itself one of the key mysteries.

The general idea of making an amorphous material is based on the fact that the amorphous state is thermodynamically less favorable than the crystalline state; that is, it is characterized by a greater free energy [Kolobov 2001].

![Fig.1.1. Structural arrangement of SiO_2 tetrahedra: (a) Crystalline SiO_2 (quartz); (b) non-crystalline SiO_2 (glass).](image)

1.2.2 Glasses.

The term amorphous solid is the general one, applicable to any solid having a non-periodic atomic array. A big and an important subclass of amorphous solids are
glasses. The term glass has conventionally been reserved for an amorphous solid actually prepared by quenching the melt and is defined as an amorphous solid which exhibit a glass transition.

The term “glass” determined by the above definition implies that all glassy solids are strictly amorphous but not all amorphous solids are glasses or amorphous materials need not to be prepared by quench of a melt.

1.2.3 Glass formation

Consider a small volume of material at a high temperature in liquid form. Its state is given by the point “a” on the V-T diagram in Fig. 1.2. On cooling, the volume gradually decreases along the path “abc”. Point “b” corresponds to $T_m$, the melting point of corresponding crystal, which may be defined as the temperature at which the solid and the liquid have the same vapor pressure or have the same Gibbs free energy. At this temperature, an infinitely small amount of crystals is in thermodynamic equilibrium with the liquid. However, for a perceptible level of crystallization, some finite amount of undercooling of the liquid to a point “c” below $T_m$ is required. Crystallization occurs if, and only if, (i) there are a sufficiently large number of nuclei present in the mass, and (ii) a large enough crystal growth rate exist. The location of the point “c” below $T_m$ varies depending upon when the thermodynamic driving force created by the undercooling causes a particular group of atoms to transform from the liquid state to the crystal state, and upon the velocity at which the atoms from the liquid can be transported to crystal-liquid interface. For these reasons, we have shown a wide, shaded region with varying probability representing the crystallization path. Volume shrinkage generally accompanies the crystallization. Upon further cooling, the crystals so formed shrink along the crystal line to the point “e”.

If crystallization does not occur below $T_m$ (mostly because the cooling rate is high), the liquid mass moves into the supercooled liquid state along the line “bcf”, which is an extrapolation of the line “abc”. No discontinuities in the V-T are observed.
CHAPTER 1: Fundamentals of the glassy state

Fig. 1.2. Volume-Temperature diagram: • a – the material is in liquid form (high temperature); • b – corresponds to \( T_m \), the melting point of corresponding crystal, • d-e – crystal line; • c – corresponds to a new metastable undercooled or supercooled liquid state; • b-c-f – line of the supercooled state, which ends at either: • g - when cooled fast and at • h – when cooled slowly; • \( T_g \), \( T_{g1}, T_{g2} \) – glass-transition temperature [Varshneya 1994].

The volume, however, shrinks continuously, i.e., the structure of the liquid rearranges itself into a lower volume along the line “bcf” required by the lower energy corresponding to a lowered temperature. As cooling continues, the molecules become less and less mobile, i.e., the viscosity of the system rapidly increases. At sufficiently low temperatures, the molecular groups cannot rearrange themselves fast enough to reach the volume characteristic of that temperature. The state line then starts a smooth departure from “bcf” and soon become a near-straight, low-temperature part of the curve behaves essentially as a solid. This is a glassy state.

The smooth curve between the onset of departure from the supercooled liquid line and the completion to a seemingly rigid condition is termed the glass transition region, or the glass transformation range. It must be emphasized that the transition to the glassy state does not occur at a single, sharp value of the temperature. In the
upper regions, glass has a viscosity of $\sim 10^8$ Pa·s ($= 10^9$ poise) or less, whereas in the glassy state the viscosity exceeds $10^{15}$ Pa·s or more to qualify for appearance as a solid. The intersection of the extrapolated glass line and the supercooled liquid line is termed the fictive temperature ($T_f$). One may imagine that $T_f$ is the temperature at which the structure of the supercooled liquid is instantly frozen into the glass.

The departure from the supercooled liquid line is dependent upon the rate of cooling. Slower cooling allows the structure to rearrange itself to stay on “bcf” somewhat longer, and hence the more slowly cooled glass at “h” would be expected to have a lower volume (higher density) and a lower fictive temperature than a more quickly cooled glass.

When the glass at “h” is reheated, the state smoothly moves through the transition region along the dashed curve to the supercooled liquid state “fcb” and ultimately to the liquid state. The V-T curve never retraces its path in the transition region. Other than the gradually increasing fluidity and, perhaps, a color change due to radiative emission, in general there are no changes in the physical appearance of glass with the reheating.

If the crystals at “e” are heated, the state will move along the crystal line up to “d” (= the melting temperature, $T_m$) past the shaded region, melt at $T_m$ to reach point “b”, and subsequently follow the liquid path “ba”. One may question whether it is possible to superheat a crystal or not. Melting produces atomic disorder in a substance and proceeds from the surface inwards. Hence, crystals may be superheated to temperatures beyond $T_m$ if the heat is provided internally or if melting produces a very high-viscosity liquid phase such that atoms within the interior of the crystal do not have “room or time to disorder”. Ordinarily, the melting of a crystal is much sharper (on the temperature scale) than the freezing of a liquid.
1.2.4 Glass forming ability

Glass formation is a poorly-understood phenomenon [Elliott 1991], and many factors appear to be important in determining whether or not a particular material readily vitrifies. Among these factors are:

- **Thermodynamic aspects related to the melt:** The existence of a sharp decrease in the liquidus temperature associated with eutectic formation in alloy facilitates glass formation due to the relatively low amount of thermal energy present in such melts which is available for atomic migration and which could lead to the formation of crystalline nuclei. However, in chalcogenide glasses, such behavior does not seem to be prevalent, instead, compound formation and the resulting atomic structure seems to be dominant controlling influences.

- **Viscosity of the melt:** Generally speaking, the more viscous the melt at a given temperature above the melting point, the greater is the propensity for glass formation.

- **Kinetics of the quenching process:** In general, the faster the rate of quenching of a melt, the greater is the likelihood of forming a glassy and not a crystalline product. Thus, some materials can only be produced as bulk glasses with extreme difficulty, and then only using very high quenching rates.

- **Process of frustration:** Crystallization in a multicomponent melt is prevented from occurring readily, either by a completion between the formation of several different types of crystal (with different compositions) or simply due to the (entropic) difficulty of rearranging many different types of atoms to form a multicomponent crystal.

Chemical factors can also determine the case of glass formation for chalcogenide materials. Thus, it is generally found that glass formation becomes progressively more difficult as an element in a given group of the Periodic table is substituted by heavier elements in the same group. This trend has already been seen in the case of chalcogen substitution (S → Se → Te), but it is also true, for example, for the case pnictogens. In general, only a few atomic percent of Bi can be incorporated in a multicomponent chalcogenide material before the devitrification occurs, whereas a
few tens of percent of Sb can be so introduced. In contract, As-containing glasses are generally relatively much better glass formers.

1.3 Preparation of amorphous materials

1.3.1 Melt quenching

Preparing bulk glasses by rapidly cooling (quenching) the melt is, perhaps, the oldest established technique for making amorphous materials and glasses. Whether a particular material crystallizes upon cooling or form a glass depends on various conditions of which the most important are the temperature of the oven and the rate of cooling. Some materials form glasses easily whereas others can be made amorphous only under extreme conditions such as an extra high cooling rate. This process is illustrated in Fig. 1.2.

1.3.2 Vapor Deposition

Although the technique of melt quenching is much used for obtaining bulk glasses, there are also several techniques based on vapor-deposition methods which can yield amorphous thin films deposited onto substrates. These techniques can be regarded as having extremely fast quenching rates and therefore can be used to produce chalcogenide materials in amorphous form which are difficult to vitrify or to extend the compositional range for which a given system can be made amorphous compared with that attainable using conventional melt-quenching techniques.

Such vapor-deposition techniques can be divided into two categories, depending on whether the process involved is physical in nature, i.e. atomic or molecular species are converted into the vapor phase from either solid or liquid sources with no chemical modification, or alternatively reactive, in which either the vapor species are chemically modified with respect to the source material or a solid-vapor reaction occurs in the condensation process of the vapor on the substrate. Thus, three different vapor-deposition techniques can be identified which can fall
into either or both of the above categories. These are thermal evaporation, sputtering and chemical vapor deposition.

1.3.2.1 Thermal evaporation

Thermal evaporation is perhaps the simplest vapor-deposition technique, and involves resistive or electron-beam heating in vacuum of a boat containing the material to be evaporated (Fig. 1.3). The melt so produced then evaporates and the vapor is condensed onto a substrate, forming a thin amorphous film if the adatom mobility is sufficiently restricted to preclude atomic reconstruction leading to crystallization. Chalcogenides are particularly suitable materials for use in evaporation deposition because of their relatively low melting points. The technique is widely used, as for example in the deposition of the selenium-rich alloys onto cylindrical drums used until recently as the photo-sensitive component in the xerographic process [Elliott 1991].

![Fig. 1.3. Schematic illustration of a thermal evaporation chamber; B – boat, S – substrate, H – heater.](image)

A number of complications can arise in the use of this technique:

- Differential evaporation, in which the various elements in a (non-compound) multicomponent melt can evaporate at substantially different rates due to the differing melting temperatures and hence vapor pressures of the constituents. As a result, the chemical composition of the deposited thin film can differ appreciably from that of the melt and also vary significantly through the thickness
of the film. In order to obviate this problem, the variant, termed *flash* evaporation, may be used, in which powder of the material to be evaporated is dropped from a hopper onto a very hot filament, and the material is thereby volatilized almost instantaneously. Since a melt-vapor equilibrium is not established in this process, differential evaporation effects can be minimized [Elliott 1991].

- Structural inhomogeneity occurring in the case of thin evaporated films deposited at oblique angles of incidence, where adatom mobility on the surface of the substrate is minimized. A shadowing effect of material on the substrate for incoming evaporant atoms incident at an oblique angle of incidence leads to the formation of a columnar-growth morphology (Fig. 1.4). In general, the direction of the columns in the films (at an angle $\beta$ to the film normal) and the evaporant beam direction (at an angle $\alpha$) do not lie parallel to each other. Instead, they are found to obey the empirical relation [Leamy 1980],

$$\tan \alpha = 2 \tan \beta$$  

(1.1)

observed for many different types of evaporated materials. In chalcogenide materials this effect is particularly prevalent for the Ge chalcogenides [Rajagopalan 1982, Spence 1989], but curiously seems to be much less pronounced for the case of, say, the As chalcogenides. Consequently, the film porosity increases and the density decreases as the angle of incidence of the evaporant beam ($\alpha$) increases [Rajagopalan 1982, Spence 1989]. Such obliquely-evaporated chalcogenide films possessing a columnar microstructure exhibit enhanced irreversible photostructural effects.

---

**Fig. 1.4.** Schematic illustration of the formation of a columnar growth morphology for thin films evaporated at oblique angles of incidence. Note that the columns do not lie parallel to the evaporation beam direction.
1.3.2.2 Sputtering

The technique of sputtering is also widely used to prepare amorphous thin films. In this, an r. f. electric field (in the case of non-metallic materials such as chalcogenides) is applied between the target material and the substrate in a vacuum chamber in which a low pressure of an inert gas (e.g. Ar) is present at a pressure of ~10 mTorr (Fig. 1.5). After plasma is struck, ions are accelerated by the field onto the target, material from which is then (physically) sputtered away and condensed onto the substrate. The advantage of this technique is that differential deposition rates for multicomponent systems are much lower than for the case of evaporation because sputtering rates are comparable for most elements. Thus, r. f. sputtering has been used to deposit STAG (Si-Te-As-Ge alloys) and similar component chalcogenide films. Furthermore, this technique is advantageous in that reactive sputtering can take place when a reactive gas, e. g. H₂, is introduced into the sputtering chamber, and which then can react chemically with the material sputtered from the target, and the incorporated into the growing film.

![Schematic illustration of sputtering apparatus](image)

**Fig. 1.5.** Schematic illustration of sputtering apparatus; T – target electrode, S – substrate electrode, P – plasma, V – vacuum system, H – heater;

1.3.2.3 Chemical vapor deposition.

Another technique which can be used to deposit thin films from the vapor phase is chemical vapor deposition (CVD). In its simplest form, precursor materials in the vapor phase either decompose or react together in a heated reactor tube on a
heated substrate. The reactions involved can be homogeneous (nucleated in the gas phase) or heterogeneous (occurring at the surface of the substrate). A variant uses plasma enhancement (PECVD), or equivalently glow discharge decomposition, in which plasma excitation rather than thermal energy provides the driving force for the reaction. Some chalcogenide films obtained by using PECVD method are $\text{As}_2\text{S}_3\cdot \text{H}$ and $\text{As}_2\text{Se}_3\cdot \text{H}$, which have been prepared by the glow-discharge decomposition of mixtures of $\text{AsH}_3$ with $\text{H}_2\text{S}$ or $\text{H}_2\text{Se}$, respectively [Smid 1980] and Ge-Se films prepared from $\text{GeCl}_4$ and $\text{Se}_2\text{Cl}_2$ [Blanc 1985].

1.3.3 Pulsed Laser Deposition (PLD)

1.3.3.1 Characteristics.

A typical set-up for PLD is schematically shown in Fig. 1.6. In an ultrahigh vacuum (UHV) chamber, elementary or alloy targets are struck at an angle of 45° by a pulsed and focused laser beam. The atoms and ions ablated from the target(s) are deposited on substrates. Mostly, the substrates are attached with the surface parallel to the target surface at a target-to-substrate distance of typically 2-10 cm [Krebs 2003].

![Scheme of pulsed laser deposition.](image)

The excimer lasers are gas-based lasers [Chrisey 1994] that generate intense short ultraviolet pulses. The medium of the laser is composed of inert and halogen gases or of pure fluorine. When the radiation from an intense pulse of ultraviolet
excimer laser; namely of F2 – 157 nm (7.89 eV); ArF – 193 nm (6.64 eV); KrF – 248 nm (5 eV); XeCl – 308 nm (4.02 eV); XeF – 351 nm (3.53 eV); or from other suitable laser system is absorbed by surface of a solid-state material, the energy of photons is converted into thermal, chemical, and mechanical energy of the surface molecules, atoms, ions or particles and fragments that are formed; it causes evaporation, dissociation of the material and its vapors, excitation of particles, their ionization and plasma formation (Fig. 1.6, [Schenck 2003]).

The energy of excimer laser pulses (from 3.5 to 7.9 eV, or from 337 to 762 kJ/mol) is mostly higher than the energies of individual chemical bonds practically in any material. The chemical bonds of the material can be then interrupted by high-energy photons; material is atomized and evaporated independent of partial vapor pressures of its parts and fragments. The effective temperature of the surface of target material can be very high. It was estimated that the surface temperature of many metals and oxides during PLD is higher than 3000 K [Gupta 1994]. Chalcogenides are generally more volatile, and the temperature of their surface could be lower. (see, e.g. [Cheung 1994] and papers cited in).

The PLD process is controlled by parameters of the target, by laser and deposition operating parameters (laser wavelength and power density, laser spot size on target, duration of light pulses, frequency of repetition of pulses, background pressure and background gas in the evaporator, etc.). Usually the pulses of nanosecond duration are used. Recently, very short high-power femtosecond pulses have been applied (e.g. [Rode 2002, Pronko 2003, Loir 2003, Amoruso 2002, Zoubir 2003]). When the femtosecond pulses are used, the thermal diffusion into the material during the pulse duration is nearly negligible [Zoubir 2003], the material has no time to melt. With short pulses better spatial resolution can be achieved, e.g. for holes drilling.
1.3.4 Sol-Gel process

The process of sol-gel involves seven different steps. A schematic illustration of these seven steps is given in Fig. 1.7 for three different methods used to derived silica monoliths.

**Fig. 1.7. Gel-silica glass process sequence.**

*Step 1: Mixing of the components:* In the case of preparation of silica monoliths the size of the sol particles and the cross-linking within the particles (i.e., density) depend mainly upon the pH and $R$ ratio ($R = [\text{H}_2\text{O}]/[\text{Si(OR)}_4]$). When sufficient interconnected Si-O-Si bonds are formed in a region, they respond cooperatively as colloidal (submicrometer) particles or a sol.

*Step 2: Casting.* Since the sol is a low-viscosity liquid, it can be cast into a mold. The mold must be selected to avoid adhesion of the gel.

*Step 3: Gelation.* With time the colloidal particles and condensed silica species link together to become a three-dimensional network. The physical characteristics of the gel network depend greatly upon the size of particles and extent of cross-linking prior to gelation. At gelation, the viscosity increases sharply, and a solid object results in the shape of the mold. With appropriate control of the time-
dependent change of viscosity of the sol, fibers can be pulled or spun as gelation occurs.

**Step 4: Aging.** Aging of a gel, also called syneresis, involves maintaining the cast object for a period of time, hours to days, completely immersed in liquid. During aging, polycondensation continues along with localized solution and reprecipitation of the gel network, which increases the thickness of interparticle necks and decreases the porosity. The strength of the gel thereby increases with aging. An aged gel must develop sufficient strength to resist cracking during drying.

**Step 5: Drying.** During drying the liquid is removed from the interconnected pore network. Large capillary stresses can develop during drying when the pores are small (<20nm). These stresses will cause the gels to crack catastrophically unless the drying process is controlled by decreasing the liquid surface energy by addition of surfactants or elimination of very small pores, by hypercritical evaporation, which avoids the solid-liquid interface, or by obtaining monodisperse pore sizes by controlling the rates of hydrolysis and condensation.

**Step 6: Dehydration or Chemical Stabilization.** The removal of surface silan (Si-OH) bonds from the pore network results in a chemically stable ultraporous solid. Porous gel-silica made in this manner is optically transparent with interconnected porosity and has sufficient strength to be used as unique optical components when impregnated with optically active polymers such as fluor-containing polymers, wavelength shifters, dyes, or nonlinear polymers [Hench 1988, Hench 1989].

**Step 7: Densification.** Heating the porous gel at high temperatures causes densification to occur. The pores are eliminated, and the density ultimately becomes equivalent to fused quartz. The densification temperature depends considerably on the dimensions of the pore network, the connectivity of the pores, and surface area.

1.3.5 Other preparation methods

A number of other techniques can be used to prepare chalcogenide materials in amorphous form, many of which are only of academic interest. The simple act of
grading a powder can introduce such a degree of shear-induced strain that crystals are transformed into an amorphous phase. This effect occurs for the case of GeSe$_2$, for example. The solid precipitated products of reactions occurring in solution can also be amorphous. Thus, a-As$_2$S$_3$ is formed by passing H$_2$S gas through a solution of As$_2$O$_3$ in dilute hydrochloric acid. Similarly, powdered a-WS$_3$ and a-MoS$_3$ can be produced by the thermal decomposition of ammonium tetrathiotungstate [Deroide 1986] or tetrathiomolybdate [Bhattacharya 1987] or the acid-catalysed decomposition of solutions of these compounds. Finally, thin films of chalcogenides have been prepared by *spin-coating*, i.e. by placing on a substrate a solution of chalcogenide material dissolved in a suitable solvent, rapidly spinning the substrate to produce a thin uniform film of the liquid and then finally evaporating the solvent to leave a solid chalcogenide layer. This technique has been used by Hajto [1987] to prepare thin films of a-As$_2$S$_3$ using anhydrous n-propylamine as a solvent.

### 1.4. Phase separation and liquid immiscibility in glasses

A glass often appears homogeneous. There is considerable evidence, however, that, the microstructure of glass, on the scale of few hundred atoms, is not as homogeneous as that of a perfect single crystal or a liquid solution. There are two processes leading to the development of inhomogeneous microstructure in glass. One of these ways is the crystallization or devitrification where definite crystalline forms nucleate and grow from a supercooled liquid mass. To cause a molten liquid mass to devitrify, the mass needs to be heat-treated to below the liquidus and above the glass transition. By cooling sufficiently rapidly through this range of temperatures to below $T_g$, the liquid turns into a glass.

The second type of microstructural inhomogeneity is related with the crystalline theory attributed to Lebedev in the Soviet Union in 1921 [Pollard 2008]. This model maintained that a glass is made up of small crystalline regions varying in size from 10 Å (three to four silica units) up perhaps to 300 Å. A critical preview of these two competing views of nature on the glass was published by Porai-Koshits
CHAPTER 1: Fundamentals of the glassy state

1990. The experimental work of [Warren 1937, Warren 1938] specifically ruled out the existence of crystalline regions larger than about 10 Å, but it is appreciated that random network theory presents only an average picture, and says nothing about the local distribution of ions. Porai-Koshits argues that regions of maximum order in the continuous network may be conveniently termed “crystallites”, and, using this definition of crystallite, the two theories are seen to blend to one another. In 1971, Soviet academicians concluded that modern methods of analysis made it impossible to hold on to the original concept of crystallites in glass [Porai-Koshits 1985] and yet direct evidence for structural inhomogeneity on the sub-micron to micron scale has subsequently been obtained using transmission electron microscopy and small angle X-ray scattering (SAXS). Application of this technique to glasses, together with the direct evidence by electron spectroscopy, has conclusively demonstrating phenomena of phase separation in many vitreous systems [Vogel 1977]. The composition of the vitreous phases in multi-component glasses has been confirmed using electron microprobe analysis. The current understanding of the structure of glasses may be summarized by combining the comments of Vogel [Vogel 1977] and Porai-Koshits [Porai-Koshits 1977]:

(i) In one component system, such as pure vitreous silica, no inhomogeneous structure occurs, except for frozen thermal density fluctuations corresponding to the situation in the melt at the glass transformation temperature. These glasses are adequately described by random network theory of Zachariassen and Warren.

(ii) All multi-component glasses whose composition is intermediate between two stable compounds exhibit phase separation, with the compositions of each phase approximating the stable compositions. Maximum phase separation occurs in compositions which are furthest removed from the stable compositions.

(iii) The addition of further components such as colorants does not lead to a homogeneous distribution of additives. Highly charged cations will concentrate in anion-rich phases.
There is now ample evidence to support the view that glasses cannot simply be regarded as a homogeneous continuous network, as predicted by random network theory, but nor is it a series of domains of highly ordered crystallites, as originally proposed by Lebedev.

1.4.1 Thermodynamics of mixing.

Assume that components A and B are mixed at a temperature, T, and pressure, P, to yield a solution of certain composition. The system containing components A and B clearly, has three options: to stay unmixed, i.e., remain no more than a physical mixture; to mix on the atomic scale and form a complete solution of A and B or to mix in preferential ratios to form various compounds of A-B. The choice, in equilibrium under isothermal and isobaric conditions, depends on the sign of the term $\Delta G_m$, which is in the change in the Gibbs free energy of the system under mixing [Varshneya 1994]. The change is defined as free energy of the mixed system, $G_{AB}$, minus the free energy of unmixed system. In other words:

$$
\Delta G_m = G_{AB} - [(1 - c)G^0_A + cG^0_B]
$$

(1.2)

where $G^0$ are the free energies of the pure components, and $c$ is the mole fraction of component B (Fig.1.8). If $\Delta G_m$ is positive, then the system will remain separated. If on the other hand, $\Delta G_m$ is negative for a certain range of compositions, then the mixing will take place in that range. In the unlikely event that $\Delta G_m = 0$, none of the options will be preferred choice over the other.

The free energy change upon mixing, or simply the free energy of mixing is given by

$$
\Delta G_m = \Delta H_m - T\Delta S_m
$$

(1.3)

where $\Delta H_m$ and $\Delta S_m$ are the enthalpy (or simply the heat) and the entropy of mixing, respectively. (Changes in thermodynamic variables are defined as the value of the variable in the final state minus the value of the variable in the initial state. It
is more convenient to plot the changes rather than the absolute values of the thermodynamic variables.

For instance, since \( \frac{\partial G^0}{\partial T} = -S^0 \) and \( S^0 \) is positive, \( G^0 \) rises with decreasing temperature. However, \( \Delta G_m \) only need to be plotted relative to zero at all temperatures). Now, the entropy of mixing \( \Delta S_m \) in a two-component system is given by

\[
\Delta S_m = -R[(1-c)\ln(1-c) + clnc]
\]  

(1.4)

where \( R \) is the gas constant. Since \( c < 1 \), the expression in the square brackets in Eq. (1.4) is a negative number, and hence \( \Delta S_m \) is always a positive number. In other words, the entropy always increases upon mixing. For ideal solutions, \( \Delta H_m = 0 \). Hence, \( \Delta G_m \) is negative at all temperatures, and the resultant material will be a mixed solution of the molar formula \( A_{(1-c)}B_c \).

For regular solutions, \( \Delta S_m \) is given by Eq. (1.4) and \( \Delta H_m \neq 0 \), and \( \Delta S_m \) is not symmetric about \( c = 0.5 \) as implied in Eq. (1.4). For simplicity, let us focus our attention on regular solutions. The heat of mixing for regular solutions is given by

\[
\Delta H_m = ac(1-c)
\]  

(1.5)

where \( a \equiv \) the excess interaction energy = \( NZ[E_{AB} - (E_{AA} - E_{BB})/2] \); \( N \equiv \) Avogadro’s number; \( Z \equiv \) coordination number, and \( E \)'s are the energies of the
various bonds between atoms. According to this model then, $\Delta H_m$ is symmetric about $c = 0.5$. There are two possibilities depending on whether $\Delta H_m$ is negative or positive (which depends upon the sign of $\alpha$).

◧ In case I, when $\Delta H_m$ is negative, i.e., when the system gives off heat upon mixing (exothermic), $\Delta G_m$ is negative at all temperatures (Fig. 1.9). This implies that a mixed AB system will be again encouraged.

![Diagram](image)

**Fig. 1.9. Free energy of mixing when the heat of mixing is negative [Varshneya 1994].**

◧ In case II, when $\Delta H_m$ is positive, i.e., when mixing is endothermic, the shape of the $\Delta G_m$ variation with $c$ depends upon the temperature, $T$. At very high temperatures, the term $-T\Delta S_m$ is greater than $\Delta H_m$, and so $\Delta G_m$ is negative everywhere (Fig. 1.10). In other words, a system is always a single-phased at sufficiently high temperatures. As the temperature is decreased to $T_1$, $\Delta G_m$ begins to look like a saddle (Fig. 1.11 (a)). Although the mixed system has a lower $\Delta G_m$ than unmixed end compositions A and B, it is clear that between points “a” and “b” (at which the common tangent representing lowest free energy touches the two free energy lobes), $\Delta G_m$ of the fully mixed system is higher than those of “a” and “b”. In other words, the free energy $G_M$ of composition M lying between “a” and “b” can be lowered to $G_M$ by separating into compositions “a” and “b”. The line joining “a” and “b” is called a tie-line. In multicomponent systems, all compositions lying on the tie-line “ab” will tend to separate into terminal compositions “a” and “b”. The
amounts of “a” and “b” are determined by the lever rule: the amount of “a” times the distance a-M is equal to the amount of “b” times the distance b-M.

The corresponding phase equilibrium diagram is shown in Fig. 1.11. Above the critical temperature $T_c$ (also called the upper consolute temperature), the system is single-phased for all compositions. At $T_1 (< T_c)$, the composition M splits into two phases of compositions “a” and “b”.

![Diagram](image1.png)

**Fig. 1.10.** Free energy of mixing when the heat of mixing is positive and: temperature is high (a) or $T_1 < T_c$ (b) [Varshneya 1994].

![Diagram](image2.png)

**Fig. 1.11.** Free energy of mixing when the heat of mixing is positive, and $T_1 < T_c$. Phase diagram corresponding to Fig. 1.10 (a) and (b) [Varshneya 1994].

Up to now no assumptions have been made regarding the kinetics of the separation process or the mechanisms by which it takes place. Atoms only have to possess sufficient mobility to separate over the experimental times. In a simple situation, M could simply be a liquid that undergoes demixing as it cools. Neither “a” nor “b” has to be crystalline; they merely have to be some compositions at
which the free energy displays minima. When both “a” and “b” are liquids, the phase separation process is termed “liquid-liquid immiscibility”. The immiscibility is termed stable or metastable depending upon whether it occurred above the liquidus or below the liquidus, respectively.

1.4.2 Mechanism of phase separation

Upon rapid cooling after phase separation, the material will be a composite of two glasses, “a” and “b”. If M is nearer to “a”, one would have to nucleate “b” to make a radical change in composition from M to “b”. Since the amount of “a” will be larger than that “b”-the microstructure would look like droplets of “b” in a matrix of “a”. This is the case of nucleated growth of phase separation. When there is sufficient fluidity in the system, the lighter phase may float upon the denser phase.

The locus of “a” and “b” on the phase diagram is called immiscibility dome phase boundary or the binodal (the region inside is sometimes referred to as the miscibility gap). Within the immiscibility dome, there exists a spinodal dome that is the locus of points “d” and “e”, which are inflection points on the G (or the $\Delta G_m$) curve (Fig. 1.12). The inflection points have an interesting property. This can be seen as follows. Let us define G as the total Gibbs free energy of a binary A-B system in which free energy density (free energy per molecule) of a uniform solution of composition, $c$, is $G(c)$. We assume that $G(c)$ is a continuous function of the composition $c$ (which is the mole fraction of B). For an infinitesimal fluctuation in composition, $h$, about the mean composition, $\bar{c}$, the free energy $G(c)$ can be expanded using a Taylor series as

$$G(c) = G(\bar{c} + h) = G(\bar{c}) + h \left[ \frac{dG}{dc} \right] + \left[ \frac{1}{2!} \right] h^2 \left[ \left( \frac{d^2G}{dc^2} \right) \right] + \left[ \frac{1}{3!} \right] h^3 \left[ \left( \frac{d^3G}{dc^3} \right) \right] + \ldots$$

The total energy of the system may be written as

$$G = N_v \int_v G(c) dv$$
where \( N \) is the number of molecules per unit volume. Since fluctuations must average to zero over the entire system, i.e.,
\[
\int h \, dv = 0
\]  
(1.8)
the change in the free energy of the system with fluctuations over a perfectly homogeneous system is given by (neglecting higher-order terms)
\[
\Delta G = G(c) - G(\bar{c}) = \frac{1}{2} \left( \frac{d^2 G}{dc^2} \right) \int h^2 \, dv
\]  
(1.9)

Fig. 1.12. Details of the (a) phase diagram, (b) free energy of mixing at \( T_1 \), (c) the first derivative of the free energy at \( T_1 \), and (d) the second derivative of free energy at \( T_1 \) when immiscibility occurs [Varshneya 1994].

Now, since \( h^2 \) is always positive, it can be seen that when \( \frac{d^2 G}{dc^2} \) (\( \) is positive, minor fluctuations in the composition
M lead to an increase of the free energy, and hence such fluctuations die out. This is the situation when the composition M lies between a-d and e-b (see Fig. 1.12 (b)). It can be seen that minor composition changes about the composition M lead to the increase of the free energy from \( G_M \) to \( G_{M'} \). One clearly needs to nucleate a composition, p, far away such that the average energy would be lowered to \( G_{M''} \). Regions a-d and e-b are thus regions of metastability with respect to compositional changes. Thermodynamics require M to separate to attain the lowest-energy state that is a mixture of a and b. However, because of the energy barrier, the kinetics may be sluggish.

On the other hand, if \( \frac{d^2G}{dc^2} \) is negative then \( \Delta G < 0 \). This happens if the starting composition, \( M_1 \), lies within d-e (see Fig. 1.12 (a), (d)). It also means that any small fluctuation in composition \( M_1 \) leads to lowering of the free energy from \( G_{M_1} \) to \( G_{M_1'} \), and hence such fluctuation will grow with time. In this case the system decomposes spinodally. Since the composition fluctuations are always present because of the thermal fluctuations, there is no need for a nucleated growth of the phase separation. Thus, the inflection points “d” and “e”, at which \( \frac{d^2G}{dc^2} = 0 \), mark the boundary of instability with respect to small fluctuations, and hence the locus of “d” and “e” is termed the chemical spinodal (or simply the spinodal), and

---

**Fig. 1.13.** Microstructure of (a) soda lime silica glass heated at 740°C for 7.25 h (14,000x) showing nucleated droplet phase separation; (b) Vycor glass heated at 700°C for 5.5 h (24,000x) showing spinodal decomposition [Rawson 1980].
the points “d” and “e” are called spinodes. Within the spinodal, the fluctuation that grows may itself decompose further depending upon whether its composition is within the inflection points or outside. Given sufficient time at temperature T, the compositions of the separated phases will gradually change until the equilibrium compositions “a” and “b” have been reached. Again, the separated phases do not possess crystalline order. Figure 1.13 contrasts the microstructure of a spinodally decomposed glass from that of a nucleated phase-separated glass. The primary difference from the nucleated phase separation is the presence of interconnected, wormlike morphology. This distinction between microstructures, however, is likely to decrease as the time allowed for phase separation increases.

Table 1.1 lists the differences between the characteristics of nucleated separation and those of spinodal decomposition. Figure 1.14 schematically shows the development of nucleated separation and spinodal decomposition. Note how, in the case of the spinodal decomposition, growth occurs by some material moving against its own concentration gradient – a phenomenon called uphill diffusion. The diffusion coefficient, \( D \), is proportional to \( \frac{d^2G}{dc^2} \), and so wherever the curvature

<table>
<thead>
<tr>
<th>Nucleation and growth</th>
<th>Spinodal decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invariance of second-phase composition with time at constant temperature</td>
<td>Continuous variation of both extremes in composition with time until equilibrium compositions are reached</td>
</tr>
<tr>
<td>Interface between phases has always same degree of sharpness during growth</td>
<td>Interface between phases initially is very diffuse, eventually sharpens</td>
</tr>
<tr>
<td>Tendency for random distributions of particle sizes and positions in matrix</td>
<td>Regularity of second-phase distribution in size and position characterized by a geometric spacing</td>
</tr>
<tr>
<td>Tendency for separation of second-phase spherical particles with low connectivity</td>
<td>Tendency for separation of second-phase, nonspherical particles with high connectivity</td>
</tr>
</tbody>
</table>
Fig. 1.14. Growth of the phase separation for (a) nucleated-type and (b) spinodal-type mechanisms with time at a given temperature. Note that in the nucleated-type mechanism, the droplets have a fixed composition “b” with an interfacial composition “a”. The growth is in the physical size of the droplet. In the spinodal-type mechanism, a small fluctuation in composition gradually grows over a period of time via “uphill” diffusion. The terminal compositions in each case are “a” and “b”. The ratio of the two phases depends upon the starting composition [Varshneya 1994].

is negative, \( D \) is negative (i.e., the material moves up the concentration gradient).

The theory of spinodal decomposition was developed by Cahn and Hilliard [Cahn 1959; Chan 1960] and Hiller [Hiller 1961] for metals, and was later extended to ceramic systems by Cahn and Charles [Cahn 1965].
CHAPTER 1: Fundamentals of the glassy state

References of Chapter 1:
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CHAPTER 1: Fundamentals of the glassy state

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2.1 Types of disorder in a solid.

Randomness in solids can occur in several forms, of which topological, spin, substitutional, and vibrational disorder are most important. Disorder is not unique property; it must be compared to some standard, and that standard is the perfect crystal. This can be defined in the following way:

A perfect crystal is that in which the atoms (or group of atoms or “motifs”) are arranged in a pattern that repeats periodically in three dimensions to an infinite extent.
With this definition, an imperfect crystal can simply be one which is finite and ends at surfaces (non-infinite extent), or one which possesses a defect, e.g. a vacancy or interstitial foreign atom or a dislocation (non-periodic). However, the forms of disorder with which we are concerned are more drastic than these small perturbations to perfect crystallinity.

- Topological (or geometric) disorder is shown in Fig 2.1 (a):

That form of randomness in which there is no translational periodicity is topological disorder. There are “degrees” of topological disorder: Short-range order, medium-range order, and long-range order, these terms will be discussed in Section 2.3. Amorphous materials have considerable short-range order. Thus, all amorphous solids are distinguished by their lack of periodicity.

- Another variety of randomness is spin (or magnetic) disorder (Fig. 2.1 (b)), in which the underlying perfect crystalline lattice is preserved, but each atomic site possess a spin or magnetic moment, and this is oriented randomly. The local moments are frozen into particular, but random, orientations because the “exchange” interaction between moments in a metal has an oscillatory spatial dependence, and so randomly distributed moments in a metallic host suffer a corresponding distribution of exchange interactions, and hence become randomly oriented. These, and those materials which are topologically disordered and posses a randomly oriented spin, are termed “spin glasses”, and must not be confused with true glasses which were defined in Chapter 1. This is a deviation from the perfect crystal.

- Substitutional disorder:

This a kind of disorder in which although the underlying crystalline lattice is preserved, the material is in fact an alloy with one type of atom randomly substituting for the other in the lattice (Fig. 2.1 (c)).
Vibrational disorder:

A perfect crystal can only occur at the absolute zero of temperature, because at any finite temperature the random motion of atoms about their equilibrium position destroys the perfect periodicity (Fig. 2.1 (d)). It is important to note, however, that vibrational disorder is not another form of topological disorder, since although the atoms are vibrating, they do so about their equilibrium crystalline positions which of course are not topologically disordered.

Fig. 2.1. Types of disorder: (a) Topological disorder; (b) Spin disorder; (c) Substitutional disorder; (d) Vibrational disorder [Elliott 1990].

2.2 Chemical ordering in covalent systems

The question of chemical ordering in covalent systems is most simply discussed for the case of binary alloy systems such as $A_xB_{1-x}$, where, if the elements A and B are in columns $a$ and $b$ in the Periodic table, they will have coordination numbers $n_a = 8 - a$ and $n_b = 8 - b$ dictated by the 8 - $N$ rule (neglecting the effect of
any coordination defects such as dangling bonds). In general, \( A - A \), \( A - B \), and \( B - B \) bonds can coexist in an alloy with an arbitrary composition, and two extreme models can describe the distribution of such bond types [Lucovsky 1977].

### 2.2.1 Random covalent network (RCN) model.

This model treats the distribution of bond types in purely statistical terms, determined only by the local coordination numbers \( n_a \) and \( n_b \) and the concentration variable \( x \), and which neglects any preferential ordering effects (e.g. arising from differences in bond energies). The RCN model, therefore, admits \( A - A \), \( A - B \), and \( B - B \) bonds at all compositions except at \( x = 0 \) and \( 1 \). Thus, for a 4:2 alloy (e.g. \( A = Ge, B = Se \)), the RCN model predicts the following relations for the numbers of the different types of bond [Lucovsky 1977]:

\[
\begin{align*}
N_{AA} &= 4(1 - x)^2/(2 - x) \quad (2.1a) \\
N_{AB} &= 4x(1 - x)/(2 - x) \quad (2.1b) \\
N_{BB} &= x^2/(2 - x) \quad (2.1c)
\end{align*}
\]

These bond-counting statistics are shown in Fig. 2.2 with solid lines, together with those for a 3:2 system (e.g. \( As_{x}Se_{1-x} \)).

**Fig. 2.2.** Bond-counting statistics for (a) 3:2 networks (e.g. \( As_{2}Se_{3} \)) and (b) 4:2 networks (e.g. \( GeSe_{2} \) [Lucovsky 1977].
2.2.2 Chemically-ordered network model.

In this model heteropolar A-B bonds are favoured. A completely chemically-ordered phase thus occurs at the stoichiometric composition

\[ x_c = \frac{n_a}{n_a + n_b} \]  

(2.2)

(e.g. as in As₂Se₃, GeS₂). In contrast to the RCN model, only A - A and A - B bonds are allowed for A-rich compositions \( 1 > x > x_c \) and only B - B and A - B bonds for \( 0 < x < x_c \). Thus, the bond statistics for the CON model for a 4:2 alloy are, for the A-rich region:

\[
\begin{align*}
N_{AA} &= 2 - 3x \\
N_{AB} &= 2x \\
N_{BB} &= 0 
\end{align*}
\]

(2.3a)

(2.3b)

(2.3c)

and for the B-rich region

\[
\begin{align*}
N_{AA} &= 0 \\
N_{AB} &= 4(1 - x) \\
N_{BB} &= 3x - 2 
\end{align*}
\]

(2.4a)

(2.4b)

(2.4c)

These bond-counting statistics are also shown in Fig. 2.2 as dashed lines, together with those for a 3:2 network.

2.3 Topological disorder

2.3.1 Short-range order

In covalently-bonded amorphous materials with strongly directed bonding, such as chalcogenides, short-range order (SRO) can be defined in terms of rather well-defined coordination polyhedra as we can see in Fig. 2.3 (a). The parameters which are sufficient to describe topological SRO are the number of nearest neighbors \( j \) around an origin atom of type \( i \), (as shown in Fig. 2.3 (a)) the nearest - neighbors
bond length $r_{ij}$, bond angle subtended at atom $i$, $\theta_i$, and the corresponding quantities of when atom $j$ is regarded as the origin, $N_i$ and $\theta_j$ (Fig. 2.3 (b)).

An additional parameter is required if the degree of chemical SRO also needs to be described, e.g. when different types of atoms constitute the coordination polyhedron centered on a given origin atom. Thus, for non-stoichiometric compositions, for example, excess atoms must be accommodated by the introduction of “wrong” (homopolar) bonds (in the absence of coordination or valence changes), and the chemical order which might otherwise occur at the stoichiometric composition is thereby broken. The parameter of relevance here would be the proportion of wrong bonds. A related type of chemical SRO is when the different types of atomic species in the coordination shell around a given atom are the same element, but each atom has a different charge state, bonded connectivity, etc. An example of this is the formation of non-bridging oxygens in silicate glasses by the incorporation of alkali modifier atoms.

![Diagram](image)

**Fig.2.3.** *Schematic illustration of the parameters describing short-range order in covalent amorphous materials:* (a) when an origin atom is of type $i$ and nearest neighbors are type $j$; (b) when atom $j$ is regarded as an origin [Elliott 1990].
2.3.2 Medium-range order

The medium-range order (MRO) can be defined as the next highest level of structural organization beyond SRO, existing on a length 5-20 Å. The question of MRO in amorphous materials is currently extremely contentious; even a definition of MRO is subject to much debate and it is very difficult experimentally to investigate MRO. It is convenient in practice, particularly for covalent materials where MRO is more prevalent, to divide MRO into three categories, corresponding to the progressively increasing length scales.

2.3.2.1 Short-range medium-range order (SRMRO).

If we define SRO in terms of well-defined coordination polyhedra, SRMRO is therefore concerned with the type of connection of coordination polyhedra as well as their relative orientation. Thus, corner-, edge- or face- sharing (Fig. 2.4 (a), (b), (c)) of polyhedra lead to very different ordering schemes on the relatively local scale, as well as pronounced differences at larger distances in terms of the network.

![Fig. 2.4. Types of connections between polyhedra in Medium – Range Order (a) corner - sharing; (b) edge – sharing; (c) edge – sharing and face-sharing connection](image)
As an example consider the AX$_2$ family of glasses, where A=Si, Ge and X=S, Se. In all cases, the SRO is characterized by AX$_4$ tetrahedra, but the type of connection between polyhedra can differ in each case. Thus, SiO$_2$, in both glassy and crystalline states, is characterized by corner-sharing connections between neighboring tetrahedral, leading to a 3D (giant molecule) structure. In contrast, both GeSe$_2$ and GeS$_2$ have a proportion of edge-sharing connections in the crystalline state, and there is considerable evidence that this situation exists in the glassy state also. Such edge-sharing of tetrahedral can lead to (locally) 2D structural characteristics. Finally, SiSe$_2$ and SiS$_2$ have crystalline polymorphism in which only edge-sharing of tetrahedra occurs. There is evidence that this type of connection predominates also in amorphous phases, in this case leading to locally 1D structures. Thus, it can be seen that there is often a strong link between MRO at the various length scales.

Obviously, MRO is most pronounced when the degrees of freedom associated with the relative orientation of neighboring polyhedra are restricted in some way, e.g. by the occurrence of edge-sharing connections. However, even with corner-sharing units, where free rotation about the common bonds could occur in principle, certain orientations may be more probable than others. A structural parameter which is measure of such orientational correlations between corner-, edge- or face- shared neighboring polyhedra in covalent systems with well-defined bonds is the dihedral (or torsion) angle $\phi$. This, as shown in Fig. 2.5, is the angle of rotation about a common bond required to bring into coincidence the projections, onto the plane perpendicular to this bond, of the two bonds either side of the common bond forming parts of the connected polyhedral units. Departures from a uniform (i.e.
random) distribution, \( P(\phi) \), are correspondingly a hallmark of MRO. Consequently, preferred values of \( \phi \) are associated with features of MRO such as (small) rings. However, this need not always be the case: for example, it appears from structural modeling studies [Corb 1982] and considerations of features in the electronic density of states that the structure of a-Se is not representative of a freely rotating chain (with constant \( P(\phi) \)), but instead \( \phi \) takes more-or less (\( \approx 102^\circ \), as in the crystal), with the sign of \( \phi \) varying either alternately or randomly in a chain.

2.3.2.2. Intermediate-range medium-range order (IRMRO)

At the next largest length scale (5-10 Å) IRMRO is determined by the type and extent of SRMRO present. IRMRO (5-10 Å) is associated with correlations between pairs of dihedral angles for neighboring bonds, as shown in Fig. 2.6, i.e. it accounts for triplet correlations between connected polyhedra, or equivalently five-atom
Fig. 2.6. Correlation between neighboring dihedral angles [Wright 1985].

correlations. It is characterized by the presence of “super-structural” units, consisting of several basic SRO units, e.g. forming rings or clusters of atoms of particular shapes or sizes, which occur in a considerably higher proportion than would be expected on purely statistical (random) basis. In certain cases, such superstructural units can be regarded as forming the essential building blocks of the amorphous structure.

One example of regular rings acting as superstructural units is associated with the edge-sharing form of connection of tetrahedra. Such edge-sharing units can equally be regarded as four-fold (e.g. Ge$_2$Se$_2$) rings. These four-membered rings may be the structural origin of the MRO responsible for so-called “companion line” in the Raman spectrum of glassy GeSe$_2$ observed at 220 cm$^{-1}$, next to the main A$_1$ breathing mode of the GeSe$_4$ tetrahedra at ~ 200 cm$^{-1}$ [Sugai 1987]. The companion line is unusually narrow and is strongly polarized, and moreover shows an unusual compositional dependence of the intensity varying as ~ $x^5$ in the alloys Ge$_x$Se$_{1-x}$; the intensity of the normal tetrahedral mode varies linearly with $x$, as would be expected for a symmetric breaking-up of GeSe$_4$ tetrahedra as the composition becomes non-stoichiometric.
Other type of superstructural units which can contribute to IRMRO in amorphous materials, namely clusters. In covalent bonded systems, clusters can be regarded as aggregates of regular rings.

2.3.2.3 Long-range medium range order (LRMRO).

Next larger length scale (greater than 10 Å) can be associated with the local dimensionality of a covalently-bonded amorphous network (Fig. 2.7) or the existence of domains in metallic systems. A local dimensionality different from 3D in a covalent network can arise from two causes: either the type of connection between coordination polyhedra may impose such a reduced dimensionality, or it may result from network depolymerization resulting from the introduction of network modifying atoms into the structure.

An example of the former occurs in a-SiSe$_2$, where edge-sharing SiSe$_4$ tetrahedra are predominant, leading to the chain-like configurations. Structures emerging from computer simulation for this glass are represented in Fig. 2.7.

![Fig. 2.7. Illustration of the elements of medium-range order contributing to various regions of the radial distribution function for a-SiS$_2$ or a-SiSe$_2$ [Elliott 1990].](image)
2.3.2.4 First sharp diffraction peak (FSDP).

MRO is generally prevalent in amorphous chalcogenide materials due to the low (two-fold) coordination associated with the chalcogen atoms. As a result, the degree of cross-linking is sufficiently low so that a three-dimensionally isotropic structure does not necessarily result, and superstructural units may form. However, it is difficult to probe quantitatively the type and the extent of MRO in glass. In general, those techniques, such as diffraction and EXAFS, which are sensitive to pair correlations of atoms are rather insensitive to MRO, and instead it is techniques such as vibrational spectroscopy (e.g. Raman scattering), which probe the collective behaviour of several atoms, which are more useful in this regard.

Nevertheless, one aspect of the diffraction results on chalcogenide materials has been ascribed to the influence of MRO, and this is so-called *first sharp diffraction peak* (FSDP) or a *pre-peak* in the structure factor, $S(Q)$. This peak almost invariably occurs at a value of scattering vector $Q \sim 1 \text{ Å}^{-1}$ in amorphous compound chalcogenides. This feature is referred to as a pre-peak because Fourier transformation of $S(Q)$, both including and omitting this peak, produces essentially indistinguishable real-space correlation functions, indicating that the peak does not contain structural information about SRO, being associated instead with subtle MRO structural arrangements.

The FSDP is anomalous in a number of ways. It is observed in a wide variety of mixed chalcogenide materials, e.g. $\text{As}_2\text{S}_3$, $\text{As}_2\text{Se}_3$, $\text{GeS}_2$, $\text{GeSe}_2$, as well as the corresponding oxide materials (e.g. $\text{SiO}_2$, $\text{B}_2\text{O}_3$) and also a-$\text{P}$ and a-$\text{As}$, but it is not present for the case of pure chalcogen a-Se, or Ge or Si. Although the position of the FSDP is at $Q_1 \sim 1 \text{ Å}^{-1}$ for the case of chalcogenides (and As and P), it is somewhat larger ($Q_1 \sim 1.5 \text{ Å}^{-1}$) for oxide materials. Nevertheless, if the structure factor is plotted against the reduced variable $Q/r_1$, where $r_1$ is the nearest-neighbour bond length, the FSDP’s of chalcogenides and oxides alike fall at approximately the
value, viz. $Q_1 r_1 \sim 2.5$ [Wright 1985] (see Fig. 2.8), which perhaps is indicative of a common origin.

The FSDP alone of all the peaks in $S(Q)$ shows anomalous behavior as a function of temperature and pressure. The intensity of the FSDP increases with increasing temperature in for example a-As$_2$S$_3$ [Busse 1984], As$_2$Se$_3$ [Busse 1981] and GeS$_2$ [Lin 1984], as well as in SiO$_2$ [Soklakov 1967]. All other peaks in $S(Q)$ decrease in intensity with increasing temperature, in accordance with the normal behaviour of the Debye-Waller factor. Indeed, the FSDP is still pronounced even in the liquid state of chalcogenide materials, e.g. GeSe$_2$ [Uemura 1978, Susman 1988]. The application of pressure also produces an anomalous behaviour of the FSDP in amorphous chalcogenide materials [Tanaka 1987, Tanaka 1989a]. Its intensity decreases and the position of the peak shifts to higher values of $Q$ with increasing pressure.

The intensity of the FSDP increases as the atomic number of the chalcogen $Ch$ decreases for a particular type of chalcogenide glass, e.g. Ge$Ch_2$, As$_2$Ch$_3$ [Susman 1988]. Furthermore, it appears that cation-cation correlations are primarily responsible for the FSDP. Anomalous X-ray scattering results for a-GeSe$_2$, indicate that Ge-centered correlations (Ge-Ge, Ge-Se) contribute predominantly to the FSDP intensity [Fuoss 1981].

There has been, and remains, much controversy over the structural origin of the FSDP in covalent glasses, and a number of explanations have been proposed. These can be effectively divided into two categories, depending on how the peak in $S(Q)$ is assumed to originate.

One model assumes that the FSDP is separate from the rest of $S(Q)$, i.e. it is regarded as a single Fourier component in reciprocal space arising, therefore, from a (quasi-)periodic correlation function in real space characteristic of the MRO.
width of the pre-peak in $S(Q)$ then arises from the damping in the amplitude of the real-space oscillations, and the Debye-Scherer equation relating diffraction line broadening to crystallite size can be used to provide a relationship between the FSDP peak width $\Delta Q$ and $D$, a characteristic coherence length over which the periodicity in real space is maintained:

$$D \approx \frac{2\pi}{\Delta Q} \quad (2.5a)$$

Using this relation, correlation lengths in the range $D \sim 20 - 30$ Å are inferred from the width of the FSDP. In addition, the position of the FSDP in this picture is determined by the periodicity in the real space via

$$d \sim \frac{2\pi}{Q_1} \quad (2.5b)$$
where \( d \) is the spatial repeat distance. For \( Q_1 \sim 1 \, \text{Å}^{-1} \), this implies a repeat distance of \( d \sim 5 - 6 \, \text{Å} \).

This model, essentially based on the micro- or quasi-crystalline approach in which regions of the structure have a more- or less-ordered structural arrangement, has some appeal since many crystalline chalcogenides are layered materials, and the repeating element is then taken to be the interlayer separation which is assumed to persist into amorphous phase [e.g. Vaipolin 1963, Leadbetter 1974, Busse 1984]. Various variants of this picture involving interlayer correlations have been proposed, e.g. that involving crumpled layers, and that of [Cervinka 1988] in which a parallel ordering in a particular orientation of pair of configurations of between two and five connected coordination polyhedra (effectively formed layers) is assumed to occur.

The second interpretation of the FSDP is in terms of a cluster picture which is, in Fourier terms, the converse of the above model. In the simplest case, there is a single (broad) peak in real space at \( r_m \) characterizing the MRO, which produces a strongly damped sinusoidal function in reciprocal space of which the observed FSDP is simply the first, most intense peak. Thus in this picture, the FSDP in itself has no structural significance (c.f. Eq. 2.5). This approach is therefore similar to that used in the interpretation of the scattering from molecular liquids such as CCl\(_4\). In this case, the total measured structure factor can be written as the sum of the two terms

\[
S(Q) = f_m(Q) + D_m(Q)
\] (2.6)

where \( D_m(Q) \) is the molecular-packing structure factor describing the intermolecular interference arising from the scattering of neutrons or X-rays from structural (molecular) entities separated by an average distance \( r_m \), and \( f_m(Q) \) is the molecular form factor describing the intra-molecular scattering. \( D_m(Q) \) is dominant at low \( Q \) values and is highly damped because of the large fluctuations in \( r_m \), whereas \( f_m(Q) \) is much less damped, because the fluctuations in intra-molecular
covalent bond lengths are considerably smaller than those for $r_m$, and it is therefore dominates at high values of $Q$.

The cluster picture has been proposed for the case of amorphous chalcogenides in general by [Moss and Price 1985], and [Fowler and Elliott 1987], perhaps associated with the packing of coordination polyhedra (although the precise clusters are not identified). Veprek et al. [Veprek 1981] have further proposed that, whilst the FSDP peak may result from many Fourier components of the real-space correlation function, nevertheless it may be associated with regions of low atomic occupancy characterized by the minimum in the radial distribution function (RDF) beyond the SRO correlations (related to the packing of coordination polyhedra and the interstitial voids between them). However, one incontrovertible example of a cluster origin for the FSDP is provided by thin evaporated films of As-S materials. These contain quasi-spherical $\text{As}_4\text{S}_4$ molecules and the very intense FSDP in the diffraction pattern of such films has been convincingly explained in terms of scattering from such clusters [Wright 1985].

Whilst the explanation of the FSDP in terms of scattering from a quasi-ordered stacking of layers is appealing, it is unlikely to be a general solution for several reasons: a FSDP is observed at approximately the same value of reduced coordinate ($Qr_1$) even for those cases (e.g. $\text{SiO}_2$) where there is no evidence whatsoever for layering in either crystalline or amorphous phases. Furthermore, a quasi-regular stack of layers extending over a correlation length $D \sim 20$ Å would not be expected to survive in the liquid state. Finally, if such a quasi-microcrystalline stacking of layers were not occurring in the glassy phase, many more peaks would be expected to be observed in the structure factor, $S(Q)$ [Wright 1987]. Conversely, in the absence of well-defined molecular species such as $\text{As}_4\text{S}_4$ in the structure, it is difficult to associate particular structural features with clusters. For instance, such clusters cannot be related to just the coordination polyhedra themselves, but instead may be defined by exclusive volume, i.e. the interstitial space, surrounding a
CHAPTER 2: TYPES AND DEGREE OF DISORDER

STRUCTURAL ORGANIZATION AND DEFECTS IN COVALENT GLASSY MATERIALS

particular coordination polyhedron and which results from steric effects [Galeener 1985].

2.4 Glass formation theories.

Chemical factors can determine the case of glass formation for chalcogenide materials. Thus, it is generally found that glass formation becomes progressively more difficult as an element in a given group of the Periodic table is substituted by heavier elements in the same group. This trend has already been seen in the case of chalcogen substitution (S → Se → Te), but it is also true, for example, for the case pnictogens. In general, only a few atomic percent of Bi can be incorporated in a multicomponent chalcogenide material before the devitrification occurs, whereas a few tens of percent of Sb can be so introduced. In contrast, As-containing glasses are generally relatively much better glass formers.

2.4.1 Zachariasen random network theory.

One possible reason for this decrease in glass-forming tendency with increasing metallicity (or equivalently atomic number in a given group of the Periodic table) stems from the fact that, in general, heavy elements such as Sn or Pb, Bi and Te tend to adopt structures (in the crystalline state) with high coordination numbers, e.g. (quasi-) octahedral rather than trigonal or tetrahedral, as a result of the delocalization of the bonding charge associated with the increased metallicity. The empirical rules for glass formation proposed by [Zachariasen 1932] asserted that glass formation was favourable only for those materials whose structure consist of cation-centered polyhedra having a small number (three or four) of anionic ligands (in this case chalcogen atoms) surrounding a cation such as As and Ge etc. [Cooper 1978] has shown that these rules in fact arise from topological consideration. Topological disorder can readily be introduced into structures consists of corner-
sharing triangular or tetrahedral polyhedra, and even also into one consisting of such polyhedra connected together in an edge-sharing fashion (thereby forming chains), but not if the connection between such small polyhedral is by means of sharing of faces, or if large (e.g. octahedral) polyhedral constitute the structural units (even with corner-sharing connections). In the latter cases, insufficient degrees of geometrical freedom remain after the connections between units (polyhedra) are all satisfied for disorder to be introduced and consequently only crystalline structures are possible.

2.4.2 Phillips’s topological constraints theory.

The glass-forming ability of chalcogenide materials can be discussed in term of constraint theory [Phillips 1979]. Most inorganic, covalently-bonded glass-forming systems have relatively low values of (average) coordination number-chalcogenides are canonical example. The propensity for glass formation can then understood in terms of the mechanical constraints, i.e. the degree of freedom associated with bond-stretching and bond-bending interactions, in a perfectly connected structure.

An atom having all covalent bonds satisfied obeys so-called $8 - N$ rule [Mott 1967], where $N$ is the number of valence electrons and the coordination number $n_c$ is given by the relation (1.1)

$$n_c = 8 - N$$

(2.7)

Strictly speaking, this relation is only valid for elements from Groups IV-VII of the Periodic table, although Liu and Taylor [Liu 1989] have generalized this expression taking account of (formal) charge-transfer effects. Thus, a chalcogen (from Group VI) will have a coordination number $n_c = 2$. For a binary alloy $A_xB_{1-x}$, the average coordination number, $m$, is given by

$$m = x n_c(A) + (1 - x) n_c(B)$$

(2.8)

In general, of course, $m$ is non-integral. For example, for GeSe$_2$ $m = 2.67$ and for As$_2$S$_3$ $m = 2.4$. Thus, $m$ can be regarded as being the coordination number of a
hypothetical pseudoatom forming a structure whose topology is identical to that of the real material.

Phillips [1979] proposed that the glass-forming tendency is maximized when

\[ N_c = N_d \]  

(2.9)

where \( N_c \) is the number of (mechanical) constraints experienced by each atom (due to interatomic forces acting on it), and \( N_d \) is the number of available degrees of freedom. The number of constraints per atom depends on the coordination number, and the number of degrees of freedom is related to the dimensionality of the system. A material is said to be overconstrained if \( N_c > N_d \), and cannot then easily form a glass (by quenching from a melt), although an amorphous structure may still be obtained by employing very rapid (vapour) quenching technique.

2.4.3 Valence-force-field model.

The mechanical constraints experienced by an atom can be considered in terms of an interatomic forces acting on an atom in the valence-force-field model, in which the (strain) potential energy \( U_s \) is expressed as a sum of contributions from bond-stretching and bond-bending:

\[ U_s = \frac{1}{2} \alpha_s \Delta r^2 + \frac{1}{2} \beta r_0^2 \Delta \theta^2 \]  

(2.10)

where \( \alpha_s \) and \( \beta \) are the bond-stretching and bond-bending force constants, respectively, and \( \Delta r \) and \( \Delta \theta \) represent small deviations in bond length and bond angle from the equilibrium values for the bond length, \( r_0 \), and bond angle, \( \theta_0 \).

For a binary alloy, \( A_xB_{1-x} \), there is only one bond-stretching interactions (\( \alpha_s \)), but there are two bond-bending force constraints, \( \beta (B A B) \) and \( \beta (A B A) \), for bending motions centered on atoms A and B, respectively. For simplicity it is assumed at the outset that \( \beta (B A B) = \beta (A B A) \), and that all three force constants act as rigid mechanical constraints. Then, the number of constraints per pseudoatom is given by [Phillips 1979]:

49
CHAPTER 2: TYPES AND DEGREE OF DISORDER.

STRUCTURAL ORGANIZATION AND DEFECTS IN COVALENT GLASSY MATERIALS

\[ N_c = \frac{m}{2} + \frac{m(m - 1)}{2} = \frac{m^2}{2}, \quad m \leq N_d - 1 \]  

(2.11)

where the first term is associated with \( \alpha_s \) interactions (the factor of \( \frac{1}{2} \) arises because a bond-stretching mode involves two atoms) and second term arises from \( \beta \) interactions. Equation (2.11) is only valid for \( m \leq N_d - 1 \) [Döhler 1980]. Otherwise, the fact that \( N_d + 1 \) bond angles (in \( N_d \)-dimensional space) are not linearly independent must be taken into account [Döhler 1980]. For a two-fold coordinated atom (such as a chalcogen), there is one angular constraints associated with the second term in Eq. 2.10, whereas adding each additional bond gives two more constraints because the angles with two existing bond must be specified [Thorpe 1983]. This yields:

\[ N_c = \frac{m}{2} + (N_d - 1)(2m - N_d)/2 \]

(2.12)

and

\[ m \geq N_d - 1 \]

For ideal glass formation, \( N_c = N_d \) (Eq. 2.9), also so from Eq. 2.12 the optimum average coordination number is given by

\[ m_c = \frac{N_d(N_d + 1)}{(2N_d - 1)} \]

(2.13)

and

\[ m \geq N_d - 1 \]

For a system in 3D space, \( N_d = 3 \), and so from Eq. 2.13 \( m_c = 2.4 \). Thus, the stoichiometric composition for V-VI materials, e.g. As\(_2\)S\(_3\), corresponds, in this picture, to the optimum glass-forming condition itself. Experimentally, it appears to be the case. For IV-VI materials, such as Ge\(_x\)Se\(_{1-x}\), use of Eq. 2.8 together with the Eq. 2.13 yields for the optimum glass-forming composition \( x_c = 0.2 \), i.e. GeSe\(_4\).

However, this simple model has to be treated with some caution, for it predicts that glass formation in the Si\(_x\)O\(_{1-x}\) system should also be favoured at \( x = 0.2 \), instead
of the stoichiometric composition \( x = 0.33 \) (viz. SiO\(_2\)) as is found experimentally. This contradiction can be circumvented by noting that the distribution of Si-O-Si bond angles is rather wide, and so the constraints associated with this bond angles should be relatively weak. If these are neglected, Eq. 2.13, suitably modified, then yields \( x_c = 0.33 \) [Thorpe 1983]. [Tanaka 1989b] has also modified the constraints model to take account of the presence of 2D-like MRO, and obtains the value \( m_c = 2.67 \).

### 2.5 Ideal glass and defects in a glassy state.

#### 2.5.1 Ideal glass

The notation of a defect in the structure of an amorphous solid might at first sight seem somewhat strange. If the structure of the solid is random, is it not rather a contradiction in terms to talk about a defect in an amorphous matrix? Or phrased in a different way, might not the structure of a non-crystalline solid be thought of as being completely defective? Studies have shown that the concept of a defect in an amorphous material is a valid one, although of course any given defect can only be defined with reference to some non-defective state.

We shall call a glass in which all atoms satisfy their valence requirements an ideal glass. To achieve this, the atoms have to obey the so-called 8 – N rule when \( N \geq 4 \), where \( N \) is the number of the valence electrons and the coordination number is given by 8 – \( N \).

- **8 - N rule when \( N \geq 4 \)**
- \( N \): the number of the valence electrons
- \( 8 - N \): coordination number.

The importance of defects lies on the fact that many properties of amorphous materials can be defect controlled. Among these are magnetic properties, opto-electronic behavior, vibrational and mechanical properties. In many cases the
behavior resulting from the presence of defects can completely dominate that due to the intrinsic material. Furthermore, for certain materials, e.g. the chalcogenide glasses, the “ideal” amorphous state appears to be impossible to achieve experimentally since structural defects are present even in thermal equilibrium in the melt and are consequently frozen-in on vitrification.

2.5.2 Coordination defects

In covalently bonded materials with pronounced directional bonding and consequently a well-defined local geometry, one type of point defect (i.e. that in which the deviation from the ideal structure is localized to a volume containing one or two atoms) concerns the atomic coordination. Such kind of defects might be of two types: either under-coordination or over-coordination with respect to the normal coordination of the ideal structure.

(i) Over-coordinated defects:

Over-coordinated defects can arise when an additional covalent bond is formed datively between a normally coordinated atom and another (utilizing non-bonding lone – pair electrons) atom. The formation of such defects provides the mechanism for producing a negative effective correlation energy for dangling bonds in chalcogenide glasses. A similar type of over-coordinated site has been postulated to exist in tetrahedrally coordinated materials, e.g., a-Si. This is the fivefold-coordinated site [Pantelides 1986], which can be regarded either as a Si self-interstitial configuration or, equivalently, as a close interaction between a dangling bond and a normally bonded, fourfold-coordinated site.

(ii) Under-coordinated defects:

Under-coordinated defects in covalent solids are dangling (or broken or unsatisfied) bond. Such a concept has no validity for materials containing non-directional bonds, such as metals, ionic salts or rare-gas solids.
Fig. 2.9 (a) Schematic representation of the origin of valence and conduction band states for a tetrahedrally bonded semiconductor (i) atomic s- and p-states; (ii) sp$^3$-hybrid state; (iii) bonding (σ) and antibonding (σ$^*$) states; (iv) broadening of σ- and σ$^*$-states into valence band and conduction band.

(b) Density of states for such a band scheme, showing the localized band-tail states. A dangling-bond band is also near mid-gap, together with the band for double occupancy higher by $U$ in energy (for a positive-$U$ system) [Elliott 1990].

If dangling bonds occur at voids they can reconstruct so as to lower the total energy, thereby changing the electron occupancy and hence the charge state of the defects.

There is an important difference between coordination defects in amorphous and crystalline solids. Isolated defects can occur in the non-crystalline state, but not in ordered structures. The energy levels for electron states associated with an isolated dangling bond may be discussed in terms of a simple molecular orbital picture. If we consider the case of a tetrahedral semiconducting material, e.g. a-Si, having an atomic electronic configuration s$^2$ p$^2$, the atomic levels hybridize to form four sp$^3$ molecular hybrids, each of which may admit a bonding or antibonding orbital. Solid-state interactions then broaden the molecular levels into bands separated by a bandgap (Fig. 2.9). A dangling bond, or non-bonding orbital, containing a single electron will therefore have an energy level lying at the zero energy for the sp$^3$ hybrids, viz. near the middle of the gap (if atomic relaxations are neglected). Thus,
structural defects such as dangling bonds are expected to introduce electron states deep into the gap, which is otherwise empty in the ideal case.

2.5.3 Wrong bonds

In multicomponent glasses any deviation from stoichiometry is also a defect. Thus an As$_2$S$_3$ glass should ideally contain only As-S bonds whereas real glasses possess a large fraction (up to 10%) of so-called wrong homopolar bonds: As-As and S-S bonds whose concentration is especially pronounced in as-made evaporated films of amorphous chalcogenides [Karataev 1988, Treacy 1980]. The presence of wrong bonds plays a decisive role in some applications of chalcogenide glasses such as photoresists and electron-beam resists.

2.5.4 Density of defects

The structural defects that are presented in this section cannot be categorized as point defects, such as dangling bonds, mono- or divacancies, for example. These density defects range from voids (of size $< 100$ Å), which may be regarded as an aggregate of a non-fixed number of vacancies, to fluctuations in density (or free volume), which may be regarded as vacancies which have become disturbed throughout the material and which therefore cannot be regarded any more as well-defined point defects.

The free volume may be associated with a single atom (Fig. 2.10 (a)), which may hop from one site to another (accomplishing diffusive motion) with concomitant collapse of the original cage of neighboring atoms (producing a local shear strain). Alternatively, the free volume defect may be associated with more than a single atom, Fig. 2.10(b). The motions of two atoms which can undergo a shear transformation and hence also contribute to diffusion and flow. The diffusion and flow defects are rather localized in this case.
2.5.5 Negative-U defects

For the sake of simplicity we shall refer to defects in elemental selenium. The most straightforward kind of a defect in such a monoatomic, amorphous solid would be atoms with unsatisfied, or broken, or dangling bonds. Once broken, the dangling bond contains one electron and is electrically neutral. Such defects should be present in large quantities in an amorphous network and the fact that the Fermi level in chalcogenide glasses is pinned near the middle of the gap [Mott and Davis 1979] seems to confirm this statement. This is likely situation in unhydrogeneted a-Si or a-Ge, which are characterized by large photoinduced electron spin resonance (ESR) signals ($\sim 10^{20} \text{ cm}^{-3}$). However, in amorphous chalcogenides a dark ESR signal is usually not observed (with the exception of Ge-S glasses) whereas a large concentration of defect states has been demonstrated by such techniques as photoluminescence [Street 1976] and alternating current (ac) conductivity [Elliott 1978].

To explain this controversy of coexistence of a large concentration of defects on the one hand with high transparency and absence of an ESR signal on the other hand, Anderson has postulated [Anderson 1975] that, due to a strong electron-phonon coupling, electron pairing becomes energetically favorable despite the endothermic cost in energy required to place two electrons on one site. Such defects
are called negative-U centers. The Anderson model is similar to the Cohen-Fritzsche-Ovshinsky (CRO) model [Cohen 1969] in a sense that the gap is filled with the tail states. An important difference is that in the Anderson model the states are two-electron and there is a real gap in the one-electron states density.

Street and Mott [Street 1975] have applied this model to a case example of simple chalcogen. According to their arguments the majority of defects in a chalcogen are pairs of positively and negatively charged dangling bonds, \( D^+ \) and \( D^- \) (Eq. 2.14):\

\[
2D^0 \rightarrow D^+ + D^- \tag{2.14}
\]

Within this approach, the system is diamagnetic (all electrons are paired), which explains the absence of an ESR signal. These two electron states are not accessible experimentally.
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CHAPTER 2: TYPES AND DEGREE OF DISORDER.

STRUCTURAL ORGANIZATION AND DEFECTS IN COVALENT GLASSY MATERIALS


Zachariansen W. H., J. Am. Chem. Soc. 54, 3841 (1932)
Chapter 3

PHOTOINDUCED PHENOMENA IN NON-CRYSTALLINE CHALCOGENIDES

3.1 Introductory Remarks

Illumination of semiconductors and insulators with light, having a photon energy comparable with that of the bandgap of the material, creates electron-hole pairs. Such optically excited carriers can subsequently separate, thereby contributing to the electrical response of the material (e.g. photoconductivity), or recombine, either radiatively (giving rise to photoluminescence (PL)) or nonradiatively. Non-radiative recombination of photoexcited electron-hole pairs can, leave the material in a different state from that characteristic of the unilluminated state. For example, structural defects can be created in this way, with the energy liberated in the non-radiative recombination event helping overcome any activation barriers to defect formation.

In crystals, essentially because of the constraints imposed by lattice periodicity on the positions that atoms may occupy, the number of pathways available to be
explored after an electron-hole creation event may be rather limited. In contrast, amorphous semiconductors and insulators can exhibit a much richer variety of photoinduced phenomena, both because of the freedom and flexibility associated with the atomic structure resulting from the relaxation of crystallographic constraints, and also because the presence of structural disorder can lead to localization of electron and hole states at the band edges in the vicinity of the gap (Mott and Davis 1979). Such disorder-induced localization of the charge carriers greatly facilitates the likelihood that metastable changes can be induced. In crystals, where such a mechanism is absent, it is only in certain cases that the otherwise extended wavefunctions associated with the charge carriers can become sufficiently localized that local structural changes can readily occur.

3.2 Transient and metastable photoinduced phenomena

It is convenient to divide photoinduced phenomena into transient and metastable effects, although in many cases this is simply a matter of definition depending on the relative times of observation and decay of the photoinduced effect after cessation of illumination: processes where the characteristic decay time is less than the observation time can be regarded as being transient, whereas those for which the converse is true can be regarded as being metastable. Conventionally, observation times are of the order of seconds (or longer). Hence, in such a case, transient optically induced phenomena include photoluminescence (PL) and photoconductivity, whereas metastable phenomena include photostructural changes and related effects, e.g. photodarkening (PD) or photobleaching (PB), and metal photodiffusion.
CHAPTER 3: PHOTOINDUCED PHENOMENA IN NON-CRYSTALLINE CHALCOGENIDES

Figure 3.1. Schematic configuration-coordinate diagram representing the ground state (I), a transient excited state (II) reached after optical excitation and a metastable state (III) to which the system can transfer by means of a structural change (equivalent to a change in the configurational coordinate q). The energy barrier $W$ between III and I ensures metastability as long as $W > kT$, [Shimakawa 1995].

A number of microscopic mechanisms have been proposed to account for metastable photoinduced effects in amorphous semiconductors and insulators. In most cases, metastability is imparted to the electronic photoexcitation event by an accompanying change in the atomic structure; this change in microscopic structure can be represented by a configuration-coordinate diagram (Figure 3.1), in which the configurational coordinate $q$ is some measure of the extent of the structural change. The energy barrier, of height $W$, separating the resultant photoexcited state (III) from the ground-state configuration (I) is responsible for the metastability, as long as the thermal energy available is sufficiently low, that is $kT \leq W$.

The double-potential-well representation of metastable-state and ground-state configurations (cf. I and II in Figure 3.1) is ubiquitous. Examples of this approach include the “bonding-twisting” mechanism for photostructural changes in (elemental) chalcogen glasses in which the conformation of a chalcogen chain is changed after optical excitation (owing to the changes in the interactions between
lone-pair (LP) electrons on the chalcogen atoms), and the model for the so-called Staebler-Wronski effect in a-Si:H.

In the next paragraphs of this chapter we will briefly refer to some of the most important photoinduced effects in non-crystalline chalcogenides. The chapter ends with some applications of these materials.

3.3 Reversible photostructural changes.

3.3.1 Photodarkening and photobleaching

The reversible photodarkening (PD) phenomenon was reported by De Neufville et al. [De Neufville 1973/1974] almost 40 years ago. If an amorphous chalcogenide film (e.g. As$_2$S$_3$) is irradiated by light with the photon energy near its energy bandgap $E_g$ (2.4 eV) then one observes a shift of the absorption edge towards lower energies up to a saturation limit. The new state called darkened state due to the lower transparency of the film. Because the photoconductivity spectrum shifts also towards lower energies (red shift) [Babacheva 1984] it was assumed that the photodarkening phenomenon is the photoinduced decrease of the optical gap which can be recovered by annealing. The recovery was called photobleaching (PB).

The photodarkening is a common phenomenon in many glass materials and especially in chalcogenide ones. The chalcogens themselves show such phenomena (amorphous selenium is a typical example) but they exhibit specific features [Bogomolov 1983, Katayama 1989]. The hydrogenated As-S and As-Se films show also photodarkening [Popescu 2008]. The amorphous tetrahedral materials, as e.g. a-Si:H do not exhibit photodarkening. As regarded the pnictide materials, the experimental results are differ for the particular element: the arsenic does not show darkening [Mytilineou 1980] but the phosphorus exhibits such effect although the response rate is rather small when compared to that of amorphous chalcogens [Kawashima 1987]. Although the oxygen belongs to the same chalcogen group of the Periodic Table, it is not considered as a chalcogen element. The studies of oxide
glasses, such as $\text{As}_2\text{O}_3$ and $\text{GeO}_2$, have not issued in a definite answer concerning the existence of the photodarkening in these materials [Pontushka 1981, Schwartz 1989].

The photodarkening can be practically detected only in amorphous films thinner than $10 \div 20 \mu\text{m}$ because this effect enhances the absorption coefficient for the light of wavelength corresponding to optical gap and, consequently, the effective depth of light penetration in the sample is diminished [Tanaka 1977a].

In most chalcogenide films was observed a bleaching phenomenon under the influence of light: photobleaching. In order to get photobleaching it is important to illuminate the sample at temperatures a little bit larger than those, which favour the photodarkening [Averyanov 1980]. In some cases, as e.g. in the $\text{As}_2\text{Se}_3$ films, the photobleaching is characterized by a thermal threshold which means that the bleaching can be observed only above a given temperature called the optical bleaching threshold, that is lower than the thermal bleaching temperature.

3.3.2 Photo-induced anisotropy

Amorphous materials are essentially isotropic while the crystals show anisotropy, i.e. most of the properties depend on the crystal orientation. The photo-induced anisotropy was originally discovered by [Weigert 1920]. The chalcogenide amorphous films [Zhdanov 1979, Zhdanov 1980, Hajtó 1982) and bulk glasses [Tikhomirov 1995] show quasi-stable optical and electronic anisotropy when illuminated by polarized light. The main photo-induced anisotropy phenomena, called also vectorial phenomena are \textit{dichroism} and \textit{birefringence}. The other are: difference in the intensity of the photoluminescence and difference in the fine structure of the X-ray absorption edge for polarizations of the control light beam parallel and perpendicular to the direction defined by the polarization of the beam used in photodarkening.
The photo-induced anisotropies can be reversibly reproduced after annealing, and the axes defining the optical anisotropy can be rotated by turning the polarization direction of the exposing light. These anisotropic phenomena differ from the isotropic photo-structural changes in their induction and annealing kinetics as well as in their dependence on temperature and on photon energy.

### 3.4 Photoinduced volume change

A change in the volume (thickness) of chalcogenide films (As$_2$S$_3$) was first reported [Hamanaka 1977] and was one of the first indications that structure of the material changed as a result of the photo-excitation. The observed increase in the thickness of about 0.5% can be explained by the assumption that light “pumps in” energy to the system, leading to its further disordering. The unharmonicity of the interatomic potential provides a simple explanation of the result. Another possible explanation includes the photo-induced creation of “wrong” As-As bonds that are longer (2.57 Å) than heteropolar As-S bonds (2.24 Å). Note that S-S bonds (2.05 Å) are shorter than the heteropolar bonds. Heteropolar-to-homopolar bond conversion therefore does not necessarily result in the volume expansion.

For a long time it was believed that photodarkening and photo-expansion were two different sides of the same phenomenon. However, parallel studies of photodarkening and photo-expansion [Tanaka 1998] have demonstrated that photo-expansion under bandgap irradiation increases earlier than photodarkening. In contrast, under sub-bandgap irradiation, photo-expansion increases more gradually than photodarkening. This result clearly demonstrates that there is no one-to-one correlation between the two phenomena.

Parallel studies of photoconductivity and photo-expansion [Ganjoo 1999] have found that upon photo-exitation the As$_2$S$_3$ thickness increases rapidly, reaches maximum, and then decreases slowly with time. This behaviour resembles the degradation of photocurrent in amorphous chalcogenides [Shimikawa 1990] which
suggests that presence of free carriers is essential for photo-expansion. A possible explanation can be given within a model [Shimakawa 1998] based on the suggestion that photo-structural changes are caused by Coulomb repulsion of crystal-like fragments of the glass due to different mobilities of electrons and holes.

3.5 Photo-induced fluidity

The relatively recently reported photo-induced fluidity (PiF) is one of the most fascinating yet less studied photo-plastic effects [Hisakuni 1995]. PiF pertains to the plastic deformation or permanent shape changes of a chalcogenide glass (manufactured in the form of a fiber or a flake) induced by light illumination in a purely athermal way. The athermal increase in a material’s plasticity is achieved through the combined effect of sub-band-gap light illumination and the simultaneous application of external mechanical stress, as was demonstrated for the As$_2$S$_3$ glass [Hisakuni 1995]. Perhaps the most provocative feature of PiF is its anomalous temperature dependence, namely, the fact that PiF is hindered at higher temperatures.

The macroscopic changes observed (i.e., fiber elongation) imply that PiF is the cumulative effect of structural rearrangements occurring at the molecular level.

The nature of PiF is purely photo-electronic and the atomic rearrangement might involve changes of either intramolecular (covalent, strong) and/or intermolecular (van der Waals, weak) bonds. However, intramolecular and intermolecular mechanisms cover actually any kind of structural mechanisms that can be envisaged [Hisakuni 1995].

This kind of transformation can be realized by the combined action of light and stress, which can untie As-As knots, resulting in an effective unfolding of the cage-like As$_4$S$_4$ molecule. The As atoms suspended at the ends of the As$_4$S$_4$ planar cluster are now amenable to bonding with S atoms. The latter are the excess S atoms needed to fulfil the stoichiometry of the As$_2$S$_3$ glass, which reside in the interstices of the
structure. It is possible that the intermediate cluster with one broken As-As bond can be further modified and the linkage of the other two As atoms to network units might contribute to the substantial polymerization of the structure [Yannopoulos 2003].

The proposed model is compatible with two key features of PiF. First, it can account for the length increase of the fiber through an opening of the ‘‘closed’’ \( \text{As}_4\text{S}_4 \) configuration. An attempt to quantitatively estimate the fractional length increase due to this model is presented below. Second, the specific atomic transformation engenders anisotropy through the transformation of a highly symmetric molecule to an asymmetric planar-like configuration, as is clearly evidenced in the depolarization ratio increase. These findings are important because they show that homopolar As-As bonds most likely dissociate rather than form during the time that photo-plastic effects take place, a procedure that is reminiscent of that of thermal annealing.

### 3.6 Microscopic nature of photo-structural changes

In order to understand the microscopic nature of photo-structural change, various structural-sensitive techniques have been used and, based on their outcomes, different models have been suggested.

A reversible change in the intensities of Raman peaks in stoichiometric \( \text{As}_2\text{S}_3 \) on illumination, situated at 231 and 187 cm\(^{-1}\) was reported in [Frumar 1984]. This change was attributed to an increase (~6%) in the number of heteropolar As-As bonds. The important role of As-As bonds in the process of photo-structural changes is in agreement with the conclusion based on the observation that an increase in arsenic content leads to a substantial increase of photo-induced changes of various parameters of As-based chalcogenides [Gurevich 1975]. The result, however seemed to contradict the experimental fact that the optical gap of chalcogenides decreases on illumination, because any deviation from the stoichiometry in the As-S(e) system
should lead to an increase of the optical gap [Myers 1967]. In addition, the formation of wrong bonds completely fails to explain photodarkening in elemental chalcogenides.

EXAFS is a local probe that has the advantage of being able to probe independently the surroundings of different chemical constituents. The EXAFS study confirms [Yang 1987] that there is a small (~1%) increase in the concentration of As-As bonds but found no other changes in the first coordination sphere. The main changes occur in the second coordination sphere of arsenic. The interatomic distance between the two arsenic bridged by a chalcogen atom reversibly increases, which means that the valence angle subtended at a chalcogen atom opens up on illumination. Interestingly, the distances in the third coordination sphere (S-As-S) remains unchanged, which allowed [Yang 1987] to conclude that the dihedral angle between the two adjacent AsS$_3$ pyramids changed simultaneously with the increase of the valence angle at the bridging chalcogen atom.

An important step in understanding the mechanism of photo-structural changes is the suggestion that both interatomic (covalent) and intermolecular (van der Waals) bonds should be considered. It is argued that the action of light in producing the photo-structural effect is to weaken and ultimately break the bonds [Pfeiffer 1991, Averyanov 1981, Likholit 1984, Elliott 1986, Hisakuni 1995]. A unified model for photo-structural changes has been suggested in [Elliott 1986]. It was suggested that not just the primary covalent (intramolecular) bonds but also weaker (intermolecular) “back-bonds” between non-bonded chalcogen atoms in neighbouring layers should be considered in this process. Within this approach, after absorption of a photon and subsequent excitation of an electron into the conduction band (anti-bonding state), the attractive interaction decreases. This changes the balance between the attractive and repulsive interactions and causes an increase in the intermolecular bond length. One consequence of this model is that a reversible increase in volume is predicted on illumination. An estimation of the expected
expansion of the glass using experimental data for the photo-induced change in the elastic moduli gives a value for photo-induced expansion of 0.63% in As$_2$S$_3$, which should be compared with the experimentally observed volume expansion of 0.6% [Hamanaka 1977]. Intramolecular bond-breaking processes, such as homopolar-to-heteropolar bond conversion (and vice versa) and self-trapped excitons have also been considered in details and has been concluded that intermolecular, rather than intramolecular, bond-breaking processes are predominant in the As-based chalcogenides.

A different approach was suggested in [Shimakawa 1998]. These authors argue that remnants of crystalline layers are presented in the glass. Upon photo-excitation, electron-hole pairs are generated. The holes diffuse apart while the electrons get trapped. The Coulomb repulsion between trapped electrons changes the interlayer interaction and, consequently, the geometry, resulting in repulsion of the layers (photo-expansion) and a slip motion along the layers. Such a change in the layer geometry results in the photodarkening through the mechanism proposed in [Watanabe 1988] and discussed previously here.

The observed formation of wrong bonds upon irradiation can be explained within the following approach. When a thin chalcogenide film is prepared by vapour deposition (e.g., thermal evaporation) there are many different molecular species in the vapour [Tanaka (b) 1977]. Upon annealing, homopolar bonds present in as-made films are broken and energetically more favourable heteropolar bonds are formed instead [Treacy 1980]. In an extreme case, the film can even crystallize on annealing near T$_g$. However, changing bond topology in a solid phase introduces strain that is most likely to occur in places where initially homopolar As-As bonds were present because it was there that the bond switching and hence the largest atomic displacement took place.

Should the annealed film now be illuminated, the bonds would weaken and the structure would be able to relax. Because the strain originated from the conversion
of As-As to As-S bonds on annealing, it is probable that As-As bonds will be formed again. This probability is higher at sites where wrong As-As bonds were initially present [Shpotyk 1990, Kolobov 1994]. Photoinduced relaxation of stress was demonstrated experimentally in [Koseki 1982].

3.7 Photoinduced change in the Phase State

3.7.1 Photo-crystallization

Several works have been reported on photo-crystallization of a-Se. Dressner and Stringfellow [Dressner 1968] reported that the radial growth rates of spherulitic crystals in a-Se films are sharply enhanced, by an order of magnitude, upon irradiation with light whose wavelengths are less than a critical value. They have concluded that this behaviour reflects primarily the photo-, rather than the thermal, effect of the irradiation. The transformation of Se from the amorphous to crystalline state depends strongly on the power of laser irradiation with pronounced threshold behaviour [Baganich 1991].

Photo-excitation results in creation of ESR-active defect pairs [Bishop 1975, Biegelsen 1980, Hautala 1988, Kolobov (a) 1997, Kolobov 1998]. The constituents of such pairs (dangling bonds at T > 100 K) are electrically neutral and can diffuse away from the place of origin. Because the diffusion occurs by bond-switching it does not require much energy after the initial momentum has been supplied by energy released upon breakdown of the triply coordinated pair. Arguments in favour of defect diffusion in a-Se have also been put forward [Grenet 1983, Larmagnac 1982] based on photocurrent studies. As time elapses (or as the temperature is increased) neutral defects are converted into charged defects with Coulombic interaction between them attracting the two defects toward each other. If the concentration of photo-induced defects (roughly proportional to the light intensity) is small, the photo-created defects recombine geminately and their recombination results in recovery of the initial structure.
CHAPTER 3: PHOTONIC IN NON-CRYSTALLINE CHALCOGENIDES

If, on the other hand, the light intensity is high, the inverse concentration of the photo-induced defects becomes smaller than the distance between the diffused defects originating from the same site. In such a case, after acquiring the charged state the defects find themselves under the action of Coulomb potential centered at a place different from that of their origin. The recombination between charged defects that originated at a different place becomes plausible. In such a case the structure resulting after recombination is different from the initial structure. Because the process develops in the direction that lowers the total energy, the material gradually crystallizes. This process is facilitated at high excitation levels when the local changes can take place collectively.

Photo-crystallization has been shown to have a complicated behaviour if induced by simultaneous irradiation of the two lasers (Kr\(^+\), \(\lambda = 676\) nm, Ar\(^+\), \(\lambda = 488\) nm) [Roy 1998]. It has been suggested that crystallization induced by sub-bandgap light (Kr\(^+\) laser) and cross-bandgap light (Ar\(^+\) light) have different mechanisms and opposite polarization dependence. Crystallites induced by one light source can be either enhanced or destroyed by the other light source. The observed photoamorphization of a partly crystallized selenium film [Roy 1998] supports this suggestion.

3.7.2 Photoamorphization

An As\(_{50}\)Se\(_{50}\) film crystallized on a silica glass substrate becomes amorphous again if irradiated by continuous low-intensity light [Elliott 1991, Kolobov 1995a, Kolobov 1995b]. This change appears to be athermal because the light-induced heating is negligible. Amorphization therefore does not take place by local melting and subsequent quenching to the vitreous phase.

Each As\(_4\)Se\(_4\) molecule [Goldstein 1974] has two intramolecular homopolar As-As bonds. The As-As bond within such molecule (2.57 Å) is significantly longer than in, let say, a-As (2.49 Å) and the As-As-Se bond angle subtended at as atoms
comprising the as-As bonds (101.2°) is also larger than the average bond angle in a-As (98°). One can conclude, therefore, that such intramolecular bonds are rather strained, and, as a result the electronic states associated with these bonds are likely to be at, or just above, the top of the valence band. Thus, optical illumination might be expected preferentially to involve the excitation of such states, leading to bond scission. As-Se bond formation could then occur between closest atoms of neighbouring molecules, resulting in a more cross-linked, and amorphous, structure.

The X-ray diffraction patterns (relative peak intensities) vary with the peak thickness [Kolobov (b) 1995], which implies that the surface and/or interface effects play a role in the process. This was further confirmed by simultaneous annealing of a film on a silica glass substrate and a film scraped off the substrate prior to annealing. Whereas the film on the exhibits crystallization after 1 h annealing at 180 °C, the scraped powder does not show any trace of crystallization even after 50 h annealing at this temperature.

The fact that attachment to the substrate is very important for the process implies that the mechanical strain, accumulated in the film, may play a role. This strain can be so strong that on light illumination, when the bonds are weakened, it becomes energetically more for the film to go back to the amorphous state, thereby reducing the strain. This result is rather unusual because the interface strain is normally relaxed in a thickness of about 1000 Å, whereas in the case of As$_{50}$Se$_{50}$ it affects much thicker films (several microns thick).

Photoinduced amorphization also has been observed in As$_2$S$_3$ [Frumar 1995] and a-Se [Roy 1998]. In the case of As$_2$S$_3$ the starting material was natural orpiment crystals. When irradiated by Kr$^+$ laser light ($\lambda = 568$ nm) the spectrum gradually transforms [Frumar 1995] and a broad feature characteristic of a glass comes out. Investigation of the temperature dependence of the process has led the authors to conclude that amorphization has essentially an electronic and not a thermal origin.
Although photoamorphization has been observed in different chalcogenides it is not quite clear whether it is a common feature of all chalcogenide glasses or limited to the previously mentioned examples.

### 3.7.3 Photo-melting

Similarities in structure of photo-excited (solid) selenium and liquid selenium have led the authors of [Kolobov 1997b] to conclude that the general mechanism of photo-structural changes is based on local athermal quasi-melting. This conclusion is in very good agreement with the photo-enhanced fluidity observed in As$_2$S$_3$ when the glass was found to become viscous in the illuminated area [Hisakuni 1995].

It has been found that, selenium, both amorphous and crystalline, can be melted by light [Poborchii 1999]. The photo-melting was studied visually using an optical microscope and by Raman scattering. Special care was taken to exclude the possibility that this effect is caused by heating due to light absorption. It was found that the “amorphous” peak at 252 cm$^{-1}$ was strongly polarized. This result implies that quasi-free chains produced as a result of photo-illumination are strongly oriented with respect to the polarization of the exciting light. It was concluded that photo-melting of selenium is associated with breaking of interchain bonds between Se chains oriented parallel to the polarization plane of the inducing light.

### 3.8 Applications of amorphous chalcogenide materials

#### 3.8.1 Lithography

Chalcogenide glasses have been shown as potential high resolution resists for photo, electron and X-ray lithography. For certain processing conditions these glasses may even be superior due to their greater hardness, resistance to acids, easy fabrication in thin film form, or the unique phenomena that they exhibit like photo-doping or photo-diffusion.
Due to the high sensitivity of chalcogenide glass resists, exceptionally thin (10s nm) films are sufficient which are expected to yield better control of geometry than possible with polymer resists. Chalcogenide glass resists are suitable for selective etching of SiO₂, Si, Cr, etc., which is used in microelectronic processing [Jain 2008].

- Photoresists

Several chalcogenide glasses exhibit the unique property of photo-diffusion, such that on exposure to bandgap light certain metals (e.g. silver, zinc, copper and indium) diffuse rapidly from the surface into the bulk (Fig. 3.3) [Tanaka 1991]. Due to the radiation induced diffusion, which is highest for silver, the chemical composition as well as the structure of irradiated region is dramatically modified compared to the unirradiated region. As a result, the selectivity or contrast of the resist is greatly enhanced [Yoshikawa 1976, Yoshikawa 1977].

Chalcogenide photoresists [Lyubin 2008] in which Ag-doped As₂S₃ chalcogenide film was used, showed to have superlinear dissolution characteristics.
Fig. 3.3 SEM image of test masks obtained on Cr layer with contact printing through evaporated photoresist based on vacuum evaporated layers of chalcogenide semiconductor $\text{As}_2\text{S}_3$.

Increasing of the dose of irradiation led to very strong super-linear increase of dissolution time. Such photoresists, having giant contrast, are prospective for many photolithographic processes like holographic lithography, zone-plate lithography and other cases of maskless photolithography, especially for interference lithography of photonic crystals, directly written in the high index resist materials.

- Gratings

A diffraction grating [Palmer 2002] is a collection of reflecting (or transmitting) elements separated by a distance comparable to the wavelength of light under study. It may be thought of as a collection of diffracting elements, such as a pattern of transparent slits (or apertures) in an opaque screen, or a collection of reflecting grooves on a substrate.

Diffraction gratings are often used in monochromators, spectrometers, wavelength division multiplexing devices, optical pulse compressing devices, and many other optical instruments. Ordinary pressed CD and DVD media (Fig. 3.4) are every-day examples of diffraction gratings and can be used to demonstrate the effect by reflecting sunlight off them onto a white wall.
**Fig. 3.4** A CD and DVD have a single spiral track of data, circling from the inside of the disc to the outside.

In the work of [Stronsky 2000] the authors showed that \( \text{As}_40\text{S}_{60-x}\text{Se}_x \) layers provided adequate etching selectivity and the formation of high-quality grating surface relief (Fig. 3.5). These layers can be used for the industrial fabrication of the diffractive optical elements and thus as recording media for holography as well.

**Figure 3.5.** *SEM image of the holographic grating of \( \text{As}_{40}\text{S}_{60-x}\text{Se}_x \) layers with spatial frequency 1200 mm\(^{-1}\) [Stronsky 2000]*
Other chalcogenide material which is appropriate for holographic gratings is amorphous \( \text{As}_{0.55}\text{Se}_{0.45} \) thin film. This composition has shown a strong dependence of the diffraction efficiency of the gratings on the readout light wavelength (650 nm, 805 nm and 1150 nm) and film with thickness of 1 µm appear to have high efficiency gratings.

- **Microlenses**

  Chalcogenide-glass microlens appear to be promising for controlling red and infrared light emitted from optical fibers [Saitoh 2002]. Microlens and microlens arrays can be found in an increasing number of optoelectronic applications, such as optical communication and computing, CCD cameras, faxes, imaging systems and IR technology [Lyubin 2004]. Both spherical and cylindrical IR microlens arrays were successfully fabricated using As–S and As–Se photoresists.

![Schematic representation of a microlens.](image)

**Fig. 3.6** Schematic representation of a microlens.

### 3.8.2 *Ovonic devices*

- **Phase-change switches**

  Among the most important applications of the electrical conduction in chalcogenide glasses are the switches with and without memory. The switching
phenomenon is an old observation. The current controlled negative resistance, a relative feature, was observed in boron as early as 1913. Switching has been found in polycrystalline materials such as nickel oxide and antimony sulphide, in single crystals of GaAs [Popescu 2008]. Amorphous switching was discovered and applied by Ovshinsky in 1959 [Ovshinsky 1959].

➢ Thermo-switches

The thermo-switches are devices, which operate as thermistors on the basis of the exponential dependence of the electrical conductivity on temperature. Ternary ovonic glasses with tellurium have being tried in preparing thin films switches: Si$_{35}$As$_{30}$Te$_{35}$, Ge$_{18}$As$_{42}$Te$_{40}$, Si$_{37}$As$_{30}$Te$_{33}$ and Si$_{12}$As$_{24}$Te$_{64}$. The highest thermostability was obtained for thermo-switches based as Si$_{37}$As$_{30}$Te$_{33}$ [Loireau-Lozac’h 1976].

3.8.3 Fiber optics

Virtually all fibers share the same fundamental structure. The centre of the fiber is the core, which has a higher refractive index than the cladding that surrounds it. The difference in refractive index causes total internal reflection that guides the light along the core [Hecht 1999].

➢ Laser power delivery

Among the most important applications of chalcogenide fibers (Fig. 3.7), based on their ability to transmit in the 2-20 $\mu$m region, is their use as transmitters of laser power in this region for military applications such as in infrared countermeasures (IRCM) and laser threat warning systems.

Recent efforts have considered delivery of energy from a medical free electron laser (MFEL) operating between 2 and 10 $\mu$m through chalcogenide fiber [Sanghera 1998], as well as, performing surgery using light transmitted by chalcogenide fibers.
Aside from this use, laser power can be used for machining materials and biological samples by tuning the wavelength and transmitting the laser power through the chalcogenide fibers to remote areas.

- Chemical sensing
  Chalcogenide fibers are well suited for chemical sensing applications since practically most molecular species vibrate in the infrared region. They can be used in fiber optic chemical sensor systems for quantitative remote detection and identification as well as detecting chemicals in mixtures. Numerous systems have been studied and a plethora of species have been detected including aqueous, non-aqueous and toxic liquids as well as solids [Sanghera 1999]. Examples include oil, freon, soap, paints, polymer curing reactions, glucose/water, benzene and derivatives, chlorinated hydrocarbons, alcohols, carboxylic acids, aqueous acids, perfumes and pharmaceutical products.

- Temperature monitoring, thermal imaging and hyperspectral imaging
  Ueda [Ueda 1992] have used As±S fibers with a teflon cladding to measure temperature increases of up to 200°C on the surface layer of ceramic plates during grinding. Kapany and Simms [Kapany 1996] first suggested the use of chalcogenide fibers for thermal imaging. Saito et al. [Saito 1985] recorded the image of an electric iron at 773 K, with some degree of coherency through a 1000 fiber bundle. Nishii et
al. [Nishii 1991] fabricated a flexible fiber bundle containing 8400 teflon coated fibers and recorded the thermal image of an operating integrated circuit in 3±5.4 μm region using an InSb detector.

- Rare earth doped fibers

The 1.3 μm wavelength is of interest for telecommunications [Yamada 1992]. The gain coefficient obtained from the single mode fiber at 1.34 μm was 0.8 dB/mW and the efficiency was about 30%. The fiber loss at 1.34 μm was about 1 dB/m [Yamada 1992]. In the work of [Shaw 1998] has shown that Dy doped selenide glasses are better candidates for 1.3 μm fiber amplifiers due to the smaller phonon energy of the host glass, and the larger absorption and emission cross-sections for Dy. Amplification has been demonstrated using Nd at 1.08 μm [Mori 1997] and Pr at 1.34 μm [Tawarayama 1997] in sulfide glass hosts.
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CHAPTER 3: PHOTOINDUCED PHENOMENA IN NON-CRYSTALLINE CHALCOGENIDES


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4.1 RAMAN SCATTERING.

4.1.1 Scattering phenomena

A scattering process is an interaction of electromagnetic radiation with atoms, molecules, or their aggregates, by which a secondary light quantum (photon) is produced, with a different phase and polarization and maybe another energy when compared to that of the primary light quantum. The scattering process occurs with extremely short time delay. In emission spectroscopy, the molecule drops from a higher energy state to a lower one, and the energy lost in this process is emitted as a photon [Schrader 1997].

Light scattering is one of the two major physical processes that contribute to the visible appearance of most objects, the other being absorption. Two types of scattering processes both elastic (Rayleigh) and inelastic (Stokes and anti-Stokes Raman) are shown in Fig. 4.1.
An elastic scattering process produces radiation with the same energy as that of the primary light photons. Depending on the size of a scattering particle and its refractive index relative to that of the surrounding medium, the processes are called Rayleigh or Mie scattering [Schader 1997]. Rayleigh scattering is a process in which electromagnetic radiation (including light) is scattered by a small spherical volume of variant refractive index, such as a particle, bubble, droplet, or even a density fluctuation. This effect was first modeled successfully by Lord Rayleigh, from whom it gets its name.

\[ \lambda \]

**Fig. 4.1.** A typical diagram showing elastic and inelastic effects through transitions between the molecules energy levels.

In order for Rayleigh's model to apply, the sphere must be much smaller in diameter than the wavelength (\( \lambda \)) of the scattered wave; typically the upper limit is taken to be about 1/10 the wavelength. In this size regime, the exact shape of the scattering center is usually not very significant and can often be treated as a sphere of equivalent volume. The inherent scattering that radiation undergoes passing through a pure gas is due to microscopic density fluctuations as the gas molecules move around, which are normally small enough in scale for Rayleigh's model to apply. This scattering mechanism is the primary cause of the blue color of the Earth's sky on a clear day, as the shorter blue wavelengths of sunlight passing overhead are more strongly scattered than the longer red wavelengths according to Rayleigh's famous $1/\lambda^4$ relation. Along with absorption, such scattering is a major cause of the attenuation of radiation by the atmosphere. The degree of scattering
varies as a function of the ratio of the particle diameter to the wavelength of the radiation, along with many other factors including polarization, angle, and coherence.

For larger diameters, the problem of electromagnetic scattering by spheres was first solved by Gustav Mie, and scattering by spheres larger than the Rayleigh range is therefore usually known as Mie scattering. In the Mie regime, the shape of the scattering center becomes much more significant and the theory only applies well to spheres and, with some modification, spheroids and ellipsoids. Closed-form solutions for scattering by certain other simple shapes exist, but no general closed-form solution is known for arbitrary shapes.

An inelastic scattering process produces secondary light quanta with different energy. One such process is the Raman effect. During the interaction of the primary light with a molecule or crystal, the energy of vibrational and/or rotational states may be exchanged and a secondary light quantum of lower or higher energy is emitted. The energy difference is equal to the vibrational energy $E_{\text{vib}}$ of a molecule or crystal and/or the rotational energy $E_{\text{rot}}$ of a molecule. It may be recorded, if monochromatic radiation is used for the primary excitation, as a vibrational, rotational or rotation-vibration Raman spectrum. The inelastic interaction of a primary light quantum with a molecule or crystal in its rotational or vibrational ground state produces the Stokes Raman spectrum, a red-shifted spectrum. Due to thermal excitation according to the Boltzmann equation, some molecules are in their vibrational (or rotational) excited states. The interaction of the primary light with these molecules may produce a blue-shifted Raman spectrum, the anti-Stokes Raman spectrum. The relative intensity of the Raman lines in the Stokes and anti-Stokes Raman spectra may be employed using the Boltzmann equation for the determination of the vibrational (or rotational) temperature [Schrader 1997].

### 4.1.2 Origin of molecular spectra

All collective vibrations that occur in crystals can be viewed as the superposition of plane waves that virtually propagate to infinity [Kittel 1996]. These
plane waves, the so-called normal modes of vibration are commonly modeled by quasi-particles called phonons. In this sense, all motions of the nuclei in a molecule relative to other nuclei in the same molecule can be considered to be a superposition of normal vibrations for which all nuclei are vibrating with the same normal frequency.

As a first approximation [Nakamoto 1986], it is possible to separate the energy of a molecule into three additive components associated with (1) the rotation of the molecule as a whole, (2) the vibrations of the constituent atoms, and (3) the motion of the electrons in the molecule. The translational energy of the molecule may be ignored in this discussion. The basis for this separation lies in the fact that the velocity of electrons is much greater than the vibrational velocity of nuclei, which is again much greater than the velocity of molecular rotation. If a molecule is placed in an electromagnetic field (e.g., light), a transfer of energy from the field to the molecule will occur when Bohr’s frequency condition is satisfied:

$$\Delta E = h\nu$$  \hspace{1cm} (4.1)

where \(\Delta E\) is the difference in energy between two quantized states, \(h\) is Planck’s constant, and \(\nu\) is the frequency of the light. The frequency, \(\nu\), is converted to the wave number, \(\bar{\nu}\), or the wavelength \(\lambda\), through the relation:

$$\nu = \frac{c}{\lambda} = \frac{c}{\bar{\nu}}$$  \hspace{1cm} (4.2)

where \(c\) is the velocity of light. If,

$$\Delta E = E^f - E^i$$  \hspace{1cm} (4.3)

where \(E^f\) is quantized state of higher energy than \(E^i\), the molecule absorbs radiation when it is excited from \(E^i\) to \(E^f\) and emits radiation of the same frequency as given in Eq. 4.1 when it reverts from \(E^f\) to \(E^i\).

Because rotational levels are relatively close to each other, transitions between these levels occur at low frequencies (long wavelengths). In fact, pure rotational spectra appear in the range between 1 cm\(^{-1}\) (10\(^4\) µm) and 10\(^2\) cm\(^{-1}\) (10\(^2\) µm). The
Fig. 4.2. Energy level diagram of a molecule. (The actual spacing of the electronic levels are much larger and those of rotational levels much smaller, than those shown in the figure.) [Nakamoto 1986].

separation of vibrational energy levels is greater, and transition occurs at higher frequencies (shorter wavelengths) than do the rotational transitions. As a result, pure vibrational spectra are observed in the range $10^2$ cm$^{-1}$ ($10^2$ µm) and $10^4$ cm$^{-1}$ (1 µm). Finally, electronic energy levels are far apart, and electronic spectra are observed in the range between $10^4$ cm$^{-1}$ (1 µm) and $10^6$ cm$^{-1}$ (10$^2$ µm). Figure 4.2 illustrates transitions of the three types mentioned for a molecule. As the figure shows, rotational intervals tend to increase as the rotational quantum number $J$ increases, whereas vibrational intervals tend to decrease as the vibrational quantum number $\nu$ increases. The dotted line below each electronic level indicates the zero point energy that exists even at a temperature of absolute zero as a result of nuclear
vibration. It should be emphasized that not all transitions between these levels are possible. To see whether the transition is allowed or forbidden, the relevant selection rule must be examined. This, in turn, is determined by the symmetry of the molecule. Vibrational problems like these can be solved for polyatomic molecules in an elegant manner by the use of group theory.

Although vibrational spectra are observed experimentally as infrared and Raman spectra, the physical origins of these two types of spectra are different. Infrared spectra originate in transitions between two vibrational levels of the molecule in the electronic ground state and are usually observed as absorption spectra in the infrared region. On the other hand, Raman spectra originate in the electronic polarization caused by ultraviolet or visible light. If a molecule is irradiated by monochromatic light of frequency $\nu$, then, because of electronic polarization induced in the molecule by this incident light, light of frequency $\nu$ (Rayleigh scattering) as well as of $\nu \pm \nu_i$ (Raman scattering) is emitted ($\nu_i$ represents a vibrational frequency). Thus the vibrational frequencies are observed as Raman shifts from the incident frequency $\nu$ in the ultraviolet or visible region (Fig. 4.3).

![Fig. 4.3. Raman excitation level vs. IR excitation level.](image-url)
Some basic aspects of the Raman effect can be explained by elementary classical theory. Consider a light wave of frequency $\nu$ with an electric field strength $E$. Since $E$ fluctuates at frequency $\nu$, we can write

$$E = E_0 \cos 2\pi \nu t$$

(4.4)

where $E_0$ is the amplitude and $t$ the time [Nakamoto 1986].

If a diatomic molecule is irradiated by this light, the dipole moment $P$ induced in the molecule is given by:

$$P = \alpha E = E_0 \cos 2\pi \nu t.$$  

(4.5)

Here $\alpha$ is a proportionality constant and is called the polarizability. If the molecule is vibrating with frequency $\nu_1$, the nuclear displacement $q$ is written as

$$q = q_0 \cos 2\pi \nu_1 t$$

(4.6)

where $q_0$ is vibrational amplitude. For small amplitudes of vibration, $\alpha$ is linear function of $q$. Thus we can write

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q$$

(4.7)

Here $\alpha_0$ is the polarizability at equilibrium position, and $\left(\frac{\partial \alpha}{\partial q}\right)_0$ is the rate of change of $\alpha$ with respect to the change in $q$, evaluated at the equilibrium position. If we combine Eqs. 4.5-4.7 we have,

$$P = \alpha E_0 \cos 2\pi \nu t = \alpha_0 \cos 2\pi \nu t + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \cos 2\pi \nu t \cos 2\pi \nu_1 t =$$

$$\alpha_0 E_0 \cos 2\pi \nu t + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \{\cos[2\pi(\nu + \nu_1)t] + \cos[2\pi(\nu - \nu_1)t]\}$$

(4.8)

According to classical theory [Nakamoto 1986], the first term describes an oscillating dipole which radiates light of frequency $\nu$ (Rayleigh scattering). The second term gives the Raman scattering of frequencies $\nu + \nu_1$ (anti-Stokes) and $\nu - \nu_1$ (Stokes). If $\left(\frac{\partial \alpha}{\partial q}\right)_0$ is zero, the second term vanishes. Thus the vibration is not Raman active unless the polarizability changes during the vibration.

An interesting feature of Eq. 4.8 is to reveal the dual sensitivity of Raman scattering to the electronic ($\alpha$) and mechanical ($\nu_1$) properties of the investigated materials. Two kinds of parameters will therefore influence the spectra:
(i) parameters acting on the “mechanics” like atomic mass, bond strength or the system geometry (coordination numbers, interatomic distances, atomic substitutions) will set the peaks’ positions (the eigenfrequencies of matter vibrations).

(ii) parameters acting on the “charge transfer” (iono-covalency, band structure, electronic insertion) will set intensity, on the basis of the vibration-induced charge variations occurring at the very bond scale.

**Fig. 4.4.** Mechanisms of normal and resonance Raman scattering: S: stokes, A: anti-Stoke, The dashed lines represents the virtual state. The shaded areas indicate the broadening of rotational-vibrational levels [Nakamoto 1986].

Figure 4.4 illustrates the mechanism of normal and resonance Raman (RR) scattering. In the former, the energy of the exciting line falls far below that required to excite the first electronic transition. In the latter, the energy of the exciting line coincides with that of an electronic transition. If the photon is absorbed and then emitted during the process, it is called resonance fluorescence (RF). Although the conceptual difference between resonance Raman scattering and resonance fluorescence is subtle, there are several experimental differences which can be used to distinguish between these two phenomena. For example, in RF spectra all lines
are depolarized, whereas in RR spectra some are polarized and others are depolarized. Additionally, RR bands tend to be broad and weak compared with RF bands. In the case of Stokes lines, the molecule at $\nu = 0$ is excited to the $\nu = 1$ state by scattering light of frequency $\nu - \nu_1$. Anti-Stokes lines arise when the molecule initially in the $\nu = 1$ state scatters radiation of frequency $\nu + \nu_1$ and reverts to the $\nu = 0$ state. Since the population of the molecule is larger at $\nu = 0$ than $\nu = 1$ (Maxwell-Boltzmann distribution law), the Stokes lines are always stronger than the anti-Stokes lines.

According to the selection rule for the harmonic oscillator, any transitions corresponding to $\Delta \nu = \pm 1$ are allowed. Under ordinary conditions, however, only the fundamentals that originate in the transition from $\nu = 0$ to $\nu = 1$ in the electronic ground state can be observed because of the Maxwell-Boltzmann distribution law. In addition to the selection rule for the harmonic oscillator, another restriction results from the symmetry of the molecule. Thus the number of allowed transitions in polyatomic molecules is greatly reduced. The overtones and combination bands of these fundamentals are forbidden by the selection rule of the harmonic oscillator. However, they are weakly observed in the spectrum because of the anharmonicity of the vibration.

4.1.3 **Introduction to group theory.**

Group theory is a useful mathematical tool which is required to understand the symmetry and selection rules of normal vibrations in polyatomic molecules. Let us consider for an example a pyramidal $\text{XY}_3$ molecule (Fig. 4.5) for which the symmetry operations $I, C_3^+, C_3^-, \sigma_1, \sigma_2$ and $\sigma_3$ are applicable. Here $C_3^+$ and $C_3^-$ denote rotation through $120^\circ$ in the clockwise and counter clockwise directions, respectively, and $\sigma_1, \sigma_2$ and $\sigma_3$ indicate the symmetry planes that pass through $X$ and $Y_1$, $X$ and $Y_2$, and $X$ and $Y_3$, respectively. For simplicity, let these symmetry operations be denoted by $I, A, B, C, D$, and $E$, respectively. Other symmetry operations are possible, but each is equivalent to some one of the operations mentioned. For instance, a clockwise rotation through $240^\circ$ is identical with
operation $B$. It may also be shown that two successive applications of any one of these operations are equivalent to some single operation of the group mentioned. Let operation $c$ be applied to the original figure. This interchanges $Y_2$ and $Y_3$. If operation $A$ is applied to the resulting figure, the net result is the same as application of the signal operation $D$ to the original figure. This is written as $CA = D$. If all the possible multiplicative combinations are made, Table 4.1, in which the operation applied first is written across the top, is obtained. This is called the multiplication table of the group.

![Image](image.png)

**Fig. 4.5** Pyramidal $XY_3$ molecules.

It is seen that a group consisting of the mathematical elements (symmetry operations) $I, A, B, C, D,$ and $E$ satisfied the following conditions:
1. The product of any two elements in the set is another element in the set.
2. The set contains the identity operation that satisfies the relation $IP = PI = P$, where $P$ is any element in the set.
3. The associative law holds for all the elements in the set, that is, $(CB)A = C(AB)$, for example.
4. Every element in the set has its reciprocal, $X$, which satisfies the relation $XP = PX = I$, where $P$ is any element in the set. This reciprocal is denoted by $P^{-1}$.

These are necessary and sufficient conditions for a set of elements to form a group. It is evident that operations $I, A, B, C, D,$ and $E$ form a group in this sense. It should be noted that the commutative law of multiplication does not necessarily hold. For example, Table 4.1 shows that $CD \neq DC$. 

94
The six elements can be classified into three types of operations: the identity operation I, the rotations $C_3^+$ and $C_3^-$, and the reflections $\sigma_1$, $\sigma_2$ and $\sigma_3$. Each of these sets of operations is said to form a class. More precisely, two operations P and Q, which satisfy the relation $X^{-1}PX = P$ or $Q$, where X is any operation of the group and $X^{-1}$ is its reciprocal, are said to belong to the same class. It can easily be shown that $C_3^+$ and $C_3^-$, for example, satisfy the relation. Thus, the six elements of the point group $C_{3v}$ are abbreviated as I, 2$C_3$ and 3$\sigma_v$.

Table 4.1 Multiplication table of the group

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>B</td>
<td>I</td>
<td>D</td>
<td>E</td>
<td>C</td>
</tr>
<tr>
<td>B</td>
<td>B</td>
<td>I</td>
<td>A</td>
<td>E</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>C</td>
<td>C</td>
<td>E</td>
<td>D</td>
<td>I</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>D</td>
<td>D</td>
<td>C</td>
<td>E</td>
<td>A</td>
<td>I</td>
<td>B</td>
</tr>
<tr>
<td>E</td>
<td>E</td>
<td>D</td>
<td>C</td>
<td>B</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

The relations between the elements of the group are shown in multiplication table, Table 4.1. Such a tabulation of a group theory is, however, awkward to handle. The essential features of the table may be abstracted by replacing the elements by some analytical function that reproduces the multiplication table. Such an analytical expression may be composed of a simple integer, an exponential function, or a matrix. Any set of such expressions that satisfies the relations given by the multiplication table is called a representation of the group and is designated by $\Gamma$. The representations of the point group $C_{3v}$ discussed above are indicated in Table 4.2. It is easily proved that each representation in the table satisfies the multiplication table.
In addition to the three representations in Table 4.2, it is possible to write an infinite number of other representations of the group. If a set of six matrices of the type $S^{-1}R(K)S$ is chosen, where $R(K)$ is a representation of the element $K$ given in Table 4.2, $S (|S| \neq 0)$ is any matrix of the same order as $R$, and $S^{-1}$ is the reciprocal of $S$, this set also satisfies given by the multiplication table. The reason is obvious from the relation

$$S^{-1}R(K)SS^{-1}R(L)S = S^{-1}R(K)R(L)S = S^{-1}R(KL)S$$

(4.9)

Such a transformation is called a similarity transformation. Thus it is possible to make an infinite number of representations by means of similarity transformations.

**Table 4.2 Representations of the point group $C_{3v}$ by matrix**

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$A_{1}(\Gamma_1)$</th>
<th>$A_{2}(\Gamma_2)$</th>
<th>$A_{3}(\Gamma_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
<td>$\left(\begin{array}{cc} 1 &amp; 0 \ 0 &amp; 1 \end{array}\right)$</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>1</td>
<td>$\left(\begin{array}{cc} -\frac{1}{2} &amp; 0 \ 0 &amp; -\frac{1}{2} \end{array}\right)$</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>-1</td>
<td>$\left(\begin{array}{cc} 1 &amp; 0 \ 0 &amp; 1 \end{array}\right)$</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>-1</td>
<td>$\left(\begin{array}{cc} 1 &amp; 0 \ 0 &amp; 1 \end{array}\right)$</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>-1</td>
<td>$\left(\begin{array}{cc} 1 &amp; 0 \ 0 &amp; -1 \end{array}\right)$</td>
</tr>
</tbody>
</table>


On the other hand, this statement suggests that a given representation may be broken into simpler ones. If each representation of the symmetry element $K$ is transformed into the form

$$
R(K) = \begin{bmatrix}
Q_1(K) & 0 & 0 & 0 \\
0 & Q_2(K) & 0 & 0 \\
0 & 0 & Q_3(K) & 0 \\
0 & 0 & 0 & Q_4(K)
\end{bmatrix}
$$

(4.10)

by similarity transformation, $Q_1(K)$, $Q_2(K)$, … are simpler representations. In such a case, $R(K)$ is called reducible. If a representation cannot be simplified any further, it is said to be irreducible. The representations, $\Gamma_1$, $\Gamma_2$ and $\Gamma_3$ in Table 4.2 are all irreducible representations. It can be shown generally that the number of irreducible representations is equal to the number of classes. Thus only three irreducible representations exist for the point group $C_{3\nu}$. These representations are entirely independent of each other. Furthermore, the sum of the squares of the dimensions ($l$) of the irreducible representations of a group is always equal to the total number of the symmetry elements, namely, the order of the group ($h$). Thus

$$\sum l_i^2 = l_1^2 + l_2^2 + \cdots = h
$$

(4.11)

In the point group $C_{3\nu}$, it is seen that

$$1^2 + 1^2 + 2^2 = 6
$$

(4.12)

A point group is classified into species according to its irreducibility representations. In the point group $C_{3\nu}$, the species having the irreducible representations $\Gamma_1$, $\Gamma_2$, and $\Gamma_3$ are called the $A_1$, $A_2$ and $E$ species, respectively.

The sum of the diagonal elements of a matrix is called the character of the matrix and is denoted by $\chi$. It is to be denoted in Table 4.2 that the character of each of the elements belonging to the same class is the same. Thus, using the character, Table 4.2 can be simplified to Table 4.3. Such a table is called the character table of the point group $C_{3\nu}$.
Table 4.3 The character table of the point group $C_{3v}$

<table>
<thead>
<tr>
<th></th>
<th>$I$</th>
<th>$2C_3(z)$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1(\chi_1)$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2(\chi_2)$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E(\chi_3)$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

4.1.4 Symmetry of normal vibrations and selection rules

Fig. 4.6 indicates the normal modes of vibration in a linear and a bent molecule. In each normal vibration, the individual nuclei carry out a simple harmonic motion in the direction indicated by the arrow, and all the nuclei have the same frequency of oscillation (i.e., the frequency of the normal vibration) and are moving in the same phase. Furthermore, the relative lengths of the arrows indicate the relative velocities and amplitudes for each nucleus (in this respect, all the normal modes of vibration shown are only approximate). The $\nu_2$ vibrations in CO$_2$ are worth comment, since they differ from the others in that two vibrations ($\nu_{2a}$ and $\nu_{2b}$) have exactly the same frequency. Apparently, there are infinite numbers of normal vibrations of this type, which differ only in their directions perpendicular to the molecular axis. Any of them, however, can be resolved into two vibrations such as $\nu_{2a}$ and $\nu_{2b}$, which are perpendicular to each other. In this respect, the $\nu_2$ vibrations in CO$_2$ are called **doubly degenerate vibrations**. Doubly degenerated vibrations occur only when a molecule has an axis higher than twofold. **Triply degenerated vibrations** also occur in molecules having more than one $C_3$ axis.

The symmetry properties of the normal vibrations of the H$_2$O molecule shown in Fig. 4.6 are classified as indicated in Table 4.4. Here, +1 and -1 denote symmetric and antisymmetric, respectively. In the $\nu_1$ and $\nu_2$ vibrations, all the symmetry properties are preserved during the vibration. Therefore, they are symmetric vibrations and are called, in principle, **totally symmetric vibrations**. In the $\nu_3$ vibration, however, symmetry elements such as $C_2$ and $\sigma_v(xz)$ are lost. Thus it
is called \textit{nonsymmetric vibration}. If a molecule has a number of symmetry elements the normal vibrations are classified as various species according to the number and the kind of symmetry elements preserved during the vibration.

\begin{table}[h]
\centering
\caption{The symmetry properties of the normal vibrations of the H$_2$O molecule.}
\begin{tabular}{|c|c|c|c|c|}
\hline
C$_{2v}$ & I & C$_2$(z) & $\sigma_{\nu}(xz)$ & $\sigma_{\nu}(yz)$ \\
\hline
Q$_1$, Q$_2$ & +1 & +1 & +1 & +1 \\
Q$_3$ & +1 & -1 & -1 & +1 \\
\hline
\end{tabular}
\end{table}

\textbf{Fig 4.6.} Normal modes of vibration in CO$_2$ and H$_2$O molecules. (+ and – denote vibrations going upward and downward, respectively, in the direction perpendicular to the paper plane) [Nakamoto 1986].

To determine the activity of vibrations in the infrared and Raman spectra, the selection rule must be applied to each normal vibration. From a quantum mechanical point of view, a vibration is active in the infrared spectrum if the dipole moment of the molecule is changed during the vibration, and is active in the Raman spectrum if the polarizability of the molecule is changed during the vibration. As was already mentioned, the induced dipole moment $P$ is related to the strength of the electric field $E$ by the Eq. 4.5. If we resolve $P$, $\alpha$ and $E$ in the $x$, $y$ and $z$ directions, simple relationships such as

$$P_x = \alpha_x E_x, \quad P_y = \alpha_y E_y \quad \text{and} \quad P_z = \alpha_z E_z$$

(4.13)
do not hold, since the direction of polarization does not coincide with the direction of applied field. This is so, because the direction of chemical bonds in the molecule also affects the polarization. Thus, instead of Eq. 4.13 we have the relationships:

\[ P_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \]  
\[ P_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \]  
\[ P_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z. \]  

In matrix form, eqs. 4.14a-4.14c is written as:

\[
\begin{bmatrix}
P_x \\
P_y \\
P_z
\end{bmatrix} =
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
\]

and the first matrix on the right-hand side is called the polarizability tensor. In normal Raman scattering, the tensor is symmetric; \(\alpha_{xy} = \alpha_{yx}, \alpha_{yz} = \alpha_{zy},\) and \(\alpha_{xz} = \alpha_{zx}\). This is not so, however, in the case of resonance Raman scattering.

According to quantum mechanics, the vibration is Raman active if one of these six components of the polarizability changes during the vibration. Similarly, it is infrared active if one of the three components of the dipole moment \((\mu_x, \mu_y,\) and \(\mu_z)\) changes during the vibration. Changes in dipole or polarizability are not obvious from inspection of the normal modes of vibration in most polyatomic molecules.

In simple molecules, however, the activity of a vibration may be determined by inspection of the normal mode. For example, it is obvious that the vibration in a homonuclear diatomic molecule is not infrared active but is Raman active, whereas the vibration in a heteronuclear diatomic molecule is both infrared and Raman active. It is also obvious that all three vibrations of \(\text{H}_2\text{O}\) and \(\nu_2\) and \(\nu_3\) of \(\text{CO}_2\) are infrared active. Except for \(\nu_1\) of \(\text{CO}_2\), the Raman activity is not easy to predict even for such simple molecules.

The polarizability tensor can be visualized easily if we draw a polarizability ellipsoid by plotting \(1/\sqrt{\alpha}\) in any direction from the origin. This gives a three-dimensional surface such as is shown in Fig. 4.7. If we orient this ellipsoid with its principal axes along the \(X, Y, Z\) axes of the coordinate system, Eq. 4.15 is simplified to
These three axes are called the principal axes of polarizability. In terms of the polarizability ellipsoid, the Raman selection rule can be stated as follows: The vibration is Raman active if the ellipsoid changes in size, shape, or orientation during the vibration. Consider the $\nu_1$ vibration of CO$_2$. As shown in Fig. 4.7, the ellipsoid changes its size during this vibration (or $\alpha_{xx}$, $\alpha_{yy}$, and $\alpha_{zz}$ change during the vibration). Thus it is Raman active. Although the size of the ellipsoid changes during the $\nu_3$ vibration, they are identical in two extreme positions, as shown in Fig. 4.7. If we consider a limiting case where the nuclei undergo very small displacement, there is effectively no change in the polarizability; hence the $\nu_3$ vibration is not Raman active. The same is true for the $\nu_2$ vibration.

In the case of H$_2$O, both the $\nu_1$ and $\nu_2$ vibrations are Raman active because the size and the shape of the ellipsoid change during these vibrations. The $\nu_3$ vibration of H$_2$O is different from the other vibrations in that the orientation of the ellipsoid changes ($\alpha_{xy}$ changes) during the vibration. Thus all three normal vibrations of H$_2$O are Raman active.

It should be noted that in CO$_2$ the vibration symmetric with respect to the center of symmetry ($\nu_1$) is Raman active and not infrared active, whereas the vibrations antisymmetric with respect to the center of the symmetry ($\nu_2$ and $\nu_3$) are infrared active but not Raman active. In a polyatomic molecule having a center of symmetry, the vibrations symmetric with respect to the center of symmetry (g vibrations) are Raman active and not infrared active, but the vibrations antisymmetric with respect to the center of symmetry (u vibrations) are infrared active and not Raman active. This rule is called the mutual exclusion rule. It should be noted, however, that in polyatomic molecules having several symmetry elements in addition to the center of symmetry, the vibrations that should be active according to this rule may not necessarily be active, because of the presence of other symmetry elements. An example is seen in a square-planar XY$_4$-type molecule of
D$_{4h}$ symmetry, where the $A_{2g}$ vibrations are not Raman active and the $A_{1u}$, $B_{1u}$, and $B_{2u}$ vibrations are not infrared active.

Fig. 4.7. Change of polarizability ellipsoid during the normal vibrations of CO$_2$ and H$_2$O [Nakamoto 1986].

4.1.5 Depolarization of Raman lines

Experimentally, measurements of the infrared dichroism and polarization properties of Raman lines of an orientated crystal provide valuable information about the symmetry of normal vibrations. Here we consider the polarization properties of Raman lines in liquids and solutions in which molecules or ions take completely random orientations.

Suppose that we irradiate a molecule fixed at the origin of a space-fixed coordinate system with natural light from positive-$y$ direction, and observe the Raman scattering in the $x$ direction as shown in Fig. 4.8. The incident light vector $E$ may be resolved into components, $E_x$ and $E_z$, of equal magnitude ($E_y = 0$). Both components give induced dipole moments, $P_x$, $P_y$, and $P_z$. However, only $P_y$ and $P_z$
contribute to the scattering along the $x$ axis, since an oscillating dipole cannot radiate in its own direction. Then, from Eqs. 4.14a-4.14c we have

$$P_y = \alpha_{yx} E_x + \alpha_{yz} E_z$$

$$P_z = \alpha_{zx} E_x + \alpha_{zz} E_z$$

(4.17)  

(4.18)

The intensity of the scattering light is proportional to the sum of squares of the individual $\alpha_j E_j$ terms. Thus the ratio of the intensities in the $y$ and $z$ directions is:

$$\rho_n = \frac{I_y}{I_z} = \frac{\alpha_{yx}^2 E_x^2 + \alpha_{yz}^2 E_z^2}{\alpha_{zx}^2 E_x^2 + \alpha_{zz}^2 E_z^2}$$

(4.19)

where $\rho_n$ is called depolarization ratio.

![Schematic representation of experimental condition for measuring depolarization ratios.]

Fig. 4.8. Schematic representation of experimental condition for measuring depolarization ratios.

In a homogeneous liquid or gas, the molecules are randomly orientated, and we must consider the polarizability components averaged over all molecular orientations. The results are expressed of two quantities: $\bar{\alpha}$ (mean value) and $\gamma$ (anisotropy):
CHAPTER 4: BASIC CONCEPTS FOR TECHNIQUES PROBING THE STRUCTURE AND THERMAL PROPERTIES OF GLASSES

\[
\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\]

(4.20)

\[
\gamma^2 = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2) \right]
\]

(4.21)

These two quantities are invariant to any coordinate transformation. It can be shown that the average values of the squares of \( \alpha_{ij} \) are

\[
\overline{(\alpha_{xx})^2} = \overline{(\alpha_{yy})^2} = \overline{(\alpha_{zz})^2} = \frac{1}{45} \left[ 45(\bar{\alpha})^2 + 4\gamma^2 \right]
\]

(4.22)

\[
\overline{(\alpha_{xy})^2} = \overline{(\alpha_{yz})^2} = \overline{(\alpha_{zx})^2} = \frac{1}{15} \gamma^2
\]

(4.23)

Since \( E_x = E_z = E \), Eq. 4.19 can be written as

\[
\rho_n = \frac{l_y}{l_z} = \frac{6\gamma^2}{45(\bar{\alpha})^2 + 7\gamma^2}
\]

(4.24)

The total \( I_n \) is given by

\[
I_n = I_y + I_z = const \left\{ \frac{1}{45} \left[ 45(\bar{\alpha})^2 + 13\gamma^2 \right] \right\} E^2
\]

(4.25)

If the incident light is plane polarized (e.g. laser beam), with its electric vector in the \( z \) direction (\( E_x = 0 \)), Eq. 4.24 becomes

\[
\rho_p = \frac{l_y}{l_z} = \frac{3\gamma^2}{45(\bar{\alpha})^2 + 4\gamma^2}
\]

(4.26)

where \( \rho_p \) is the depolarization ratio for polarized light (\( p \)). In this case, the total intensity is given by

\[
I_p = I_y + I_z = const \left\{ \frac{1}{45} \left[ 45(\bar{\alpha})^2 + 7\gamma^2 \right] \right\} E^2.
\]

(4.27)

The symmetry property of a normal vibration can be determined by measuring the depolarization ratio. From an inspection of character table, it is obvious that \( \bar{\alpha} \) is nonzero only for totally symmetric vibrations. Then Eq. 4.24 gives \( 0 \leq \rho_n < \frac{6}{7} \), and the Raman lines are said to be polarized. For all nontotally symmetric vibrations, \( \bar{\alpha} \) is zero, and \( \rho_n = \frac{6}{7} \). Then the Raman lines are said to be depolarized. If the exciting line is plane polarized, these criteria must be changed according to Eq. 4.26. Thus 0
≤ ρ_p < \frac{3}{4} \text{ for totally symmetric vibrations, and } \rho_p = \frac{3}{4} \text{ for nontotally symmetric vibrations. Fig. 4.9 shows the Raman spectra of CCl}_4\text{ (500 - 150 cm}^{-1}\text{) in two directions of polarization obtained with the 488 nm excitation. The three bands at 459, 314, and 218 cm}^{-1}\text{ give } \rho_p \text{ values of approximately 0.01, 0.75, and 0.75, respectively. Thus it is concluded that the 459 cm}^{-1}\text{ band is polarized } (A_1), \text{ whereas the two bands at 314 } (F_2) \text{ and 218 cm}^{-1}\text{ (E) are depolarized.}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{raman_spectra}
\caption{Raman spectra of CCl}_4\text{ (500 - 150 cm}^{-1}\text{) in two directions of polarization (488 nm excitation, 1.5 cm}^{-1}\text{ resolution).}
\end{figure}

The polarizability tensors are symmetric in normal Raman scattering. If the exciting frequency approaches that of an electronic absorption, some scattering tensors become antisymmetric. A tensor is called antisymmetric if \(\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = 0\) and \(\alpha_{xy} = -\alpha_{yx}, \alpha_{yz} = -\alpha_{zy},\text{ and } \alpha_{zx} = \alpha_{xz}\). In this case resonance Raman scattering can occur and Eq. 4.26 must be written in a more general form [Spiro 1972]:

\begin{align*}
\alpha_{\text{res}} &= \alpha_{\text{norm}} + \alpha_{\text{int}} \\
\alpha_{\text{int}} &= \sum \frac{\mu_i^2}{\rho_i^2} \delta \omega
\end{align*}
where

\[ g^o = 3(\bar{a})^2 g^s = \frac{1}{3} \left[ (a_{xx} - a_{yy})^2 + (a_{xx} - a_{zz})^2 + (a_{yy} - a_{zz})^2 \right] \]
\[ \quad + \frac{1}{2} \left[ (a_{xy} + a_{yx})^2 + (a_{xz} + a_{zx})^2 + (a_{yz} + a_{zy})^2 \right] \]  
(4.29)

\[ g^a = \frac{1}{2} \left[ (a_{xy} - a_{yx})^2 + (a_{xz} - a_{zx})^2 + (a_{yz} - a_{zy})^2 \right] \]

If we define

\[ \gamma_s^2 = \frac{3}{2} g^s \text{and} \gamma_{as}^2 = \frac{3}{2} g^a \]  
(4.30)

Eq. 4.28 can be written as

\[ \rho_p = \frac{3\gamma_s^2 + 5\gamma_{as}^2}{10g^o + 4g^s} \]  
(4.31)

In normal Raman scattering, \( \gamma_s^2 = \gamma^2 \) and \( \gamma_{as}^2 = 0 \). Then the Eq. 4.31 is reduced to Eq. 4.26.

The symmetry properties of resonance Raman lines can be predicted on the basis of Eq. 4.31. For totally symmetric vibrations, \( \bar{a} \neq 0 \) and \( \gamma_{as} = 0 \). Then Eq. 4.31 gives \( 0 \leq \rho_p < \frac{3}{4} \). Nontotally symmetric vibrations (\( \bar{a} = 0 \)) are classified into two types: those which have symmetric scattering tensor, and those which have antisymmetric scattering tensors. If the tensor is symmetric, \( \gamma_{as} = 0 \) and \( \gamma_s \neq 0 \). Then the Eq. 4.31 gives \( \rho_p = \frac{3}{4} \) (depolarized). If the tensor is antisymmetric, \( \gamma_{as} \neq 0 \) and \( \gamma_s = 0 \). Then the Eq. 4.31 gives \( \rho_p = \infty \) (inverse polarization). In the case of the \( D_{4h} \) point group, the \( B_{1g} \) and \( B_{2g} \) representations belong to the former type, whereas the \( A_{2g} \) representation belongs to the latter [McClain 1971].

### 4.2 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) is a thermal analysis technique in which a difference in heat flow between a sample and an inert reference (see Fig. 4.10) is measured as a function of time and temperature as both the sample and the
reference are subjected to a controlled environment (pressure, purge gas). DSC measurements provide qualitative and quantitative information regarding *phase transitions* in materials that invoke endothermic processes, or changes in heat capacity. It is applicable to a variety of materials including polymers, pharmaceuticals, foods and inorganics. Some of the advantages contributing to the widespread usage of DSC are the ease of sample preparation, the applicability to both solids and liquids, fast analysis time and wide temperature range.

In conventional thermal analysis, the sample temperature is either ramped linearly at a constant heating or cooling rate or kept constant (as in isothermal experiments). Total heat flow is the quantity that is available and hence it is the only quantity that is always measured in conventional DSC experiments \[\text{van Herwaarden 1999}\] and it is described by the eq. 4.41:

\[
\frac{dQ}{dt} = C_p b + f(T, t)
\]  

(4.41)

where \(\frac{dQ}{dt}\) : resultant heat flow, \(C_p\) : heat capacity of the sample, \(b\) : rate of temperature change \(\left(\frac{dT}{dt}\right)\) and \(f(T, t)\) : heat flow from kinetic processes.

Fig. 4.10. A typical set-up for DSC.
To increase the sensitivity (i.e. signal–to-noise) for the detection of a weak transition either the sample mass or the scan rate can be increased. For obtaining a better resolution in separating transition occurring at close temperatures, either smaller samples are used or the scan rate is lowered. So, increased sensitivity is always at the expense of the resolution and vice versa.

**Drawbacks that characterized the conventional DSC are:**

- Difficulty in the interpretation of the DSC thermograms, when multiple processes are involved over the same temperature range. In a single component material, different types of transitions can overlap such as, for example, melting and recrystallization in a semi-crystalline material and changes in heat capacity during the exothermic cure reaction of a thermoset. In a multicomponent material, transitions of the different compounds can overlap.

- It is not always straightforward to identify the nature of a transition: an enthalpic relaxation peak superimposed on the heat capacity variation at the glass transition temperature can be so large that the transition is confused with a melting transition.

- The detection of the weak transitions is strongly influenced by the baseline curvature and stability. The determination of a small jump in heat capacity, for example, is much more difficult when it is superimposed on a curved baseline than if the baseline is straight. Often the baseline is not straight due to, for example, moisture evaporation from the sample, variations in thermal contact between the sample and the DSC pans during the scan and overall baseline characteristics of the specific DSC cell. Some quantities such as the absolute value of the material’s heat capacity and its thermal conductivity cannot determined straightforwardly with DSC and requires multiple experiments. Moreover, the heat capacity cannot be determined in an isothermal experiment with DSC [Verdonck 1999].

Recently a greatly enhanced version of the DSC method called *temperature modulated differential scanning calorimetry* (MDSC) has been introduced [Reading (a) 1993, Reading (b) 1993]. The MDSC method incorporates not only the capability of conventional DSC but it also provides significant and distinct advantages over
traditional DSC. The benefits of MDSC technique includes: increased resolution and sensitivity for the detection of weak transitions, separation of complex transitions into easily interpreted components, measurements of heat flow and heat capacity in a single experiment, ability to determine more accurately the initial crystallinity of the studied materials, measurement of thermal conductivity [Wagner 1996].

In contrast to conventional DSC method, in MDSC, the sample temperature is modulated sinusoidally about a constant ramp so that the temperature, $T$, at time $t$ is

$$T = T_0 + rt + A \sin\left(\frac{2\pi t}{P}\right)$$

(4.42)

where $T_0$: starting temperature, $r$: the heating rate (or a cooling ramp, $q$), $A$: the amplitude of the modulation and $P$ the period. The average heating rate, corresponding to the rate for a conventional DSC experiment, is called the underlying heating rate. The modulated heating rate, $dT/dt$, varies between a minimum and a maximum value; these are determined by the value of the underlying heating rate, the period (or frequency) and the amplitude of the superimposed temperature wave. Depending on the combination of these three parameters, the minimum modulated heating rate is positive (heat-only), zero (heat-isothermal), or negative (heat-cool). Resultant heat flow is composed of two components:

(i) reversing heat flow (RHF) component which is a function of the sample’s heat capacity and rate of temperature change;

(ii) non-reversing heat flow (NHF) component that is a function of absolute temperature and time.

Since the reversing component is related to the sample’s heat capacity a glass transition event is detected in the reversing heat flow. On the other hand processes such as enthalpic relaxation, crystallization, evaporation, decomposition, and cure are resolved into the non-reversing heat flow. For a melting transition the interpretation is not straightforward. Melting can occur in the reversing heat flow as well as in the non-reversing heat flow, and moreover the fraction of melting in both
of these signals depends on the experimental conditions (underlying heating rate, modulation period, modulation amplitude, sample thickness) [Verdonck 1999].

**Fig. 4.11** (a) Deconvoluted signals (total heat flow, reversing heat flow, non-reversing heat flow) for the MDSC heating experiment of a quenched polyethylene terephthalate (PET) sample. (b) Modulated heating rate (input) and modulated heat flow (output) for the MDSC heating experiment of a quenched PET sample [Verdonck 1999].
A good example [Verdonck 1999] of the additional information obtained from MDSC is illustrated in Fig. 4.11 (a), where conventional DSC and MDSC studies of quenched polyethylene terephthalate (PET) is presented. The conventional DSC signal (equivalent to the total heat flow from the MDSC experiment) subsequently shows the glass transition, the cold crystallization exotherm, and the melting of the formed crystals. In the region between crystallization and melting the heat flow seems to return to its baseline. However, when looking at the reversing and non-reversing components, it becomes clear that in this region endothermic melting (displayed in the reversing heat flow) and exothermic (re)crystallization (displayed in the non-reversing heat flow) compete, resulting in a net ‘zero’ effect in the total heat flow. In this example, the experimental parameters are chosen to provide a heat-isothermal modulated heating rate profile. At the moment that the modulated heating rate is zero, the heat flow is entirely due to kinetic processes (see Eq. 4.41, with $b = 0$). The heat flow at the lowest heating rate (zero in this case) is in fact the top of the modulated heat flow signal (Fig. 4.11 (b)). The kinetic process of (re)crystallization during heating can thus also be verified from the top of the modulated heat flow in Fig. 4.11 (b). This example illustrates the ability of MDSC to gain more insight into the crystalline structure of semi-crystalline polymers. Moreover, from the total heat flow it is difficult to calculate the initial crystallinity (i.e. crystallinity at room temperature, prior to heating) of the sample, because it is not clear how to choose the baseline for peak integration. In essence one needs to compare the enthalpies of crystallization and melting.

4.3 SCANNING ELECTRON MICROSCOPY

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals, that are derive from electron-sample interactions, include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted
backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence--CL), and heat.

Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly [Swapp].

**Fig. 4.12** Scanning electron microscope
In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20x to approximately 30,000x, spatial resolution of 50 to 100 nm) [Swapp].

The electron gun thermionically emits electrons with energies up to 40 keV (Fig. 4.12). The electrons are focused by condenser lenses to a spot about 0.4nm to 5nm in diameter. This primary beam then passes through scan coils, which deflect the beam so that it scans in a raster fashion over the area of sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by random scattering and absorption in specimen, extending from about 100 nm to 5µm into the sample. This depth depends on the electron energy, the atomic number of the specimen and the density of the specimen. The energy exchange between the electrons and sample results in the reflection of electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation. Each of those can be detected by specialized detectors.

4.4 X-RAY DIFFRACTION.

In analogy to liquids and gases, amorphous solids irradiated by monochromatic X-rays shows a diffraction pattern that can be described by a distribution function of the scattered intensity, depending on the angular variable $s = 4\pi \sin \theta / \lambda$ [Feltz 1993]. The intensity at a given angle results from a superposition of those wave fronts that are diffracted at all atoms of the specimen into a defined direction, and it contains information on the distribution of distances between the scattering particles in the substance concerned.

The intensity function is expressed by Debye’s sum formula:
Here: $r_{mn}$ stands for the magnitude of the distance vector between atoms $m$ and $n$, $f_m$ and $f_n$ are the scattering amplitude functions of atoms $m$ and $n$.

If the sample has $N$ equal atoms in identical environments, Eq. 4.43 can be reduced as follows:

$$ I = N f^2 \sum_m \cos \frac{s r_{mn}}{sr_{mn}} $$ (4.44)

With the approximation $sr_{mn} \to 0, \cos \frac{s r_{mn}}{sr_{mn}} \to 1$, and with the introduction of the density function $\rho(r)$, this leads to

$$ I = N f^2 \left[ 1 + \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin sr}{sr} dr \right] $$ (4.45)

$g(r)$ is the volume density of atoms at distance $r$ from the reference atom, and $4\pi r^2 \rho(r) dr$ is the number of atoms in a spherical shell of radius $r$ and thickness $dr$.

Introducing $\rho_0$, the average density of atoms in the sample investigated, the second integral in the equation

$$ I = N f^2 \left\{ 1 + \int_0^\infty 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin sr}{sr} dr + \int_0^\infty 4\pi r^2 \rho_0 \frac{\sin sr}{sr} dr \right\} $$ (4.46)

can be neglected in the range of values of $s$ acquired in a wide angle measurement.

Application of Fourier’s integral theorem eventually leads to

$$ 4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty s \left( \frac{1}{Nf^2} - 1 \right) \sin sr ds $$ (4.47)

The radial distribution function (RDF) can be determined by calculating the integral over the limits of measured values $s$.

Fig. 4.13 shows the radial distribution function for vitreous selenium according to [Krebs 1964]. The averaged curve $4\pi r^2 \rho_0$ describes the distribution that would result if the substance were a hypothetical continuum without an atomic structure. In this case all the distances between the scattering particles, which are assumed to be of point form, would occur in a random distribution. The deviation of the RDF from this averaged curve contains the structural information. It can be that there is no distance between two atoms smaller than the chemical bond length. The integral of the area of the first maximum gives the number of particles in the first coordination sphere, and thus yields information on the short-range order.
number of atoms in the present case is two, so that a chain-like linkage and, consequently, a short-range order can be inferred, which is comparable with the structure of crystalline selenium. The second maximum too can be interpreted in a relatively unambiguous way. The bond length between a particular selenium atom and the adjacent four atoms, which in crystalline selenium belongs to three selenium chains in the immediate vicinity, is extended in selenium glass to the van der Waals distance, which happens to coincide with the two next but one distances in the same chain, so that this region contains six atoms altogether. However for more distant maxima, attempts to assign these to specific atomic configurations are subject to increasing ambiguity, owing to the great variety of similar configurations. Consequently, with increasing distance from the reference atom the RDF approximates ever more closely to the averaged curve.

For heteronuclear systems with \( N \) identical structural units, eq. 4.43 leads to

\[
I = N \sum_p f_p^2 + \sum_m \sum_{n \neq m} f_m f_n \frac{\sin \sigma_{mn}}{\sigma_{mn}}
\]

\[ (4.48) \]

Fig. 4.13 Radial distribution function for selenium [Krebs 1964]
CHAPTER 4: BASIC CONCEPTS FOR TECHNIQUES PROBING THE STRUCTURE AND THERMAL PROPERTIES OF GLASSES

The first sum must be calculated for all atoms of a structural unit, while the second covers all atom pairs in the specimen. The distribution of atoms in the vicinity of the reference atom is again regarded as continuous. On the plausible assumption that the numbers of atoms \( m, n \) in the spherical shell with radius \( r \) and thickness \( dr \) are \( a_m \) and \( a_n \) respectively a weighted density function \( 4\pi r^2 \rho_m(r)dr = \sum a_m f_m \) can be defined. This and the above equation lead to

\[
I = N \left[ \sum m f_m^2 + \sum f_m \int_0^\infty 4\pi r^2 \rho_m(r) \frac{\sin sr}{sr} dr \right]
\]  

(4.49)

\( \rho_m(r) \) and \( f_m \) in this expression depend on \( s \), so that of Fourier transformation is not yet possible in this form.

For systems composed of different atoms, an approximation must therefore be introduced. Because of the closely similar \( s \)-dependence of the atomic scattering amplitude functions, this is permissible if the atomic numbers do not differ too much. A multiple of the scattering factor of the free electron is assumed for the scattering amplitude function of each species of atoms. The proportionality factors then represent the effective electron numbers of the atoms:

\[
f_m(s) = K_m f_e(s)
\]  

(4.50)

and the atomic density distribution function \( \rho_m(r) \) can be replaced by an electron density function \( g_m(r) \):

\[
g_m(r) = f_e g_m(r)
\]  

(4.51)

Introducing an average electron density \( g_0 \), and neglecting the small-angle portion of the scattering leads to

\[
\frac{1}{N} - \sum n f_n^2 = 4\pi f_e^2 \int_0^\infty \sum m K_m [g_m(r) - g_0] r^2 \frac{\sin sr}{sr} dr
\]  

(4.52)

and applying Fourier’s integral theorem then gives

\[
4\pi r^2 \sum m K_m g_m(r) = 4\pi r^2 g_0 \sum m K_m + \frac{2r}{\pi} \int_0^\infty s \frac{1}{f_e^2} \sum m f_m^2 \sin sr \, ds
\]  

(4.53)

with the approximation chosen here, the RDF is found to be a representation of \( e^2/r \) as a function of distance \( r \). The expression on the left of the equation, the RDF, can also be described by a set of partial pair functions, which for example, represent the frequency of the distances A-A, A-B, and B-B in the noncrystalline solid \( A_x B_y \). This enables one to investigate the contributions of different
CHAPTER 4: BASIC CONCEPTS FOR TECHNIQUES PROBING THE STRUCTURE AND THERMAL PROPERTIES OF GLASSES

interelement distances to the integral RDF, when attempting to simulate the experimental RDF from distance distributions based on the known bounding properties of the atoms and subassemblies that make up the system.

4.5 EXAFS

EXAFS is another method for structural exploration of amorphous materials [Feltz 1993]. Sayers, Lytle and Stern [Sayers 1972] developed this method by interpreted the fine structure of the X-ray K absorption edge as a structural effect of the environment of the atom concerned.

Fig. 4.14 Difractogramms of \((1-x)WO_3-y\cdot xReO_2\) mixtures (a) XRD spectra (b) Experimental EXAFS \(x(k)k^2\) spectra of the W and Re \(L_3\) edge [Kuzmin 1998].
If the absorption coefficient is denoted by $\alpha$ and the sample thickness by $x$, then

$$\alpha x = \ln(I_0/I)$$  \hspace{1cm} (4.54)

exhibits periodic fluctuations on the high-energy side of the absorption edge (Extended X-ray Absorption Fine Structure), which are related to the arrangement of atoms in the immediate neighborhood of the absorbing atom. This is a special case of electron diffraction, in which a photoelectron with energy

$$E = h\nu_k - E_k$$  \hspace{1cm} (4.55)

$E_k$ is the bonding energy of the K electron) is emitted from the atom in which the absorption event occurs. The electron wave interferes with a partial wave generated by diffraction at the atoms in the immediate neighborhood. This interference is most pronounced in the region of origin of the emission, so that a partial overlap with the wave function of the initial state can be observed. According to this interpretation, the matrix that determines the transition probability for a change in a dipole moment undergoes oscillations depending on the wavelength of the photoelectron, resulting in a corresponding oscillation of the absorption coefficient. Fig. 4.14 reveals the different view of the two diffractogram types $(1-x)WO_{3-y} \cdot xReO_2$ system [Kusmin 1998].

The analytical expression describing the oscillation of the X-ray absorption coefficient can be subjected to a Fourier transformation. This allows the bond distances and coordination number of the first coordination sphere to be determined separately for each atom type.

4.6 Neutron diffraction.

Neutrons are diffracted at the atomic nuclei, whose geometric dimensions are much less than the neutron wavelength [Feltz 1993]. The diffraction intensity is spherically symmetric. In other words, the atomic scattering amplitude functions $f_N$ are independent of the diffraction angle, which greatly facilitates interpretation. The
neutrons used have a wavelength of 0.07 nm, whereas the wavelength of thermal neutrons is about 0.12 nm. The scattering cross-section is relatively small, and consequently larger samples are required than for recording of X-ray scattering curves. Dimensions of some centimetres have been found to be sufficient. Also the measuring time required for plotting neutron scattering curves is relatively long.

On an average, the atomic scattering amplitude functions show a slight increase with the atomic number, in proportion to $Z^{1/3}$. However, the fluctuations from one element to the next, and the differences between various isotopes, are often quite large, and in such cases the contributions of different nuclear species to the scattering intensity can readily be identified, for example by varying the isotopic composition of the sample. Such investigations are very laborious and have as yet been carried out in only a few cases.

### 4.7 Reverse Monte Carlo simulation.

The aim of Reversible Monte Carlo method is to produce a structural model (i.e. an ensemble of atoms, usually referred to as a configuration) which is consistent with one or more sets of experimental data within their errors and subject to a set of constraints. The errors are assumed to be purely statistical and to have a normal distribution [McGreevy 2001].

1. $N$ atoms are placed in a cell with periodic boundary conditions, i.e. the cell is surrounded by images of itself. Normally cubic cells are used but other geometries may be chosen, e.g. to make a supercell of a crystalline unit cell. The cell dimensions should be as equal as possible. The atomic number density should be the same as the experimental value. The positions of the atoms may be chosen randomly; they may have a known crystal structure or they may be taken from a different simulation or model. The combination of atom coordinates and cell geometry/dimensions is known as a configuration.

2. Calculate $C$ the partial radial distribution functions (also known as the pair distribution functions) from the configuration:

$$g_{\alpha\beta}^{C}(r) = \frac{n_{\alpha\beta}^{C}(r)}{4\pi r^2 \rho_{\alpha} \rho_{\beta}}$$  (4.56)
$\rho$ is the atomic number density, $c_\alpha$ is the concentration of atoms type $\alpha$ and $n_{\alpha \beta}^\circ(r)$ is the number of atoms type $\beta$ at a distance between $r$ and $r + dr$ from a central atom of type $\alpha$, averaged over all atoms as centres. Superscript $o$ means ‘old’ and its significance will become clear in the following steps.

(3) Fourier transform $g_{\alpha \beta}^\circ(r)$ to obtain the partial structure factors:

$$A_{\alpha \beta}^\circ(Q) = \rho \int_0^\infty 4\pi r^2 \left( g_{\alpha \beta}^\circ(r) - 1 \right) \frac{\sin qr}{qr} \, dr$$

(4.57)

where $Q$ is the momentum transfer.

(4) Calculate the total structure factor

$$F^\circ(Q) = \sum c_\alpha c_\beta b_\alpha b_\beta \left( A_{\alpha \beta}^\circ(Q) - 1 \right)$$

(4.58)

where $b_\alpha$ is the coherent neutron scattering length for atom type $\alpha$.

(5) Calculate the difference between the measured total structure factor, $F^E(Q)$, and that determined from the configuration, $F^\circ(Q)$:

$$\chi^2_0 = \sum_{i=1}^m \left( F^\circ(Q_i) - F^E(Q_i) \right)^2 / \sigma^2(Q_i)$$

(4.59)

where the sum is over the $m$ experimental points and $\sigma$ nominally represents the experimental error. Note that the minimum $Q_i$-value used should be larger than or equal to $2\pi/L$, where $L$ is the minimum dimension of the configuration.

(6) Move one atom at random; in practice there is a maximum move distance. If any two atoms approach closer than a predefined (cut-off) distance, then the move is rejected, a new atom is chosen and a new move is made.

(7) Calculate the new partial radial distribution function, $g_{\alpha \beta}^\circ(r)$, the new partial structure factors, $A_{\alpha \beta}^\circ(Q)$, the new total structure factor $F^\circ(Q)$, and the difference

$$\chi^2_n = \sum_{i=1}^m \left( F^\circ(Q_i) - F^E(Q_i) \right)^2 / \sigma^2(Q_i)$$

(4.60)

(8) If $\chi^2_n < \chi^2_0$, then the move is accepted, i.e. the ‘new’ configuration becomes the ‘old’ configuration. If $\chi^2_n > \chi^2_0$ it is accepted with probability $\exp\left(- (\chi^2_n - \chi^2_0) / 2 \right)$. Otherwise it is rejected.

(9) Repeat from step 6.
CHAPTER 4: BASIC CONCEPTS FOR TECHNIQUES PROBING THE STRUCTURE AND
THERMAL PROPERTIES OF GLASSES

References of Chapter 4:
Swapp Susan, University of Wyoming, Geochemical Instrumentation and Analysis: http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html
van Herwaarden S., Calorimetry Measurements, CRC Press LLC (1999)
5.1 Sample preparation

5.1.1 Sb$_x$Se$_{100-x}$ (x: 0, 2, 5, 10, 15, 20, 25, 30) glassy system.

Glasses with composition 0 < $x_{\text{Sb}}$ < 30 % were prepared from high purity (99.9999 %) Sb and Se. Appropriate amounts of the elements, of a total mass of ~1.5 g were calculated by using eq. 5.1.

$$A = \frac{A_{\text{at}}A_{\text{mol}}\%}{A_{\text{at}}A_{\text{mol}}\%+B_{\text{at}}B_{\text{mol}}\%+C_{\text{at}}C_{\text{mol}}\%} \times 2.10^{-3} \quad (5.1)$$

where $A$ is the mass of the substance A, $A_{\text{at}}$, $B_{\text{at}}$, $C_{\text{at}}$. – atomic mass of the substances A, B, and C, respectively; $A_{\text{mol}}\%$, $B_{\text{mol}}\%$, $C_{\text{mol}}\%$ – mol fraction of the substances A, B, and C, respectively, in %
The materials were weighted and loaded in silica tubes with 6 mm outside diameter – 4 mm inside diameter in an appointed order, depending on their volatility, molar mass, solid state (species, powder). Silica tubes were thoroughly cleaned by dilute hydrofluoric acid and rinsed several times with triple distilled water. Finally, the tubes were baked by an oxygen-butane flame at 1100 °C in order to enhance their optical quality and to remove impurity inclusions. The Raman cells with the appropriate material amounts were heated under dynamic vacuum at ~200 °C (see Fig. 5.1) for few hours in order to remove traces of humidity and then were sealed under vacuum. The cells were placed in a furnace heated at high temperature with periodic shaking to ensure homogenization before being quenched in water. For the low Sb concentration ($x_{\text{Sb}} = 2, 5 \%$) (see Table 5.1) the melting and quenching cycle was performed once to ensure homogenization and amorphization. For composition $x_{\text{Sb}} = 10, 15, 20$ two cycles of melting and quenching were needed in order to minimize the concentration gradient between the top and the bottom part of the tube. For the two highest compositions $x_{\text{Sb}} = 25$ and $30$, quenching took place from 1000 °C in silica tubes with 4 mm outside diameter – 2 mm inside diameter and to the lower glass-forming ability of these mixtures. Photos of materials from Sb$_x$Se$_{100-x}$ system are shown in Fig. 5.2.
Fig. 5.2 Photos of materials from $\text{Sb}_x\text{Se}_{100-x}$ system.

Table 5.1: Experimental details for sample preparation of the $\text{Sb}_x\text{Se}_{100-x}$ binary system

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Temper. $[^{\circ}\text{C}]$ and time [h] of melting</th>
<th>Temper. $[^{\circ}\text{C}]$ of quenching</th>
<th>Temper. $[^{\circ}\text{C}]$ and time [h] of annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$ in $\text{Sb}<em>x\text{Se}</em>{100-x}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>400$^{\circ}$/2 h</td>
<td>400$^{\circ}$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1) 730$^{\circ}$/17 h</td>
<td>650$^{\circ}$</td>
<td>55$^{\circ}$/2 h</td>
</tr>
<tr>
<td>5</td>
<td>1) 700$^{\circ}$/2.5 h</td>
<td>700$^{\circ}$, waiting 5s</td>
<td>62$^{\circ}$/1.5 h</td>
</tr>
<tr>
<td>10</td>
<td>1) 700$^{\circ}$/3h</td>
<td>1) 700$^{\circ}$, waiting 5s</td>
<td>2) 740$^{\circ}$</td>
</tr>
<tr>
<td></td>
<td>2) 740$^{\circ}$/15 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1) 715$^{\circ}$/3.5h</td>
<td>1) 715$^{\circ}$/2$^\text{h}$</td>
<td>Small piece 45$^{\circ}$/1.5h</td>
</tr>
<tr>
<td></td>
<td>2) 760$^{\circ}$</td>
<td>2) 760$^{\circ}$</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1) 715$^{\circ}$/245</td>
<td>1) 715$^{\circ}$/2$^\text{h}$</td>
<td>765$^{\circ}$</td>
</tr>
<tr>
<td></td>
<td>2) 765$^{\circ}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>In 6-4 mm cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1) 590$^{\circ}$/14h</td>
<td>650$^{\circ}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>→750$^{\circ}$ →650$^{\circ}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>In 4-2 mm cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1) 620$^{\circ}$/18h →800$^{\circ}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2) 950$^{\circ}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3) 1000$^{\circ}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>In 6-4 mm cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1) 650$^{\circ}$/20$^{\text{h}}$ →750$^{\circ}$/1$^3$</td>
<td>750$^{\circ}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2) 825$^{\circ}$/3h</td>
<td>825$^{\circ}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In 4-2 mm cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1) 624$^{\circ}$/22h</td>
<td>810$^{\circ}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2) 1000</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>
5.1.2 As\textsubscript{x}Se\textsubscript{100-x} (x: 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 57, 60, 65, 70) glasses.

Appropriate amounts of the substances, calculated by following eq. 5.1, were weighted and prepared from high purity (99.9999 %) As and Se. Because of their toxic nature, the weighting took place in a Glove Box, (Braun, model MB 200) (Fig. 5.3).

![Glove Box, model MB 200](image)

Fig. 5.3 *Glove Box, model MB 200*

Then materials were loaded in previously cleaned silica tubes. The lasts were bathing with dilute hydrofluoric acid, washed out with triple distilled water, degassed by flame to remove traces of humidity and sealed under vacuum. Then the ampoules were placed in a furnace in which the temperature was raised up to 650-700 °C (which is above their liquidus). At that temperature the materials were melted and kept for 20 h with periodic shaking to ensure homogenization (*Table 5.2*). Afterwards ampoules were quenched in water and annealed at temperature, which depends on their glass-transition temperature. Photos of materials from this system may be seen in Fig. 5.4.
Fig. 5.4 Photos of materials from $\text{As}_x\text{Se}_{100-x}$ system.

Table 5.2: Experimental details for sample preparation of the $\text{As}_x\text{Se}_{100-x}$ binary system

<table>
<thead>
<tr>
<th>$x$ in $\text{As}<em>x\text{Se}</em>{100-x}$</th>
<th>Temper. [°C] and time [h] of melting</th>
<th>Temper. of Quenching [°C]</th>
<th>Temper. [°C] and time [h] of annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>400°/2h</td>
<td>400°</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>670°/20h→430°/0.5h</td>
<td>430°</td>
<td>65°/3h</td>
</tr>
<tr>
<td>10</td>
<td>560°/0.5h→496°/1h</td>
<td>496°</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>670°/20h→430°/0.5h</td>
<td>430°</td>
<td>1) 65°/3h→95°/4.5h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2) 110°/20h</td>
</tr>
<tr>
<td>20</td>
<td>560°/0.5h→513°/1h</td>
<td>513°</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>700°/24h→430°/0.5h</td>
<td>430°</td>
<td>1) 120°/2.5h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2) 130°/20h</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>700°/24h→430°/0.5h</td>
<td>430°</td>
<td>1) 120°/2.5h,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140°/48h 2) 160°/12h, 170°/6h</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 45 | 1) 720°/24h  
2) 820° | 1) 720°  
2) 820° | 1) 170°/3h, 80°/12h  
2) 125°/63h  
3) 190°/23h |
| 50 | 1) 700°/24h  
2) 810°  
4) 792°/13h | 1) few sec, 700°  
2) 810° | 1) 170°/3h, 80°/12h  
2) 150°/18h  
3) 185°/22h |
| 57 | 1) 650°/72h→550°  
2) 830°/40 min | 1) 550°  
2) 830° | 2) 120°/2h, 101°/15h, 117°/2h |
| 60 | 1) 650°/72h→550°  
2) 820°/1.20h | 1) 550° | 2) 120°/2h, 101°/15h, 117°/2h |
| 65 | 1) 510°/15h→610°/1.5h  
→834°/3.5h; crystallization at 210°  
2) 870° (immediately)  
3) 960°→920° | 870°  
920° (in l-N₂) | 140°/16h, 180°/2h |
| 70 | 1) 750°/15h→815°/2h, crystallization at 210°  
2) 870° (immediately)  
3) 960° | 815°  
870°  
917° (in l-N₂) | 150° |

### 5.1.3 As\textsubscript{x}Te\textsubscript{100-x} (20 ≤ x ≤ 60) glassy system.

The amorphous alloys As\textsubscript{x}Te\textsubscript{100-x} for x: 20, 34, 40, 50, and 60 were calculated (by using eq. 5.1) and prepared from high purity (99.9999%) As and Te. Pre-weighed amounts of As and Te were loaded in thoroughly cleaned and baked at high temperatures silica tubes and sealed under vacuum. Due to the moderate glass-forming ability of As-Te mixtures thin walled and small diameter silica tubes were
used, i.e. 4 mm outer diameter – 3 mm inside diameter. Samples preparation took place in an inert atmosphere glove box filled with pure Argon in order to avoid oxidation of As metal. Before sealing the tubes the mixture was heated under vacuum at 250 °C for several hours to remove any oxide formed at the surface or other volatile substances. The mixtures were heated slowly to temperatures well above the corresponding liquidus where they were kept for at least 24 h. To ensure homogenization the tubes were shaken frequently. All samples were melted at temperature above liquidus in order to enhance fluidity and to ensure homogenization. Finally, the samples were quenched in water or liquid nitrogen depending on the glass-forming ability of each composition.

5.1.4 Ge_{x}S_{100-x}, (x = 33, 34, 35, 40)

Glasses with composition 33 < x_{Ge} < 40 % were prepared from high purity (99.9999 %) Ge and S. Appropriate amounts of the elements, of a total mass of ~1 g were calculated by using eq. 5.1. The materials were weighted and loaded in silica tubes with 6 mm outside diameter – 4 mm inside diameter (for x_{Ge} = 40 %) and 8 mm outside diameter – 6 mm inside diameter for x_{Ge} = 33, 34, and 35 %) in an appropriate order, depending on their volatility, molar mass, solid state (species, powder). Silica tubes were thoroughly cleaned by dilute hydrofluoric acid and rinsed several times with triple distilled water. Finally, the tubes were baked by an oxygen-butane flame at 1100 °C in order to enhance their optical quality and to remove impurity inclusions. The cells with the appropriate material amounts were sealed under vacuum 0.01 mbarr. Afterwards, the cells were placed in a furnace heated at high temperature with periodic shaking to ensure homogenization before being quenched in water. At samples concentrations higher than the stoichiometric (x_{Ge} >34, 35) the melting and quenching cycle was performed more than once to ensure homogenization and amorphization (Table 5.3). In addition, in order to enhance the homogeneity the furnace was rocked frequently. The vitrification for these two compositions was achieved more difficult, probably due to bigger
material amount and bigger cell size. Raman cells from this glassy system are shown in Fig. 5.5

![Fig. 5.5 Photos of materials from Ge$_x$S$_{100-x}$ system.](image)

Table 5.3: Experimental details for sample preparation of the Ge$_x$S$_{100-x}$ binary system

<table>
<thead>
<tr>
<th>procedure</th>
<th>x in Ge$<em>x$S$</em>{100-x}$</th>
<th>Temperature and time of melting</th>
<th>Temp. of quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>830°/27 h</td>
<td>830°, water</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>1) 830°/27 h 2) 710°/14 h + 900°/9 h 3) 760°/12 h + 900°/1 h</td>
<td>1) 830°, water 2) 900°, water 3) 900°, water</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>1) 750°/12 h +895°/ 5h 2) 750°/14 h + 920°/10 h 3) 610°/17 h + 890°/5 h</td>
<td>1) 895°, water 2) 900°, air 3) 890°, 5s waiting water</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>890°/96 h</td>
<td>890°, water</td>
<td></td>
</tr>
</tbody>
</table>
5.1.5 \((\text{GeS}_{1.5})_{100-x} (\text{AgI})_x, x = 5, 10, 15, 20 \text{ mol.}\%, (y: \text{S}/\text{Ge}), y = 1.5\)

Bulk glasses from the system \((\text{GeS}_y)_{100-x} (\text{AgI})_x\) where \(x = 5, 10, 15, 20\) mol.% and ratio \((\text{S}/\text{Ge}) y = 1.5\) were synthesized. The samples were prepared in evacuated (~10\(^{-5}\) –3 Pa) and sealed quartz ampoules from elemental Ge and S with 4N purity and AgI (5N, Merck) by conventional direct monotemperature synthesis in a rotary furnace. Stepwise heating regimes were employed for the preparation of the glassy materials, as follows: (i) heating to 473 K with a rate of 4 K/min and temperature maintenance for 1800 s, (ii) heating to 673 K with a rate of 3 K/min, (iii) increasing the temperature up to 973–1123 K with a rate of 2 K/min (applying vibrational stirring), (iv) heating up to 1273 K with a rate of 1 K/min, (v) quenching in a mixture of ice and water. The annealing conditions (temperature regimes and heating rates) have been chosen in accordance with the melting points of the initial components.

\[
\text{Ge/S} = 1.5:
\]

![Image](image.png)

**Fig. 5.6 Materials from \((\text{GeS}_{1.5})_{100-x} (\text{AgI})_x, where x = 5, 10, 15, 20 \text{ mol.}\%\)**

These samples were prepared in the Institute of Electrochemistry and Energy Systems, Solid State Electrolytes, Bulgarian Academy of Science (BAS), Sofia, Bulgaria.

5.1.6 Quasi binary chalcogenide systems containing Ag and AgI:

[a] \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x, (x = 0, 5, 10, 15, 20, 25, 30, 40 \text{ mol.}\%\),

[b] \((\text{As}_2\text{S}_3)_{100-x}\text{Ag}_x (x = 0, 5, 15, 25, \text{ mol.}\%\)

The bulk glasses from the following chalcogenide systems : \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x, (x = 0, 5, 10, 15, 20, 25, 30, 40 \text{ mol.}\%\), \((\text{As}_2\text{S}_3)_{100-x}\text{Ag}_x (x = 0, 5, 15, 25, \text{ mol.}\%\),
were prepared by two-stage synthesis: (i) preparation of binary \( \text{As}_2\text{S}_3, \text{As}_{50}\text{Se}_{50}, \text{GeSe}_4 \) and \( \text{GeSe}_6 \) compounds from the elements with 5N purity; (ii) synthesis of quasi binary alloys from the previously obtained matrix and commercial Ag, AgI and In (Alfa Aesar, Johnson Matthey), respectively. The preparation process were identical for both binary and quasi-binary alloys: the initial materials in appropriate amounts were placed in quartz ampoules evacuated to \( \sim 10^{-3} \text{ Pa} \), further subjected to.

<table>
<thead>
<tr>
<th>Element/compound</th>
<th>Melting point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>850 (sublimes)</td>
</tr>
<tr>
<td>S</td>
<td>112</td>
</tr>
<tr>
<td>AgI</td>
<td>557</td>
</tr>
<tr>
<td>Ag</td>
<td>962</td>
</tr>
</tbody>
</table>

Fig. 5.7 Materials from (a): \( (\text{As}_2\text{S}_3)_{100-x}\text{AgI}_x, (x = 0, 5, 10, 15, 20, 25, 30, 40 \text{ mol.}) \), (b): \( (\text{As}_2\text{S}_3)_{100-x}\text{Ag}_x, (x = 0, 5, 15, 25, \text{ mol}) \) regular increase of the temperature with a rate of 10 K/min in a rotary furnace.

The temperature was kept constant at the melting point of each component (see Table 5.4) for around 3 h and the melt was continuously stirred for better homogenization. The binary glasses were obtained by slowing cooling inside the furnace, while for the pseudo-binary glasses the quenching took place in a mixture of ice and water.
These samples were prepared in the Institute of Electrochemistry and Energy Systems, Solid State Electrolytes, Bulgarian Academy of Science (BAS), Sofia, Bulgaria. A photo of some of them is represented in Fig. 5.7.

5.1.7 \( \text{As}_{33}\text{S}_{67} \) - butylamine solutions.

5.1.7.1 Bulk \( \text{As}_{33}\text{S}_{67} \) glasses.

The bulk chalcogenide glass with composition of \( \text{As}_{33}\text{S}_{67} \) was prepared by mixing 5N elements of appropriate weights in evacuated quartz ampoules placed in a rocking furnace (at 650 °C for 24 hours). The glass was prepared by quenching the melt to room temperature.

5.1.7.2 Spin-coated \( \text{As}_{33}\text{S}_{67} \) amorphous films.

Chalcogenide glass solutions with three different concentrations \( c_1 = 16.6, c_2 = 83, \) and \( c_3 = 166 \) mg/ml of \( \text{As}_{33}\text{S}_{67} \) were obtained by dissolution of bulk glass in butylamine (BA) solvent (Sigma-Aldrich, 99.9%). Thin films were coated on silica glass substrates by spinning solutions with concentrations \( c_1 \) and \( c_2 \) for 30 seconds at a spin speed of \(~3000\) rpm. Film thicknesses were estimated of about 100 and 1700 nm, respectively. The annealing procedure that was applied to some of the spin coated films involved heating at 90 °C under moderate vacuum at 5 Pa for 1 hour.

5.1.7.3 \( \text{As}_{33}\text{S}_{67} \) - butylamine solutions for DLS.

The preparation of solutions for the DLS study was considered with care so as to avoid the presence of undesired dust particles that interfere with the scattered signal which originates from the Brownian motion of the chalcogenide glass clusters. The \( \text{As}_{33}\text{S}_{67}/\text{BA} \) solutions were passed through 0.2 \( \mu \)m PTFE filters into pre-cleaned, dust-free pyrex tubing of 10 mm inner diameter. All measurements took place at ambient temperature and right angle scattering.
5.2 Raman scattering

5.2.1 Experimental details

Raman spectra were recorded with the aid of a Fourier Transform (FT) Raman spectrometer (model FRA 106/S, Bruker) shown in Fig. 5.8. The two major components required to do FT-Raman spectroscopy are a CW Nd: YAG laser and a conventional FT-IR. The HeNe laser beam is made collinear with the invisible Nd: YAG beam via a dichroic beamsplitter. The 632.8 nm line is used for alignment of the instrument and positioning of the sample. The signal is detected by cooled Ge and InGaAs detectors which exhibit high sensitivity and low noise for the near-infrared region (5000 - 10 000 cm\(^{-1}\)). This choice of laser provides a stable source of infrared photons whose energy is too low to excite photoidnduced effects in chalcogenide glasses (see chapter 3 for details) but whose intensity is high enough to compensate for the fall off in Raman scattering intensity due to its proportionality to \(v^4\). The standard backscattering geometry with lenses for both focusing the excitation and collecting the scattered radiation was used. The collection apparatus is mated to an input port of the interferometer, and a series of dielectric cutoff filters to reject the Rayleigh scattering is placed within the interferometer sample compartment.

Fig.5.8 A photo, representing a FT infrared spectrometer which has been used for analyzing the samples.
The role of the interferometer is to spectrally analyze the Stokes-shifted scattering from the sample which has been illuminated with the Nd : YAG (9395 cm\(^{-1}\)) laser.

In the present study the excitation source was a laser operating at 1064 nm. The signal was detected and analyzed by a liquid-nitrogen–cooled charge-coupled device (Ge-type CCD detector). The backscattered light was analyzed employing two scattering geometries: the polarized (VV, vertical polarization of the incident beam, vertical analysis of scattered light); and the depolarized one (VH, vertical polarization of incident beam, horizontal analysis of scattered light). Polarization calibration was checked by liquid CCl\(_4\). In order to get maximum spectral accuracy a resolution 1 cm\(^{-1}\) was used for all spectra.

### 5.2.2 Analysis of Raman spectra

Because the intensities of the various Raman bands depends on the sample temperature and the individual band energy it is important to remove this effect so as to isolate the vibrational density of states (weighted of course by the Raman coupling coefficient or cross section of each vibrational mode). To achieve this, one has to employ the so-called reduced representation. Due to the Boson–like statistical description obeyed by phonons, their mean number at any temperature is given by

\[ n(\tilde{\nu}, T) = \left[ \exp \left( \frac{\hbar \tilde{\nu}}{k_B T} \right) - 1 \right]^{-1} \]

where \( \hbar \) and \( k_B \) are the Planck and Boltzmann constants, respectively. Therefore, the Stokes–side reduced Raman intensity \( I^{\text{red}} \) is related to the experimentally measured one \( I^{\text{exp}} \) via the equation [Galeener 1978]:

\[ I^{\text{red}} (\tilde{\nu}) = (\tilde{\nu}_0 - \tilde{\nu})^{-4} \tilde{\nu} [n(\tilde{\nu}, T) + 1]^{-1} I^{\text{exp}} (\tilde{\nu}) \]  

(5.2)

where the term in the fourth power is the usual correction for the wavelength dependence of the scattered intensity; \( \tilde{\nu} \) is the Raman shift in cm\(^{-1}\), and \( \tilde{\nu}_0 \) denotes the wavenumber of the incident radiation.

The depolarization ratio is calculated via:

\[ \rho = \frac{I^{\text{VH}}}{I^{\text{VV}}} \]  

(5.3)
We used polarization analysis in order to be able to isolate the isotropic and anisotropic components of the Raman spectrum. Therefore, we can correctly estimate the isotropic component of the Raman spectrum which originates from the diagonal elements of the polarizability tensor. In essence, the isotropic component is the one that is associated with the pure vibrational spectrum devoid of any rotational contributions, and thus it is the isotropic spectrum that has to be analyzed:

\[ I^{\text{iso}}(\tilde{\nu}) = I^{VV}(\tilde{\nu}) - \frac{4}{3} I^{VH}(\tilde{\nu}) \]

(5.4)

where \( I^{VV} \) and \( I^{VH} \) represent the intensity of the signal in vertical and horizontal polarization, respectively and \( \tilde{\nu} \) is the Raman shift in \( \text{cm}^{-1} \).

5.3 Thermal studies by convention DSC

5.3.1 Sb\(_x\)Se\(_{100-x}\) system.

First series of measurements (DSC runs at ICE/HT) were performed with the aid of DSC-Q100 from TA Instruments, Inc (Fig.5.9). The device is equipped with a liquid nitrogen cooling accessory and a nitrogen gas DSC cell purge and allows both heating and cooling scans in the modulated or non-modulated DSC regime. The instrument was calibrated for enthalpy and temperature readings using a standard of high purity elemental indium. The instrument was also calibrated for specific heat capacity \( (C_p) \) with a standard sample of sapphire using the same heating rate in the temperature range of interest as those used in the subsequent experiments. The reference value for \( C_p \) of sapphire was obtained from the manufacturer. Samples were placed in a standard crimped aluminum pans. The undertaken DSC measurements are with a rate of 10 °C/min for all samples studied. The temperature interval was between 10 and 500 °C for Sb\(_x\)Se\(_{100-x}\) system, between 25 - 500°C for (GeS\(_{1.5}\))\(_{100-x}\)(AgI)\(_x\) and (GeS\(_{1.2}\))\(_{100-x}\)(AgI)\(_x\), and between 25 - 350°C for (As\(_2\)S\(_3\))\(_{100-x}\)(AgI)\(_x\). Pure Se that was studied in the range 10-250 °C.
Extra DSC measurements for the Sb$_x$Se$_{100-x}$ binary system were undertaken at University of Thesaloniki. Experiments were performed at scan rate of 5 °C/min for samples with Sb content 2, 5, 10, 15, 20, 25 and 30, as well as for pure Se. The material was chosen from bottom part of the ampoules. The temperature interval presented here is between 40 and 180 °C for all samples studied. Samples were put in standard aluminum pans. The instrument used in this case was model DSC141 Setaram.

5.3.2 As$_x$Te$_{100-x}$ system

The glass transition temperature $T_g$ of amorphous As-Te alloys was determined by conventional differential scanning calorimetry (NETZSCH DSC 404). DSC measurements were performed on powdered samples (~ 35 mg) under argon gas flow. Non-isothermal annealing was carried out from 40 °C to 250 °C at the heating rate of 20 K/min. Temperature calibration of the calorimeter was performed with high pure elements supplied with the equipment. The measurements took place Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany.

5.3.3 Temperature-Modulated Differential Scanning Calorimetry.

These experiments were performed with the aid of DSC-Q100 from TA Instruments, Inc (Fig. 5.9). The instrument was calibrated for baseline slope by
heating an empty cell through the entire temperature range expected in subsequent experiments. Next calibration that was performed was enthalpy and temperature readings using a standard of high purity elemental indium. The instrument was also calibrated for specific heat capacity (\(C_p\)) with a standard sample of sapphire using the same pan type, heating rate, oscillation period and modulated amplitude in the temperature range of interest as those used in the subsequent experiments. The reference value for \(C_p\) of sapphire was obtained from the manufacturer. Samples were placed in a standard crimped aluminum pans. The undertaken DSC measurements are with a rate of 10 °C/min for all samples studied. The temperature interval was between 10 and 500 °C for Sb\(_x\)Se\(_{100-x}\) system, between 25 - 500°C for (GeS\(_{1.5}\))\(_{100-x}\)(AgI)\(_x\), and (GeS\(_{1.2}\))\(_{100-x}\)(AgI)\(_x\) and between 25 - 350°C for (As\(_2\)S\(_3\))\(_{100-x}\)(AgI)\(_x\). The pure Se that was studied in the range 10-250 °C. The typical scanning conditions that were used are: heating/cooling rate 5°C/min; modulation period 80 s; modulation amplitude of ± 1.062°C.

For a glass transition endotherm with width of about 24°C one takes about \((24\,\text{°C})/(5\,\text{°C/min}) = 4.8\text{min}\) to go across the transition. And for a modulation period of 80s, one then has about 5 full periods which are more than sufficient to get a reliable Fourier transform of the modulated heat flow. All samples were equilibrated for 5 min at some initial temperature prior to each modulated ramp data acquisition.

5.4 X-ray Diffraction (XRD)

5.4.1 Sb\(_x\)Se\(_{100-x}\) and (As\(_2\)S\(_3\))\(_{100-x}\)(AgI)\(_x\)

The amorphous nature of the glasses from the systems Sb\(_x\)Se\(_{100-x}\) and (As\(_2\)S\(_3\))\(_{100-x}\)(AgI)\(_x\) was tested by x-ray diffraction measurements using a Bruker D8 Advance diffractometer (Fig. 5.10). The sample stage of this device allows for many different sample environments. These range from 10 K Helium closed-cycle cryostats up to non-ambient sample conditions with high temperature and humidity. For ambient conditions, the flip-stick sample stage and the auto changer provide the capability of measuring a batch of up to 90 samples in transmission as well as in reflection.
geometry. The D8 ADVANCE that measures powders and thin films in the two theta configuration while controlling the sample temperature anywhere from room temperature to 1500° C. Samples may be measured in air, under vacuum, or in a user controlled atmosphere.

![A photo of Bruker D8 Advance type.](image)

**Experimental setup:**

- Vertical theta-theta goniometer in powder XRD setting; lowest step size \(2\theta\) = 0.0002; horizontal sample carrier; nine-position multiple stage with automatic sample changer; fixed slit system.
- One-dimensional detector (LynxEye type) with collection rate about two orders of magnitude higher than that of conventional point detectors and very good angular resolution (default setting), or NaI(Tl) scintillation counter.
- Copper target X-ray tube used with nickel K\(\beta\) filter or with curved-graphite monochromator (default setting) or molybdenum target tube - if large scattering vector ranges are required.

Bulk materials were grind into fine powder. The fine crush is important for achieving accurate diffraction signal. The powder was placed in a plexiglass holder.
The Sb$_x$Se$_{100-x}$ system was scanned within 8-90° range with scan speed of 0.5 s/step, while (As$_2$S$_3$)$_{100-x}$(AgI)$_x$ and (As$_2$S$_3$)$_{100-x}$Ag$_x$ were scanned within 20-90° range with scan speed of 1 s/step for. Increment (step) was 0.0200267. The radiation source was a Cu Kα line at 1.5405 Å and the signal was measured by LynxEye, PSD detector.

5.4.2 XRD (As$_x$Te$_{100-x}$ system)

The X-ray diffraction experiments on As$_{20}$Te$_{80}$, As$_{34}$Te$_{66}$, As$_{40}$Te$_{60}$, As$_{40}$Te$_{50}$ and As$_{60}$Te$_{40}$ were carried out at the BW5 experimental station [Bouchard 1998] at HASYLAB, DESY. The sample material was filled into thin walled (0.02 mm) quartz capillaries of 2.0 mm inner diameter. The energy of the incident beam was 99.8 keV. The size of the incident beam was 1 x 4 mm$^2$. Raw data were corrected for background, polarization, detector dead-time and variations in detector solid angle [Poulsen 1995].

5.5 Extended X-ray Absorption Fine Structure (EXAFS).

The EXAFS measurements on As$_{20}$Te$_{80}$, As$_{34}$Te$_{66}$, As$_{40}$Te$_{60}$, As$_{50}$Te$_{50}$ and As$_{60}$Te$_{40}$ were carried out in transmission mode at the beamline A1 of HASYLAB. Samples were finely ground, mixed with cellulose and pressed into pellets. The sample quantity in the pellets was adjusted to the composition of the sample and to the selected edge.

5.6 Neutron diffraction.

The neutron diffraction measurements on As$_{20}$Te$_{80}$, As$_{40}$Te$_{60}$, As$_{50}$Te$_{50}$ and As$_{60}$Te$_{40}$ were carried out at the 7C2 diffractometer (LLB, France). Samples were filled into thin walled (0.1 mm) vanadium containers with 5 mm diameter. Raw data were corrected for detector efficiency, empty instrument background, scattering
from the sample holder, multiple scattering and absorption using the standard procedures.

5.7 Scanning Electron Microscopy

The images of the samples presented were investigated by aid of field emission scanning electron microscopy (FESEM) Zeiss Supra 35VP, equipped with an Advanced Schottky Field Emission Source and GEMINI Electron Optical Column. ZEISS’s unique variable pressure (VP) capability enables one to examine a variety of non-conducting samples without time consuming preparation. The signal was detected by back-scatter electron detector CENTAURUS. The X-ray micro-analyses were performed with the aid of QUANTAX 200 model, Bruker AXS.

5.8 RMC Modeling of $\text{As}_x\text{Te}_{100-x}$ system.

Simulation boxes used in these simulations contained 16,000 atoms. The minimum As–As, As–Te, and Te–Te distances were set to 2.3, 2.4, and 2.5 Å, respectively. Density values were taken from [Borisova 1981]. A single EXAFS curve may distinguish between different types of neighbors if the difference of their phase shifts is large enough. X-ray atomic form factors were taken from [Waasmaier 1994]. The EXAFS backscattering amplitudes and phases needed to determine $\chi(k)$ from the partial pair distribution functions $g_{ij}(r)$ were calculated using the FEFF8.4 code [Ankudinov 1998]. At first, unconstrained runs were carried out (without constraining the total number of neighbors of As or Te), while in the second step different coordination constraints were applied to As and Te.

5.9 Far-IR spectroscopy.

Samples appropriate for far-IR measurements were prepared by grinding the glasses and dispersing the powder in low-density polyethylene. The IR spectra of the investigated glasses were recorded by spectrophotometer (model IFS 113 Bruker) in the transmittance regime in the frequency range 80-500 cm$^{-1}$ of the far infrared
spectral region. The spectrometer resolution was 2.0 cm$^{-1}$ and the number of accumulations was of about 70 in order to obtain smooth spectra. All far-infrared measurements were performed at room temperature.

### 5.10 Optical Absorption

The electronic absorption spectra were measured with a Perkin–Elmer (model Lambda 900) spectrophotometer equipped with reverse optics and a large sample compartment. Fused silica square optical cell (Ultrasil/Helma, Germany) with an optical path length of 1.00 cm was used. The electronic absorption spectra of all solutions were recorded in the region 200 – 800 nm. The solutions were measured before and after passing through the filter in order to check for possible concentration change during filtering.

### 5.11 Dynamic light scattering

Normalized intensity time correlation function $g^{(2)}(q, t) = \langle I(q, t) I(q, 0) \rangle / \langle I(q, t) \rangle^2$, were measured over a broad time scale (from $10^{-8}$ s to $10^4$ s) using a full multiple tau digital correlator (ALV–5000/FAST) with 280 channels spaced quasi-logarithmically. The scattering wavevector $q = 4\pi n \sin(\theta/2) / \lambda_0$ depends on the scattering angle $\theta$ ($\theta = 90^\circ$ was used in the present work), the laser wavelength $\lambda_0$, and the refractive index of the medium $n$. Various light sources were used in order to check for possible photo-induced effects in the chalcogenide glass solutions. In particular, the following laser wavelengths were used: the 496, 488 and 514. 5 nm lines from an Ar$^+$ ion laser (Spectra Physics 2020), the 632.8 nm line from a He-Ne laser and the 671 nm line form a diode pumped solid state laser. Various power levels were used when possible. The scattered light was collected by a single mode optical fiber and transferred to a photo-multiplier and then to the digital correlator for analysis.
5.12 Atomic force microscopy

The AFM images of As-S film surfaces were recorded using an Atomic Force Microscopy (AFM) equipment Dimension 3100 (Digital Instruments - Veeco Metrology Group). An area of 250 x 250 nm was scanned at a high-resolution tapping mode to reveal films surface morphology. In addition an area of 5 x 5 μm was scanned in order to determine the magnitude of the root mean square roughness of the films.
References of Chapter 5


Chapter 6

Structural and thermal studies of the 

$\text{Sb}_x\text{Se}_{100-x}$ binary glassy system

6.1 Brief literature survey

Binary selenide glasses, mainly those of As and Ge, have intensively been investigated over the last decades owing to the ease of glass-formation and the plethora of applications that these materials find [Borisova 1981, Feltz 1993, Kolobov 2003]. On the contrary, considerably fewer efforts have been dedicated on Sb-Se binary glasses. The lack of systematic studies has a two-fold origin. First, Sb-Se materials are not good glass-formers exhibiting high crystallization tendency. Second, even in the case of glass-formation under rapid cooling of the melt, the obtained glasses are phase separated on a microscopic scale.

Phase separation is generally considered as drawback to applications and further complicates the study of the $\text{Sb}_x\text{Se}_{100-x}$ binary system. Phase separation is
avoided in thermally evaporated amorphous films [Myers 1972] where the non-
crystalline range can be extended beyond the range of the bulk glasses, i.e. the
stoichiometric Sb$_2$Se$_3$ is the limiting composition that can be prepared in bulk form.
However, using splat-cooling techniques, foils of glasses were prepared for Sb
content up to 50 at. % [Brasen 1974]. Despite the above-mentioned shortcomings
the non-crystalline phases of antimony selenides meet a number of applications in
view of their interesting optical properties [Shaaban 2007] and could be potentially
used as phase change nonvolatile memory materials [Kang 2005].

The phase diagram of the Sb$_x$Se$_{100-x}$ binary system, illustrated in Fig. 6.1(a) in
full the composition range. A part of this phase diagram in the composition range of
interest in this work is shown in Fig. 1(b). The phase diagram reveals an incipient
(or metastable sub-liquidus) immiscibility over the concentration range 4< x$_{\text{Sb}}$ <35
[Myers 1972]. In particular, while the binary alloy forms a homogeneous liquid
above the liquidus curve, the decrease of temperature towards the glass transition
temperature $T_g$ causes decomposition of the mixture via the spinodal decomposition

![Phase Diagram](image)

**Fig. 6.1.** (a) Full-composition range phase diagram of the Sb-Se binary system.
(b) Se-rich part of the phase diagram of the binary Sb$_x$Se$_{100-x}$ system,
reproduced form [Myers 1972]. The liquidus of this system exhibits an
inflection point, which is indicative of a hidden miscibility gap. The binodal
and spinodal curves are shown by solid and dashed lines, respectively. The
vertical arrows indicate the glass compositions studied in this work.
mechanism as described in Chapter 1. As a result, the alloy separates in two different glassy phases with compositions similar to those defined by the immiscibility dome limits, i.e. a Se-rich phase which contains 4-5 at. % of Sb and a near-stoichiometric-like phase Sb$_2$S$_3$. Despite the interesting physics in understanding the formation of heterogeneous glassy materials and the fact that antimony selenides could meet a number of applications, a limited number of studies on bulk glasses have been undertaken, devoted mainly to their thermal properties [Myers 1972, El-Zaidia 1987, Tonchev 1999, Mehta 2006, Holubová 2007]. Indeed, structural studies on bulk Sb-Se glasses are completely absent, while few studies have been reported for Sb-Se amorphous thin films [Sagara 1976].

6.2 Results

6.2.1 Raman scattering

Stokes-side unpolarized Raman spectra of the Sb-Se glasses studied in this work are presented in Fig. 6.2. It should be stressed that attempts to record polarized and depolarized Raman spectra for the glasses of this binary system failed. The reason will become clear below in this chapter. The spectra have been normalized at the peak maximum of the 250 cm$^{-1}$ band characteristic of the Se chain vibrational mode. The enhanced baselines of the two highest glass compositions at high wavenumbers originate from the second order scattering mechanism of the Sb-Se band, which peaks at ~380 cm$^{-1}$.

It is obvious from Fig. 6.2 that the intensity of the vibrational mode at about 195 cm$^{-1}$, characteristic of the Sb-Se bond in SbSe$_{3/2}$ pyramidal units, increases systematically with respect to the intensity of the Se chain peak, upon increasing $x_{\text{Sb}}$. Two important observations emerge from this figure: (a) The energy of the vibrational mode of the Se matrix remains practically constant over the very wide range of Sb content. (b) The broad band of SbSe$_{3/2}$ pyramids exhibits an unusual self-similarity, i.e. its shape and energy is essentially the same for all glasses studied except for $x_{\text{Sb}} = 2$. Both observations are unique for this binary system since
the Raman spectra of other structurally similar arsenic-chalcogen glasses (i.e. As-S, As-Se, etc.) do not share common features with antimony selenide glasses. This distinction reflects structural heterogeneity due to phase separation as will become clear in next sections.

6.2.2 Thermal studies.

(A) DSC thermograms obtained from the first series (see chapter 5.3.1) of experiments are shown in Fig. 6.3.
CHAPTER 6: Structural and thermal studies of the Sb$_x$Se$_{100-x}$ binary glassy system

![Figure 6.3 DSC thermogram of Sb$_x$Se$_{100-x}$ glasses (0 $\leq$ x $\leq$ 10 at %) using a heating rate of 10 °C/min. (a) T$_g$ (endothermic peaks) and crystallization (exothermic peaks); (b) melting points](image)

The assignment of the various peaks in the above thermograms is as follows:

1) The first endothermic peak (around 50 °C) is assigned to the glass transition temperature of the Se-rich phase. In comparison with the T$_g$ of pure Se (at 49 °C), these positions of the peaks of the mixtures change only slightly. In particular, both T$_g$(Sb$_5$Se$_{95}$) and T$_g$(Sb$_{10}$Se$_{90}$) are at ~57 °C. We use here the peak minimum for T$_g$ instead of the onset of glass transition that is sometimes alternatively used. The later can be estimated by the slope change when the curve levels-off from the background.

2) The exothermic peaks just above 100 °C indicate crystallization processes. The peak maximum shifts with increasing Sb content: Se: 109 °C, x$_{Sb}$ = 5%; 129 °C, x$_{Sb}$ = 10%; 131 °C. As can be seen from the thermogram, the glass
for $x_{\text{Sb}} = 5\%$ reveals two peaks. The first one has a sharp maximum. The edge of this peak is covered by a second one, so as together they form a very broad peak. Furthermore, the glass for $x_{\text{Sb}} = 10\%$ exhibits two peaks, one emerged clear peak, the edge of which extends and turns to a second peak. The last is very broad, of small height and with hardly distinguishable peak maximum.

3) The second endothermic peaks on thermograms are close to 221 °C. This temperature is the melting point of pure selenium or the Se-rich phase. As is expected the area of this peak decreases with increasing antimony content. Moreover, the peak position moves towards lower temperature.

4) At higher temperatures (450-500 °C) in studied glasses few endothermic peaks are distinguishable, which can be attributed to decomposition of the glass due to the appreciable volatility of Se at such temperatures. This effect was confirmed by thermogravimetric (TGA) experiments. The curves from this study are shown in Fig. 6.4. It is seen that at temperature just exceeding 400°C the masses of the materials start to decrease confirming loss of solid material.

![Fig. 6.4 Thermogravimetric curves of Se and Sb$_5$Se$_{95}$.](image)
(B) A more complete thermal study was undertaken at University of Thesaloniki (see 5.3.2). The DSC thermograms are shown in Fig. 6.5 and their assignment is as follows:

1) The first endothermic peak (around 50 °C) is assigned to the glass transition temperature of the Se-rich phase. In comparison with the $T_g$ of pure Se these peaks are slightly shifted. The $T_g$ values for whole measured range of composition are shown in Table 6.1. Again, peak minimum for $T_g$ is used here.

2) The exothermic peaks just above 100 °C indicate crystallization processes; the peak maximum shifts with increasing Sb content. The peak area continuously decreases with increasing antimony concentration. The thermogram of the $x_{Sb} = 2\%$ glass shows two peaks. The first one has a well-defined maximum and overlaps partly with a second peak. The last one is characterized by very long tail at higher temperature. The second peak is at the moment a puzzling finding because for the $x_{Sb} = 2\%$ – which according to the phase diagram is a homogeneous glass – only one crystallization peak should be expected.

![Fig. 6.5 DSC thermograms of Sb$_x$Se$_{100-x}$ glasses (0 ≤ x ≤ 30 at %). Heating rate: 5 °C/min](image)
CHAPTER 6: Structural and thermal studies of the Sb\textsubscript{x}Se\textsubscript{100-x} binary glassy system

Table 6.1: \(T_g\) values of Sb-Se glasses

<table>
<thead>
<tr>
<th>Sb content [at. %]</th>
<th>(T_g) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>51.0</td>
</tr>
<tr>
<td>2</td>
<td>55.9</td>
</tr>
<tr>
<td>5</td>
<td>57.4</td>
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<tr>
<td>10</td>
<td>52.4</td>
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<tr>
<td>15</td>
<td>51.6</td>
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<tr>
<td>20</td>
<td>52.1</td>
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<tr>
<td>25</td>
<td>49.2</td>
</tr>
<tr>
<td>30</td>
<td>49.5</td>
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</tbody>
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The first peak in \(x_{\text{Sb}} = 5\%\) glass thermogramm shifts and almost overlaps with the second one. Furthermore, for the \(x_{\text{Sb}} = 10\%\) glass the two peaks overlap strongly and hence one broader peak is formed. For the \(x_{\text{Sb}} = 15\%\) glass composition a long tail at lower temperature and one broad peak appears. On the contrary, at higher concentration, i.e. \(x_{\text{Sb}} = 20\%\), three peaks are revealed. The first one is positioned at lower temperature, near the crystallization of selenium, the second one appears near the first peak of \(x_{\text{Sb}} = 2\%\) glass, and the third peak is near the second peak of \(x_{\text{Sb}} = 2\%\) and \(x_{\text{Sb}} = 5\%\) glasses. For the concentration \(x_{\text{Sb}} = 25\%\) again two peaks are

Table 6.2: Crystallization temperatures of Sb-Se glasses

<table>
<thead>
<tr>
<th>Sb content [at. %]</th>
<th>(T_c) [°C]</th>
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<tr>
<td></td>
<td>1\textsuperscript{st} peak</td>
</tr>
<tr>
<td>0</td>
<td>97.0</td>
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<tr>
<td>2</td>
<td>117.1</td>
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<td>5</td>
<td>122.3</td>
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<td>10</td>
<td>120.2</td>
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<td>15</td>
<td>127.0</td>
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<tr>
<td>20</td>
<td>86.8</td>
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<td>25</td>
<td>122.8</td>
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<tr>
<td>30</td>
<td>123.4</td>
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</tbody>
</table>
displayed. The first one is very broad at lower temperature, while the second one appears at higher temperature. Finally, for \( x_{\text{Sb}} = 30\% \) thermogram one very broad peak appears and a second one which is hardly distinguishable. The crystallization temperatures of the Sb-Se glasses are summarized in Table 6.2.

3) The second endothermic peaks on thermograms are close to 221 °C. This temperature is the melting point of pure selenium or the Se-rich phase. As is expected the area of this peak decreases with increasing antimony content. Moreover, the peak position moves towards lower temperature.

### 6.2.3 X-ray Diffraction measurements

Figure 6.6 contains obtained diffraction patterns. Traces of crystallinity were observed only for the two highest concentrations studied in this work.

### 6.3 Analysis of the Results and Discussion

#### 6.3.1 Structural study by off-resonance Raman spectroscopy

Raman spectra of Sb-Se bulk glasses have recently been reported for Sb-Se glasses for a very limited composition range \( 0 \leq x_{\text{Sb}} \leq 8 \) [Holubova 2007] (see Fig. 6.7). However, in that work the Sb-Se band is rather sharp indicating partial crystallinity of the glass. In the course of the present study we have also measured correspondingly sharp Sb-Se Raman peaks only in cases where the quenching rate was not enough to ensure the absolute absence of crystallinity. However, by increasing the quenching rate we were able to record the Raman spectra of the purely glass phase.

#### 6.3.1.1 On the structure of elemental Se

As mentioned in Section 6.2.1, the Raman spectra are dominated by the Se-Se vibrations at least for the Sb-poor compositions. Therefore, before proceeding to
the discussion of the obtained Raman data in terms of structural features of Sb-Se glasses it is important to briefly refer to the vibrational modes assignment of elemental Se which is already complicated despite the fact that Se is a monomatomic system. An extensive analysis of this issue has been presented elsewhere [Yannopoulos 2004a; Yannopoulos 2004b]. The Raman spectrum of Se can be divided in two spectral regions: in the bond-bending region [70-150 cm\(^{-1}\)] and the bond stretching one [200-300 cm\(^{-1}\)]; the latter is the main focus of the present study.

**Fig. 6.6** Representative diffraction patterns for the glasses for \(x_{\text{Sb}}=2, 10 \) and 20. Scan rate: 25 s/degree.
CHAPTER 6: Structural and thermal studies of the Sb$_x$Se$_{100-x}$ binary glassy system

Fig. 6.7 Raman spectra of Sb$_x$Se$_{100-x}$ bulk glasses [Holubova 2007].

The high-frequency region is separated from the low frequency one by a gap in VDoS between 150 and 200 cm$^{-1}$. The Raman intensity in the high frequency spectral range is characteristic of the Se–Se bond stretching vibrational modes. Both long Se chains and eight-membered Se$_8$ rings coexist in g-Se. In analogy with the case of liquid sulfur we will symbolize the polymer content or the chains of selenium as Se$_\mu$. However, contrary to what happens in sulfur, [Mayer 1976, Kalampounias 2003] the polymer content is the dominant species of selenium’s structure at any temperature. Most of these chains are found in a highly disordered arrangement but there is also a non-negligible portion of closely packed chains whose strong interchain interaction gives rise to a peak at energies comparable to the corresponding peak in the trigonal modification of crystalline Se, i.e. t-Se. Therefore, the high-frequency spectral regime is dominated by bond-stretching vibrations of Se atoms incorporated into three different local environments, namely, rings, disordered chains, and strongly interacting chains. To get an accurate determination of peak areas, the high frequency spectral region has been fitted using mixed Gauss and Lorentz curves [Yannopoulos 2004(b)]. A representative example of decomposed spectra into the individual components is shown in Fig. 6.8.
CHAPTER 6: Structural and thermal studies of the Sb<sub>x</sub>Se<sub>100-x</sub> binary glassy system

Fig. 6.8. A characteristic example of the fitting in the bond-stretching regime, using the procedure described in the text. Open circles: reduced polarized Raman spectrum at 343 K; thick solid line: total fit curve; dashed line: t-Se component; thin dotted line: Se<sub>µ</sub> chain species component; dashed-dotted line: Se<sub>8</sub> ring species component. Only a part of the experimental data points (25%) is shown for clarity, [Yannopoulos 2004b].

An elucidation of the origin of the vibrational peaks appearing in this best of our knowledge, attempts to analyze the (200–300 cm<sup>-1</sup>) spectral envelope in the glass with more than two lines are not known yet. At the beginning, it was considered that the peak at 250 cm<sup>-1</sup> was a manifestation of Se<sub>8</sub> rings while the low energy shoulder at 235 cm<sup>-1</sup> was due to long chains [Schottmiller 1970, Carini 1980]. In the work by Carini 1980 it was attempted an estimation of the relative ring-to-polymer ratio by fitting the 200–300 cm<sup>-1</sup> region with two Gaussian lines; one at 235 cm<sup>-1</sup> accounting for the polymer content and one at 250 cm<sup>-1</sup> accounting for the ring concentration. The relative increase of the 235 cm<sup>-1</sup> peak as a function of temperature above <i>T_g</i> was interpreted as an increase in chain population. Although the latter conclusion is true, Carini 1980 were misled by the fact that in Se glass the
crystallinity has also the tendency to increase above $T_g$. Latter, it was suggested that
the bond stretching vibrational mode of both the chains and the rings are located at
about 250 cm$^{-1}$, and the 235 cm$^{-1}$ mode was assigned to chains arranged in trigonal-
like form [Richter 1973, Martin 1976].

The presence of three distinct peaks in the frequency range 200–300 cm$^{-1}$ has
been found in studies of polarized Raman spectra of Se species confined in
nanochannels of AlPO-5 single crystals [Poborchii 1997]. The authors assigned the
peaks found at 237, 259, and 268 cm$^{-1}$ to $t$-Se, $s_{\mu}$ chains and $s_8$ rings,
respectively. The same authors found a forth peak at 250 cm$^{-1}$ while working on the
same AlPO4-5/Se system [Poborchii 1999] and they attributed it to an amorphous-
like component of Se chains, which together with the crystalline component forms
in the mesoporous channels of the structure.

The lower frequency region (70–150 cm$^{-1}$) originates from bond-bending
vibrational modes and as recent molecular dynamics simulations [Nakamura 2003]
have shown a large piece of information about the medium-range structural order of
the glass and the supercooled liquid can be obtained by a quantitative analysis of
the peaks in this region. In this frequency regime three main peaks are evident in
the Raman spectrum at 82, 112, and 138 cm$^{-1}$. The presence of these three
vibrational modes is not enough to account for the broadness of the scattered
intensity background taking into account the sharpness of the three aforementioned
peaks.

Up to now, the presence of the 112 cm$^{-1}$ in the intermediate or bond-bending
frequency range is considered as the only direct proof of the existence of $s_8$ rings
in the glass structure [Brodsky 1978]. However, given the above context, we
propose here that the bond-stretching frequency range can also serve as a source of
ring/chains species equilibrium. The fact that our spectra were recorded with high
resolution has made it possible to resolve a weak peak situated at the high-energy
side of the dominant 250 cm$^{-1}$ peak. Therefore, we follow the idea that the shoulder
located at 234 cm$^{-1}$ (that is, on the low-energy side of the main 250 cm$^{-1}$ peak) is
assigned to the intrachain bond-stretching vibrational mode of the chains disposed at a \( t \)-Se-like conformation as is already known.

Our proposition is that the dominant peak at 250 cm\(^{-1} \) could be attributed to the intrachain bond-stretching vibrational mode of the disordered Se\(_{\mu} \) chains, while the low intensity shoulder located at \( \sim 260 \) cm\(^{-1} \) is attributed to the intraring bond-stretching vibrational mode of Se\(_8 \) species. Although this latter peak is not well resolved, its presence becomes indisputable if one tries to fit the 220–270 cm\(^{-1} \) spectral envelope with only two peaks associated with the Se\(_{\mu} \) and \( t \)-Se-like vibrational modes. This suggestion is also supported by the nature of vibrational modes in liquid sulfur where a close resemblance is noticed. In particular, a peak located at \( \sim 460 \) cm\(^{-1} \) is attributed in polymeric sulfur chains while a stronger peak located at \( \sim 470 \) cm\(^{-1} \) is assigned to intraring S\(_8 \) vibrations [Kalampounias 2003].

Fig. 6.9 Reduced Raman spectra of Sb\(_x\)Se\(_{100-x} \) glassy system for various Sb contents as shown in the legend. The spectra have been normalized with respect to the Se-Se symmetric stretching vibrational mode. The inset shows for comparison the corresponding spectra of the binary As-Se glasses [Kostadinova 2009].
6.3.1.2 Structural details of Sb-Se glasses

Given the above context as regards the structure and the analysis of the spectral features of elemental Se, the corresponding analysis of the spectra of the Sb-Se binary glasses is now straightforward because the Sb-Se band, albeit much broader than the previous one, is quite featureless.

![Graph of Raman spectra for Sb-Se glasses with varying Sb content.](image)

**Fig. 6.10.** Fitting of $\text{Sb}_{x}\text{Se}_{100-x}$ Raman spectra with the aid of Gaussian distribution function.

In order to present quantitative results, which will be useful for the subsequent discussion, we analyzed the reduced data shown in Fig. 6.9 by fitting the broad bands with Gaussian distributions, demonstrated in Fig. 6.10. A more detailed fit is shown in Fig. 6.11 for the $\text{Sb}_{10}\text{Se}_{90}$ glass. The dependence of the intensity ratio of Sb-Se and Se-Se ($I_{\text{Sb-Se}}/I_{\text{Se-Se}}$) modes, the position of this peak and its bandwidth on Sb-content are shown in Fig. 6.12. The following experimental facts suggest that
phase separation in Sb-Se glasses for $x_{\text{Sb}} > 5$ occurs which is in agreement with the phase diagram of this binary system.

![Raman shift vs. Reduced Intensity graph]

**Fig. 6.11.** Representative fitting example for $\text{Sb}_{10}\text{Se}_{90}$. Only 20% of the experimental data (open circles) are shown for clarity.

![Graph showing Sb content vs. Sb-Se peak position, bandwidth, and intensity ratio]

**Fig. 6.12.** Dependence of the fit parameters (full width of the Sb-Se peak, ratio of the intensity of the Sb-Se mode to the intensity of the Se-Se modes, and the peak position of the Sb-Se peak) as a function of $x_{\text{Sb}}$.

(i) The composite band at $\sim 250$ cm$^{-1}$ exhibits neither a shift in energy nor a change in bandwidth with increasing Sb concentration for glasses in the phase separation regime. A contrasting behavior occurs for similar concentrations in As-Se binary glasses (see inset in Fig. 6.9) where As atoms are homogenously...
dispersed within the Se matrix preventing phase separation in the As-Se binary system. The Se-Se Raman band exhibits an appreciable blue-shift with increasing As content as a result of the effect of chains’ interconnection by means of As atoms. On the contrary, the existence of Se rich phase, in Sb-Se glasses, with a negligible amount of Sb atoms linking Se chains results in an insignificant influence of Sb atoms on Se chains’ vibrational properties and hence justifies the constant energy of the symmetric bond stretching Se-Se mode at 250 cm\(^{-1}\).

(ii) The broad band at \(\sim 195\) cm\(^{-1}\) is characteristic of the Sb-Se stretching mode of the SbSe\(_{3/2}\) pyramidal units. This band exhibits two noticeable features. Its width is practically constant for all \(x_{\text{Sb}} \geq 5\). The mode frequency exhibits a slight red-shift for \(0 < x_{\text{Sb}} < 10\) while it remains constant for higher \(x_{\text{Sb}}\). The effect of self-similarity in shape (constant width) can be accounted for by considering the existence of only one kind of species for all antimony concentrations. This is a near-stoichiometric-like environment which builds-up in the glass structure for \(x_{\text{Sb}} > 5\).

Figure 6.13 illustrates the frequency dependence of selected depolarization ratio spectra. As it is evident, the depolarization ratio of elemental Se exhibits fine structure as expected for a homogeneous medium whose structural units obey different symmetry operations in the course of vibrational motion. The fine structure of \(\rho\) is gradually lost when entering the phase separation regime, i.e. for the Sb\(_5\)Se\(_{95}\) glass and is completely absent for higher \(x_{\text{Sb}}\) contents, lending support to the heterogeneity of glass structure.

The loss of fine structure in the depolarization ratio might originate from “optical stresses” or gradients in the refractive index trapped in the glass structure as a results of fast quenching. However, after sufficient annealing these optical inhomogeneities are eliminated and the depolarization ratio attains the correct form. In the present case where the annealed glass structure is phase separated, fluctuations in the refractive index originate from the different compositions of the two phases. Therefore, light will be depolarized due to these inhomogeneities and mainly due to the scattering that light undergoes at the interfaces of the two phases.
Fig. 6.13. Frequency dependence of the depolarization ratios for three glasses.

The aforementioned observations provide compelling evidence for the decoupling of two glassy phases. Regions of Sb$_2$Se$_3$ (or slightly sub-stoichiometric concentration) are immersed into a Se-rich (or slightly Sb-doped) phase. Considering this and taking into account the details of the Sb-Se phase diagram the following picture can be envisaged for the structure of the Sb$_x$Se$_{100-x}$ binary glasses. For $x_{Sb} \geq 5$ the glass structure is organized in two phases, the Se-rich and the stoichiometric-like one whose compositions are determined by the limits of the immiscibility dome shown in Fig. 6.1. The two phases are characterized by such spatial extent, presumably some tens of nanometers, so that their vibrational modes are decoupled.

Up to now, no direct evidence has been provided for the shape and size of the two phases. However we know that in the present case the growth of phase separation is the spinodal-type mechanism. Nucleation and growth is characterized by distinct spherical droplets of the nucleated phase in a continuous matrix of a second phase. Preliminary scanning electron microscopy measurements in our
laboratory showed no evidence for such droplets, implying a composition fluctuation spatial profile much smaller than one micron. On the other hand, the non-preservation of the depolarization ratio indicates that the spatial extent of composition fluctuation cannot be smaller than few tens of nanometers because otherwise the structure should be “seen” as homogeneous by the laser light. The addition of Sn reduces the population or the volume of the Se-rich phase in a way proportional to $x_{Sn}$. Thus the system behaves as a “mechanical” mixture of two phases that exchange population, while maintaining their local structure unchanged.

The experimental finding shown in Fig. 6.12 supports this conclusion. Indeed the ratio of the intensity of the Sn-Se mode to the intensity of the Se-Se modes grows almost linearly with $x_{Sn}$. Given the above context, the Raman spectrum of any glass in the phase separation regime can be written as a linear combination of the Raman spectra that correspond to the two phase, i.e. the Sn-poor one and the Sn$_2$Se$_3$-like one. The present study also suggests that the depolarization ratio is indeed a sensitive indicator of monitoring phase separation at the nanoscale.

### 6.3.2 Study of thermal properties using DSC

The $T_g$ values determined from our measurements as well as other literature values for glasses of the same binary system are summarized in Fig. 6.13 (a). Our data show qualitative similarities with the most complete study by Tonchev et al. [Tonchev 1999] who used TMDSC. In particular, the $T_g$ values exhibit an increasing trend at low Sn content up to the composition of the low concentration limit of the immiscibility dome where phase separation should take place. Up to this point the structure is locally homogenous because Sn is randomly distributed in the Se structure. Therefore, DSC probes single $T_g$ whose magnitude increases as it also happens in other similar binary glasses, i.e. As-Se. Above the Sn$_5$Se$_{95}$ glass composition phase separation occurs and then the $T_g$ peak seen in the thermograms corresponds to the Se-rich phase. This is the reason why the $T_g$ value remains practically independent from composition for Sn content larger than 5%.

163
finding indicates that the Se-rich phase has practically the same concentration in the whole range of glass-formation studied here.

It is interesting to compare the \( T_g \)’s obtained from bulk glasses and those obtained from thin films produced by thermal evaporation. In the second case, the structure of the obtained amorphous binary Sb-Se films is homogeneous at all compositions and the \( T_g \)’s are monotonically increasing as a function of Sb content. This is because Sb atoms are uniformly distributed in the Se structure coordinated by three Se in a pyramidal configuration leading to a rigid network structure.

The \( T_g \) values of thin films produced by thermal evaporation are shown in Fig. 6.13(a). The red circle is the composition at the higher limit of the immiscibility dome and the \( T_g \) value for this glass is expected to occur as high as ~ 150 °C. This means that the stoichiometric-like phase should exhibit a \( T_g \) in the DSC thermograms at about this temperature. However, we never observed a second \( T_g \) in the DSC data because this “putative” \( T_g \) falls within the broad crystallization range of the Se-rich phase. Another interesting observation is that when thin films are

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**Fig. 6.14 (a)** Dependence of \( T_g \) of Sb-Se glasses on the Sb content compiled from different sources as shown in the legend. **(b)** Enlarged part of the phase separated glasses. The vertical dashed line denotes the low limit of the immiscibility dome.
annealed then they become phase separated and their $T_g$ values follow the trend of bulk glasses, see the half-filled circles in Fig. 6.14(b).

As mentioned above, thermal studies [Myer 1972, El-Zaidia 1987, Tochev 1999, Mehta 2006, Holubova 2007] have provided the only available data on Sb-Se bulk glasses. In most of the studies the $T_g$ values exhibit unusual temperature dependence. Specifically, the expected increase up to $x_{Sb} \approx 4$ is followed by a decrease and practically constant trend for higher $x_{Sb}$ values. Similar behavior was exhibited by other thermodynamic parameters, such as thermal stability, crystallization temperature, etc. To account for these observations [Mehta 2006] considered the highly unlikely scenario that in glasses with $x_{Sb} > 4$ homopolar Sb-Sb bonds start to form at the expense of Sb-Se bonds. Further, they considered that at this critical composition ($x_{Sb} = 4$) a dimensionality change (from 1D to 2D) occurs. Evidently, Raman spectra show evidence against this suggestion. In another thermal study [Tonchev 1999] the maximum in the $T_g'$ vs. $x_{Sb}$ curve was observed at somewhat low composition, i.e. $x_{Sb} \approx 1.5$. The authors suggested that initially up to this limit Sb is bonded to terminal Se atoms and that up to this limit all Se chains ends have been saturated by Sb atoms. For high compositions Sb atoms are incorporated into Se chains.

An illuminating thermal study has been presented by [Myers 1972] where both bulk glasses and evaporated films were examined. As can be seen from Fig. 6.13(a), in the case of as-prepared films $T_g$ values increase almost linearly with $x_{Sb}$ as expected for a homogeneous, non-phase-separated binary mixture. This is because Sb atoms are uniformly distributed in the Se structure coordinated by three Se atoms in a pyramidal configuration. Indeed, producing films through thermal evaporation one avoids the incipient liquid state immiscibility, which is a genuine feature of the melt-quenched glasses. However, when the homogeneous films are annealed at $T>T_g$ phase separation takes place and the thermal features of these films are practically similar to those of the bulk glasses [Myers 1972].
6.4 Conclusions

Structural studies of bulk antimony selenide glasses are largely absent. This has been the motivation to undertake a detailed Raman spectroscopic study of the structural details of $\text{Sb}_x\text{Se}_{100-x}$ bulk glasses over a wide composition range, which was presented in this chapter. The main conclusions of this chapter can be summarized as follows:

- Glass formation in the Sb-Se binary system is possible for a wide composition range from pure Se up to the stoichiometric compound $\text{Sb}_2\text{Se}_3$. This is an important result since even in recent studies glass formation was considered either to be limited only over a narrow composition range close to elemental Se [Tonchev 1999, Holubova 2007] or be completely absent [Popescu 2008].

- The Raman spectra of Sb-Se bulk glasses exhibit unusual spectral features when compared with other structurally similar binary systems, such as As-S and As-Se glasses. The experimental findings that the Sb-Se and Se-Se bond stretching frequencies and widths are independent from the glass composition are consistent with the phase separation that takes place in bulk, melt-quenched Sb-Se glasses over the composition range $4 < x_{\text{Sb}} < 35$.

- The particular frequency dependence of the depolarization ratio is an important factor which can be used as a sensitive indicator for detecting nanoscale phase separation in condensed media, such as glasses. The loss of fine structure in the $\rho(\tilde{\nu})$ function in well-annealed glasses is a rather reliable sign of phase separation in the scattering medium.

- The results of thermal studies also point to the outcome that bulk Sb-Se glasses are phase separated. Indeed, the independence of $T_g$ on the Sb content for $x_{\text{Sb}} \geq 5$ is a clear indication that the extra Sb atoms are not homogenously dispersed in the Se glass matrix. Therefore, the observed near-constant $T_g$ values correspond to the glass transition temperature
of the Se-rich phase. The $T_g$ of the stoichiometric-like phase is probably hidden under the crystallization peak of the Se-rich phase.
CHAPTER 6: Structural and thermal studies of the Sb$_x$Se$_{100-x}$ binary glassy system

References of Chapter 6:

Feltz, A., Amorphous Inorganic Materials and Glasses, VCH, Weinheim (1993)
CHAPTER 6: Structural and thermal studies of the $\text{Sb}_{x}\text{Se}_{100-x}$ binary glassy system

Chapter 7

Structural aspects of the As$_x$Se$_{100-x}$ glassy system: A Raman scattering study

7.1 Brief literature survey

Despite the enormous number of structural studies carried out for As-Se binary glasses and amorphous films using various experimental techniques such as nuclear magnetic resonance (NMR), x-ray diffraction, neutron diffraction, EXAFS [Bureau 2003, Mastelaro 1992], IR absorption, Raman scattering [Lucovsky 1977; Ohsaka 1974, Holubova 2007, Onari 1986] and other techniques, the detailed structural organization and the type of the evolved structural species as a function of the As content is still is not fully elucidated, [Hosokawa 1999, Ahn 2006, Reinninger 1973, Leadbetter 1974, Ahn 2002, ].

One of the most powerful, but not always the easiest, techniques for studying materials’ structure is light scattering. In particular, Raman scattering is used to probe local structural arrangement and molecular species that constitute the so
CHAPTER 7: Structural aspects of the $\text{As}_x\text{Se}_{100-x}$ glassy system: A Raman scattering study

called short- and medium-range structural order of the glass. The study of the structure of elemental selenium and of As-Se glassy system by means of Raman spectroscopy has been subject of many works, [Onari 1985, Kovanda 2003, Holubova 2007, Yannopoulos 2004a, Yannopoulos 2004b]. However, as regards the binary As-Se glasses, the details suggested about the atomic structure are self-contradictory. The main reason for the difficulty in approaching a consensus about the structure of As-Se glasses has to be traced to the proximity in the masses of As and Se atoms (74.92 and 78.96, respectively). This proximity and the similar bonding strengths of As-Se and Se-Se bonds, has as a consequence a strong overlap of the vibrational modes of the pyramidal unit and those of Se chains and rings. As a result many authors have misinterpreted the vibrational modes of the pyramidal network that builds-up with increasing As content with the vibrations of pure Se.

G. Lucovsky et al. [Lucovsky 1977] have shown that the infrared and Raman spectra of the amorphous $\text{As}_x\text{Se}_{100-x}$ ($40 \leq x \leq 60$) are well described by the vibration of the AsSe$_3$ stretching mode. The analysis of the infra-red and Raman spectra indicates that the 8-N coordination rule applies at all glassy compositions, and that heteropolar bonds are always favored. The infrared and Raman spectra for the arsenic-rich region does not show, relative to the stoichiometric composition, a significant difference as they observed for the $\text{As}_x\text{S}_{100-x}$ system; this is explained by the large similarities of the physical properties presented by the As and Se atoms. Moreover, the authors conclude that the tendency toward ordering is less in the As-rich region.

Later on, still using Raman, T. Mori et al. [Mori 1980] showed that in the selenium-rich region of the $\text{As}_x\text{Se}_{100-x}$ ($0 \leq x \leq 50$) system, AsSe$_3$ pyramids dominate as fundamental structural units due to energetic factors (the As-Se bond is quite stable). As the selenium content is increased, the number of Se-Se bonds increases. In the region between stoichiometric $\text{As}_2\text{Se}_3$ and elemental Se, the AsSe$_3$ pyramids and Se-Se bonds are distributed homogeneously and randomly in space. They supposed in this case the existence of Se-Se bonds along As-Se-Se-As chains. However, since the frequency of this mode is similar to that of the stretching mode
of the AsSe₃ pyramidal unit, the identification of the Se-Se stretching mode is not clear. For the arsenic-rich region, when the arsenic concentration is increased above that of the stoichiometric As₂Se₃ composition, the number of As-As bonds due to the extra arsenic atoms increases. Hence, they suggested that As₂Se₄ structural type may be constructed.

In the one of the most recent works, [Holubova 2007], unpolarized Raman spectra of AsₓSe₁₀₀₋ₓ glasses (x = 1, 2, 4, 8, 16) have been deconvoluted and the authors have reported four bands in the range 200 – 300 cm⁻¹. The fact that three of these modes are at the same energies with corresponding peaks in glassy Se (239, 252 and 262 cm⁻¹) led the authors to attribute these modes to the same structural species as those in elemental g-Se. In agreement with [Lucovsky 1967, Carini 1980, and Yannopoulos 2004a], the authors assigned the band at 239 cm⁻¹ to the vibration of trigonal selenium chains (trans-conformation). The intensities of both peaks at 252 and 262 cm⁻¹, which create a composite band, decrease when the glass is dissolved in CS₂. The latter is a good solvent for monoclinic Se (Se₈) and hence the authors concluded that the two abovementioned bands are related to Se₈-like vibrations. The fourth band, which they report, appears at ~ 230 cm⁻¹. The intensity of this band increases with increasing the As content and the band position slightly shifts to lower energies. This band has been attributed to the As-Se vibrational mode of the AsSe₃ pyramids [Lucovsky 1977, Ohsaka 1979, Mikla 1993]. Contrary to [Mikla 1993], who have found this band in As-Se system only for arsenic content higher than 2 at.%, [Holubova 2007] have identified this one even at composition containing 1 at.% As. They also have found that the peak at 262 cm⁻¹ of glassy Se which is assigned to the vibrations of fragments (chains) originating from Se₈ rings, moves significantly to higher energies when arsenic content is higher than 8 at.%. The authors suppose that As atoms can bind readily these fragments and joining selenium chains in cis-conformation by AsSe₃ pyramids into a compact net. As a result, the bond-stretching vibrational modes of these selenium chains are affected by adjacent arsenic atoms and their energy increases. For As₁₆Se₈₄ glass they found the energy at 273 cm⁻¹.
The atomic radial distribution functions of the As-Se glasses have been studied by Renninger et al. [Renninger 1973] the As$_x$Se$_{100-x}$ glasses with $0.0 \leq x \leq 0.5$. They found that the first neighbor correlation peak shifts linearly from 2.34 Å for elemental Se to 2.41 Å for $x = 36$ and remains constant at higher arsenic concentration. Peak areas increase linearly with arsenic concentration and their magnitudes agree well with a model which assumes that Se is twofold coordinated and that As is threefold coordinated. Moreover, they found that at $x = 40$ and $x = 50$ the first and second neighbor peaks are very similar to that obtained from the crystals As$_2$Se$_3$ and As$_4$Se$_4$. This suggests that local crystalline configurations, possibly made of AsSe$_3$ units and As$_4$Se$_4$ molecules, also exist in bulk glasses. However, significant differences between the crystalline and amorphous distributions are observed after the second peak. They conclude then that models based on the existence of microcrystalline regions of As$_2$Se$_3$ and As$_4$Se$_4$ observed for those two compositions do not give satisfactory agreement with the experimental distributions.

Later on, Leadbetter et al. [Leadbetter 1974] studied As$_x$Se$_{100-x}$ glasses ($30 \leq x \leq 50$) by X-ray and neutron diffraction. They showed that for selenide glasses the sheet structure becomes more pronounced when increasing the arsenic concentration. For all the glasses, the data are consistent with full satisfaction of the respective two- and threefold covalency requirements of chalcogenide and arsenic atoms. The distribution of arsenic-chalcogenide bond lengths is shown to be symmetrical about the average values of 2.44 Å.

The structure of differently prepared vacuum deposited As$_2$Se$_3$ films and As$_2$Se$_3$ and As$_2$Se$_2$ melt-quenched glasses have been investigated by Notholt et al. [Notholt 1989] using X-ray diffraction experiments. For all the films they studied, no significant structural variations were observed: the structure remained similar to the As$_2$Se$_2$ glass composition. Moreover, it was impossible to find a distinct peak due to the As-As distance in the correlation functions, and they observed that the As-As bonding existence just yields an increase of the halfwidth of the first peak in the As$_2$Se$_2$ composition.
A detailed description about the short- and medium-range structural order in chalcogenide alloys can be found in two papers published by J. C. Phillips [Phillips 1979, Phillips 1981]. The conditions for the formation of microcrystals or clusters in chalcogenide glasses are emphasized. Concerning the As\textsubscript{x}Se\textsubscript{100-x} system, an analysis of the variation of the glass transition temperature $T_g$ showed that a maximum is observed for $x = 40$. This was explained by a competition between As\textsubscript{4}Se\textsubscript{4} units and As\textsubscript{2}Se\textsubscript{3} cross-linked chains. The As\textsubscript{4}Se\textsubscript{4} molecular units are stable in the gas phase and are always present in evaporated As\textsubscript{x}Se\textsubscript{100-x} films. These molecules can be destroyed (polymerized in the glass structure) by annealing. The As-As bonds present in these alloys are however very difficult to break.

Later, Elliott et al. [Elliott 1990] using EXAFS, compared an amorphous As\textsubscript{50}Se\textsubscript{50} film and the corresponding bulk glass. They found that the local structural changes in the first coordination sphere are relatively insignificant. The arsenic atoms are coordinated on the average by 2.4 selenium atoms with a mean bond length $R_{\text{As-Se}} = 2.40 \text{ Å}$ and by 0.7 arsenic atoms with a mean bond length $R_{\text{As-As}} = 2.80 \text{ Å}$. Selenium is coordinated to 1.8 arsenic atoms. The uncertainties in the values of coordination numbers were estimated to be approximately $\pm 0.5$.

More detailed EXAFS studies for the binary glasses As\textsubscript{x}Se\textsubscript{100-x} glasses ($20 \leq x \leq 57$) have been undertaken by Mastelaro et al. [Mastelaro 1992]. The analysis of the data revealed the existence of homopolar bonds. For the Se-rich region ($x < 40$), the local structure consists of AsSe\textsubscript{3} pyramidal units and Se-Se homopolar bonds which may form the Se\textsubscript{n} chains and/or Se\textsubscript{8} rings. On the As-rich region side ($x > 40$) the local structure consists of both AsSe\textsubscript{3} pyramidal units and As-As homopolar bonds, the origin of which was not specified in detail. This behavior is different from what has been observed for the arsenic-rich sulfide glassy system. The existence of homopolar bonds for enriched selenium and arsenic glasses is in good agreement with the chemical ordering network model.

Structural detailed of As-Se binary bulk glasses were studied in an indirect way, i.e. through thermal studies of the glasses using TMDSC [Georgiev 2000]. This work revealed that the glass transition temperature $T_g(x_{As})$ variation at $x < 12$ is
linear with a slope $\frac{dT_g}{dx_{As}} = 4.1 \degree C / \text{at.}\% \text{ As}$. This is much lower than the value 7.7 $\degree C / \text{at.}\% \text{ As}$ which is predicted by the stochastic agglomeration theory. Moreover, the nonreversing heat flow almost vanishes in the $29.1 < x < 37$ composition range, thus the rigidity onset occurs at $<r_c> = 2.29$, i.e. substantially below the usual mean-field value of 2.40. These thermal results interpreted in terms of the agglomeration theory and constraint theory led to the conclusion that in addition to AsSe$_3$ pyramidal units, quasitetrahedral (QT) Se=AsSe$_3$ (where $=$ denotes a double bond) units also serve to crosslink Se$_n$ chains at $x < 40$. To account for the observed differences between experiments and the stochastic agglomeration theory, the authors [Georgiev 2000] suggested that almost 30% of As atoms must be 4-fold coordinated. This is an unrealistically high fraction which conflicts the findings of Raman scattering.

The quest for such QT units is quite old. According to Diemann (1979), in As$_2$S$_5$, vibrational and photoelectron spectroscopic investigations as well as the radial distribution curves indicate the presence of QT units S=AsS$_{3/2}$ in the short-range structural order of glassy As$_2$S$_5$. Each As-atom is bonded to the bridging S atoms at a distance of 230 pm and to one terminal S atom at 212 pm. In the first TMDSC study of the As-Se binary glasses, Wanger et al. [Wagner 1996] presume that a similar structure can be expected in As$_2$Se$_5$ glass, with Se=AsSe$_{3/2}$ QT structural units. They suggested that when the As-Se system reaches the composition As$_{16.6}$Se$_{84.4}$ the structure of the glass can be represented as As$_2$Se$_{10}$, with five-fold coordinated As atoms, two-fold coordinated Se atoms and structural units AsSe$_{5/2}$ in short range order. They conclude that in the As-Se glass system the addition of As into Se leads initially to branching of selenium chains. They considered that the local maxima in the $T_g$ vs. $x_{As}$ curve can be accounted for by considering 5-fold As units of the form AsSe$_{5/2}$ and the QT units Se=AsSe$_{3/2}$ appearing at $x_{As} = 16.6 \text{ at.}\%$ and 28.5 at.\% As, respectively. Further addition of As-atoms destroys the Se=As double bonds, which leads to the formation of pyramids in the structure. The number of these pyramidal units increases and they are clearly seen at 40 at.\% As.
The preceding survey indicates, in fact, that there is still discrepancy about the detailed atomic structure of As-Se binary glasses. Table 7.1 is a brief summary of the structural studies. In general, the various techniques “agree” on the fact that AsSe$_3$ is the basic unit for all glassy compositions. Polarization-analyzed Raman spectra have not yet been recorded. Therefore, in the rest of the present chapter we

### Table 7.1 Some results found by others’ works

<table>
<thead>
<tr>
<th>Compositions $\text{As}<em>x\text{Se}</em>{100-x}$</th>
<th>Se rich</th>
<th>As rich</th>
<th>Molecular model propositions</th>
<th>Form</th>
<th>Techniques</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>$0.40 \leq x \leq 0.50$</td>
<td>-</td>
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<td>Bulk</td>
<td>IR, Raman</td>
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<tr>
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<td>No</td>
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<td>Bulk</td>
<td>Raman</td>
<td>Mori 1980</td>
</tr>
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<td>XRD</td>
<td>Renninger 1973</td>
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<tr>
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<td>-</td>
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<td>Bulk</td>
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<td>Bulk</td>
<td>MCS</td>
<td>Phillips 1979, Phillips 1981</td>
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<tr>
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<td>$\text{AsSe}_3$</td>
<td>Thin films</td>
<td>Modeling</td>
<td>Phillips 1979, Phillips 1981</td>
</tr>
<tr>
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<td>Thin films</td>
<td>XRD</td>
<td>Notholt 1989</td>
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<td>-</td>
<td>-</td>
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<td>Thin films</td>
<td>EXAFS</td>
<td>Elliott 1990</td>
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</tbody>
</table>
provide detailed, high-resolution, polarization-analyzed Raman spectra and analyze them in order to get some more insight into the structure of As-Se glasses. Some of the most interesting questions to be answered regarding the structure of these glasses are: (i) The existence of Se$_8$ rings, (ii) (2) Slope change of $T_g$ and other properties at $x_{As} \approx 15$, and (iii) The existence of quasi-tetrahedral S=As(Se$_{1/2}$)$_3$ units.

### 7.2 Results

Figure 7.1 illustrates the polarized, depolarized, and isotropic Raman spectra of the As$_x$Se$_{100-x}$ binary system for a wide range of compositions from elemental Se ($x_{As} = 0$) up to the stoichiometric glass ($x_{As} = 40$). Isotropic Raman spectra were calculated using Eq. 5.4. For clarity, the spectral range has been divided in low and high frequency parts, shown in the left and right panels, respectively. The spectral resolution was set to 1 cm$^{-1}$. The Raman band intensities of the lower frequency range have been magnified by a factor of 10 in relation to the spectra of high frequency range. The high frequency bands (200 – 300 cm$^{-1}$) represent bond-stretching vibrations while the low frequency spectra (below 150 cm$^{-1}$) originate mainly form bond bending and torsional vibrations.

Due to the proximity of the As and Se masses As-Se and Se-Se vibrational frequencies are of the same magnitude. This is evident from Fig. 7.1 where it is observed that with the progressive addition of As, new Raman bands appear overlapping, at both sides of the main vibrational mode of Se locate at ~250 cm$^{-1}$. Changes occur also in the low energy spectra, though less dramatic compared with those in the high energy spectral range. In particular, the sharp polarized band at ~110 cm$^{-1}$ in the spectrum of elemental Se gradually disappears when alloying with As at concentrations $x_{As} > 15$. New weak bands appear near 155 cm$^{-1}$ associated with the bending modes of AsSe$_3$ pyramidal units. It is noteworthy that there is a spectral gap in the vibrational modes for all glasses shown in Fig. 7.2. For elemental Se this gap amounts to ~70 cm$^{-1}$. Although this phonon-band-gap zone exhibits systematic decrease upon increasing the As content it is still evident in the Raman spectrum of the stoichiometric glass.
The frequency dependence of the depolarization ratio, \( \rho(\tilde{\nu}) = I^{\text{VH}}(\tilde{\nu}) / I^{\text{VV}}(\tilde{\nu}) \), for the glasses studied here is shown in Fig. 7.2. The spectral region of the gap has been omitted from the figure for clarity. As expected, Raman bands originating from stretching vibrational modes are more polarized in comparison to the bands assigned to bending/torsional modes. As reported in the experimental section, several annealing procedures took place in order to get the correct form of \( \rho(\tilde{\nu}) \).

**Fig. 7.1.** Polarized (black), depolarized (red), and isotropic (blue) Raman spectra of the As\(_x\)Se\(_{100-x}\) binary glasses. The As content (at. %) is given in each case. The left panel contains the low energy spectra magnified by a factor of 10 in relation to the high frequency spectra (right panel).
As mentioned in Section 5.22 it is common in Raman studies to address issues related to the population of various species or structural units composing the glass structure. It is therefore of particular importance to advance line shape corrections to the raw, experimental intensities. For an accurate determination of the correct Raman band intensities two types of spectra transformation are considered: the “isolation” of the isotropic and the anisotropic parts of the Raman
tensor, and the removal of the temperature, laser wavelength and mode frequency
dependence from the band intensities using the reduced representation.

A representative example of the aforementioned data manipulation is
illustrated in Fig. 7.1 for the As$_{30}$Se$_{70}$ and As$_{35}$Se$_{65}$ glasses. The advantage of using
different polarization geometries is evident. As it is seen, the breadth of the Raman
spectra makes rather tricky the recognition of the number and exact energy of the
various modes if only the polarized (VV) spectrum is examined. On the other hand,
combining information from the depolarized spectrum and in particular from its
frequency dependence, peak identification becomes more reliable.

For facilitating the comparison between the various forms of Raman spectra
vertical dashed lines have been added at wavenumbers where peaks positions are
evident. Lines “1” and “5” in Fig. 7.3 reveal hidden vibrational modes which are
only identified only in the $\rho(\vec{\nu})$ spectrum (which exhibits distinct minima) while
the VV spectrum reveals the existence of three peaks (lines “2”, “3” and “4”). It is
therefore obvious the imperative need to analyze all three functions $I^{\text{VV}}(\vec{\nu})$, $I^{\text{VH}}(\vec{\nu})$
and $\rho(\vec{\nu})$ for a reliable peak identification in Raman spectra. The correct number of
peaks is important in order to identify the structural units (short-range structural
order) and their connectivity (medium-range structural order) because group theory
[Nakamoto 1986] predicts the number of vibrational modes and their polarization
character given the point group symmetry of the structural unit.

Another noteworthy point seen in Fig. 7.3 is that the corrected spectra have
appreciable changes in both band intensities and mode frequencies. As regards the
former, it is clear that the relative band intensities in reduced isotropic spectra are
considerably different than those in the raw data. This fact must be taken into
account when “species” populations are associated to Raman band areas determined
by curve fitting. Concerning band energies, Fig. 7.3(a) illustrates a typical example.
For example, the high frequency peak (vertical line “4”) is situated at 254, 256, and
258 cm$^{-1}$ in the VV, isotropic, and reduced isotropic spectra, respectively. Although
these differences are not practically significant in understanding the structure of
glasses, the knowledge of accurate mode frequencies is important in cases where
these parameters are used to characterize rigidity transitions where shifts of the order of 1 cm\(^{-1}\) are taken into account [Selvanathan 2000].

![Raman spectra of As\(_{35}\)Se\(_{65}\) and As\(_{30}\)Se\(_{70}\)](image)

**Fig. 7.3.** Representative examples of Raman spectra treatment. Black, red and blue lines represent the VV, VH and isotropic spectra, respectively. Cyan and magenta lines represent the reduced isotropic and anisotropic spectra, respectively. The spectrum of the depolarization ratio has also been added to reveal the different symmetry character of the vibrations in the broad 200-300 cm\(^{-1}\) Raman band.
7.3 Analysis of the Results and Discussion

7.3.1 Analyzing Raman spectra as superposition of Se chains and AsSe$_3$ pyramids network structures

Reduced-isotropic (R$^{iso}$) and reduced-anisotropic (R$^{aniso}$) Stokes-side Raman spectra are illustrated in Fig. 7.4 for all glass compositions ranging from elemental Se to the stoichiometric glass As$_2$Se$_3$. The spectra have been scaled in an arbitrary way in order to reveal better the spectral changes brought about by the increasing As concentration. In particular, for low $x_{As}$ the spectra have been matched at the intensity of the strongest peak in the Raman spectrum of elemental Se. It is easily made out that new peaks grow at both sides of the main vibrational mode of elemental Se upon increasing the As content in the glass.

Before proceeding to a deconvolution analysis of the individual lines hidden under this complex Raman band profile for both R$^{iso}$ and R$^{aniso}$ spectra we will try to get some quantitative results. As became clear from the literature survey given in Section 7.1 the main building blocks in elemental Se and the stoichiometric glass As$_2$Se$_3$ are the Se$_n$ chains and the AsSe$_3$ trigonal pyramids. The structures of the intermediate compositions are mixtures of these two structural units. Using this as a starting-point and assuming that the structure of the glasses between elemental Se and the stoichiometric composition is a linear combination of Se chains and pyramidal units, we can “theoretically” reproduce the Raman spectra of the intermediate compositions. This way of analyzing the Raman data was also followed by Onari et al. [Onari 1985]. The spectra obtained by this procedure are shown in Fig. 7.5. The steps followed are:

(i) The contribution of the spectrum due to the presence of AsSe$_3$ pyramids to the spectrum at each intermediate glass composition was calculated. To achieve this, the As$_2$Se$_3$ spectrum was multiplied by $x_{As}/40$ and normalized to the spectrum of each glass at 220 cm$^{-1}$ where only AsSe$_3$ pyramids are expected to contribute. This is denoted as the “theoretical” spectrum in Fig. 7.5.
(ii) The difference between the experimental and the “theoretical” spectrum was calculated; denoted as the “difference” spectrum in Fig. 7.5.

(iii) The $R^{iso}$ spectra of Se were also added in Fig. 7.5. for comparison later having been normalized to the height of the difference spectrum.
Fig. 7.5 Representative reduced isotropic spectra of the binary glasses $\text{As}_x\text{Se}_{100-x}$ ($x = 5, 20, 35$) analyzed with the procedure described in the text.

The main idea behind this qualitative analysis of the Raman spectra is to see whether the structure of the intermediate compositions can be satisfactorily described as linear combinations of the two “limiting” glasses, i.e. Se and $\text{As}_2\text{Se}_3$. To check this hypothesis one has to compare the “difference” spectrum which stands for the expected modes of the Se-Se vibrations for the intermediate compositions with the normalized Se spectrum. Dissimilarities between these two spectra are indications of two main factors: (i) Structural correlations or
perturbations effects due the presence of As atoms. Indeed, Raman spectra are sensitive to the medium-range effects and hence the Se-Se vibrational modes have different frequencies depending on the local environment surrounding these bonds. The addition of As causes an interconnection of the Seₙ chains which eventually leads to a severe length shortening of the latter. As in the case of sulfide glasses, short chains vibrations are different than long ones due to the redistribution of the electrons’ overlap.

Inspecting Fig. 7.5, we observe that the similarity between the “difference” and the experimental spectrum of Se is significant at low values of \( x_{\text{As}} \), while it is gradually lost with increasing the As content. The dissimilarity between these two spectra pertains to their difference in peak frequency and halfwidth as well. Figure 7.6 shows the calculated “difference” spectra for all glass compositions.

**Fig. 7.6.** Subtraction between raw data and “theoretical” spectra of As-Se system are denoted as “Difference” spectra.
demonstrating the changes we have just described. Apart from the peak position and halfwidth, the area also exhibits a strong decrease as expected due to the decrease of the number of Se-Se bonds at high As contents. Making the above arguments more quantitative, we present in Fig. 7.7 the As-content dependence of the spectral features (energy, width, and area) of the “difference” spectrum which stands for the Se-Se vibrations for the intermediate glasses.

Fig. 7.7. As-content dependence of the spectral features (energy, width, and area) of the “difference” spectrum. The shaded rectangular denotes the composition range where changes occur in the trends of the plotted spectral parameters.
In order to check the validity of the procedure described above we plot in Fig. 7.8 the dependence of the quantity $\Delta \nu_{\text{Se-Se}}$ on $x_{\text{As}}$. $\Delta \nu_{\text{Se-Se}}$ is the difference in the Raman shifts between the peaks associated with Se-Se vibrations in elemental Se and the corresponding component (i.e. the frequency mode assigned to Se$_\mu$ chains in pure selenium, at 250.5 cm$^{-1}$) in the R$^{\text{iso}}$ spectra (solid squares) and the “difference” spectra (open circles). It is readily seen that the symbols for the data sets in Fig. 7.8 match very well until 15 at% As. Above this composition the agreement is not so satisfactory.

![Graph showing the arsenic-content dependence of the quantity $\Delta \nu_{\text{Se-Se}}$.](image)

**Fig. 7.8.** Arsenic-content dependence of the quantity $\Delta \nu_{\text{Se-Se}}$; see text for details.

It is clearly seen from Fig. 7.7 that all three spectral parameters exhibit different trends at $x_{\text{As}}$ values exceeding 15 at.% in As. This behavior leads us to the conclusion that close to this point there is a change in the “rule” that controls the building of structure upon adding As in the glassy Se. In particular, at very low $x_{\text{As}}$ values the addition of As atoms leads to the creation of AsSe$_3$ pyramidal units which are initially well separated spatially. This procedure follows up until, at some intermediate concentration of As atoms, a fraction of these pyramidal units become interconnected by a Se atom; a situation that brings As atoms in the second
CHAPTER 7: Structural aspects of the As\textsubscript{x}Se\textsubscript{100-x} glassy system: A Raman scattering study

coordination sphere. Obviously this situation changes the initial “rule” that governs structure formation at low \(x\text{As}\).

It interesting to notice that several decades ago [Nemilov 1964] in thermodynamic and viscosity studies of As-Se melts Nemilov found that the activation entropy of viscous flow for binary As-Se melts exhibits a discontinuity when plotted as a function of \(x\text{As}\) when exceeding \(x\text{As} = 17\). To account for this finding Nemilov considered changes in the character in the glass structure at this composition. In particular, it was found that the activation entropy dependence on composition follows three distinct regions, suggesting that at low arsenic concentrations the structure was primarily that of amorphous selenium, while at concentrations above 20 at.\% As an \(\text{As}_2\text{Se}_3\)-type structure predominated, with a mixture of the two structures in the region 10-20 at.\% As. A similar result was obtained by Myers and Felty [Myers 1967] in a study of glass transition temperature \(T_g\) vs. composition. In addition, the above composition threshold matches nicely with the eutectic point of the binary As-Se glasses at \(x\text{As} = 20\).

7.3.2 On the existence of the quasi-tetrahedral Se=AsSe\textsubscript{3} unit

Qualitative changes at about \(x\text{As} = 15\) are also demonstrated in the as-content dependence of other parameters related to the rigidity of the glass. In particular, the curve of \(T_g\) vs. \(x\text{As}\) exhibits a plateau in the range \(15 < x\text{As} < 20\) [Georgiev 2000]. The authors considered that at this region there is a transition from a stochastic mechanism of structure formation to a non-stochastic one at \(x\text{As} > 15\) as dictated by stochastic agglomeration theory [Kerner 1994, Miccoulaut 1999]. Stochastic agglomeration theory provides an attractive framework to analyze the observed \(T_g(x\text{As})\) trends in the low As content range. The theory identifies \(T_g\) with the temperature at which covalent agglomeration processes between local structural units are frozen. Thus, a selenium chain-glass network stochastically crosslinked by three-fold coordinated As, should result in a linear increase of \(T_g\) with slope of about \(dT_g/dx\text{As} = 7.7 \degree C / \text{at.}\%\) As predicted by the theory. This value is appreciably higher than the experimental finding value \(4.1 \degree C / \text{at.}\%\) As in the range \(0 < x\text{As} < 12\).
To account for the observed discrepancy between theory and experiment it was considered [Georgiev 2000] that the mechanism of the three-fold coordination of As atoms must be reconsidered. Adopting the presence of Se=AsSe$_3$ QT units (as mentioned in Section 7.1) it was found that the theoretical slope of $T_g$ vs. $x_{As}$ curve should match the experimental value if $\sim$30% of As atoms participate in QT units.

The existence of a fraction of $\sim$30% of As atoms forming QT units should be observable in Raman scattering especially in view of the presence of the double As=Se bond which is expected to give a distinct fingerprint in the Raman spectrum. It should be instructive here to use an analogy from other systems whose Raman spectra of single and double bonds are known, so as to predict the spectral range where the As=Se vibration is to be expected. Solid evidence for the presence of double bonds exists for phosphorous selenide glasses (Se=PSe$_3$) while no clear evidence exists for As-Se glasses (see Section 7.1). A double bond between As and Se atoms has a length considerably smaller than that of a single bond. Besides, a repulsive interaction of double bonding electrons with single bonding ones around As atom in the Se=AsSe$_3$ QT structural unit also affects the equilibrium parameters of the single bonds. Thus, Thus, in a Se=AsSe$_3$ structural unit, one should expect some increase in single bonding length compared with the corresponding bonds in trigonal pyramidal units AsSe$_3$ pyramid and hence the angles $\alpha$ and $\beta$ [see Fig. 7.9(a)] will differ from the of the perfect tetrahedral symmetry (109.5$^o$), being $\alpha > 109.5^o > \beta$. Geometrical calculations easily result in the following relation between these angles, i.e. $\sin(\beta/2) = (3/2)^{1/2} \sin (180^o - \alpha)$. Using the above arguments and analyzing radial distribution function of selected compositions from the As-Se binary system Luksha et al. [Luksha 1991] concluded that QT units could be found in thin films’ structure produced by flash evaporation. They suggested that the comparatively higher evaporation temperatures, in comparison with normal thermal evaporation methods, are capable of exciting such atomic complexes with subsequent electron orbital hybridization of As and Se atoms necessary for the formation of the structural units with double As=Se bonding.
As mentioned in Section 7.1. Diemann [Diemann 1976] studied glassy As$_2$S$_5$ using vibrational spectroscopy, electronic absorption, photoelectron spectroscopy, and x-ray diffraction. Interpreting the Raman and IR spectra Diemann considered erroneously that the 463 cm$^{-1}$ mode in the Raman spectrum is indication of the As=S$_t$ (terminal) double bond. Obviously, this interpretation is flawed since the strong, sharp line at 463 cm$^{-1}$ is the symmetric stretching S-S vibrational mode of this S-rich glass. Therefore, Diemann considered that the structure of this glass is based on the molecular unit As$_4$S$_{10}$ (see Fig. 7.9) which is composed of four QT units S$_t$=AsS$_3$. The x-ray diffraction analysis of the authors resulted in two interatomic arsenic-sulfur distances at 2.12 and 2.30 Å for As-S$_t$ and As-S$_b$ (bridged) bonds, respectively.

![Fig. 7.9. (a) Ball and stick draw of the QT unit; the red Se atom denotes the bonded via a double bond to As. (b), (c) Ball and stick draws of the HF fully optimized structures of highly symmetric As$_{4}$Se$_{6}$ and As$_{4}$Se$_{10}$ cage-like molecules.](image)

To support our arguments we use evidence from ab initio calculations [Chrissantopoulos 2009a] of the geometrical and vibrational properties of As-Se cage-like molecules. The Hartree-Fock (HF) molecular orbital theory as implemented in the GAUSSIAN 03 program package is utilized in the present study in order to calculate the structural details of the two cage-like molecular units As$_4$Se$_n$ (n= 6, 10). The accuracy of the computational method and the basis sets, which have been chosen for the investigated systems, has been tested by comparing the calculated properties with other theoretical and experimental structural data that
are available in the literature. The electronic structure of the atoms participating in the investigated structures are described by the Ahlrichs TZV basis sets [Schafer 1994] For a more accurate description of the nature of the chemical bond between atoms and for a better determination of the vibrational energies, a polarization d-Gaussian-type function (GTF) has been added on arsenic and selenium set. (Basis sets were obtained from the EMSL Basis Set Exchange Library [Feller 1996; Schuchardt 2007].

Using the method described above we have undertaken a full optimization of the structures of the cagelike “molecules” shown in Figure 7.9. The $\text{As}_4\text{Se}_6$ molecule contains four pyramidal units interconnected through the $\text{Se}$ atoms situated at the pyramids’ bases. Table 7.2 contains the structural parameters of the cagelike units as estimated by the HF method. $\text{Se}_t$ stands for the terminal $\text{Se}$ atoms connected to $\text{As}$ atoms via double bond.

Table 7.2. Structural parameters of the fully optimized structures of $\text{As}_4\text{Se}_6$ and $\text{As}_4\text{Se}_{10}$ cagelike molecules. For comparison the geometrical parameters of the corresponding sulfide molecules [Chrissantopoulos 2009b] are shown. $\text{Se}_t$ denote terminal $\text{Se}$ atoms connected via double bond with $\text{As}$ atoms.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\text{As}_4\text{X}_6$ ($T_d$)</th>
<th>$\text{As}<em>4\text{X}</em>{10}$ ($T_d$)</th>
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<tr>
<td>$R(\text{As-As})$ /Å</td>
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<td>$X=\text{Se}$ HF</td>
</tr>
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<td></td>
<td>$X=\text{S}$ HF</td>
<td>$X=\text{Se}$ HF</td>
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<tr>
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<td>$\angle \text{X-As-X}_t$ /°</td>
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</table>

Vibrational analysis has been performed at the HF level theory of the $\text{As}_4\text{Se}_6$ and $\text{As}_4\text{Se}_{10}$ cagelike molecules at $T_d$ symmetry in order to obtain the harmonic frequencies of particular vibrational modes. The symmetric breathing mode of the
As$_4$Se$_6$ cage which involves mainly the radial motion of Se atoms (As atoms are practically frozen) is found at 213.4 cm$^{-1}$ characterized by Raman activity (RA): $60.5 \times \text{a.m.u.}^{-1}$ and depolarization ratio $\rho = 0$. The corresponding vibration of the As$_4$Se$_{10}$ cage is located at 232.9 cm$^{-1}$ with RA: $27.6 \times \text{a.m.u.}^{-1}$ and $\rho = 0$. The higher Raman frequency in the case of the As-Se$_b$ bond in the As$_4$Se$_{10}$ cage is in agreement with the shorter bond length of this bond in comparison to the corresponding As-Se$_b$ bond length in the As$_4$Se$_6$ cage. The vibrational motion that involves mainly the As-Se$_t$ bond stretching with minor displacements of other atoms was estimated at a high energy as expected, i.e. at 376.6 cm$^{-1}$ with RA: $0.08 \times \text{a.m.u.}^{-1}$ and $\rho = 0$. The RA of the As-Se$_t$ bond stretching vibrational mode is almost two orders of magnitude smaller than the corresponding of the As-Se$_b$ bond stretching. This situation is unique for the As$_4$Se$_{10}$ molecule since for the sulfide counterpart (As$_4$S$_{10}$) the RA of the two bonds are comparable. By scaling the calculated As-Se frequencies to experimental ones (the main As-Se vibrational mode of AsSe$_3$ pyramids is located at ~230 cm$^{-1}$) we find that the As-Se$_t$ mode should be located in the experimental Raman spectrum at an energy range not lower than ~406 cm$^{-1}$. At present, the Raman data show no evidence for such a peak in the above spectral range. However, this could also be due to the very low Raman activity of the As=Se$_t$ bond vibration.

Concluding, the presence of QT units with double As=Se bonds in binary As-Se glasses is highly questionable. No evidence exists from Raman scattering about the double bond. If such molecules exist are present in the glass structure their concentration must be negligible. Therefore, the 30% percentage suggested by DSC studies [Georgiev 2000] is an unrealistically high fraction.

7.3.3 On the existence of Se$_8$ rings in the structure of As-Se glasses

A detailed discussion has been presented in Section 6.3.1.1 concerning the structure of glassy Se. The presence of rings in elemental Se was studied in detail with Raman scattering [Yannopoulos 2004a, Yannopoulos 2004b] using analogies from corresponding studies of elemental S [Kalampounias 2003] where the
vibrations of the $S_8$ rings and $S_\mu$ chains are better resolved. The fraction of Se atoms participating in $Se_8$ rings in elemental Se has been estimated to about 15% much below $T_g$ exhibiting a monotonic decrease with temperature rise [Yannopoulos 2004b]. The only approximation made was the equivalence of the Raman scattering efficiencies of these two species which is however justified to some extent by the similarity of the Raman and neutron data in this frequency region. A valuable contribution to the ring/chain picture has been made by Misawa et al. [Misawa 1978] who developed a disordered chain model for $g$-Se. These authors put forward the idea that the structure of $g$-Se is not composed solely by isolated rings and chains but contains also molecular fragments having both ringlike and chainlike conformations. The model advanced by Misawa et al. appeared almost at the same time with, however independently of, Luckovský’s suggestion that a single macromolecular species can be composed by both helixlike and ringlike arrangements [Lucovský 1979]. Therefore, the fraction of the “$Se_8$” component estimated by Raman scattering contains both the isolated $Se_8$ rings and the ringlike arrangements that can be found in chains.

In an effort to analyze the unpolarized Raman spectra of As-Se glasses at low As concentrations [Holubova 2007] it was suggested that the Raman peak on the high wavenumber side of the main peak at 250 cm$^{-1}$, i.e. at 262 cm$^{-1}$ and beyond is a manifestation of ringlike arrangements in chains. However, since the intensity of the Raman bands in the spectral range 260-280 cm$^{-1}$ increases continuously with the increase of $x_{As}$, we consider that the above explanation is erroneous. We believe that the increased Raman intensity in the above spectral range has a twofold origin: (i) The pyramidal unit AsSe$_3$ with $C_{3v}$ symmetry is characterized by four active Raman modes. Therefore, some of these modes may contribute to the range 260-280 cm$^{-1}$. (ii) It is known from Raman studies of the binary As-S glasses [Kyriazis 2009] that at very high concentrations, just below the stoichiometry threshold, the presence of disulfide bonds of the form S$_2$AsS-SAsS$_2$ (i.e. two pyramids joint by an S-S bond) gives rise to a band which is situated at a frequency ~7% higher than the S-S frequency of long chains. Using this scaling
factor for the isostructural As-Se glasses we find that the diselenide bonds Se₂AsSe-SeAsSe₂ that will appear at high $x_{\text{As}}$ values will contribute to ~268 cm⁻¹, i.e. at the spectral range under consideration.

To check the above arguments we advance below a comparison of the Raman spectra between As-Se and Sb-Se glasses at the same compositions. We expect that since the SbSe₃ pyramid is much heavier than the AsSe₃ one, all four vibrations of this unit [see (i) above] will shift to much lower frequencies. Indeed,

![Graph showing Raman spectra comparison between Sb-Se and As-Se glasses](image)

**Fig. 7.10.** Comparison between $R^{iso}$ spectra for selected compositions of binary $\text{As}_x\text{Se}_{100-x}$ and $\text{Sb}_x\text{Se}_{100-x}$ ($x_{\text{As}}=5, 10$) glasses.
Fig. 7.10 illustrates the $R^{iso}$ Raman spectra of Sb-Se and As-Se glasses for $x_{As} = 5, 10$. The comparison reveals that the high wavenumber side of the band in As-Se glasses (apart from exhibiting blue-shift) broadens proportionally to the $x_{As}$ content. This observation shows that the modes at this energy region are probably associated with As-Se units, which in the case of the heavier Sb mass are present at lower wavenumbers in the case of Sb-Se glasses.

7.3.4 Quantitative analysis of Raman spectra

Two main structural models of vitreous $As_xS_{100-x}$ (X: S, Se) can be found in the literature. Both models involve severe approximations yet each stresses a different aspect of the known structural features of these glasses.

(i) Planar-Random-Network Model: Bermudez has extrapolated from the layer character of both crystalline and vitreous $As_xS_3$, to a two-dimensional computer-generated disordered network model of the amorphous phase [Bermudez 1972]. A portion of the network is shown in Fig. 7.11(a). Note that the distribution in As-S-As bond angles is Gaussian while the S-As-S angle is fixed at 120°. Using this

![Fig. 7.11. Schematic representation of the atomic arrangements in (a) the planar-random-network model and (b) the molecular model, [Kobliska 1973].](image)

structural model and a two-parameter potential function involving nearest-neighbor central and noncentral interactions, Bermudez generated and solved the equations
of motion and calculated the density of vibrational states of vitreous As$_2$S$_3$. His calculated density of states has a reasonable agreement with experiment. Bermudez’s model was also found to give a satisfactory explanation of the symmetry of the observed vibrational modes by predicting rather well the frequency dependence of the depolarization ratio spectrum [Kobliska 1973].

(ii) Molecular Model: Lucovsky and Martin have proposed a molecular model based on the local atomic arrangement shown in Fig. 7.11(b) to explain the optical spectra of amorphous As$_2$X$_3$ glasses [Lucovsky 1972]. They associate bands in the Raman and infrared spectra of vitreous As$_2$X$_3$, with the intramolecular and intermolecular vibrations of a basic structural unit, the AsX$_3$, pyramid. The intermolecular modes are identified with deformations of the triatomic bent chain As-S-As “waterlike molecule”. (In this respect the planar-random-network model and molecular model are quite similar). The intermolecular coupling is presumed to be sufficiently weak that the pyramidal modes and the bridging chain As-X-As modes can be treated independently. In addition, from a group theoretical point of view, the AsX$_3$ and As-X-As units have the well-known point-group symmetries C$_{3v}$, and C$_{2v}$, respectively. The Raman active modes of the pyramidal and the bent molecules are illustrated in Fig. 7.12.

![Diagram of Raman active modes](image)

Fig. 7.12. Schematic representation of the Raman active modes of the (A) pyramidal AsX$_3$ and (B) the “waterlike molecule” As-X-As.
ν₁, ν₃ and ν’₁ are the symmetric and anti-symmetric bond-stretching modes and ν₂, ν₄, ν’₂, and ν’₃ are bond-bending or deformation modes. The latter are doubly degenerate. Table 7.3 contains experimental frequencies taken from Raman and IR spectra and theoretical ones calculated by force-field models for the two isostructural stoichiometric glasses As₂Se₃ and As₂S₃ (values in parentheses). Frequencies for As₂Se₃ are solely from IR spectroscopy. The vibrational frequencies obtained from the present study are also included in the last column. An asterisk besides a frequency means that this frequency has been determined visually while the other values are taken from fits. We should remind again at this point that FT-Raman intensities are useful up to a lower cut-off limit of ~120 cm⁻¹. Therefore, it is not possible to provide frequencies for the ν₂ and ν’₂ modes.

Table 7.3. Experimental (Raman and IR) and calculated frequencies for As₂Se(S)₃ glasses, compared with those assigned in the present study. Calculated frequencies are from [Lucovsky 1972]; experimental frequencies for As₂S₃ are from [Shastry 1993], while for As₂Se₃ are from various sources given in [Shastry 1993].

<table>
<thead>
<tr>
<th></th>
<th>Calculated frequency [cm⁻¹]</th>
<th>Experimental frequency [cm⁻¹]</th>
<th>Experimental present work [cm⁻¹]</th>
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<tbody>
<tr>
<td>AsSe(S)₃</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pyramidal molecule</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>C₃ᵥ symmetry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₁</td>
<td>227 (344)</td>
<td>227 (345)</td>
<td>133*</td>
</tr>
<tr>
<td>ν₂</td>
<td>102 (162)</td>
<td>101 (160)</td>
<td>149*</td>
</tr>
<tr>
<td>ν₃</td>
<td>220 (310)</td>
<td>216 (310)</td>
<td>210</td>
</tr>
<tr>
<td>ν₄</td>
<td>78 (133)</td>
<td>75 (120-150)</td>
<td>217</td>
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<td></td>
<td></td>
<td></td>
<td>234</td>
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<tr>
<td>As – Se(S) – As</td>
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<tr>
<td>“water molecule”</td>
<td></td>
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</tr>
<tr>
<td>C₂ᵥ symmetry</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ν’₁</td>
<td>178 (218)</td>
<td>170 (230)</td>
<td>250</td>
</tr>
<tr>
<td>ν’₂</td>
<td>39 (55)</td>
<td>45 (55)</td>
<td>263</td>
</tr>
<tr>
<td>ν’₃</td>
<td>282 (438)</td>
<td>290 (400)</td>
<td>277</td>
</tr>
</tbody>
</table>

In order to accurately determine the vibrational frequencies from our Raman spectra we have undertaken a quantitative analysis using Gaussian lines to deconvolute the complex and broad spectral envelops of the R¹iso and R²aniso spectra.
that develop upon increasing the concentration of As. Some representative examples of the analysis are given in Fig. 7.13. In all cases the least number of fitting components was used in order to get a satisfactory description of the experimental spectra. Open symbols represent the experimental data. The red lines passing through the data points are the best-fit curves. Only 25% of the experimental points are shown for clarity. Blue and dark green solid lines stand for the various spectral components of the $n R^{iso}$ and $R^{aniso}$ spectra, respectively. The experimental depolarization ratio $\rho$ is also plotted in the figures. The importance of the frequency dependence of this parameter has been adequately described in section 7.2. Actually, as is easily made out from Fig. 7.13 the local extrema (minima or maxima) of $\rho$ coincide very well with the peak positions as determined by the fits. The vertical dashed lines are used to reveal this finding. Two more varieties of $\rho$ are also indicated in the figure; $\rho^{iso}_{fit}$ and $\rho^{iso}_{exp}$ represent the ratios of $R^{aniso} / R^{iso}$ for the best-fit curve (red lines) and the experimental data, respectively. In the region of interest, i.e. where the Raman intensity is considerably higher than the background signal, the two spectra $\rho^{iso}_{fit}$ and $\rho^{iso}_{exp}$ match almost perfectly showing that the obtained fit results are realistic.

As regards elemental Se, the interpretation of the various fitting components has been amply described elsewhere [Yannopoulos 2004a]. In brief, in the previous reference it was for the first time suggested that the composite 220–280 cm$^{-1}$ spectral envelope contains three (instead of two) peaks as considered in the existing literature. The 234 cm$^{-1}$ peak it is well-established so far that it originates from Se chains in a configuration resembling the crystalline trigonal configuration, t-Se. The peaks at 250 cm$^{-1}$ and 262 cm$^{-1}$ were assigned to Se-Se bond stretching vibrations in disordered chains and rings.

The situation becomes more complicated for the spectrum of the As$_{10}$Se$_{90}$ glass. There are two more new peaks that appear at this glass composition. The peak at 226 cm$^{-1}$ comes from the symmetric stretching As-Se bond in AsSe$_{3/2}$
Fig. 7.13. Deconvolution analysis of the $R^{iso}$ and $R^{aniso}$ Raman spectra of selected glass compositions. Red lines: final fit curves; blue lines: $R^{iso}$ fit components; green lines: $R^{aniso}$ fit components; the various depolarization ratios are described in the text.
Fig. 7.13. Continued (see previous page for description).
pyramidal units. The peak at 237 cm\(^{-1}\) is mainly depolarized and is situated at exactly the same energy with the peak we assigned to Se-Se bond stretching vibrations in t-Se-like environments in the elemental Se glass. Despite this, it is highly unlikely that these two peaks have the same origin. A fraction of 10 at.\% of As is quite high (i) to induce disorder to the more ordered t-Se-like environments thus perturbing the oriented chains and (ii) to increase the density of the branching points between the one dimensional Se chains, hence reducing the -Se\(_n\)- segments between such branching points. Further, this frequency does not seem to match any one of the frequencies of the molecular model given in Table 7.3. Therefore, this vibrational mode has to be assigned to a new species formed at this composition whose origin is at present not known. Finally, an extra vibration mode appears at high energies, 274 cm\(^{-1}\) which is highly polarized. The frequency of this mode is near the \(\nu_3\) mode of the C\(_{2v}\) symmetry water-like molecule (see Table 7.3). However, we can not assign the 274 cm\(^{-1}\) peak to the \(\nu_3\) mode of the water-like molecule because the possibility to find two AsSe\(_3\) pyramids connected by a common Se atom at such low As concentrations is negligible. In other words, the As atoms, being dispersed randomly in the glassy Se matrix, will form AsSe\(_3\) pyramids which will be separated by short Se chains. The fact that this is the vibrational mode with the highest energy it is more reasonable to assume that it might be related to Se-Se bond stretching vibrations of Se atoms in ring-like environments.

The analysis becomes more complicated for the spectra of the As\(_{30}\)Se\(_{70}\) glass. A new peak appears at low energy, i.e. at 210 cm\(^{-1}\). The other bands are almost at the same energies as in the previous composition while their relative intensities have change drastically. The band at 210 cm\(^{-1}\) can be assigned to the anti-symmetric stretching vibrational mode of the AsSe\(_3\) pyramid (\(\nu_3\) mode), with the 219 cm\(^{-1}\) band representing the symmetric stretching mode of the same unit (\(\nu_1\) mode). If the assignment is correct then the \(\nu_3\) band should also be observed in the spectrum of the As\(_{10}\)Se\(_{90}\) glass. However, since the intensity of this band is lower than that of the \(\nu_1\) mode it was fitted under the profile of the latter which is quite broad in the
$R^{iso}$ spectrum of the As$_{10}$Se$_{90}$ glass. The depolarized band at 238 cm$^{-1}$ exhibits a strong increase and becomes the dominant band in the spectrum. Further, the Se chain band at 254 cm$^{-1}$ decreases appreciably as expected while the intensities of two highest in frequency modes increase.

The picture still remains puzzling even for the stoichiometric compound, As$_{40}$Se$_{60}$. The growing part of the spectrum at 220-225 cm$^{-1}$ which we associated with the increasing fraction of AsSe$_3$ pyramidal units has now shifted to 235 cm$^{-1}$. We should recall here the Chemically-Ordered Network (CON) model (see Section 2.2.2). In this model heteronuclear (As-Se) bonds are favored. A completely chemically-ordered phase thus occurs at the stoichiometric composition and hence only heteronuclear As-Se bonds should exists for the stoichiometric glass. The breadth of the spectra shows that the CON model is not a good candidate to describe the structure of the As$_2$Se$_3$ glass. An alternative candidate, i.e. the Random Covalent Network (RCN) model (see Section 2.2.1) treats the distribution of bond types in purely statistical terms, determined only by the local coordination numbers (3 for As and 2 for Se) and the concentration variable $x_{As}$, and which neglects any preferential ordering effects (e.g. arising from differences in bond energies). According to the RCN all types of bonds As-As, Se-Se, and As-Se can be found for all compositions. RCN predicts that at the stoichiometric composition almost 50% of the bonds are of As-Se type and the rest 50% is divided equally to As-As and Se-Se bonds. As-As vibrations in bulk amorphous As [Lannin 1977] form a broad band (180-270 cm$^{-1}$) centered at about 235 cm$^{-1}$. Therefore, it is quite reasonable to assume that the strong increase of the 234 cm$^{-1}$ band in the As-Se binary alloys when approaching the stoichiometric threshold might arise from the abrupt increase of the As-se bonds.

The above idea is also supported by recent ab initio molecular dynamics simulations for As$_2$Se$_3$ [Drabold 2003] where it was found that that 61% of the atoms are part of pyramids, the residue being mostly the Se$_2$As–AsSe$_2$ structure. Where the ‘8-N’ rule is concerned, simulations showed that As is nearly always threefold-coordinated (96.5 %). On the other hand only about 60% of the Se atoms
are twofold coordinated in both systems and there are nearly identical numbers of singly and triply coordinated Se (supporting the valence alternation pair picture, even in binary Se glasses). Where chemical order is concerned, As$_2$Se$_3$ has 77% As–Se bonds, 11% As–As bonds, and 12% Se–Se bonds. An overview of the structures obtained by simulation [Biswas 2009] can be seen in Fig. 7.14. The figure shows the formation of stable vulcanized (interconnected) units at three different concentrations, 5%, 10% and 15% in As. It is clear from the figure that, with increasing concentration, more and more non-bonded As atoms connected to

Fig. 7.14. Formation of amorphous As–Se networks at three different concentrations: (a) the initial 64-atom glassy Se (green) network, (b) Se network with 3% of As (red) atoms, (c) Se network with 10% of As (red) and (d) Se network with 15% As (red) atoms. As–Se–As cross-links are clearly visible in (d), [Biswas 2009].

the network and formed 3D-like structures. Selenium chains were broken and cross-linking units of As–Se were formed until the long chains were tightly connected together. It is apparent from the figure that at 15% there is significant change in the original structure, particularly via formation of “As–Se–As” triplets. One can expect that at higher concentrations such changes might be more prominent and
would cause the 1D chain structure to evolve into a complex 3D continuous network. This might lead to the formation of new structural units and possibly phase transitions.

### 7.4 Concluding Remarks

The content of the present chapter made clear that despite the large numbers of experimental and theoretical works, which have appeared so far in the literature, devoted on the elucidation of the structure of binary As-Se glasses there are still many issues of the subject poorly understood. Raman scattering was chosen here to study closely spaced glass compositions of the \( \text{As}_x\text{Se}_{100-x} \) (\( 0 \leq x_{\text{As}} \leq 40 \)) binary system. Off-resonant conditions (laser energy \(~1.17 \text{ eV}\)) was used to avoid undesired photoinduced effects (the optical bandgaps of all compositions studied are larger than 1.6 eV) and thus to study the equilibrium structure of the glasses. In addition, the present study is the first Raman scattering investigation where polarization analysis was employed and reduced isotropic and anisotropic spectra were analyzed. Some of the puzzling issues of the As-Se glass structure were dealt with the aid of \textit{ab initio} calculations which provided help to support or discard suggestions by other authors on the existence of certain structural arrangements.

The main conclusions of the present chapter are summarized as follows:

- The high frequency part of the Raman spectrum of elemental Se consists of three peaks associated with Se-Se bond stretching vibrational mode in three different environments. The two lowest modes correspond to Se-Se bond vibration in chains either in a disordered form (250 cm\(^{-1}\)) or in a more ordered chain arrangement resembling that of the crystalline form t-Se (237 cm\(^{-1}\)). The highest energy mode (262 cm\(^{-1}\)) is related to Se-Se vibrations in Se\(_8\) or ringlike 4-atom arrangements in a chain.

- The addition of the trivalent As atoms induced chain crossing and the formation AsSe\(_{3/2}\) pyramidal units as evidenced from the new peaks that appear in the Raman spectra. The pyramids are randomly or
homogeneously dispersed in the structure for low As content increasing the rigidity of the glass.

- A qualitative analysis of the intermediate glass spectra ($5 \leq x_{As} \leq 35$) took place by considering each spectrum as a linear combination of the basic structural units of the limiting glasses, i.e. the Se$_n$ chain of elemental Se and the AsSe$_{3/2}$ pyramidal unit of the stoichiometric glass. The analysis showed that the linear combination of the two limiting spectra is not a good model to describe the structure of the intermediate glass compositions. The difference between each experimental spectrum and the corresponding linear combination increased with increasing As content revealing structural correlations effects due to the presence of As atoms and the generation of new structural units.

- The spectral features, i.e. position, width, intensity, of the spectra that describe the difference between each experimental spectrum and the corresponding linear combination show an interesting dependence of $x_{As}$. All the above spectral parameters exhibit different trends at $x_{As}$ values exceeding $x_{As} = 15$. This behavior has been interpreted as a change from a stochastic to a non-stochastic building process of the structure. In particular, we proposed that at $x_{As}$ above that threshold the addition of As atoms leads to the creation of AsSe$_3$ pyramidal units which are bridged by a common Se atom. Computer simulation studies show also a similar effect.

- The presence of the quasi-tetrahedral (QT) unit Se=AsSe$_{3/2}$ in the structure of binary As-Se glasses is a long-standing issue of this field. We tried to resolve this issue using \textit{ab initio} calculations of the geometrical and vibrational properties of As-Se cage-like molecular units As$_4$Se$_n$ ($n=6,10$). The n=10 molecule is a realistic representative of a structure that contains the As=Se double bond because the QT unit cannot exist as an isolated molecule in the glass structure. \textit{Ab initio} calculations showed that the As=Se mode should be located in the
experimental Raman spectrum at an energy range not lower than \( \sim 406 \) cm\(^{-1}\). At present, the Raman data show no evidence for such a peak in the above spectral range. However, this could also be due to the very low Raman activity of the As-Se bond vibration. Therefore, the presence of QT units with double As-Se bonds in binary As-Se glasses is highly questionable. If such molecules exist, they are present in the glass structure their concentration must be negligible. Therefore, the 30% percentage suggested by DSC studies is an unrealistically high fraction.

For a more quantitative analysis of the glass structure we used a set of Gaussian peaks to fit the complex, broad band profiles of the \( \text{R}^{\text{iso}} \) and \( \text{R}^{\text{aniso}} \) Raman spectra. A tentative assignment of the various components was attempted and the glass structure was discussed in the framework of various structural models, i.e. the molecular model, which does not seem to successfully describe the structure of the stoichiometric glass. Furthermore, the dramatic change of the Raman spectra lineshape for glass composition near the stoichiometric one led us to the conclusion of the presence of an appreciable fraction of As-As bonds for the stoichiometric glass. This finding is supported by recent \textit{ab initio} molecular dynamics simulations for this glass pointing to the inadequacy of the CON model. On the other side, the bond statistics of the RCN seem to better reflect the structure of the As\(_2\)Se\(_3\) glass.
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Chapter 8

Structure of $\text{As}_x\text{Te}_{100-x}$ ($20 \leq x \leq 60$) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation

8.1 Literature survey

At present, amorphous tellurides find a number of applications in phase change optical data storage, radiometry and optical transmission of information (infrared transmitting optical fibers) and as random access memory devices [Kolobov 2003, Danto 2006, Lankhorst 2005]. As research in these fields is strongly driven by the needs of high-tech industry, physical properties related to the applications are much more systematically investigated than the atomic structure, which is ultimately related to the macroscopic properties, itself. This may be the reason why the microscopic origin of fascinating physical phenomena is still not completely understood. A shortcoming of not having yet established microstructure-properties relations in non-crystalline tellurides is the lack of a strategic design of new materials for specific applications. As a result, trial-and-error methods are frequently employed to obtain materials’ compositions with the desired functionality.

Elucidating the structure of non-crystalline phases is not an easy and straightforward task. Major structure-probing techniques include x-ray and neutron diffraction as well as x-ray absorption fine structure (EXAFS). Further, vibrational spectroscopy (Raman and infrared) can also provide an important piece of information
CHAPTER 8: Structure of As$_x$Te$_{100-x}$ ($20 \leq x \leq 60$) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation

on selected aspects of structural details [Elliott 1990, Feltz 1993]. The problem becomes more complicated in multicomponent alloys where the description in terms of the partial pair correlation functions (or at least coordination numbers and nearest neighbor distances) is indispensable. The number of these parameters increases steeply with increasing number of components. Already a binary alloy is characterized by three partial pair correlation functions, the separation of which is a tedious task, especially if the nearest neighbor distances of both components are alike as is the case in As-Te glasses.

A challenging aspect of arsenic telluride glasses which makes their structural studies intriguing is the fact that these materials are among the very few substances where the densities of the crystalline and glassy phases differ appreciably (of about 13% for As$_{40}$Te$_{60}$; the difference for As$_{40}$Se$_{60}$ and As$_{40}$S$_{60}$ is about 4% and 8%, respectively [Feltz 1993, Borisova 1981]) as a result of the different short-range structural order between the two phases. GeTe is another typical example which shows a contrasting local structure in the amorphous and crystalline phase [Yannopoulos 2006]; a fact that has been considered as an advantage for the enhanced phase-change properties of this material. GeSe is also characterized by large differences between the local order of different phases. In the crystalline state it is characterized by octahedral coordination. As it was revealed by the neutron diffraction with isotopic substitution study of Petri et al. [Petri 1999] upon melting the octahedral structure collapses and the Ge-Se coordination number decreases to 3.2±0.2.

Crystalline As$_2$Te$_3$ was investigated by single crystal X-ray diffraction [Carron 1963]. The structure is monoclinic with two non-equivalent As and three non-equivalent Te sites. Nearest As-Te distances range from 2.68 Å to 2.93 Å. As-As and Te-Te bonds do not exist in crystalline As$_2$Te$_3$. Due to the presence of non equivalent sites the variety of nearest As-As and Te-Te distances is also large (from 3.56 Å to 4.61 Å for As-As pairs and from 3.70 Å to 4.43 Å for Te-Te distances).

CHAPTER 8: Structure of As\textsubscript{x}Te\textsubscript{100-x} (20 ≤ x ≤ 60) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation

references therein). Evaluating the conclusions of these structural studies one is faced with contradictory structural models. For example, there is still a confusing picture even for the structure of the stoichiometric As\textsubscript{2}Te\textsubscript{3} composition. It has been suggested, on one side, that the glass consists of As\textsubscript{Te}\textsubscript{3/2} pyramidal units distributed at random (meaning that the sample is ‘chemically ordered’ but lacks long range order) [Cornet 1973a, Cornet 1973b, Fitzpatrick 1971] and on the other side, that the amorphous alloy is chemically disordered in view of the presence of homonuclear As-As or Te-Te bonds [Ma 1993, Wasse 2001, Dongol 2006, Sen 2008]. The disadvantage of many of the previous works is that a limited number of compositions (sometimes just one alloy) were studied and often only one experimental method was applied, see for example Refs. [Dongol 2006, Sen 2008]. Finally, a third line of reasoning on the structure of As\textsubscript{2}Te\textsubscript{3} glass invokes the existence of a fraction of As atoms that are octahedrally coordinated in direct analogy with its crystalline counterpart [Tverjanovich 1998, Cornet 1977]. However, evidence against the existence of octahedral As sites has been presented in [Cornet 1973a, Cornet 1973b].

The most detailed study of As\textsubscript{x}Te\textsubscript{100-x} glasses (x = 20, 30, 40, 50 and 60) carried out so far is that by Ma et al. [Ma 1993] who applied extended X-ray absorption fine structure (EXAFS) at the As and Te K-edges and anomalous X-ray scattering. The main conclusions of that study are summarized in the following: (i) As atoms are threefold coordinated over the whole composition range studied; (ii) Te atoms are twofold coordinated in As-rich alloys (x > 40), and about 40% of Te are threefold coordinated in the alloys with x ≤ 40; (iii) the glasses are chemically disordered for all compositions as is evidenced by the existence of homonuclear As-As and Te-Te bonds.

8.2. Results

8.2.1 Unconstrained simulations

Bond distances and coordination numbers obtained by unconstrained simulation runs are listed in Table 8.1. It can be observed that \( <N_{As} > \) – the average number of As atom’s neighbors – is close to 3, while \( <N_{Te} > \) – the average number of Te atom’s
neighbors – is close to 2 over the whole composition range investigated. In the case of As coordination numbers the largest discrepancy (~9%) is found for As$_{20}$Te$_{80}$.

Table 8.1. Average number of neighbors of As and Te (denoted with $<N_{As}>$ and $<N_{Te}>$) and average coordination numbers $<N>$ obtained by the unconstrained RMC simulation. The estimated uncertainty of $<N>$ is 5% while that of $N_{As}$ and $N_{Te}$ is about 10%.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$&lt;N_{As}&gt;$</th>
<th>$&lt;N_{Te}&gt;$</th>
<th>$&lt;N&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$<em>{20}$Te$</em>{80}$</td>
<td>2.72</td>
<td>2.15</td>
<td>2.26</td>
</tr>
<tr>
<td>As$<em>{34}$Te$</em>{66}$</td>
<td>2.94</td>
<td>1.99</td>
<td>2.31</td>
</tr>
<tr>
<td>As$<em>{40}$Te$</em>{60}$</td>
<td>2.94</td>
<td>1.91</td>
<td>2.32</td>
</tr>
<tr>
<td>As$<em>{50}$Te$</em>{50}$</td>
<td>2.81</td>
<td>2.19</td>
<td>2.50</td>
</tr>
<tr>
<td>As$<em>{60}$Te$</em>{40}$</td>
<td>2.99</td>
<td>2.26</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Taking into account the low As concentration and the fact that the above coordination number was obtained by an unconstrained run, even this deviation is well within the experimental uncertainties.

8.2.2 Constrained simulations

Neither EXAFS nor diffraction data contain information on coordination number distributions. Even for a one component system these techniques can provide $<N>$, the average coordination number, which can be reproduced by several different coordination number distributions. A well known example is the structure factor of amorphous Si that can be fitted by 100% and 0% 4-fold coordination as well while the average coordination number is 4 in both cases [Gereben 1994]. Thus, the actual shape of the coordination number distribution obtained by an unconstrained simulation run has in general no physical meaning. It is only prior physical/chemical knowledge that can help to judge the width of a distribution. We know that $<N>$=4 is the result of a sharp distribution in a-Si but $<N>$=12 is the mean value of a broader distribution in a liquid metal. It is reasonable to assume that in a covalent glass average coordination
numbers close to 2 and 3 mean that the majority of Te and As have 2 and 3 neighbors, respectively.

**Table 8.2.** Coordination numbers and bond lengths $r_{ij}$ for As-Te glasses obtained by constrained RMC simulations. The error of bond lengths is about 0.02 Å. The estimated uncertainty of $<N>$ is 5% while that of $N_{AsAs}$, $N_{AsTe}$, $N_{TeAs}$ and $N_{TeTe}$ is about 10-15%. The $N_{ij}$ 'partial coordination numbers' can be obtained by integrating $4\pi r^2 \rho_{ij}(r)$ up to the first minimum of $g_{ij}(r)$.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$N_{AsAs}$</th>
<th>$N_{AsTe}$</th>
<th>$N_{TeAs}$</th>
<th>$N_{TeTe}$</th>
<th>$&lt;N_{As}&gt;$</th>
<th>$&lt;N_{Te}&gt;$</th>
<th>$&lt;N&gt;$</th>
<th>$r_{AsAs}$ (Å)</th>
<th>$r_{AsTe}$ (Å)</th>
<th>$r_{TeTe}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$As_{20}Te_{80}$</td>
<td>1.05</td>
<td>1.92</td>
<td>0.48</td>
<td>1.62</td>
<td>2.97</td>
<td>2.10</td>
<td>2.27</td>
<td>2.50</td>
<td>2.56</td>
<td>2.77</td>
</tr>
<tr>
<td>$As_{34}Te_{66}$</td>
<td>1.53</td>
<td>1.45</td>
<td>0.75</td>
<td>1.34</td>
<td>2.98</td>
<td>2.09</td>
<td>2.39</td>
<td>2.48</td>
<td>2.58</td>
<td>2.74</td>
</tr>
<tr>
<td>$As_{40}Te_{60}$</td>
<td>1.69</td>
<td>1.20</td>
<td>0.80</td>
<td>1.26</td>
<td>2.89</td>
<td>2.06</td>
<td>2.39</td>
<td>2.46</td>
<td>2.59</td>
<td>2.75</td>
</tr>
<tr>
<td>$As_{50}Te_{50}$</td>
<td>1.84</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
<td>2.87</td>
<td>2.06</td>
<td>2.47</td>
<td>2.46</td>
<td>2.59</td>
<td>2.74</td>
</tr>
<tr>
<td>$As_{60}Te_{40}$</td>
<td>2.16</td>
<td>0.85</td>
<td>1.28</td>
<td>1.03</td>
<td>3.01</td>
<td>2.31</td>
<td>2.73</td>
<td>2.45</td>
<td>2.59</td>
<td>2.74</td>
</tr>
</tbody>
</table>

*: values obtained without fitting Te K-edge data; **: no neutron data were available

Thus, in order to be able to make more definite statements on the structure of As-Te alloys, existing chemical information was built in the simulations in the form of the following coordination constraints: *each* As was forced to have 3 neighbors while Te atoms were allowed to have either 2 or 3 neighbors. This structural flexibility was allowed for Te atoms in view of previous studies (e.g. Ref. [Ma 1993]) which concluded that Te can be partly threefold coordinated in the Te-rich region ($x \leq 40$). The type of neighbors was not constrained in these runs. The quality of the fits did not change upon introducing constraints. The results are summarized in Table 8.2.

### 8.3 Discussion

Since the majority of As atoms (90-95%) satisfied the constraints, only small deviations from the target value ($<N_{As}> = 3.0$) were observed. It is remarkable that the average coordination number of Te is very close to 2 for $20 \leq x \leq 50$. Taking into account that Te atoms were allowed to have 2 or 3 neighbors, this is a strong evidence that Te is indeed twofold coordinated in $As_xTe_{100-x}$ glasses over the composition range $20 \leq x \leq 50$. The largest deviation was found for $As_{60}Te_{40}$ where the coordination
number of Te was 2.31. Even this value means that tellurium is mostly (~70 %) twofold coordinated.

Ma et al. [Ma 1993] also suggested that As-As and Te-Te homonuclear bonding play an important role over the whole glass forming region. They found that the number of As-As bonds increases from about 0.2 to 1.5 when As content increases from 20 to 50 at. %. In parallel, the average number of Te-Te bonds per Te atoms decreases from 1.7 to 0.4. A snapshot of the simulation box shows the presence of small clusters of atoms for the stoichiometric composition (Fig. 8.1).

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Fig. 8.1 A snapshot of the simulation box of glassy As$_{40}$Te$_{60}$ (yellow: As, grey: Te)

Our findings are in qualitative agreement with the above mentioned structural changes; however, there is a clear quantitative difference since our values are significantly higher than those reported in Ref. [Ma 1993]. Deviations are due to two main reasons. The first is the rapid development of electronic structure calculation methods. Ma et al. used the much less accurate backscattering phases and amplitudes of Mac Kale et al. available at that time [Mac Kale 1988]. Present day calculation techniques (e.g. the FEFF code [Ankudinov 1998] used in our study) provide significantly more accurate parameters. The paper of Ma et al also strongly relies on
anomalous X-ray scattering data. As it is pointed out in ref. [Ma 1993] in case of As-Te alloys elastic intensities show only a weak energy dependence which brings about noisy difference structure factors over the whole experimental range and limited useful momentum transfer range (up to about 10 Å⁻¹) even for the difference structure factors measured around the Te K-edge. As a result, the spatial resolution is low which makes the separation of close r-space contributions rather uncertain.

Partial structure factors and pair correlation functions obtained by constrained runs are shown in Figs. 8.2 and 8.3. It is evident that the height of the first peak of

![Graph showing partial structure factors for As-Te glasses obtained by the constrained simulation runs.](image)

Fig. 8.2 Partial structure factors for As-Te glasses obtained by the constrained simulation runs. solid line: As₂₀Te₈₀, dashes: As₃₄Te₆₆, dots: As₄₀Te₆₀, dash dots: As₅₀Te₅₀, short dashes: As₆₀Te₄₀
CHAPTER 8: Structure of $\text{As}_{100-x}\text{Te}_x$ ($20 \leq x \leq 60$) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation

$g_{20\text{As}20\text{Te}80}(r)$, the As-As partial pair correlation function, changes monotonously with As content. For $x = 20$ the first peak is much narrower than for other compositions. For this alloy the contribution of As-As correlations to diffraction measurements is rather low thus $g_{\text{AsAs}}(r)$ is determined mainly by the As K-edge EXAFS measurement. It is well known that EXAFS and diffraction techniques are sensitive to thermal disorder in different ways. Correlated (in-phase) motions of absorber and backscattered do not contribute to the broadening of bond length distributions [Lee 1981]. Therefore,
EXAFS peak widths are usually smaller than the values obtained by diffraction techniques. Another consequence of the low As content – and therefore the low weight of $S_{\text{AsAs}}(Q)$ in diffraction measurements – in case of $\text{As}_{20}\text{Te}_{80}$ is that $g_{\text{AsAs}}(r)$ is somewhat less structured outside the sensitivity range of EXAFS data ($r > 3 \text{ Å}$).

In the case of $g_{\text{AsTe}}(r)$ the position and shape of the first peak is practically the same for $34 \leq x \leq 60$ which means that the length of As-Te bonds is the same for two- and threefold coordinated tellurium atoms. Peak heights and positions of $g_{\text{TeTe}}(r)$ do not show any systematic variation with concentration.

Comparing our results on $\text{As}_x\text{Te}_{100-x}$ glasses ($x \leq 50$) with some recent investigations on $\text{GeSb}_2\text{Te}_4$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [Jóvári 2007, Jóvári 2008] and $\text{Si}_{40}\text{As}_{25}\text{Te}_{35}$ [Kaban 2007a] reveals a common property of these alloys. Though they possess very different glass forming abilities (As-Te can be vitrified in bulk by melt quenching while Ge-Sb-Te alloys are identified as marginal glass formers [Kalb 2003]) they equally satisfy the ‘8-N’ rule [Mott 1967]. The above finding is even more interesting if we take into account that $\text{As}_{25}\text{Si}_{40}\text{Te}_{35}$ and the Ge-Sb-Te glasses are characterized by strong heteronuclear bonding preferences (e.g. Ge-Te and Sb-Te bonds are preferred to Te-Te ones in $\text{GeSb}_2\text{Te}_4$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$), which are not present (or much weaker) in As-Te alloys, according to the results of the present work. It should be mentioned, however, that the 8-N rule is not valid for all glassy tellurides. A recent experimental study revealed that the coordination number of Te is significantly larger than 2 in $\text{Ge}_{15}\text{Te}_{85}$ [Kaban 2007b].

### 8.3.1 Assessment of RMC results

The average number of As neighbors of As atoms in the ‘constrained’ case of our study is $\sim 1$ for $\text{As}_{20}\text{Te}_{80}$ and $\sim 2$ for $\text{As}_{60}\text{Te}_{40}$. The number of Te-Te bonds decreases from $\sim 1.6$ for the glass with 80 at.% Te down to $\sim 1$ for the glass with 40 at.% Te. It can also be noticed (see Table 8.2 and Fig. 8.3) that the number of homonuclear bonds in the “constrained” case changes practically monotonically with $x_{\text{As}}$ without showing any extrema at the stoichiometric composition ($x = 40$) as it
CHAPTER 8: Structure of As$_x$Te$_{100-x}$ (20 ≤ $x$ ≤ 60) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation

should be expected if chemical ordering would play an important role in the short range order of As-Te glasses.

![Graph](image)

**Fig. 8.4.** Comparison of coordination numbers obtained by constrained RMC simulations (symbols) with the completely random bonding model (lines).

To check whether bonding in these alloys can be considered as ‘completely random’, coordination numbers of the constrained runs are compared with the values obtained by assuming random bonding. Coordination numbers for the ‘completely random’ case are given by the following simple rules:

i) each Te has 2 neighbors while each As is threefold coordinated;

ii) there is no preferential bonding in the system. Thus for As$_x$Te$_{100-x}$ the average coordination number is $2 + \frac{x}{100}$ and the probability that a selected bond connects two As atoms is given simply by \( \left( \frac{3x}{2 + \frac{x}{100}} \right)^2 \). The same for
Te-Te bonding is \[ \left( \frac{2(100-x)}{2+x/100} \right)^2 \]. Then it follows after some straightforward steps that the As-As and Te-Te coordination numbers are equal to \[ \frac{9x}{200+x} \]
and \[ \frac{4(100-x)}{200+x} \], respectively.

Coordination numbers of the completely random model are plotted in Fig. 8.4. It can be observed that the values determined by RMC are rather close to the curve representing the completely random model. The discrepancy is largest for the Te-Te coordination number at \( x=60 \). This is reasonable because one of the basic assumptions of the model calculations (each Te has 2 neighbors) does not hold. Given the estimated 10-15\% uncertainty of \( N_{\text{AsAs}} \), \( N_{\text{AsTe}} \) and \( N_{\text{TeTe}} \) our results suggest that bonding is random over the whole glass forming region. It was concluded in Ref. [Ma 1993] that Te is twofold coordinated in the As-rich region (\( x>40 \)) while the coordination number of Te is 2.4 for \( x \leq 40 \). According to our results the tendency is exactly the opposite: \( N_{\text{Te}} \) is very close to 2 for \( x \leq 50 \) while it increases to about 2.3 at \( x=60 \).

### 8.3.2 Structural details vs. physical properties

The comparison between structural details and physical properties of glasses is always a useful benchmark in order to assess the validity of the analysis of the experiments and simulations which have provided the structural information in question. In this section we attempt a comparison between the concentration dependence of certain structural parameters estimated by the constrained RMC analysis presented above with the corresponding dependence of various physical properties of the glasses studied.

Glass transition temperature, \( T_g \), is an important parameter reflecting both thermodynamic and rigidity aspects of the glass structure. The As-content dependence of \( T_g \) determined in this work by DSC is shown in Fig. 8.5(a). It is important to notice that we have used the same samples in our structural studies and DSC measurements
so as to eliminate errors induced by glass preparation details. For comparison, the corresponding dependence of the mean total coordination number, \(<N>\), is also presented showing a very good coincidence with the \(x_{\text{As}}\) dependence of \(T_g\). This plot reveals the following interesting fact. Both \(T_g\) and \(<N>\) exhibit two different slopes vs. \(x_{\text{As}}\) in the Te-rich and As-rich phases. Although there is a qualitative disagreement between these two parameters at \(x_{\text{As}} = 50\), on quantitative grounds the similarity in

![Graphs showing composition dependencies of various parameters for As,Te\(_{100-x}\) glasses.](image)

**Fig. 8.5 Composition dependencies of structural and various physiochemical parameters for As,Te\(_{100-x}\) glasses.** (a) \(<N>\) and \(T_g\) vs. \(x_{\text{As}}\). (b) \(<N>\) and \(T_c-T_g\) vs. \(x_{\text{As}}\). (c) \(<Z_{\text{AsAs}}>\) and reciprocal density vs. \(x_{\text{As}}\) [Lee 1981]. (d) \(<Z_{\text{AsAs}}>\) and \(E_g\) vs. \(x_{\text{As}}\). Closed symbols refer to structural data while open symbols stand for the respective physicochemical parameter [Lee 1981].

slope change is evident. On the contrary, in a previous study [Ma 1993] the same comparison was made using the number of homonuclear As-As bonds; in addition, another weak point of that work is that different samples for structural and thermal
studies were used. A kink in the slope of the microhardness of As-Te glasses at the stoichiometric composition has also been reported elsewhere [Cornet 1973a, Cornet 1973b] lending support to our findings for the behavior of \( T_g \) and \( <N> \) shown in Fig. 8.5(a). Apart from the glass transition temperature, the stability of the glasses is also reflected in the extent of the temperature interval above \( T_g \) into which the glass can be heated before crystallization intervenes, i.e. \( T_c - T_g \). The dependence of this parameter vs. \( x_{As} \) is shown in Fig. 8.5(b) together with the dependence of \( <N> \). Again, a mild dependence of \( T_c - T_g \) in the Te-rich phase is replaced by a stronger one in As-rich glasses. The stability of the glassy state increases with increasing As content as it is seen from Fig. 8.5(b). This is to be contrasted to the behavior of other As-chalcogenides, i.e. As-S and As-Se where the stoichiometric glass exhibits the highest \( T_g \) and structural stability where the number of As-As bonds is negligible and therefore cannot be considered as a reason for the improved glass-forming ability as was suggested for As-Te glasses in previous studies [Ma 1993, Cornet 1973a, Cornet 1973b].

The change from unstable to relatively stable glassy state around 43 at.% As for As-Te glasses has been reported in [Borisova 1981]. It should be emphasized here that the stability of the glassy state may depend on the energetics of glassy and crystalline phase as well as on the nature of chemical bonds (e.g. strength and cooperativity). The latter is especially important for high As content (\( x>50 \)) where a significant proportion of Te atoms switch from two- to threefold coordination, which may affect the strength of individual chemical bonds. In conclusion, both \( T_g \) and \( T_c - T_g \) in As-Te glasses exhibit alike concentration dependencies which both follow qualitatively the trend of the mean coordination number. Taking into account that the mean coordination number is a very crude measure of glass stability (differences in As-As, As-Te and Te-Te bond strengths are not taken into account) the above finding is remarkable.

Before turning our attention to non-thermal properties it is interesting to mention that the jump in heat capacity \( \Delta C_p \) at \( T_g \), estimated by DSC, decreases linearly with increasing \( x_{As} \) [Cornet 1973a, Cornet 1973b]. \( \Delta C_p \) is a measure of the
configurational degrees of freedom that become activated as the glass is heated above \( T_g \). Glasses with network structure, i.e. strong glasses show little change (small jump) in heat capacity at \( T_g \) while the opposite happens for fragile glasses. Therefore, the decrease of \( \Delta C_p \) at high As concentrations points to a stronger character of the As-rich glasses. This fact is in accordance with our findings and in particular with the increase of \( <N> \) and the increase of \( <N_{Te}> \) with \( x_{As} \).

Other parameters whose \( x_{As} \)-dependence show striking agreement with our structural data, and in particular with the number of homonuclear As-As bonds, \( <Z_{AsAs}> \) (=\( x_{As} \times N_{AsAs} \)) are the density and the optical energy gap \( E_g \) [Lee 1981] as shown in Figs. 8.5(c) and 8.5(d), respectively. We observe that the \( x_{As} \)-dependence of both the density and the optical energy gap exhibit a very good agreement with the number of As-As bonds estimated in this work. The optical gap of As-Te glasses shows a linear increase with increasing the As content in the glass. This is expected knowing that elemental As has a higher \( E_g \) value compared with elemental Te. Therefore, the increase of As content in the binary glasses will cause the substitution of Te-Te bonds with As-As bonds and hence the increase of \( E_g \). As has been suggested elsewhere [Elliott 1990], the magnitude of \( E_g \) correlates with the strength of the chemical bonds building-up the glass structure. The presence of the strong As-As bonds at the expense of the weaker Te-Te bonds is responsible for the band gap widening upon increasing \( x_{As} \). The striking similarity between the \( x_{As} \)-dependence of \( <Z_{AsAs}> \) and \( E_g \) indicates the validity of the analysis of the structural data obtained in this work.

To complete the comparison between structural and other physicochemical properties we illustrate in Fig. 8.6 the concentration dependence of the number of Te-Te bonds, \( <Z_{TeTe}> \) (=(1-\( x_{As} \))\times N_{TeTe}), together with parameters that depend upon the presence of such bonds in As-Te glasses. Data for electronic conductivity measured at 20 °C, \( \sigma_{20 \degree C} \), have been taken from Ref. [Borisova 1981]. Both \( <Z_{TeTe}> \) and the logarithm of conductivity exhibit a linear decrease with decreasing the number of Te-
Te bonds suggesting that the presence of homonuclear Te-Te bonds are responsible for increased conductivity in Te-rich glasses.

It was also found that the increasing number of Te-Te bonds is closely related to the increase of the mean polarizability $\langle \alpha \rangle$, [Zavetova 1982], as shown in Fig. 8.6(b). Though a detailed discussion is certainly beyond the scope of the present study the comparison of bond strengths provides a qualitative understanding of the above effect. The fact that Te-Te bonds are much weaker (38 kcal/mol) than As-Te bonds

![Diagram showing composition dependencies of structural and various physiochemical parameters for As$_x$Te$_{100-x}$ glasses. (a) $\langle Z_{TeTe} \rangle$ and conductivity vs. $x_{\text{As}}$. (b) $\langle Z_{TeTe} \rangle$ and mean polarizability vs. $x_{\text{As}}$. Closed symbols refer to structural data while open symbols stand for the respective physicochemical parameter [Borisova 1981].]
(45 kcal/mol) implies that the electron cloud along the Te-Te bond is more loosely bound than that of the As-Te bond and hence more polarizable. The dependence of \( \langle c \rangle \) on concentration is again linear and bears a very good similarity with \( \langle Z_{\text{TeTe}} \rangle \) as estimated from our structural analysis.

### 8.4 Conclusions

\( \text{As}_x\text{Te}_{100-x} \) glasses \((20 \leq x \leq 60)\) were studied by high energy X-ray diffraction, neutron diffraction, and EXAFS measurements at the As and Te K-edges. The reverse Monte Carlo simulation technique was used to generate large scale models compatible with experimental data. Analysis of the resulting atomic configurations revealed that homonuclear bonding is important over the whole glass forming region. At the stoichiometric composition \((\text{As}_{40}\text{Te}_{60})\) the average As-As and Te-Te coordination numbers amount to 1.7±0.2 and 1.3±0.1, respectively. As-As bonding is significant in the Te-rich region \((34 \geq x)\) while Te-Te bonding is considerable in the As-rich region \((x \geq 50)\) as well. It has been shown that Te is predominantly twofold coordinated for \(x \leq 50\) while As is threefold coordinated for all compositions investigated. It can be concluded that chemical ordering does not play an important role in the formation of short range order of As-Te glasses and – similarly to some other amorphous tellurides – \((\text{e.g. Ge}_2\text{Sb}_2\text{Te}_5, \text{GeSb}_2\text{Te}_4, \text{As}_{25}\text{Si}_{40}\text{Te}_{35})\) glassy As-Te alloys obey the ‘8-N’ rule for \(x \leq 50\).

The significance of a structural study lies on its power to provide structure-properties relations which are ultimately useful for materials applications. In an effort to step towards this direction we have undertaken extensive comparisons between the structural information obtained in the present study with several physicochemical properties of the As-Te glasses. In particular, the total mean coordination number \( \langle N \rangle \) was found to correlate qualitatively with thermal parameters, e.g. \( T_g \) and \( T_c-T_g \). \( \langle N \rangle \) as well as both \( T_g \) and \( T_c-T_g \) exhibit different slopes below and above the stoichiometric limit. The concentration dependence of the number of As-As bonds exhibits noticeable similarities with the corresponding dependence of the density and the optical energy.
CHAPTER 8: Structure of As$_x$Te$_{100-x}$ ($20 \leq x \leq 60$) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation gap. Finally, the number of Te-Te bonds seems to govern properties such as the conductivity and the mean polarizability of the system.
CHAPTER 8: Structure of As$_x$Te$_{100-x}$ ($20 \leq x \leq 60$) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation

References of Chapter 8:

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CHAPTER 8: Structure of As$_x$Te$_{100-x}$ (20 ≤ $x$ ≤ 60) glasses investigated with EXAFS, X-ray and neutron diffraction and reverse Monte Carlo simulation

Mott N., Adv. Phys. 16, 49 (1967)
Chapter 9

Structural study of $\text{Ge}_x\text{S}_{100-x}$, ($x_{\text{Ge}}$: 33.3, 34, 35, 40) glasses by Raman scattering

9.1 Brief Literature survey

The first structural study of vitreous GeS$_2$, with the aid of vibration spectroscopy, was reported by Kawamoto et al. [Kawamoto 1969, Kawamoto 1971]. Kawamoto et al. have examined glass-forming regions and various physical properties of glasses in the system $\text{Ge}_x\text{S}_{100-x}$. They found [Kawamoto 1969] two glass-forming regions. The first, denoted (1), spans the composition $0 < x_{\text{Ge}} < 33.3$, while the second, denoted (2), is $40 < x_{\text{Ge}} < 43.2$. Concerning the structure of glasses in these two glass-forming regimes Kawamoto et al. [Kawamoto 1971] conclude the following. Glasses in region (1): when S is added in small amounts to GeS, glass, the S forms $(-S-)_n$ chains between Ge atoms initially; then, when the $x_{\text{Ge}}$ is of about 15-20% the structure of the glasses becomes very open with many interstices in which S$_8$ ring molecules can enter. Accordingly, sulphur forms not only $(-S-)_n$ chains but also S$_8$ molecules. As the sulphur content increases, the structure of the glass progressively approaches that of plastic S. However, in glass-forming region (2) the glasses are made up of GeS$_2$ and GeS components, i.e. of
GeS₄ tetrahedra and GeS₆ octahedra. The authors [Kawamoto 1971] have associated the GeS₆ octahedra of the GeS component with the distorted rock-salt structure of the crystalline species and also assume that the GeS is of the form of Ge⁺² in this component.

A structural by X-ray diffraction study by Rowland et al. [Rowland 1972] showed that both glassy phases are characterized by covalent bonding. The radial distribution function analysis showed no evidence of an octahedrally coordinated doubly ionized Ge species. Until 1970 it was considered that GeS₂ exist on one crystal structure whose structure is a three-dimensional network composed of GeS₄ tetrahedra. In 1970, however, Viaene et al. [Viaene 1970] found that GeS₂ has two polymorphs, i.e., a high temperature, or α-phase and a low temperature, or β~phase. Subsequently, Dittmar et al. [Dittmar 1975; Dittmar 1976] determined the structures of α- and β-GeS₂ by x-ray diffraction. After these studies the following scenario was accepted: α-GeS₂ is stable in equilibrium with GeS above ~520 °C and with excess S above ~497°C and is characterized by a two-dimensional (2D) layer structure. On the other hand, β-GeS₂ is stable below this inversion temperature range and possesses a three-dimensional (3D) network structure. The GeS₂ crystal phase that has been known prior to 1970 was proved to be the low temperature modification.

Raman spectroscopy has been a valuable probing technique for the study of structure of binary glasses GeₓS₁₀₀₋ₓ (x₆: 33.3, 34, 35, 40) glasses by Raman scattering. Unambiguous assignment of the broad and overlapping Raman bands of these glasses has not always been possible, though, thus leading to diverse structural interpretations. One undisputed result concerning the S-rich (x₆<33.3) alloys is that a nanoscale phase separation occurs in these glasses. The excess sulphur forms S₈ ring molecules which are decoupled from the glassy network of corner sharing (CS) GeS₄₁₂ tetrahedra, see Fig. 9.1. It is therefore expected that in S-rich glasses Ge-S and S-S bonds should dominate while Ge-Ge should be absent. For the stoichiometric GeS₂ and the Ge-rich (x₆>33.3) binary...
CHAPTER 9: Structural study of Ge<sub>x</sub>S<sub>100-x</sub> (<i>x</i> Ge: 33.3, 34, 35, 40) glasses by Raman scattering

Ge-S glasses, Lucovsky <i>et al.</i> [Lucovsky 1974] proposed an extended three-dimensional chemically ordered network of Ge<sub>n</sub>S<sub>4-n</sub> (n=0,1,2,3,4) tetrahedra centered about Ge atoms which are bonded to S and Ge neighboring atoms at a (macroscopically average) ratio determined by the S and Ge contents. As such, this model for Ge-rich glasses excludes the presence of S-S bonds.

![Fig. 9.1. The corner-sharing (CS), edge-sharing (ES), and ethanelike (ETH) cluster models.](image)

A considerably different structural model was introduced for the stoichiometric GeS<sub>2</sub> (and its isomorphous GeSe<sub>2</sub>) glass by Bridenbaugh <i>et al.</i> [Bridenbaugh 1979] and advanced by Aronovitz <i>et al.</i> [Aronovitz 1983] based on Raman measurements and calculations of density of states in large clusters, respectively. The authors were led to their proposition by the observation in both GeS<sub>2</sub> and GeSe<sub>2</sub> of a polarized Raman line (for which, it was believed, there was no counterpart in the crystal) with a frequency of about 10% greater than the normal <i>A<sub>1</sub></i> mode (breathing mode of the tetrahedral unit). In contrast to the <i>A<sub>1</sub></i> mode, the intensity of this so-called companion <i>A<sub>i</sub></i> mode displays an anomalous composition dependence [Sugai 1987; Griffiths 1982] in Ge<sub>x</sub>S(Se)<sub>100-x</sub> alloys. Bearing in mind its polarized spectral features, it was pointed out that the <i>A<sub>i</sub></i> mode is most likely associated with symmetric motions of S atoms (different from the symmetric
breathing motions assigned to the $A_1$ mode) and that the structure of GeS(Se)$_2$ glasses could not be described by a highly disordered three-dimensional network of corner sharing GeS(Se)$_4$ tetrahedra. Instead, they proposed [Bridenbaugh 1979, Aronovitz 1983, Griffiths 1982] a model of clusters having a layered structure similar to the high temperature two-dimensional (2D) crystal phase. In this model, each cluster (called outrigger raft) is regarded as a fragment of the 2D crystal phase and consists of corner-sharing tetrahedra chains linked to each other via bridges of edge-sharing tetrahedral, see Fig. 9.2. Unlike the crystal, however, each cluster is terminated by S-S (Se-Se) dimers along a direction perpendicular to the chain axis. The $A_1^c$ mode was then attributed to symmetrical vibrations of the S-S dimers. Similar or modified terminating cluster models were adopted later by other groups [Murase 1983] which associate the $A_1^c$ companion mode with the medium-range order of the glass. However, in an alternative explanation [Sugai 1987] the $A_1^c$ companion mode was associated with the breathing vibration of the 4-atom ring in edge-sharing (ES) units, see Fig. 9.1.

Fig. 9.2. The large molecular unit (outrigger raft) which was suggested to be a dominant structural unit of Ge-S(Se) glasses. Small spheres: Ge, large spheres: S.
A third model proposed by Boolchand et al. [Boolchand 1986] suggests a broken heterogeneous network consisting of two types of molecular clusters: the first type is similar to the layered structure fragments described in the previous paragraph while the second involves chains of ethane-like (ETH) $S_3\text{Ge-GeS}_3$ structural units, see Fig. 9.1.

Apart from the stoichiometric glass, most of Raman studies have been focused on S-rich binary Ge-S glasses. Early IR studies [Kawamoto 1971] revealed the existence of two types of sulfur in S-rich Ge$_x$S$_{100-x}$ glasses. One type is insoluble in liquid CS$_2$ species (sulfur chains), and exists below $x=20$. The other type is soluble in CS$_2$ species (sulfur rings), appearing at $x>20$. Many research groups identified sulfur rings as S$_8$ using Raman spectroscopy (see, for example, [Lucovsky 1974, Lucovsky 1972]). A simple model was proposed to account for these results. (i) Excessive sulfur atoms, added to the stoichiometric glass (GeS$_2$), transform bridging sulfur into sulfur dimers. At a “saturated” composition AsS$_3$ or GeS$_4$, all tetrahedral structural units GeS$_{4/2}$ become isolated, i.e., they do not share any corners and are separated by sulfur dimers. (ii) Above the “saturated” compositions at $x>20$, the S$_8$ rings appear in the glass network, evidenced by characteristic vibrations in the Raman spectra and partial glass dissolution in CS$_2$.

This simple model was modified [Bychkov 2006] allowing both corner (CS) and edge sharing (ES), as well as association of Ge-based structural units (Fig. 9.3). The association means that even at high sulfur contents a fraction of CS and ES-structural units still persists in the glass network instead of being entirely separated by sulfur species. The “saturated” compositions can be formulated as follows: $\text{AsS}_3$-$f_{\text{ES}}$-$\delta$ and $\text{GeS}_4$-$f_{\text{ES}}$-$\delta$, where $f_{\text{ES}}$ is the fraction of the ES-structural units and $\delta$ is the concentration of the associated CS-structural units. In addition, sulfur rings seem to be inappropriate to Ge-based glass network, since S$_8$ or another cyclic sulfur species with different stoichiometry represents a self-contained molecular cluster, which are joined together by Van der Waals and not by covalent forces. Correspondingly, glasses in the domain $x>20$ are supposed to be phase separated.
CHAPTER 9: Structural study of Ge$_x$S$_{100-x}$ ($x_{Ge}$: 33.3, 34, 35, 40) glasses by Raman scattering

Fig. 9.3. Schematic 2D representation of the advanced structural model for sulfur-rich Ge$_x$S$_{100-x}$ glasses: (a) a fragment of the stoichiometric GeS$_2$ glass with CS- and ES-GeS$_{4/2}$ tetrahedra; (b) a fragment of the glass structure in the S-rich domain with CS-, ES- and isolated ISO-GeS$_{4/2}$ units, separated by S$_2$ dimers, and sulfur rings [Bychkov 2006].

The stoichiometric germanium disulphide GeS$_2$ plays a key role in the formation of the thiogermanate glass network [Julien 1994]. The GeS$_2$, when it is alloyed with other sulfides, gives a variety of glasses [Barnier 1992]. Some GeS$_2$-based glasses developed so far exhibit electrically and optically interesting properties [Hugget 1983, Leung 1985]. Further, bulk ternary glasses of the Ag-Ge-S system are solid electrolytes with a high ionic conductivity at room temperature [Souquet 1981, Tranchant 1985]; their conductivity being significantly increased by dissolution of a dopant salt. Moreover, germanium sulfide glasses are practical host materials for rare-earth ions because of their large refractive index and low maximum phonon energy. These properties result in large emission cross-sections and low nonradiative decay rates for optical transitions, respectively [Cherry 2002]. Consequently, glasses from this system doped with rare-earths are of interest for a variety of photonic applications, including optical amplifiers and near-IR sources [Turnbull 1999, Aitken 1997]. And although their physical properties are now well-known, the fundamental mechanisms of ionic transport are not yet fully understood from a microscopic point of view. This is essentially due to the fact that the structure of these glasses is still not completely established [Julien 1994].
Limited structural information exists for Ge-rich binary Ge-S glasses. The glasses with \( x = 35, 40, 45 \) were studied using Raman scattering [Kotsalas 2001]. It was found that in the moderately enriched in Ge glass \( (x=35) \), the band at 260 cm\(^{-1}\), which was hardly observed in the spectrum of the stoichiometric glass, becomes very pronounced while the other three main bands at higher frequencies maintain, more or less, their relative intensities. The band at 260 cm\(^{-1}\) has been attributed [Lucovsky 1974] to Ge-Ge bonds as the excessive Ge atoms start occupying corner sites in the tetrahedra. It is known [Lannin 1985] that the main Raman band of amorphous Ge appears at about 270 cm\(^{-1}\) and this supports the view that the band at 260 cm\(^{-1}\) in the Raman spectra has its origin in Ge-Ge bond vibrations, with the small shift towards the lower frequencies being justified by the different environments around the Ge-Ge bond in each case. Alternatively, the 260 cm\(^{-1}\) band has been assigned [Boolchand 1986] to the breathing mode of GeS\(_6\) octahedra that form the crystalline lattice of c-GeS. The authors supported the idea that G-rich Ge-S glasses are nanophase separated; the new phase that grows has structure similar to the rock-salt structure of the crystalline modification.

The above survey makes clear that even for the stoichiometric glass GeS\(_2\) there is controversy as regards the correct structure description due to the ambiguous band assignment. Obviously, the situation is more complex for the overstoichiometric, Ge-rich, binary glasses. Therefore, the present chapter focuses on a detailed analysis of the stoichiometric and Ge-rich glasses as well in an effort to clarify some not well understood issues related to the structure of these glasses.

### 9.2 Results

Stokes-side unpolarized Raman spectra of the Ge-S glasses studied in this work are presented in Fig. 9.4. Attempts to record polarized and depolarized Raman spectra for the glasses of this binary system failed. The reason is that the glasses have been produced by rapid quenching from the high temperatures melt (see Chapter 6 for details). The rapid cooling induces “optical stresses” or gradients in the refractive index trapped in the glass structure as a result of fast quenching.
CHAPTER 9: Structural study of $\text{Ge}_x\text{S}_{100-x}$ ($x_{\text{Ge}}$: 33.3, 34, 35, 40) glasses by Raman scattering

These optical inhomogeneities can be eliminated after sufficient annealing near $T_g$ and thus the depolarization ratio would attain its correct form. However, Ge-S glasses, and especially those for $x_{\text{Ge}} > 33.3$ have the disadvantage of exhibiting fast crystallization even at temperatures near but below $T_g$. This has to be contrasted to As-Se glasses where crystallization is indeed difficult to achieve even under prolonged annealing at $T > T_g$.

![Stokes-side Raman spectra of Ge$_x$S$_{100-x}$ binary glasses (33.3 $\leq x \leq$ 40) normalized at the intensity of the 342 cm$^{-1}$ mode. Intensities are attenuated below $\sim$120 cm$^{-1}$ due to the notch filter of the FT-Raman set-up.]

**Fig. 9.4.** Stokes-side Raman spectra of $\text{Ge}_x\text{S}_{100-x}$ binary glasses (33.3 $\leq x \leq$ 40) normalized at the intensity of the 342 cm$^{-1}$ mode. Intensities are attenuated below $\sim$120 cm$^{-1}$ due to the notch filter of the FT-Raman set-up.

The spectra have been normalized at the peak maximum of the 342 cm$^{-1}$ band characteristic of $A_1$ mode of the GeS$_2$ glass. We observe that the Raman spectrum of the stoichiometric compound exhibits a gap between the low- and high-frequency parts of the spectrum between 220 and 300 cm$^{-1}$. Bond-bending and
bond-stretching vibrational modes contribute to these spectral windows, respectively. At least three vibrational modes are evident in bond stretching region of the stoichiometric glass composition. The main one is located at \( \sim 342 \text{ cm}^{-1} \); this mode is accompanied by two other modes situated at \( \sim 372 \text{ cm}^{-1} \) and \( \sim 435 \text{ cm}^{-1} \). The bond-bending spectral part is broad featureless band without any discrete peaks. However, two broad, weak modes seem to be located at \( \sim 202 \) and \( \sim 155 \text{ cm}^{-1} \). Increasing Ge concentration above the stoichiometry (\( x=33.3 \)) by less than 1 at.\% in Ge we observe appreciable spectral changes over the whole frequency range. In particular, a new broad band appears in the 210-280 cm\(^{-1}\) spectral range. This band is composed of two vibrational modes at \( \sim 243 \) and \( \sim 258 \text{ cm}^{-1} \). On the high frequency side we observe a partial loss of the fine structure of the bond stretching peaks. Increasing further by little the Ge content (Ge\(_{35}\)S\(_{65}\)) the above described changes continue with the same trend. A peak seems to grow also at \( \sim 405 \text{ cm}^{-1} \) blurring the minimum between the 372 cm\(^{-1}\) and 435 cm\(^{-1}\) modes. These changes become more obvious in the Raman spectrum of the Ge\(_{40}\)S\(_{60}\) glass where the gap between the bond-bending and bond-stretching regimes is now bridged.

9.3 Analysis of Raman spectra and Discussion

As has already been mentioned in Section 9.1 the structure of Ge-Se binary glasses has been the subject of numerous investigations with the use of vibrational spectroscopy [Kotsalas 2001, Lucovsky 1974, Cai 2002]. However, not definite structural information exists still for Ge-rich binary Ge-S glasses. One of the reasons for this is that binary Ge-S glasses at the Ge-rich regime are characterized by low optical bandgaps due to the appreciable decrease of this optical property upon the addition of Ge atoms [Seki 2003]. The coloration of these glasses causes technical problems in Raman experiments where visible light is used to excite Raman spectra. Therefore, in the present work we utilized off-resonance conditions in order to be able to record with accuracy the equilibrium structure of these binary glasses.
In fact, even the assignments of the stoichiometric glass GeS\textsubscript{2} are still considered as not definite [Kotsalas 2001, Sugai 1987]. Let us now proceed to the discussion of the theoretical predictions of tetrahedrally bonded solids. For a tetrahedral symmetry ($T_d$), group theory predicts four active Raman modes: the symmetric stretching mode $\nu_1(A_1)$, the bending modes $\nu_2(E)$, $\nu_4(F_2)$ located at frequencies lower than $\nu_1(A_1)$, and the antisymmetric stretching $\nu_3(F_2)$ mode at a frequency higher than $\nu_1(A_1)$ [Nakamoto 1986]. The irreducible representation of the Raman active modes in this case is $\Gamma(T_d) = A_1 + E + 2F_2$. What is broadly accepted for the stoichiometric glass is that its main vibrational modes have been accounted for by considering both corner-sharing (CS) and edge-sharing (ES) GeS\textsubscript{4/2} tetrahedral units (see Fig 9.1). The reduced Raman spectra of the present glasses are shown in Fig. 9.5 in a normalized representation different than that used to normalize the data in Fig. 9.4. Normalization in Fig. 9.5 has been performed by considering constant area of the spectra in the range 120-500 cm\textsuperscript{-1}. We observe a transfer of the scattered intensity to the low energy modes and a narrowing of the high-frequency spectra envelope. In order to be able to describe the structural
details of the Ge-rich glasses we first attempt to clarify the structure of the stoichiometric glass.

### 9.3.1 Structural details of the stoichiometric glass GeS$_2$

Understanding the structure of the stoichiometric glass is essential for a correct description of the structure of the Ge-rich glasses. Figure 9.6 illustrates the deconvolution of reduced polarized Raman spectra into Gaussian line distributions for the stoichiometric glass GeS$_2$. Since the high frequency spectral envelope [300-480 cm$^{-1}$] is practically isolated from the low energy bending vibrations, and hence it was treated independently of these low frequency (weak) modes. Two schemes of the fitting procedure were followed. In Fig. 9.6(a) we present deconvolution of these broad spectral bands with four Gaussian peaks. It is important to notice here that in the current literature this region is still considered as being composed of three vibrational modes, i.e. those which are seen as discrete peaks. Sugai was the

![Fig. 9.6. Gaussian peak deconvolution of reduced polarized Raman spectra for GeS$_2$: (a) fit with 4 Gaussian peaks; (b) fit with 5 Gaussian peaks. The best fit parameters, i.e. frequency, halfwidth at half height and area are indicated in the legends.](image)
first (actually without followers) to fit this region with four peaks [Sugai 1987] obtaining a result similar to that shown in Fig. 9.6(a). However, Sugai did not attempt to assign the extra broad mode at 394 cm\(^{-1}\) to a vibrational mode of some specific structural unit present in the glass. Judging from the width of the vibrational line at 394 cm\(^{-1}\) it seems that the four Gaussian peaks fit is not a realistic one for the high frequency spectrum of GeS\(_2\) glass. Therefore, we present in Fig. 9.6(b) a fit with five Gaussian lines, splitting eventually the very broad 394 cm\(^{-1}\) band to two narrower ones. We observe for the values of the best-fit parameters listed in the legends of Fig. 9.6 that although the frequencies of the other peaks do not differ appreciably between the two fits, on the other hand the relative intensities of these peaks differ substantially. This is important when one uses band areas for deterring the relative fraction of CS and ES tetrahedral units.

Let us now discuss the possible origin of the above peaks. To identify the stretching frequency \(\nu_1(A_1)\) we can be based on the analogy between the Raman modes of the GeS\(_4\) and the GeCl\(_4\) tetrahedra. Since the mass ratio of germanium tetrachloride is very similar to germanium tetrarsulfide we also expect a correspondence in the respective Raman frequencies. The frequencies of the isolated GeCl\(_4\) molecule are [Clark. 1971, Clark 1975]: 125 cm\(^{-1}\) for \(\nu_2(E)\); 171 cm\(^{-1}\) for \(\nu_4(F_2)\); 397 for cm\(^{-1}\) \(\nu_1(A_1)\); and 459 cm\(^{-1}\) for \(\nu_3(F_2)\). Although the two tetrahedra have almost the same reduced mass the absolute values of frequencies differ significantly, i.e. 397 and 342 cm\(^{-1}\) for the \(\nu_1(A_1)\) mode for the chloride and the sulfide tetrahedron, respectively. This difference reflects mainly “condensed matter” effects. In particular, the isolated from its neighbors GeCl\(_4\) tetrahedron does not share electronic density with neighboring units and hence its intramolecular vibrations are at higher frequency than those of the GeS\(_4\) tetrahedron which is bonded via covalent bonds to its immediate neighbors.

Using these values we can calculate the ratio \(\nu_3 / \nu_1 = 1.156\) for GeCl\(_4\). Assuming a similar value of this ratio for the GeS\(_4\) tetrahedron and based on the fact that the \(\nu_1(A_1)\) mode of the GeS\(_4\) tetrahedron has a frequency at 342 cm\(^{-1}\) we conclude that the corresponding \(\nu_3(F_2)\) mode should be located at 395.4 cm\(^{-1}\). This
value is exactly at the frequency of the No. 3 Gaussian peak of the fit shown in Fig. 9.6(b). Following the same scaling scheme we can determine the frequencies for the bond-bending modes of the GeS₄ tetrahedra; these frequencies are at 108 and 147 cm⁻¹ for the \( \nu_2(E) \) and \( \nu_4(F_2) \) modes, respectively. As has already been mentioned at the beginning of Section 3, a broad, weak mode is seen at \(~150\) cm⁻¹. Based on the above discussion we can rather safely assign this mode to the \( \nu_4(F_2) \) mode of the GeS₄ tetrahedron. The \( \nu_2(E) \) mode is not detectable from our spectra since it is located at the spectral region where the FT-Raman spectrum is attenuated and severely distorted by the notch filter that serves to block the elastic line.

Having assigned all four vibrational modes of the CS GeS₄ tetrahedra we see that there are extra peaks in the Raman spectrum which need to be assigned. Summarizing, we still have to identify the modes at \(~202, 373, 413, \) and \(~434\) cm⁻¹ modes. As mentioned in the literature survey presented above the 373 cm⁻¹ mode, called the companion line \( A'_1 \), has been assigned to the symmetric stretching modes ES GeS₄ tetrahedra. The atomic displacements related to the vibrational modes \( A_1 \) and \( A'_1 \) are shown in Fig. 9.7(a), (b). Apart from the \( \nu_1(A_1) \) mode ( \( A'_1 \) ) of the ES tetrahedra, the \( \nu_3(F_2) \) mode should also be Raman active. Using the same scaling factor for the \( \nu_3 / \nu_1 \) ratio of CS tetrahedra we estimate that the \( \nu_3(F_2) \) of CS units should be located at \(~431\) cm⁻¹, i.e. at the frequency of the highest vibrational mode observed in the Raman spectrum, [peak No. 5 in Fig. 9.6(b)]. Ab initio simulations

![Fig. 9.7. Atomic displacements involved in the \( A_1 \) and \( A'_1 \) modes presenting symmetric-stretching vibrations of corner-sharing (a); and edge-sharing tetrahedra (b); and in the vibrational modes at 440 cm⁻¹ (c) and 200 cm⁻¹ (d) concerning edge-sharing units.](image)
[Jackson 1999] have suggested that the 434 cm\(^{-1}\) mode is the highest frequency mode of the ES unit in line with our assignment. The origin of the band at 434 cm\(^{-1}\) is still an unsolved issue in the current literature; see [Kotsalas 2001]. In the framework of a frequently adopted assignment this mode is considered to arise from S-S vibrations where the S atoms are situated either at the edges of bigger clusters or in short chains. However, this assignment can be safely excluded reckoning on the Raman spectrum of crystalline and liquid S [Kalampounias 2003a, Kalampounias 2003b] where it is shown that the stronger bands of both monomeric (S\(_8\) molecules) and polymeric (S\(_n\) chains) sulfur species in the spectral range above 400 cm\(^{-1}\) are located at 474 and 463 cm\(^{-1}\), respectively.

The mode at \(~202\) cm\(^{-1}\) has not been frequently considered in experimental studies and is rarely put under focus. In a recent molecular dynamics simulations study [Blaineau 2004] was associated with vibrations of ES tetrahedra and in particular with modes related to the atomic displacement shown in Fig. 9.7(d). It is however difficult to check experimentally this suggestion since this mode is both very weak and insensitive to variations of the Ge content in the glass. Finally, as regards the weak 413 cm\(^{-1}\) mode it is not possible at present to speculate about its origin. The analysis presented above is obviously not unique; however, we tried to fit the spectrum with the least number of peaks and assign the observed peaks to specific vibrational modes of the structural units. More peaks might be hidden under this broad spectral envelope reflecting local inhomogeneities of the glass structure. Indeed, Fig. 9.8 shows the possible bonding configurations around a GeS\(_4\) tetrahedron in the stoichiometric GeS\(_2\) glass. In (a) and (c) we see purely ES and CS units, respectively, leading to 3D (or 2D) network structures (a) and quasi-1D chain structures. There is however a new configuration where a tetrahedron is bonded to two tetrahedra via CS and to one tetrahedron via ES. Obviously the A\(_1\) and A\(_1\)' vibrational modes, which are defined for structures of type (a) and (c) in Fig. 9.8, have to be modified for the tetrahedron of type (b). This implies generation of new modes and/or broadening of the existing ones. Therefore, the 413 cm\(^{-1}\) mode might be related to the vibrational motions of such mixed structures.
CHAPTER 9: Structural study of $\text{Ge}_x\text{S}_{100-x}$ ($x_{\text{Ge}}$: 33.3, 34, 35, 40) glasses by Raman scattering

**Fig. 9.8.** The possible bonding configurations around a GeS$_4$ tetrahedron: (a) four CS tetrahedra; (b) two CS and one ES units; (c) two ES units.

The ratio of $A_1$ and $A'_1$ band intensities is frequently used to estimate the fraction of tetrahedra that are bonding in CS or ES configurations. Using the areas determined by the fit, we find that $I(A'_1)/I(A_1) = 0.38$, or alternatively almost 28% of the tetrahedra are arranged in ES bonding configuration. Molecular dynamics simulations [Blaineau 2004] have found that the fraction of ES tetrahedra is higher and amounts to about 46%. The Raman result needs correction for the Raman cross-section (polarizability matrix elements) of the the CS and ES units. *Ab initio* studies are under way to clarify this issue.

### 9.3.1 Structural details of the Ge-rich binary Ge-S glass

Given the confusion and lack of consensus concerning the assignment of Raman bands to specific vibrational modes for the stoichiometric GeS$_2$ glass described in detail in the previous Section, it is obvious that the interpretation of Raman spectra of Ge-rich Ge-S binary glasses has been even more speculative in the current literature. Actually no definite band assignments were given in previous studies [Kotsalas 2001, Lucovsly 1974] where high germanium concentrations were studied. In a recent Raman study [Cai 2002] compositions [$x_{\text{Ge}} = 32.5, 33, 33.33, 33.6, 34$] very near the stoichiometric glass were investigated. The raw Raman spectra of Cai et. al. are shown for comparison in Fig. 9.9. The interest was mainly to the spectral regions around 250 and 500 cm$^{-1}$ (see insets in Fig. 9.9) A band
detected at ~494 cm\(^{-1}\) (in the \(x_{\text{Ge}} = 32.5, 33, 33.33\) compositions) was attributed to the \(S_n\)-chains. In the 200-300 cm\(^{-1}\) spectra range two bands are observed labeled B (255 cm\(^{-1}\)) and C (236 cm\(^{-1}\)), which progressively grow in scattering strength with increasing \(x_{\text{Ge}}\), starting at a threshold Ge concentration \(x_{\text{Ge}} = 33\). They assigned the B peak to ethane-like \(\text{Ge}_2(S_{1/2})_6\) units, and the C mode to distorted rocksalt octahedra \(\text{Ge}(S_{1/6})_6\) which grow as a new nanophase in the glass structure.

![Raman scattering in indicated glass samples obtained using 514.5 nm excitation in a macro-configuration [Cai 2002].](image)

**Fig. 9.9** Raman scattering in indicated glass samples obtained using 514.5 nm excitation in a macro-configuration [Cai 2002].

Following a similar quantitative analysis for the Ge-rich glasses we illustrate in Fig. 9.10(a) the fitting result for the \(\text{Ge}_{34}\text{S}_{66}\) using again five Gaussian peaks for the high frequency range. Since the gap in the vibrational modes between low and high frequencies is still present we fit the low frequency region separately, see inset of Fig. 9.10(a). An extra broad Gaussian peak was used at the high energy range (~500 cm\(^{-1}\)) in order to fit the non-zero background which emerges in the Raman spectrum of this glass between the first and second order vibrational modes. This background was completely absent in the spectrum of the stoichiometric glass. It is obvious from Fig. 9.10 that the spectral parameters of the individual Gaussian peaks (frequencies, widths, and relative intensities) are practically unchanged in
CHAPTER 9: Structural study of Ge_{x}S_{100-x} (x_{Ge}: 33.3, 34, 35, 40) glasses by Raman scattering

Comparison with the corresponding parameters of the stoichiometric glass. The vibrational frequencies of the Ge_{34}S_{66} glass estimated from the fit are at: 343, 373, 395, 412, and 434 cm\(^{-1}\). The ratio of the population of ES to CS tetrahedra is for this glass \(I(A'_1)/I(A_1) = 0.39\) and hence almost 28\% of these units are edge-shared.

The low energy region has been fitted using six Gaussian peaks, see inset in Fig. 9.10(a). The peak at 155 cm\(^{-1}\) has been used to fit the broad background; since it is at the limits of the distortion that the FT-Raman technique induced in the spectrum it will not be discussed further. Therefore, we observe that the low energy part of the Raman spectrum is dominated by four peaks at: 180, 205, 215, 237, and 258 cm\(^{-1}\). The two modes with the highest frequency, i.e. 237 and 258 cm\(^{-1}\), are of the main importance since these peaks have been associated with Ge-Ge vibrations in ethane-like (ETH) units (see Fig. 9.1) and vibrations of Ge(S_{1/6})\(_6\) octahedral units [Cai 2002] which are building blocks of the distorted rocksalt structure of crystalline GeS. A first-principles density functional calculation of vibrational modes on selected GeS\(_n\), clusters has shown [Jackson 1999] that ethane-like units possess two strongly active Raman modes: one at 254 cm\(^{-1}\) and the other at 366 cm\(^{-1}\). These calculations provided justification to assign the mode at 258 cm\(^{-1}\) to the presence of ethane-like units [Lucovsky 1977].

Following a similar analysis we present in Fig. 9.10(b) the results of Gaussian peak deconvolution for the Raman spectrum of the Ge_{35}S_{65} glass. Because the gap between low- and high-frequency peaks is still well-defined the analysis of the two spectral regions has been conducted in two steps. The inset in Fig. 9.10(b) shows the analysis of the low frequency part. The situation is not radically different than that of the Ge_{34}S_{66} glass. The ratio \(I(A'_1)/I(A_1)\) remains unchanged implying that no detectable change in the CS and ES population has occurred. On the other hand, a new scattering contribution appears at the region of the local minimum between 400 and 420 cm\(^{-1}\). As regards the low-frequency part we observe that there is also no important change in the lineshapes apart from an increase of the intensity of the bands in the region 230-300 cm\(^{-1}\).
In contrast to the glasses with composition near the stoichiometric threshold, the continuous background that appears between the high and low frequency bands in the Raman spectrum of the Ge\textsubscript{40}S\textsubscript{60} glass necessitates the simultaneous fitting of the whole spectral range. It should be stressed all Gaussian peaks used to fit this

Fig. 9.10. Gaussian peak analysis of reduced Raman spectra for Ge-rich glasses.
spectrum are either clearly visible in the experimental Raman spectrum. The frequencies of bands in the high energy appear at 345, 369, 387, 403, 423 cm\(^{-1}\).

Therefore, we observe a slight blue-shift of the \(A_1\) mode and a corresponding red-shift of the \(A'_1\) mode. In addition, all other three modes have been softened by almost 10 cm\(^{-1}\). The lineshape of the high-frequency spectral envelope experiences appreciable changes. The ratio \(I(A'_1) / I(A_1)\) has changed considerably; its magnitude for the Ge\(_{40}\)S\(_{60}\) glass is \(\sim 0.9\) implying that almost 47\% of the tetrahedra are in ES bonding configuration. In the low-frequency region, the broad background scattering as well as the intensity of the bands in the region 230-300 cm\(^{-1}\) has increased considerably. The various analyzed peaks are quite broad and higher errors associated with their intensities does not permit a quantitative description of the structure in terms of the relevant structural units.

The addition of Ge in the stoichiometric glass causes the appearance of mixed Ge\(_n\)S\(_{100-n}\) \(n = 0,1,2,3,4\) tetrahedra. The relative population of these tetrahedral units can be estimated using statistical argument. Therefore, in the framework of the chemically ordered network [Lucovsly 1974] and under the assumption of the satisfaction 8-N rule for the coordination numbers the relative populations of the mixed tetrahedra for the glasses studied in this work are given in Table 9.1.

<table>
<thead>
<tr>
<th>Tetrahedral unit</th>
<th>GeS(_4) ((T_d))</th>
<th>GeS(_3)Ge(<em>1) ((C</em>{3v}))</th>
<th>GeS(_2)Ge(<em>2) ((C</em>{2v}))</th>
<th>GeS(_1)Ge(<em>3) ((C</em>{2v}))</th>
<th>GeGe(_4) ((T_d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge at.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>88.74</td>
<td>10.76</td>
<td>0.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>35</td>
<td>74.35</td>
<td>22.88</td>
<td>2.64</td>
<td>0.13</td>
<td>--</td>
</tr>
<tr>
<td>40</td>
<td>31.64</td>
<td>42.19</td>
<td>21.09</td>
<td>4.69</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Figure 9.11 illustrates graphically the evolution of the relative populations of the mixed tetrahedra as a function of the glass composition. It is obvious that
according to the chemically ordered network model we expect an appreciable reduction of the GeS₄ tetrahedral units even for small percentages of Ge above the stoichiometric threshold. Actually, this is evident in Fig. 9.10 where the intensity of the sharp band of the symmetric stretching mode of the GeS₄/2 tetrahedra at ~342 cm⁻¹ has decreased in comparison with the intensity of the other peaks hidden below the spectral envelope [300-430 cm⁻¹].

**Fig. 9.11.** (a) Relative distributions of the various types of GeSₙGe₁₋ₙ tetrahedra; (b) A detail of the same plot near the glass compositions studied in this work.

The intensity ratio I(A₁') / I(A₁) determined from peak areas was found to be almost constant (within experimental error) for the Glasses with x₇₄ = 33.3, 34, and 35 to a value ~0.39, while it seems to change substantially in the case of the Ge₄0S₆₀ glass where it acquires the value ~0.9. The concentration dependence of this ratio is known only for S-rich glasses [Sugai 1987] where it was reported its monotonic increase up to the stoichiometric composition. As evident from the present data, the presence of Ge atoms at concentrations exceeding the stoichiometry influences the substructures where corner sharing dominates to a higher extent than that of edge-sharing units. The drastic reduction of the GeS₄/2 corner-sharing tetrahedra does not necessarily implies that the extra Ge atoms attack the corner sharing bridges transforming CS units to ES ones. The incorporation of Ge atoms into a tetrahedron
and the formation of units of the form GeS$_3$Ge (with symmetry $C_{3v}$, i.e. lower than $T_d$) have as consequence the change of the vibrational frequency of the new unit and the reduction of the $\nu_1(A_1;GeS_{4/2})$ peak intensity. As can be seen from Table 9.1 the mixed tetrahedral units are characterized by lower symmetries which imply changes in the number of vibrational modes per unit as well as changes in the frequencies of these modes in comparison with the GeS$_4$ tetrahedron. This situation complicates further the assignment of the bands, especially for the Raman spectrum of the Ge$_{40}$S$_{60}$ glass. Therefore, the peaks in the high frequency region seen in Fig. 9.10(c) do not have (probably) the same origin with the corresponding peaks in the spectrum of the stoichiometric glass.

Concerning the low energy spectral range, i.e. below 300 cm$^{-1}$, several peaks appear in the Ge-rich glass. Apart from bending modes of GeS$_{4/2}$ units, which also exist in GeS$_2$ glass, the new modes have their origin at the symmetric stretching vibrations of Ge-enriched tetrahedral units, i.e. GeS$_n$Ge$_{3-n}$ (n = 0,1,2) tetrahedra. The bending modes of these heavier units superimpose to the corresponding modes of the other tetrahedra and form the broad, intense background seen in the low-frequency part in the Raman spectrum of the Ge$_{40}$S$_{60}$ glass.

In order to check the validity of the assignment of the peak at ~238 cm$^{-1}$ to the vibrations of the distorted rocksalt octahedra Ge(S$_{1/6})_6$ we have to attempt a quantitative estimation of the expected red-shift of the Ge-S vibrational frequency on going from the GeS$_{4/2}$ tetrahedron to the distorted Ge(S$_{1/6})_6$ octahedron. A similar analysis has been conducted for the GeTe compound whose structure is similar to that of GeS in the crystal phases (distorted rocksalt) while is dominated by GeTe$_{4/2}$ tetrahedra in the amorphous state [Andrikopoulos 2006]. At first, the red-shift from 343 cm$^{-1}$ in GeS$_{4/2}$ to 238 cm$^{-1}$ in Ge(S$_{1/6})_6$ is justified from the fact that the coordination number of Ge atoms changes from 4 to 6. This means that the electronic density of Ge is distributed to a larger number of bonds and hence the strength of the bonds is reduced. Then, we know [Zachariasen 1932] that Ge atoms are surrounded by distorted octahedra formed by sulfur atoms. The germanium atom is not lying at the center of the octahedron, but is displaced towards one of the
octahedral faces. The distance from germanium to three of the sulfur atoms in this manner is distinctly smaller than to the three others. The two distances Ge-S are: 2.58 Å for the short bond (average of 2.47, 2.64, 2.64) and 2.97 Å for the long bond (average of 2.91, 3.00, 3.00) [Zachariasen 1932]. The fact that 3 of the S atoms are situated at a larger distance results in even weaker interactions with the central Ge atom.

The change in the coordination number induces relaxation in bond energy due to change in bond length. Therefore, in our case where the change of geometry from tetrahedral to octahedral induces bond dilation we have $<d>^{\text{oct}} = c \cdot <d>^{\text{tet}}$, where $<d>^{\text{oct}}$ and $<d>^{\text{tet}}$ are the average bond length in the GeS crystal and bond length of the tetrahedron in the glassy state, respectively, and $c$ is a bond dilation coefficient with $c > 1$. The relation between the bond energy and the bond length is a power law dependence on the coefficient $c$ [Sun 2002], i.e.:

$$E(<d>^{\text{oct}}) = c^{-m}E(<d>^{\text{tet}})$$

For a number of materials, experimental facts have shown that $m \approx 4$ [Sun 2002]. Employing Eq. (2) and the bond lengths $d^{\text{tet}} = 2.20$ Å [Rowland 1972], and $<d>^{\text{oct}} = 2.775$ (which is the mean value of the aforementioned values for c-GeS) we obtain $c \approx 1.26$ and hence $E(<d>^{\text{oct}}) = 0.395 \times E(<d>^{\text{tet}})$. Considering the bond energies proportional to the bond frequencies we estimate using the above finding that the peak of the octahedral molecule if present in g-GeS$_2$ should appear at $\sim$140 cm$^{-1}$. This is at a much lower energy than the 238 cm$^{-1}$ which considered to arise from GeS distorted rock-salt nanophase.

### 9.4 Concluding Remarks

It has become evident from the introductory section of the present chapter that despite the intensive efforts from both the experimental and the theoretical point of view, the knowledge of the structure of Ge-rich binary Ge-S glasses is still not at a satisfactory level. Raman scattering has been presumably the most valuable tool in
elucidating the structure for these binary glasses in view of the variety of structural units present in their structure. It is noteworthy that even for the structure of the stoichiometric glass GeS$_2$ there are several self-contradictory aspects in the current literature. Raman scattering was used in order to study few closely spaced glass compositions of the Ge$_x$S$_{100-x}$ near and above the stoichiometric threshold. The off-resonant laser conditions were also important in view of the decreased optical bandgap of the glasses with appreciable Ge content. The main conclusions of the present chapter are summarized as follows:

- The structure of the stoichiometric glass is composed of GeS$_4$ tetrahedral units bonded either via corner or edge sharing. Using the well-defined analogies between the various frequencies of isolated tetrahedral molecules (i.e. GeCl$_4$) it has been possible to identify the Raman peaks that are associated with the four vibrational modes dictated by the tetrahedral symmetry of the GeS$_4$ molecule. The key point to this identification was the detailed analysis of the high-frequency spectral envelope with five Gaussian peaks.

- We have discussed why the highest frequency peak at 434 cm$^{-1}$, whose origin is the most controversial in relation to other peaks, cannot be associated with S-S bonds. Using scaling arguments this peak has been identified with the antisymmetric stretching vibrational mode of ES units. The broad nature of the peaks in the Raman spectrum was associated with the existence of three types of bonding around a reference GeS$_4$ tetrahedron. These types include four CS units, two CS and one ES unit, and two ES units. Using the areas determined by the fit, we find (assuming comparable polarizability matrix elements for these two species) that ~28% of the tetrahedra are arranged in ES bonding configuration.

- The Raman spectra of Ge-rich glasses change appreciably even for few percent addition of Ge. New Raman bands appear at ~237 and ~258 cm$^{-1}$ which grow fast as a function of $x_{Ge}$. The mode at ~258 cm$^{-1}$ has
been assigned to Ge-Ge bonding in ethane like units $S_3$Ge-Ge$S_3$. Using a simple model connecting bond energies with the average bond distances we have shown that it is rather incorrect to assign the Raman at 238 cm$^{-1}$, which grows fast with the addition of Ge in the spectra of Ge-rich glasses, to the nanoscale phase separation of the glass structure to GeS-like distorted rocksalt octahedral units.
CHAPTER 9: Structural study of Ge$_{x}$S$_{100-x}$ ($x_{Ge}$: 33.3, 34, 35, 40) glasses by Raman scattering

References of Chapter 9:

Cai L., and Boolchand P., Phil. Mag. 82 1649 (2002)
Zachariasen W. H., Phys. Rev. 40, 917 (1932)
Chapter 10

Structural aspects of the $(\text{GeS}_{1.5})_{100-x} (\text{AgI})_x$ glassy system: Structural Raman and IR studies.

10.1 Literature survey.

The considerable attention that has been paid on chalcogenide glasses over the last decades is due to a wide range of their potential practical applications [Kolobov 2003, Proceedings of the XV International Symposium on Non-Oxide Glasses and New Optical Glasses, Bangalore 2007]. The knowledge of the structure and the basic building units of a glassy material are essential for better understanding the composition-properties-applications relation. Vibrational spectroscopy (infrared spectroscopy and Raman scattering) is a very powerful experimental tool, which is amply used in structural investigations of glasses [Feltz 1993]. Glasses that contain both chalcogen and halogen atoms, known as chalcohalides glasses, have been intensively studied in the past in view
of their IR transparency and enhanced chemical durability when exposed to ambient conditions as has been reviewed in [Sanghera 1988, Gan 1992].

Evidently, arsenic chalcohalides are the most thoroughly studied materials, whilst only few experimental works have focus on germanium-based chalcohalide glasses [Sanghera 1988, Gan 1992]. In particular, Heo et al. [Heo 1989] have undertaken structural studies on Ge-S-I glasses and Kamistos et al. [Kamistos 1994] have studied structure and conductivity of GeS$_2$-Ag$_2$S-AgI glasses. In the former study, the sulfur-rich domain of glass composition was studied while in the latter silver compounds were added in the stoichiometric germanium sulfide glass matrix. It would therefore be interesting to investigate the nature of structural changes in Ge-rich non-stoichiometric sulfide glasses.

Elucidation of vibrational properties offers a challenging opportunity to explore changes in the structure caused by doping a chalcogenide glass matrix with binary salt – silver iodide. The introduction of the salt is attractive also from the practical point of view as has been recently demonstrated in gas sensing [Monchev 2007a]. Moreover, the basic physicochemical properties of glasses from the system Ge-S undergo changes when adding AgI [Monchev 2007b]. The density and the molar volume increase. The compositional dependence of these properties is due to the higher density and the bigger atomic radius of silver iodide, as compared to the other components. At the same time, the microhardness decreases. At macroscopic point of view, the most reasonable explanation for this ‘‘plasticizing effect’’ is connected with the very low microhardness of the silver iodide, which is about two orders of magnitude lower as compared to the microhardness values of the germanium sulfides [Gmelin (1974–1979)]. The compositional dependence of microhardness viewed at atomic scale is related to the energies of the bonds that should be broken down when the microindentor penetrates into the glassy sample. That approach supposes that the more high energetic bonds define (corresponds to) the bigger microhardness of the material. The authors assumed that, in accordance with chemically ordered covalent network, the most probable bonds presented in the studied glasses are Ge–S and Ag–I [Monchev 2007b]. In the work of
Monchev [Monchev 2005], the authors examined the change in optical properties of the Ge-S-AgI films. They observed that the transparency decreases significantly with AgI. Films with 20 mol.% AgI show 20 % lower transparency compared with film with 5 mol% AgI while the reflectivity of the films increases, respectively. All these property changes are due to the structural modification due to AgI addition into the Ge-S matrix. By considering the bond energies in Ge–S-AgI glasses [Monchev 2005] the application of random covalent network model according to which Ge-Ge bonds are possible can be excluded. Bonds such as Ag-S and S-S have also lower possibility of existence due to their lower bond energy. They suggested that the most favorable structural units are GeS$_{4/2}$ and AgI. The tetrahedral GeS$_{4/2}$ units are corner bridged with AgI clusters through three-coordinated silver atoms. The increase in the AgI amount is associated with an increase in the number of AgI clusters and increase in the number of metallic bonds in the film. Although the importance and the presented suggestions concerning structure of these glassy system, structural studies are practically absent in the literature.

![FT Raman experimental spectra of (GeS$_{1.5}$)$_{100-x}$ (AgI)$_x$ composition](image)

Fig. 10.1 FT Raman experimental spectra of (GeS$_{1.5}$)$_{100-x}$ (AgI)$_x$ composition
CHAPTER 10: Structural aspects of the $(GeS_{1.5})_{100-x} (AgI)_x$ glass system: Structural Raman and IR studies

10.2 Results

10.2.1 Raman scattering results of $(GeS_{1.5})_{100-x} (AgI)_x$ glasses

Raw spectra of the glasses containing AgI are represented in Fig. 10.1, together with the matrix spectrum. It is readily distinguishable the bond-bending part (at lower frequency) from the bond-stretching one (high frequency bands).

As it is seen, the spectra do not bear any significant changes. The main stretching bands do not show any shift in frequency in all concentration presented. The same bands displayed slight width change, which, nevertheless, is itself confusing. The 5 % spectrum increases mildly in width, whereas the next composition investigated, 10 %, decreases. The same change undergo and the highest concentrations, namely 15 and 20 mol% in AgI.

10.2.2 Infrared spectroscopy

Figure 10.2 presents the absorption coefficient spectra of $(AgI)_x (GeS_{1.5})_{100-x}$ bulk glasses for various values of AgI content. The spectrum of GeS$_{1.5}$ is also shown for

![Infrared absorption spectra](image)

**Fig. 10.2** Infrared absorption spectra of $AgI_x (GeS_{1.5})_{100-x}$ glasses. The spectra have been normalized at the energy of the strongest peak.
comparison; its spectral shape is not drastically different from the spectra of the AgI containing glasses. This implies that the addition of AgI causes mild structural modifications to GeS\textsubscript{1.5} glass network.

The main differences are the broadening of the band at high frequencies (near 400 cm\textsuperscript{-1}) and the appearance of extra vibrational lines at low frequencies, i.e. below 300 cm\textsuperscript{-1}. As regards, the spectra of the AgI-doped glasses, it is evident that they exhibit similar spectral features as regards both band shapes and band energies.

10.3 Discussion

The reduced Raman spectra of the present glasses are shown in Fig. 10.3 in a normalized representation. For more details concerning reduction of the Raman spectra see section 5.2.2. Normalization took place at the frequency of the A\textsubscript{1} band of GeS\textsubscript{4/2} tetrahedra at ~342 cm\textsuperscript{-1}.

As shown in Fig. 10.3, the addition of AgI causes mild structural changes in the structure of the GeS\textsubscript{1.5} glass. Although, AgI seems to cause subtle structural changes due to the formation of Ge-I bonds, it is also evident that AgI does not act as a real modifier that would depolymerize appreciably the Ge-S network structure. Similar effects have been recently reported in Raman and EXAFS studies of AgI-As\textsubscript{2}Se\textsubscript{3} glasses [Usuki 2002] where it was concluded that the addition of AgI into As\textsubscript{2}Se\textsubscript{3} glass is not accompanied by significant changes in the short-range structural order of the pyramidal (AsSe\textsubscript{3/2}) network.

The main Raman band shapes of the AgI-doped glasses in our case remain similar to the base glass although small, subtle changes are evident after normalizing the spectra. In the high frequency spectral range we observe a systematic intensity decrease of the bands situated at ~368 and ~407 cm\textsuperscript{-1} relative to the band of the CS GeS\textsubscript{4/2} tetrahedra. This might imply a modest decrease of the population of the ES tetrahedra upon increasing the AgI content. This is possible through the formation of mixed GeS\textsubscript{4-n}I\textsubscript{n} or the even more complex Ge\textsubscript{n}Ge\textsubscript{m}I\textsubscript{4-n-m} tetrahedra. This mechanism takes place via the partial termination
of the glass network by the iodine atoms. The formation of these mixed tetrahedra would cause, in AgI-doped glasses, increased scattering relative to the base glass (GeS$_{1.5}$) at frequencies below 300 cm$^{-1}$ as is indeed revealed in Fig. 10.3.

![Reduced Raman spectra of AgI, (GeS$_{1.5}$)$_{100-x}$ glasses. The Raman spectrum of the stoichiometric GeS$_2$ base glass has also been added for comparison. The baseline of the AgI-doped glasses has been shifted upwards for clarity.](image)

Fig.10.3 Reduced Raman spectra of AgI, (GeS$_{1.5}$)$_{100-x}$ glasses. The Raman spectrum of the stoichiometric GeS$_2$ base glass has also been added for comparison. The baseline of the AgI-doped glasses has been shifted upwards for clarity.

In a detailed study of the Raman spectra of the S-rich ternary Ge-S-I system for ratios S/Ge=3 and S/Ge=2, Heo et al. [Heo 1989] identified the vibrational modes of
mixed GeS$_{4-n}$I$_n$ tetrahedra in the frequency range 200-280 cm$^{-1}$. At the lowest part of this spectral range they identified the breathing modes of the I-rich tetrahedra, i.e. $n=2$, 3, while in the middle of this range the breathing mode of the $n=1$ tetrahedron was hypothesized. Finally, it was suggested [Heo 1989] that the antisymmetric stretching modes of I-rich tetrahedra ($n=2$, 3) are situated in the spectral range 250-260 cm$^{-1}$. However, as has been mentioned above, the addition of AgI in the Ge-rich glass in the present study complicates further the peak assignment since mixed tetrahedral units of the form GeS$_n$Ge$_m$I$_{4-n-m}$ are statistically expected to exist and to have active Raman modes in the energy range below 300 cm$^{-1}$. Apparently, these complex tetrahedral units will be partially interconnected, through S and/or Ge bridges, so as to form low dimensionality arrangements decoupled from the network glass structure.

The IR spectra of the Ge$_x$S$_{100-x}$ binary glasses were studied in detail by Lucovsky et al. [Lucovsky 1974]. It was found that for compositions $30 < x_{Ge} < 50$ the spectra display features in two frequency regimes; i.e. they show a strong composite band at ~375 cm$^{-1}$ and weaker broad band at ~150 cm$^{-1}$. The latter band is considered to be composed of two vibrational modes at ~110 cm$^{-1}$ and ~150 cm$^{-1}$ which were assigned [Lucovsky 1974] to the $v_2$ (E) and $v_4$ (F$_2$) bending modes of GeS$_{4/2}$ tetrahedral units. Similar features are observed in the IR spectrum of the GeS$_{1.5}$ glass in the present study. In detail our fitting analysis revealed the existence of vibrational lines at 110, 150, 258, 305, 341, 378, and 418 cm$^{-1}$. The first two modes are obviously assigned to the bending modes of tetrahedral units as stated above. The mode at ~258 cm$^{-1}$ is related to the presence of Ge-Ge bonds in this Ge-rich GeS$_{1.5}$ glass. The strongest band at ~378 cm$^{-1}$ is the asymmetric stretching $v_3$ (F$_2$) vibrational mode of GeS$_{4/2}$ tetrahedral units as stated above, while the band at 335 cm$^{-1}$ is located near the frequency of the $v_1$ (A$_1$) mode of such tetrahedra. The origin of the peak at 418 cm$^{-1}$ is still a controversial issue in the literature [Kotsalas 2001].

Let us now focus on the structural changes that the addition of AgI brings about. In order to present the analysis in a more quantitative way we have attempted a deconvolution procedure where the broad spectral bands were fitted to several Gaussian
peaks. The deconvoluted spectra of the base glass GeS\textsubscript{1.5} and the AgI-doped glasses with \(x_{\text{AgI}}\): 5 and 20 are presented in Fig. 10.4. As seen in this figure, the addition of 5 mol. % AgI causes a moderate band broadening of the high frequencies spectral envelope (300-450 cm\textsuperscript{-1}) as well as the emergence of a continuum of vibrational lines at frequencies below 300 cm\textsuperscript{-1}. Fitting the IR spectra of the AgI-doped glasses in a way similar to that we applied for the base glass we observe (Fig. 10.4) that there are small but systematic

**Fig. 10.4** Deconvoluted spectra of AgI\(_x\) (GeS\textsubscript{1.5})\(_{100-x}\) glasses for \(x=0\), \(x=5\), and \(x=20\). Open symbols represent the experimental data. The thick solid line through the data is the best-fit curve and the thin solid lines are the Gaussian peaks representing the various vibrational modes.
structural changes with the increase of the AgI content in the glass. One such difference between the spectra of the AgI-doped glasses is the increase of the peak at ~110 cm\(^{-1}\). Raman and IR studies [Bottger 1972] associate this peak with the transverse optical modes of \(\beta\)-AgI. This might be evidence for a possible phase separation of the AgI component from the Ge-S glass matrix as it occurs in many AgI-doped chalcogenide glasses. The peak associated with \(\beta\)-AgI is grown on top of the composite low frequency IR band which contains modes at ~110 cm\(^{-1}\) and ~150 cm\(^{-1}\) assigned to the bending modes of the tetrahedral units.

The strongest absorption mode in the IR spectra is the band centered at ~380 cm\(^{-1}\), which as mentioned above originates from asymmetric stretching \(\nu_3(F_2)\) vibrational mode of GeS\(_{4/2}\) tetrahedral units [Lucovsky 1974]. The spectra deconvolution procedure of AgI doped glasses has revealed the existence of peaks at 340 cm\(^{-1}\). This peak is quite strong in the AgI 5 at. \%, while it weakens with addition of more AgI associated with the \(\nu_1(A_1)\) mode of GeS\(_{4/2}\) tetrahedra. However, this peak is still stronger than the corresponding peak in the base glass. A similar increase in the population of GeS\(_{4/2}\) tetrahedra of AgI-doped Ag\(_2\)S-GeS\(_2\) glasses has been reported elsewhere [Kamitsos 1994]. The high frequency shoulder shifts to at ~411 cm\(^{-1}\) in AgI-doped glasses exhibiting no important intensity changes. This band was associated with the bond stretching frequency of the terminal Ge-S\(^-\) bonds in di-thio-germanate units [Kamitsos 1994] in GeS\(_2\) glass modified by Ag\(_2\)S. This mode becomes IR active owing to the reduction of the \(T_d\) symmetry of a fully polymerized GeS\(_{4/2}\) tetrahedron to \(C_{3v}\) (or lower symmetry) upon creating non-bridging S bonds. However, such an interpretation cannot be accepted here because this band exists in the undoped GeS\(_{1.5}\) glass where no such units are present.

In the frequency region between 150 and 340 cm\(^{-1}\) there are a number of modes as revealed by the deconvolution procedure. The number of these absorption peaks depends on the AgI content, as evidenced from the deconvoluted spectra. However, to keep the number of fitting peaks to minimum we have added for AgI-doped glasses only a new band at ~210 cm\(^{-1}\) where as evident from the spectra there is increased scattering in
CHAPTER 10: Structural aspects of the (GeS$_{1.5}$)$_{100-x}$ (AgI)$_x$ glassy system: Structural Raman and IR studies

Comparison with the base glass. The accurate assignment of these modes is not a trivial task especially in the present case where the base glass is a non-stoichiometric one. As mentioned above, the structure of the present base glass (GeS$_{1.5}$) can be described by a mixing of interconnected (GeS$_n$Ge$_{4-n}$ ($n = 0, 1, 2, 3, 4$) tetrahedra. The substitution of Ge for S causes a redshift of the vibrational modes of the tetrahedra; the fewer the S atoms in a tetrahedron, the lowest the energy of its breathing mode. The massive GeGe$_{4/2}$ tetrahedra (for $n=0$) have the lowest vibrational frequencies in comparison to the mixed GeS$_n$Ge$_{4-n}$ units. The $\nu_1(A_1)$ vibrational frequency of GeGe$_{4/2}$ in a-Ge is located at ~ 280 cm$^{-1}$ [Yannopoulos 2006]. Therefore, we suggest that in the spectral range 280-340 cm$^{-1}$ the observed modes arise from GeS$_n$Ge$_{4-n}$ ($n = 0, 1, 2, 3, 4$) mixed tetrahedra whose frequencies decrease with decreasing $n$.

The situation becomes more complex by adding AgI. The presence of iodine atoms and their high chemical affinity for Ge atoms renders highly probable the existence of mixed tetrahedral units GeS$_n$Ge$_m$I$_{4-n-m}$. The populations of such tetrahedra that are rich in iodine atoms, which terminate the network structure, increase with increasing the AgI content. In the limiting case where isolated GeI$_4$ units are formed, we expect their breathing mode at ~159 cm$^{-1}$ [Clark 1980]. The spectra deconvolution in our case has shown the existence of bands at ~150 cm$^{-1}$ for all glasses, which, apart from being associated with the bending modes of GeS$_{4/2}$ tetrahedra, might also be associated with I-rich GeS$_n$Ge$_m$I$_{4-n-m}$ tetrahedra, i.e. $n, m = 0, 1$. Obviously, the frequencies of the breathing modes of I-poor mixed tetrahedra of the type GeS$_n$Ge$_m$I$_{4-n-m}$ would be dispersed in the interval 150-250 cm$^{-1}$. However, other types of vibrations have also been considered to contribute at this frequency range. Ge-Ge vibrations in ethane-like units S$_3$-Ge–Ge-S$_3$ have been assigned to account for the 250-260 cm$^{-1}$ vibrational modes in Ge-rich binary Ge$_x$S$_{100-x}$ glasses [Lucovsky 1974].
10.4 Conclusion remarks.

FTIR spectroscopy and FT-Raman scattering have been employed to investigate the structural changes that are brought about by the addition of AgI on the structure of the Ge-rich GeS$_{1.5}$ glass. The structural studies reveal that addition of AgI causes mild changes in the structure of the GeS$_{1.5}$ pointing to a non-network modifier role of the AgI additive. However, although subtle, the changes brought about by the addition of AgI are systematic. The interpretation of the Raman spectra of the AgI-doped glasses suggest a mild decrease of the ES units and the concomitant increase of complex GeS$_n$I$_{4-n}$ or Ge$_m$Ge$_n$I$_{4-n-m}$ tetrahedra whose vibrations lie in the spectral range below 300 cm$^{-1}$. The presence of iodine atoms and their high chemical affinity for Ge atoms seems to be the incentive for the small but clearly seen structural changes of AgI-doped Ge-rich glasses. Weak peaks at the low energy part for the Raman spectra indicate the existence of Ge$_n$Ge$_m$I$_{4-n-m}$ tetrahedral units decoupled from the glass network.
CHAPTER 10: Structural aspects of the (GeS$_{1.5}$)$_{100-x}$(AgI)$_x$ glassy system: Structural Raman and IR studies

References of Chapter 10:

Chapter 11

Structural and thermal study of the phase separated

\[(\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\] and

\[(\text{As}_2\text{S}_3)_{100-x} \text{Ag}_x\] glasses using

Raman scattering, XRD, DSC, and SEM

11.1 Brief literature survey

Bulk chalcogenide glasses doped with solid electrolytes, \(\text{Ag}_2\text{S}\), \(\text{Ag}_2\text{Se}\), and \(\text{AgI}\) have been the focus of several experimental investigations over the last few decades [Mott 1979, Elliott, Kolobov 1991, Borisova 1981] owing to their increased ionic conductivity. The interest on such glasses has recently revived in view of the technological significance of silver-containing chalcogenides exemplified through their potential applications in memory switching [Hirose 1976, Hirose 1980] and programmable metallization devices [Kozicki 2005]. The majority of studies on the above directions have been performed to selenides [Kozicki 2005] while less attention has been paid to silver-doped arsenic sulfide glasses in view of the phase separation exhibited by the latter over a broad range of Ag concentration [Borisova 1981]. Although phase separation is an undesirable effect for most applications (e.g. in optics) its role has proved quite interesting in the peculiar behavior of the ionic conductivity as function of the silver content [Kazakova 1980].
Phase separation in bulk, silver-doped As$_2$S$_3$ glasses has been reported long ago [Borisova 1981]. Homogeneous glasses were found in the Ag-poor phase (less than 4-5 at. % in Ag) and in the Ag-rich phase (more than 18-20 at. % in Ag). Glasses also form in the intermediate concentration range being however not homogeneous. [Borisova 1981]. Ohta et al. [Ohta 1982] provided clear evidence of the phase separation effect in bulk Ag$_y$ (As$_2$S$_3$)$_{100-y}$ glasses for $2 \leq y_{Ag} \leq 9.1$ by means of scanning electron microscopy (SEM). By performing quantitative analysis it became possible to identify the concentration of the Ag-poor and Ag-rich phases [Ohta 1982], which were found to slightly depend on $y_{Ag}$. It is interesting to notice that the authors observed a percolation of the Ag-rich phase by changing the glass composition from $y_{Ag} = 7.4$ to $y_{Ag} = 9.1$. In particular, the initially fragmented Ag-rich phase at low Ag content becomes the continuous one at Ag concentration slightly greater than $y_{Ag} = 7.4$. More recent studies on Ag$_2$S-As$_2$S$_3$ glasses were conducted by Pradel and co-workers using SEM and conductivity measurements [Pradel 2003, Piarristeguy 2006] and by Bychkov and co-workers using structure probing [Bychkov 2000, Bychkov 2001] and thermal techniques [Bychkov 2001]. Combining SEM and conductivity data the huge discontinuous increase of the conductivity around 7 at. % in Ag was accounted for by a percolation of the Ag-rich phase [Pradel 2003, Piarristeguy 2006].

More recently [Kyriazis 2009a, Kyriazis 2009b] Raman scattering, SEM and x-ray microanalysis have been used to examine the structural details and morphological features of the ternary glasses Ag$_x$ · (As$_{33}$S$_{67}$)$_{100-x}$ for $0 \leq x \leq 25$. The glasses separate into two glassy phases for Ag content $4 \leq x \leq 20$. The obtained Raman results have shown a systematic reduction of the excess sulfur bonds of the As$_{33}$S$_{67}$ glass upon Ag addition. Elemental sulfur nanodomains consist of three types of S bonding arrangements, i.e. short chains, S$_8$ rings and disulfide bonds. The former seem to be the most affected with increasing Ag content. In the spectral region of the As-S bonds, Raman spectra are described satisfactorily as a linear combination of the Raman spectra of the glass for $x_{Ag} = 4$ and the AgAsS$_2$ ($x_{Ag} = 25$) glass. The Raman interpretation [Kyriazis 2009a, Kyriazis 2009b] is
consistent with the SEM observations of a robust macrophase separation of the present glasses in domains of several micrometers in extent. As it was mentioned before, at ~7 at.% Ag the Ag-rich phase percolates through the structure and this effect is related to an abrupt change of the ionic conductivity of the glasses at this composition.

A microscopic description of the transport processes which are associated with fast ion conductivity and other physical properties is directly related to the system structure on both the short and intermediate atomic length scales. This task is particularly difficult owing to the inherent structural disorder of glassy materials and the presence of four chemical species [Benmore 1994]. Key questions concern:

(i) The relative arrangement of the mobile ionic species;

(ii) The extent to which a glass network is modified when it is made a fast ion conductor by alloying with suitable component.

In the 1930’s Stock published his pioneering work leading to a qualitative understanding of the superionic conductivity properties of AgI. The ionic conductivity of the Ag\(^+\) ions above the transition temperature \(T_c = 147 \, ^\circ C\) is very large, in fact comparable to that found in aqueous electrolyte solutions. Correspondingly, Stock found that above \(T_c\), in the so called \(\alpha\) phase, AgI

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**Fig.11.1.** Schematic representation of Ag-I lattice: (a) low-temperature \(\beta\) phase; (b) high-temperature \(\alpha\) phase. The large circles are the I\(^-\) and the possible sites of Ag\(^+\) are shown but only on the front face of the cube for clarity [Burns 1977].
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and 
\((\text{As}_2\text{S}_3)_{100-x} \text{Ag}\) glasses using Raman scattering, XRD, DSC, and SEM

transforms from a wurtzite \(\beta\)-phase [see Fig. 11.1(a)] to a new high-temperature structure type, represented in Fig. 11.1(b). In this phase, two \(\Gamma\) anions form a body-centered cubic lattice and two \(\text{Ag}^+\) cations are distributed over as many as 42 possible sites in the unit cell. This open structure, with many more sites than there are \(\text{Ag}^+\) ions, gives a qualitative understanding of the unusual mechanical and electrical properties of \(\alpha\)-AgI phase.

Regardless of the wide utilization of ChG, at present much more is known about the physical properties than about their structure. Apart from some systematic studies of binary (As-Se, As-S) and ternary (As-Se-Ag and As-Se-AgI) glasses [Kovalskiy 2006, Neilson 2007, Choi 2008a, Choi 2008b, Legin 1993, Krbal 2007a, Krbal 2007b, Usuki 2002, Krbal 2006, Usuki 2007, Sanghera 2008], there is lack of detailed information concerning the As-S-AgI glassy system and works studying this system are practically completely absent.

![Diffractograms of \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glasses (0 \(\leq x_{\text{AgI}} \leq 40\) mol %).](image_url)
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and \((\text{As}_2\text{S}_3)_{100-x} \text{Ag}_x\) glasses using Raman scattering, XRD, DSC, and SEM

In this chapter we present a detailed study concerning the structure, thermal properties and morphology, at the microscale, of two glass-forming systems, i.e. \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and \((\text{As}_2\text{S}_3)_{100-x} \text{Ag}_x\).

11.2 Phase separation in \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glasses

11.2.1 Results

11.2.1.1 X-ray Diffraction measurements of \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glasses

Figure 11.2 contains diffraction patterns for the \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glasses \((x_{\text{AgI}} = 0, 5, 15, 20, 25, 35, 40)\) over a wide scattering angle range. The diffraction patterns confirm the amorphous nature of the glasses at least at low AgI concentrations. However, traces of crystallites grown in the glassy matrix are observed for AgI content exceeding 20 mol%. The peaks grow in intensity and become narrower with increasing the AgI content.

11.2.1.2 Raman scattering study of \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glasses

Figure 11.3 displays Stokes-side Raman spectra of \((\text{As}_0.4\text{S}_0.6)_{100-x}(\text{AgI})_x\) system. The Raman spectrum of crystalline \(\beta\)-AgI is also shown for comparison. The spectra of glasses have been normalized at the main band maximum of the \(341 \text{ cm}^{-1}\), which is the main vibrational bond-stretching frequency of the As-S bond in AsS\(_{3/2}\) pyramidal units. It seems at first surprising that the addition of AgI into the As\(_2\)S\(_3\) glass structure causes no appreciable changes in the Raman spectra even at AgI concentrations as high as 40 mol%. Indeed, both the energy and width of the main band at \(341 \text{ cm}^{-1}\) remain unchanged for all doping concentrations. Subtle changes are observed only in the low frequency (bond bending bands) which can be summarized as a moderate increase of the broad background intensity and the appearance of few more weak sharp peaks in comparison with the base glass As\(_2\)S\(_3\). The \(186 \text{ cm}^{-1}\) vibration mode shows more pronounced increase in intensity with increasing AgI concentration. Furthermore, new bands appear between \(200 \text{ cm}^{-1}\) and \(250 \text{ cm}^{-1}\) when adding even of 5% AgI. Finally, a weak peak emerges at \(~110 \text{ cm}^{-1}\) in the spectra of the glasses with the two highest concentrations. As mentioned above, the Raman results seem at a first glance surprising but as will be discussed
11.2.1.3 Thermal study of \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glasses

DSC thermograms obtained from \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glassy materials are shown in Fig. 11.4.

As it is seen from the figure, the undoped glass \(\text{As}_2\text{S}_3\) exhibits only one endothermic transition at about 215 °C. Except the glass transition observed in all
CHAPTER 11: Structural and thermal study of the phase separated (As₂S₃)₁₀₀₋ₓ (AgI)ₓ and (As₂S₃)₁₀₀₋ₓ Ag glasses using Raman scattering, XRD, DSC, and SEM

Fig. 11.4 DSC thermogram of (As₂S₃)₁₀₀₋ₓ (AgI)ₓ glasses (0 ≤ x ≤ 30 mol %). Heat rate is 10 °C/min.

glasses at almost the same temperature range, some other transitions emerge with the introduction of AgI in the glassy network, the origin of which will become clear below.

11.2.1.4 Morphological features of (As₂S₃)₁₀₀₋ₓ (AgI)ₓ glasses studied by Scanning Electron Microscopy

Field-emission Scanning Electron Microscopy (FE-SEM) images for the pseudo binary glassy system are shown in Fig. 11.5 and 11.6 at magnifications 2000× and 5250×, respectively. As expected, the image of the matrix (As₂S₃) reveals a homogenous glass. Homogeneity persists also for the 5% AgI doped glass.
CHAPTER 11: Structural and thermal study of the phase separated $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ and $(\text{As}_2\text{S}_3)_{100-x}\text{Ag}$ glasses using Raman scattering, XRD, DSC, and SEM

![Image](image_url)

Fig. 11.5. FE-SEM images of $(\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x$ glasses; magnification 2000x.

As can be seen from the high magnification, Fig. 11.6. Introduction of additional AgI has a profound effect on the glass morphology at the micrometer spatial scale. Practically, tiny droplets appear at $x_{\text{AgI}} = 10$ which is better seen in the corresponding image in Fig. 11.6. Light colored spots appear at this concentration.
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and 
\((\text{As}_2\text{S}_3)_{100-x} \text{Ag}\), glasses using Raman scattering, XRD, DSC, and SEM

Fig. 11.6. FE-SEM images of \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) glasses; mMagnification 5250×.

and grow progressively at high AgI contents. As it will become evident with the microanalysis results below the light and dark regions correspond to AgI-rich and AgI-poor phases, respectively. A dramatic change in the size of AgI-rich droplets
appears at a concentration threshold that lies between the 30 and 35 % in AgI. For glasses with $x_{AgI} \leq 30$ the droplet size ranges from a few tens of nm for the glasses with the lowest AgI concentration up to 100-200 nm for the $x_{AgI} = 30$ glass. Up to this point the droplets are more or less characterized by a narrow size distribution. Glasses with AgI content higher than $x_{AgI} = 30$ exhibit droplets with qualitatively and quantitatively different features. Droplet sizes are polydispersed and the diameters of the larger ones is of about 5-10 µm. In all cases, droplets have a uniform spherical shape. The black spots that appear for the larger droplets, see Fig. 11.6 for $x_{AgI} = 35$ and 40 has its origin to the AgI migration due to the electron beam. Therefore, the black spots inside the light colored droplets denote regions of lower AgI content than that of the AgI-rich phase.

11.2.2 Analysis of the results and Discussion

As it is shown in Fig. 11.2 traces of crystallites grow in the glassy matrix at AgI content 20 mol% and beyond. The peaks grow in intensity and become narrower with increasing the AgI content. These peaks correspond to $\beta$-AgI crystallites. We observe that for all glasses studied here the peaks associated with the crystallite phase are broader than the corresponding peaks of the bulk crystal AgI. This finding indicates the existence of nanocrystallites. Actually, combing the results of XRD and SEM described above we can conclude the following:

(a) The glasses with concentrations $x_{AgI} < 10$ appear homogeneous in SEM; thus AgI is randomly dispersed in the As$_2$S$_3$ glass structure.

(b) The glasses with concentrations $10 < x_{AgI} < 20$ are microphase separated. Droplets sizes are of about 100 nm or less. These droplets, presumably rich in AgI, are in an amorphous state since no “crystalline” peaks appear in the XRD pattern.

(c) The glasses with concentrations $x_{AgI} \geq 20$ are also microphase separated. Droplets sizes are of about 100 nm or less for $20 \leq x_{AgI} < 35$ whilst they grow enormously for $x_{AgI} \geq 35$. In both cases, these AgI-rich droplets are in crystalline state. The sizes of crystallites are very small for glass
compositions near $x_{AgI} = 20$, while these crystallites grow progressively at higher AgI concentrations. The latter conclusions arise from the Scherrer formula which combines the crystal size with the inverse width of the peak in the XRD pattern.

Before discussing in some detail the structural changes on As-S glass matrix caused by the addition of AgI as revealed by Raman spectra, it would be instructive to briefly refer to the structural details of the base glass, i.e. $\text{As}_2\text{S}_3$. This glass is isomorphous to the $\text{As}_2\text{Se}_3$ glass whose structure has been discussed in detail in Section 7. Therefore, the models advanced in the literature to account for the structure of the selenide glass can also be applied to the present case. The structure of arsenic-sulfide glasses has been the subject of numerous investigations with the use of vibrational spectroscopy [Ward 1968, Lucovsky 1972, Kobliiska 1973]. The $\text{As}_2\text{S}_3$ spectrum exhibits a broad asymmetric band between 250 and 400 cm$^{-1}$ accompanied by number of weak peaks in the bond-bending vibrational region.

![Raman spectra of native arsenic-sulfur crystals](image)

**Fig. 11.7** Raman spectra of native arsenic-sulfur crystals: (a) $\text{As}_4\text{S}_4$ (realgar); (b) $\text{As}_2\text{S}_3$ (orpiment); The broken line superimposed on the Raman spectrum of orpiment is a trace of the Raman spectrum of $\text{As}_2\text{S}_3$ glass. [Ward 1968].
In the number of works it is suggested that the glass spectrum bares close resemblance to the spectrum of the corresponding crystal (see Fig. 11.7) [Ward 1968, Lucovsky 1972, Yannopoulos 2003]. The principal features of the former may be approximated by a broadening of the orpiment spectrum accompanied by an over-all shift of about 30 cm\(^{-1}\) to higher energies [Ward 1968]. The broad, near-featureless band centered at 341 cm\(^{-1}\) in the spectra of the arsenic-sulfur glasses is clearly attributable to bond stretching vibrational modes of As\(_2\)S\(_3\) pyramidal units. Recalling the Raman spectra shown in Fig. 11.3 it is obvious that this spectral region is not affected by the addition of AgI in the glass matrix. A similar conclusion can be drawn also for the weak band at \(\sim 494\) cm\(^{-1}\) which originates from disulfide units S\(_2\)AsS-SAsS\(_2\), i.e. S-S stretching vibrational mode in small units composed of two As\(_2\)S\(_3\) pyramids bonded via two S atoms. Given the above two observations it is evident that the doping component, and in particular Ag atoms, fail not only to break the covalent As-S intrapyramidal bond in order to make bonds with S atoms, but also seem not to react with the most susceptible homonuclear S-S bonds.

Let us now turn our attention to the low frequency band which exhibits some subtle changes in AgI-doped glass in comparison with the pure matrix. The sharp, weak peaks in this spectral range are reminiscent of the vibrational modes of molecular or cage-like units which appear in As-rich As-S binary glasses. Actually, two such cage-like are known to be present in the structure of As-rich glasses, the As\(_4\)S\(_4\) and the As\(_4\)S\(_3\) molecules shown in Fig. 11.8. Actually, such molecules, and in particular the former one, can also be found in the structure of the stoichiometric glass under conditions where (a) the glass is produced by high quenching rate and (b) when an amorphous film is produced by thermal evaporation. Annealing the glass and the amorphous film can cause severe reduction in the population of the molecular species.

A brief survey on the vibrational modes of Raman studies of the As\(_4\)S\(_4\) molecule embedded in various environments has been presented elsewhere.
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and 
\((\text{As}_2\text{S}_3)_{100-x} \text{Ag}_x\) glasses using Raman scattering, XRD, DSC, and SEM

[Yannopoulos 2003] and reveals the following facts. The \(\text{As}_4\text{S}_4\) molecule (basic unit of the realgar crystal \(\text{As}_{50}\text{S}_{50}\), shows Raman peaks at 182, 192, 220, and 222 cm\(^{-1}\) [Yannopoulos 2003]. These values are very close to the ones 186, 210, 222 cm\(^{-1}\) observe in our study. Therefore, we can safely assign these bands to the bond bending and stretching vibrations of cage-like \(\text{As}_4\text{S}_4\) units. The small band found at \(\sim 233 \text{ cm}^{-1}\) can be ascribed to the homopolar As-As bond vibrations. The main peak of the \(\text{As}_4\text{S}_3\) molecule is at 273 cm\(^{-1}\). Therefore, judging from the Raman spectra in Fig. 11.3 we can exclude to possibility that such units form upon alloying the \(\text{As}_2\text{S}_3\) glass with AgI. Finally, a new peak emerges at \(\sim 110 \text{ cm}^{-1}\) in the two highest concentrations (shown enlarged in Fig. 11.9, where for clarity only the base glass and the mentioned concentration are presented). Owing to the fact, that this band is visible only at high AgI concentration, we can ascribe it to the most pronounced mode due to \(\text{Ag}^+\) motion in the iodine lattice [Delaney 1976].

![Fig. 11.8. Ball and stick draw of the (a) As\(_4\)S\(_4\) and the (b) As\(_4\)S\(_3\) molecules.](image)

In works concerning other structurally similar systems as AgI-\(\text{As}_2\text{Se}_3\) [Usuki 2002] it was found that the Raman spectra of the mixtures for AgI content up to 60 mol. % are almost identical with that of the base glass. Therefore, the authors suggested that the network matrix in the glass is constructed from covalent \(\text{AsSe}_{3/2}\) pyramidal units, and that a significant number of \(\text{Ag}^+\) have a tetrahedral coordination with \(\text{I}^-\), similar to the case in crystalline \(\alpha\)-AgI. They proposed the structure model for \((\text{AgI})_x(\text{As}_2\text{Se}_3)_{1-x}\) glasses to be a pseudo-binary mixture of the
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) and 
\((\text{As}_2\text{S}_3)_{100-x}\text{Ag}\) glasses using Raman scattering, XRD, DSC, and SEM

Fig. 11.9. Low frequency region of the FT Raman spectra of \((\text{As}_2\text{S}_3)_{100-x}(\text{AgI})_x\) glasses: (a) \(0 \leq x_{\text{AgI}} \leq 40\) mol %; (b) \(x_{\text{AgI}} = 0.35, 40\) mol % and AgI.

amount of AgI does not significantly affect the SRO of both the network former and modifier atoms. In a more recent study [Usuki 2007] it was reported that the interatomic distance of Ag–I pairs is similar to the case of crystalline AgI. However, the coordination number of Ag–I pairs in the present glasses seems to be somewhat smaller than that in the crystalline AgI, suggesting a heavy distortion of tetrahedral coordinates of AgI units or structural disorder of the I–I subcages in the glassy state.

Furthermore, when studying AgI-doped silver borate glasses two models were suggested. The first model is based on the Raman spectroscopy results on these systems suggest the existence of \(\alpha\)-AgI microdomains, especially at higher AgI concentrations. The second proposed model supports the existence of AgI dispersed in the interstices of the diborate network. Here, the disorder modes of the borate network are proposed to dynamically couple with the ion motion, thus enhancing ionic conduction. Structurally, the difference between the two models is the \(\text{Ag}^+\) cation environment. On the base of chemical information [Petkova 2007] it is known that Ag can be bonded with other Ag or chalcogen atom but not to an As atom. Taking into account this in the microdomain model, the \(\text{Ag}^+\) cations exist in two coordination environments, one related to the iodine anion and the other with oxygen ions (bridging or non-bridging oxygens). In the latter model, all \(\text{Ag}^+\) cations
all share a common coordination with iodide anions and oxygen atoms. In these works studying AgI-doped diborate [Kamitsos 1992] and tetraborate [Fontana 1983] silver glasses authors suggested two (or more) coordination environments for the AgI ions signifying the presence of “microdomains” of AgI within the glassy matrix.

The glass transition temperatures obtained by the onset of the step-like baseline change for the studied glasses are tabulated in Table 11.1.

Table 11.1 Glass transition temperature obtained by the onset along with other transition temperatures in (As$_2$S$_3$)$_{100-x}$ (AgI)$_x$ glasses.

<table>
<thead>
<tr>
<th>AgI content [mol%]</th>
<th>T$_g$ [°C]</th>
<th>( \beta_{AgI \rightarrow \alpha_{AgI}} ) transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>204</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>191</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>194</td>
<td>155</td>
</tr>
<tr>
<td>15</td>
<td>195</td>
<td>104</td>
</tr>
<tr>
<td>20</td>
<td>195</td>
<td>135</td>
</tr>
<tr>
<td>25</td>
<td>194</td>
<td>148</td>
</tr>
<tr>
<td>30</td>
<td>194</td>
<td>150</td>
</tr>
</tbody>
</table>

As it is expected, the undoped base glass, As$_2$S$_3$, AgI doping reveals only one endothermic transition characteristic of the glass transition temperature T$_g$. It is seen that the T$_g$ value displays a characteristic drop when a small amount of AgI is introduced in the glass matrix. Further increase of the AgI concentration does not practically affect the glass transition values. This behavior is reminiscent to the thermal properties of phase separated Sb-Se binary glasses studied in chapter 6. It seems that there is a minor structure modification for the AgI 5 mol. % glass which appears homogeneous in SEM. Then, when entering the phase separation regime, the agglomeration of AgI in the light colored droplets leaves the rest of the matrix unchanged and thus the T$_g$ of all glasses with x$_{AgI}$ > 5 are practically identical with
the $T_g$ of the homogeneous mixture, the glass with $x_{AgI} = 5$. Except the glass transition observed in all glasses, some other transitions emerge with introducing AgI in the glassy network. The low-temperature transition is attributed to $\beta_{AgI} \rightarrow \alpha_{AgI}$ [Burns 1977] occurring at 147 °C for the bulk crystal.

X-ray microanalysis was used to obtain the concentration profiles of the phase separated glasses using a scanning speed of 0.5-1 µm / s. Some representative examples are shown in Fig. 11.10 for the glasses with $x_{AgI} = 0, 30, 35, 40$. The image of the scanned region has been added for a direct comparison between the phase separated domains and the concentration profiles of the four elements. As expected the profiles of the various elements in the base glass, Fig. 11.10(a), are constant at values very close to the nominal glass composition, i.e. As/S:40/60. although the glass with $x_{AgI} = 30$ is indeed phase separated as the SEM image reveals, the microanalysis, Fig. 11.10(b), shows practically constant concentration profiles because the spatial resolution of the technique did not allow to correctly measure the concentration of the very small droplets of the AgI-rich phase.

This problem is overcome in the two highest concentrations shown in Fig. 11.10(c),(d). As mentioned above, light colored regions correspond to the AgI-rich phase and expectedly the AgI concentration is maximized at these regions. The alternating maxima of both Ag and I atoms profile fall within the range 25-30 at. %, while the ratio of S/As in the dark regions is almost equal to 2. On the other hand, the deepest minima of the Ag and I atoms profiles assume a value near 5 % characterizing the Ag-poor phase. Ag and I atoms have almost identical profiles. It seems that the Ag and I concentrations in AgI-rich and AgI-poor phases do not strongly dependent on the AgI content.

The above finding are in good accordance with the density results as well as other physic-chemical properties [Kolev 2005]. Results of measured and calculated physical-chemical characteristics of the samples are listed in Table 11.2.
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and \((\text{As}_2\text{S}_3)_{100-x} \text{Ag}\) glasses using Raman scattering, XRD, DSC, and SEM
**CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and \((\text{As}_2\text{S}_3)_{100-x} \text{Ag} \) glasses using Raman scattering, XRD, DSC, and SEM**

Fig. 11.10. Concentration profiles of Ag, As, S, and I atoms for selected glasses: (a) \(\text{As}_2\text{S}_3\); (b) \(x_{\text{AgI}} = 30\); (c) \(x_{\text{AgI}} = 35\); (d) \(x_{\text{AgI}} = 40\). The X-ray intensities of the various atoms are shown in a percentage scale.
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} \text{(AgI)}_x\) and 
\((\text{As}_2\text{S}_3)_{100-x} \text{Ag}, \) glasses using Raman scattering, XRD, DSC, and SEM

Table 11.2 Physical-chemical characteristics of the \((\text{As}_2\text{S}_3)_{100-x} \text{(AgI)}_x\) glasses.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(d ) [kg.m(^{-3})]</th>
<th>(V_M) [m(^3)]</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{As}_2\text{S}_3)</td>
<td>(3.09 \times 10^3)</td>
<td>(7.96 \times 10^{-5})</td>
<td>-0.099</td>
</tr>
<tr>
<td>((\text{As}_2\text{S}<em>3)</em>{95}(\text{AgI})_5)</td>
<td>(3.11 \times 10^4)</td>
<td>(7.9 \times 10^{-3})</td>
<td>-0.111</td>
</tr>
<tr>
<td>((\text{As}<em>2\text{S}<em>3)</em>{90}(\text{AgI})</em>{10})</td>
<td>(3.31 \times 10^4)</td>
<td>(7.4 \times 10^{-3})</td>
<td>-0.072</td>
</tr>
<tr>
<td>((\text{As}<em>2\text{S}<em>3)</em>{85}(\text{AgI})</em>{15})</td>
<td>(3.4 \times 10^5)</td>
<td>(7.19 \times 10^{-3})</td>
<td>-0.066</td>
</tr>
<tr>
<td>((\text{As}<em>2\text{S}<em>3)</em>{80}(\text{AgI})</em>{20})</td>
<td>(3.425 \times 103)</td>
<td>(7.13 \times 10^{-3})</td>
<td>-0.079</td>
</tr>
<tr>
<td>((\text{As}<em>2\text{S}<em>3)</em>{75}(\text{AgI})</em>{25})</td>
<td>(3.44 \times 103)</td>
<td>(7.06 \times 10^{-3})</td>
<td>-0.092</td>
</tr>
</tbody>
</table>

Addition of AgI exceeding 30% has a profound effect on the glass morphology at the micrometer spatial scale. Addition of AgI more than 30% leads to an enormous growth of the AgI droplets as much as two orders of magnitude, as approaching 20-30 \(\mu\)m. We should note that it was very difficult to take an image of the two highest concentrations, since the laser beam was invoking Ag diffusion in the regions nearby. As evidenced from the FE-SEM images of the glasses, the \(\text{As}_2\text{S}_3\) –AgI glasses indeed act as pseudo-binary mixtures of AgI microclusters dispersed in the \(\text{AsS}_{3/2}\) matrix and \(\text{Ag}^+\) connected with interstices of chalcogenide ions.
11.3 Phase separation in (As$_2$S$_3$)$_{100-x}$Ag$_x$ glasses

11.3.1 Results

Figure 11.11 contains diffraction patterns for the (As$_2$S$_3$)$_{100-x}$Ag$_x$ glasses ($x_{Ag} = 0, 5, 15, 25$) over a wide scattering angle range. The diffraction patterns confirm the amorphous nature of the glasses for all glass compositions. In contrast to the AgI-doped glasses no traces of crystallinity is observed here.

Stokes side Raman spectra of the matrix As$_2$S$_3$ and the glasses containing Ag ($5 \leq Ag \leq 25$ mol. %) are represented in Fig. 11.12. For comparison, the spectra of the As$_{42}$S$_{58}$ glass and the As$_4$S$_4$ realgar crystal [Kyriazis 2009b] are also shown. The inset shows an enlargement of the 494 cm$^{-1}$ band. The spectra of the glasses have
been normalized to the peak maximum intensity around 341 cm\(^{-1}\) in order to reveal the changes caused by Ag addition.

![Graph showing FT Raman spectra of (As\(_2\)S\(_3\))\(_{100-x}\)Ag\(_x\) glasses. The inset shows an enlargement of the 494 cm\(^{-1}\) band.]

**Fig. 11.12.** *FT Raman spectra of (As\(_2\)S\(_3\))\(_{100-x}\)Ag\(_x\) glasses. For comparison, the spectra of the As\(_{42}\)S\(_{58}\) glass and the As\(_4\)S\(_4\) realgar crystal are also shown. The inset shows an enlargement of the 494 cm\(^{-1}\) band.*

In contrast to the study of the previous section where the addition of AgI did not cause any significant change in the Raman spectra, in the present case it is obvious that doping the glasses even with 5 at. % Ag causes significant changes in the spectrum as evidenced from the numerous new sharp bands that appear. The frequencies of these bands match the frequencies of the main peaks of the Raman spectrum of the realgar crystal providing evidence for the creation of As\(_4\)S\(_4\) cage-like molecules due to Ag incorporation in the glass structure. The intensities of the
bands in the Ag-doped glasses increase systematically with increasing the Ag concentration. The bands are situated at 133, 145, 166, 210, and 221 cm$^{-1}$ at the bond-bending spectral region. Besides, the peak that appears at 272 cm$^{-1}$ for the $x_{Ag} = 25$ glass is evidence for the presence of As$_4$S$_3$ molecules in the corresponding glass. Continuing with the bond-stretching region, several significant spectral changes appear again at frequencies where the realgar crystal shows its main Raman bands. The most apparent modification emerges as a new band situated at 361 cm$^{-1}$. The highest frequency band located at 494 cm$^{-1}$ is related to disulfide bonds as we have discussed in the previous sections. We observe a gradual decrease of the intensity of this band with addition of Ag in the glass.

Field-emission Scanning Electron Microscopy (FE-SEM) images for the pseudo binary glassy system are shown in Fig. 11.13 and 11.14 at magnifications 2000× and 5250×, respectively. As expected, the image of the matrix (As$_2$S$_3$)
Fig. 11.13. *SEM images of (As₂S₃)₁₀₀₋ₓAgₓ glasses; magnification 2000x.*

reveals a homogenous glass. Homogeneity seems to persist even after doping the glass with Ag, apart from the case of the glass doped with 25 at.% Ag. In the latter, droplets of, probably, Ag-rich droplets appear. As in the previous study (AgI doping) the light and dark regions correspond to Ag-rich and Ag-poor phases, respectively.

Fig. 11.14. *SEM images of (As₂S₃)₁₀₀₋ₓAgₓ glasses; magnification 5250x.*

11.3.2 Discussion

The structure of the Ag-doped glasses is obviously quite different than that of the AgI-doped glasses studied in the first part of this chapter. While in the case of
AgI-doped glasses Phase separation in AgI-rich and AgI-poor phases took place even for low AgI contents, in the present case Ag seems to participate in the structure of the chalcogenide glass, thus causing appreciable structural modifications. XRD patterns revealed non-crystalline phases for all doping levels. This finding demonstrates that the droplets which appear for the most heavily doped glasses, i.e. for 25 at. % Ag, are characterized by an amorphous structure in contrast to the AgI-doped glasses where the droplets at a similar doping level were in a crystalline state. This is a reasonable finding considering similar studies for S-rich As-S glasses doped with Ag [Kyriazis 2009a]. In that paper, Raman scattering, FE-SEM and x-ray microanalysis have been used to examine the structural details and morphological features of the ternary glasses \( \text{Ag}_x \cdot (\text{As}_{33}\text{S}_{67})_{100-x} \) for \( 0 \leq x \leq 25 \). It was found that the glasses separate into two glassy phases for Ag content \( 4 \leq x \leq 20 \). The obtained Raman results have shown a systematic reduction of the excess sulfur bonds of the \( \text{As}_{33}\text{S}_{67} \) glass upon Ag addition. The same effect, i.e. the disappearance of the 494 cm\(^{-1}\) Raman peak which is associated with disulfide (S-S) bonds takes place also in the present study. The Ag-rich in the phase separation regime of the \( \text{Ag}_x \cdot (\text{As}_{33}\text{S}_{67})_{100-x} \) glasses [Kyriazis 2009a] was identified through microanalysis with the composition \( \text{AgAsS}_2 \) which is the smithite-type glass. Therefore, the lack of crystallization in the Ag-rich droplets of the present study is probably related to the fact that the composition of this phase is similar to the smithite-type glass. Unfortunately, the size of the droplets for the \( \text{Ag}_{25} (\text{As}_2\text{S}_3)_{75} \) glass (see Fig. 11.14) is very small, i.e. of about 100 nm or less, thus prohibiting a correct x-ray microanalysis.

As mentioned above, the Raman spectra show changes upon the addition of Ag, a fact that is consistent with the SEM results. A comparison of the Raman spectra of the Ag-doped glasses and the molecular crystal (realgar) \( \text{As}_4\text{S}_4 \) reveals that the main changes that take place is a transformation of some pyramidal units \( \text{AsS}_3 \) to the cage-like molecules \( \text{As}_4\text{S}_4 \) with the characteristic sharp Raman peaks. This transformation implies that Ag breaks the network of the \( \text{As}_2\text{S}_3 \) glass. Due to its high electronegativity, silver forms bonds to sulfur atoms thus leaving excess As...
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and 
\((\text{As}_2\text{S}_3)_{100-x} \text{Ag}\), glasses using Raman scattering, XRD, DSC, and SEM

Atoms in the glass structure. These excess As atoms have the tendency to form the cage like units \(\text{As}_4\text{S}_4\) shown in Fig. 11.8(a) and to a much smaller fraction the molecules \(\text{As}_4\text{S}_3\), Fig. 11.8(b), where homonuclear As-As bonds are allowed. The exact bonding features of Ag are not easy to be defined. However, what we know from previous studies [Kyriazis 2009a], is that at the phase separation regime the Ag-rich phase has the smithite-glass structure. This structure is described by three-membered rings of \(\text{AsS}_3\) pyramidal units with three terminal As-S bonds. Ag cations are situated near the charged terminal S atoms for charge compensation.

11.3.3 Concluding Remarks

Raman scattering, XRD, FE-SEM, DSC, and x-ray microanalysis have been used to examine the structural details and morphological features of the pseudo-binary glass-forming systems \([1] \ (\text{AgI})_x \cdot (\text{As}_2\text{S}_3)_{100-x} \) for \(0 \leq x_{\text{AgI}} \leq 40\) and \([2] \ \text{Ag}_x \cdot (\text{As}_2\text{S}_3)_{100-x}\) for \(0 \leq x_{\text{Ag}} \leq 25\). The main conclusion of the present study are summarized as follows:

[1] \((\text{AgI})_x \cdot (\text{As}_2\text{S}_3)_{100-x}\) glasses:

For all glasses, Raman spectra show practically no spectral changes. DSC data reveal that the glass transition temperature does not depend upon the AgI content. XRD, SEM, and x-ray microanalysis gave the most useful information for this system.

(a) The glasses with concentrations \(x_{\text{AgI}} < 10\) appear homogeneous in SEM, implying that AgI is randomly dispersed in the \(\text{As}_2\text{S}_3\) glass structure.

(b) The glasses with concentrations \(10 < x_{\text{AgI}} < 20\) are microphase separated. Droplets sizes are of about 100 nm or less. These droplets, presumably rich in AgI, are in an amorphous state since no “crystalline” peaks appear in the XRD pattern.

(c) The glasses with concentrations \(x_{\text{AgI}} \geq 20\) are also microphase separated. Droplets sizes are of about 100 nm or less for \(20 \leq x_{\text{AgI}} < 35\) whilst they grow enormously for \(x_{\text{AgI}} \geq 35\). In both cases, these AgI-rich droplets are in crystalline
CHAPTER 11: Structural and thermal study of the phase separated \((\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x\) and 
\((\text{As}_2\text{S}_3)_{100-x} \text{Ag}, \text{glasses using Raman scattering, XRD, DSC, and SEM}\)

state. The sizes of crystallites are very small for glass compositions near \(x_{\text{AgI}} = 20\),
while these crystallites grow progressively at higher AgI concentrations.

[2] \(Ag \cdot (\text{As}_2\text{S}_3)_{100-x}\) glasses:

Raman spectra of this glass forming system revealed severe structural changes
caused by the addition of Ag in the base glass. Ag atoms seem to destroy parts of
the pyramidal network of the base glass thus allowing the formation of cage-like
realgar type molecules \(\text{As}_4\text{S}_4\). XRD revealed that all samples are in the amorphous
states; no crystalline was observed. SEM detected phase separation only for the
most heavily doped glass for \(x_{\text{Ag}} = 25\). Considering findings of similar studied
systems we conclude that the structure of the droplets is in the amorphous state
since it is similar to that of the smithite-type glass.
CHAPTER 11: Structural and thermal study of the phase separated $(\text{As}_2\text{S}_3)_{100-x} (\text{AgI})_x$ and $(\text{As}_2\text{S}_3)_{100-x} \text{Ag}$ glasses using Raman scattering, XRD, DSC, and SEM

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Chapter 12

Effect of cluster size of chalcogenide glass nanocolloidal solutions on the surface morphology of spin-coated amorphous films

12.1 Literature survey.

The capability of fabricating and tailoring in a consistent way thin films of amorphous semiconductors is essential for modern electronic devices. Thin films structure and hence their properties that are important for applications depend strongly upon the deposition method. Methods that are typically employed for thin film deposition include thermal evaporation, magnetron sputtering, pulsed laser deposition, etc. Main shortcoming are encountered with the above techniques ranging from poor control of materials compositions (for evaporation techniques) or high cost of film fabrication. On the other hand, wet-chemistry methods, where film deposition is achieved through spin coating of material’s solution, have recently revived in view of their simplicity, reliability in depositing thin (and ultrathin) films and low cost of operation. Fabrication of metal chalcogenides thin films of technological importance has recently been demonstrated [Milliron 2007, Mitzi 2006].

Arsenic chalcogenide As-X (X: S, Se) bulk glasses and their amorphous thin films have been systematically investigated over the last decades [Elliott 1990, Boolchand 2001, Kolobov 2001, Kolobov 2003] owing to the wide range of applications that these materials meet. Photo-sensitivity is the key issue that can be exploited to alter and control material’s structural details which ultimately determine other macroscopic properties such as mechanical, optical (linear and nonlinear),
CHAPTER 12: Effect of cluster size of chalcogenide glass nanocolloidal solutions on the surface morphology of spin-coated amorphous films

thermodynamic, rheological, etc. [Boolchand 2001, Kolobov 2001, Kolobov 2003]. Obviously, thin films are more exploitable in the application sector (e.g. as planar waveguides) than bulk glasses and hence have attracted most of the scientific interest. This is evidenced by the fact that various routes have been employed to fabricate thin films, as mentioned above, which eventually lead to different local atomic arrangements and hence to materials with different properties. Indeed, it is now well documented that arsenic chalcogenide thin films produced by vacuum deposition techniques are characterized by different structural details.

The fact that thin films of amorphous chalcogenides can be prepared by means of the spin-coating method from solutions of chalcogenide glasses has been demonstrated long ago [Chern 1983a, Chern 1983b, Chern 1983c, Norian 1984]. Arsenic sulphide glasses can readily be dissolved in organic solvents such as amines over the concentrations range 1-10^3 mg ml^{-1}. Chalcogenide spin-coated films have demonstrated similar quality and properties [Hajto 1991, Shtutina 1995, Kohoutek 2004] to those films deposited using the vacuum techniques although subtle differences between them were also reported [Norian 1984].

Attempts to understand the mechanism of dissolution of chalcogenides in amines have been reported [Chern 1983a, Chern 1983b, Chern 1983c, Norian 1984] and the existence of the presence of chalcogenide clusters with dimensions of several nanometers was envisaged, see Fig. 12.1. Further studies were focused on the surface morphology of as-prepared spin-coated As-S chalcogenide thin films deposited from amine solutions. In particular, a nanoscale grainy character of such film surfaces was revealed using transmission electron microscopy (TEM) [Norian 1984] and atomic force microscopy (AFM) techniques [Kohoutek 2007]. The film surface morphology of as-deposited spin-coated films is probably influenced by solvent evaporation during film fabrication while film’s thickness depends mainly on spinning parameters [Birnie 1992], solution viscosity and adhesion of chalcogenide material to the substrate.

There are several factors influencing the resulting quality of surface morphology of spin-coated films which are crucial for their applications, e.g. as high resolution photoresists. Factors such as the use of suitable solvent for bulk glass dissolution
CHAPTER 12: Effect of cluster size of chalcogenide glass nanocolloidal solutions on the surface morphology of spin-coated amorphous films

Fig. 12.1 Schematic representation of As-S clusters (as envisaged by Chern et al. [Chern 1983a]) resulting from the dissolution of chalcogenide glass in amines, i.e. butylamine.

(solubility, solution viscosity, etc.), film preparation conditions (inert atmosphere), adhesion to substrate, spin speed and time, film stabilization have to be particularly considered in order to reach the desired film quality. Appreciating that film structure is usually fragmented due to the existence of large grains – an undesired outcome for applications – it would be important to ask if there is an particular relation between cluster size in the solution of the chalcogenide glass and grain size in the film morphology.

The present work aims at elucidating the above-mentioned issue by combing results from various experimental techniques including dynamic light scattering (DLS), optical absorption spectroscopy, and AFM. The main focus is to investigate physicochemical and cluster size properties of dissolved chalcogenides glasses (As$_{33}$S$_{67}$ in butylamine solutions) in order to understand possible relations in morphological properties of clusters in solution and in spin-coated films. In addition, while photoinduced effects in chalcogenides glasses are exclusively reported in the glassy state, a new interesting transient photoinduced effect which takes place in solution is revealed in the present study.
12.2 Results and Discussion

The optical absorption spectra for the three concentrations of BA/As$_{33}$S$_{67}$ glass solutions as well as for pure BA are shown in Fig. 12.2 in the form of transmittance. As expected, the transmission curves shift to lower energies with the increase of the glass concentration in BA. The energy gaps, $E_g$, of the solutions were estimated using the derivatives of the transmission curves. Eventually, the minimum of the first derivative corresponds to the inflection point of the transmission curve that is usually considered as an accurate estimation of $E_g$. In this way we obtained for $E_g$ the values: 2.74 eV, 2.58 eV, and 2.54 eV for $c_1$, $c_2$ and $c_3$, respectively. The concentration dependence of the energy gap is shown in the inset of Fig. 12.2. It is obvious that with increasing concentration – or equivalently increasing the cluster size as will become evident below – the bandgap of the solution decreases tending to that of the As$_{33}$S$_{67}$ bulk glass (~2.42 eV) denoted by the horizontal dashed line in the inset. The vertical arrows in Fig. 12.2 represent the main laser energies we employed in the present work in an effort to investigate possible photo-induced effects of the glass solutions.

![Fig. 12.2 Transmission curves of BA and the three BA/As$_{33}$S$_{67}$ solutions. The arrows indicate the energies of the laser lines used in the present work, (a) 671 nm, (b) 632.8 nm, (c) 514.5 nm, and (d) 488 nm. The inset shows the concentration dependence of $E_g$ for the studied samples, the solid line is a guide to the eye and the dashed horizontal line marks the $E_g$ of the bulk glass.](image-url)
Absorption curves were recorded also for solutions before and after filtering the liquids in order to prepare the samples for DLS studies. The results revealed that there are negligible changes in the absorption features before and after filtering presumably to the capture of some tiny “insoluble” chalcogenide clusters on the filter, which however does not practically change the sample concentration.

DLS is a useful tool for studying particle sizes in solutions exploiting the Brownian motion of the suspended particles. Under the assumption of homodyne scattering conditions, which are easily fulfilled in dust-free suspensions as in the present case, the desired normalized electric-field time auto-correlation function

\[ g^{(1)}(q,t) = \frac{\langle E(q,t) E^*(q,0) \rangle}{\langle E(q,0) \rangle^2} \]

is related to the experimentally recorded intensity auto-correlation function

\[ g^{(2)}(q,t) = \frac{\langle I(q,t) I(q,0) \rangle}{\langle I(q,0) \rangle^2} \]

through the Siegert relation [Berne 1976]:

\[ g^{(2)}(q,t) = B \left[ 1 + f^* \left| g^{(1)}(q,t) \right|^2 \right] \] (12.1)

where \( B \) describes the long delay time behavior of \( g^{(2)}(q,t) \) and \( f^* \) represents an instrumental factor obtained experimentally from measurements of a dilute polystyrene/toluene solution. In our case, the optical fiber collection results in \( f^* \equiv 1 \).

The electric-field time correlation function \( g^{(1)}(t) \) – for simplicity we drop the \( q \)-dependence in the following – was analyzed as a weighted sum of independent exponential contributions, i.e.:

\[ g^{(1)}(t) = \int L(\tau) \exp(-t/\tau) \, d\tau = \int L(\ln \tau) \exp(-t/\tau) \, d\ln \tau \] (12.2)

where the second equality is the logarithmic representation of the relaxation times. The distribution of relaxation times \( L(\ln \tau) \) was obtained by the inverse Laplace transformation (ILT) of \( g^{(1)}(q, t) \) using the CONTIN algorithm [Provencher 1982a, Provencher 1982b]. The apparent hydrodynamic radii of the suspended “particles” were determined using the Stokes-Einstein relation [Berne 1976],

\[ R_h = \frac{k_BT}{6\pi\eta D} \] (12.3)
where $k_B$ is the Boltzmann constant, $\eta$ is the viscosity of the solvent and $D$ the “particle” self-diffusion coefficient. The latter is determined by $D = 1/\tau q^2$, where $\tau$ is the relaxation time of $g^{(1)}(q,t)$.

Alternatively, $g^{(1)}(q,t)$ was fitted with a stretched exponential or Kohlrausch-Williams-Watts (KWW) function of the form:

$$g^{(1)}(t) = A \exp[-(t/\tau)^{\beta_{\text{KWW}}}]$$

(12.4)

where $A$ is the amplitude or contrast of the time correlation function (zero-time intercept) and $\beta_{\text{KWW}}$ is the corresponding stretching exponent which is characteristic of the breadth of the distribution of the relaxation times and assumes values in the interval [0, 1]. The lower the value of $\beta_{\text{KWW}}$, the more stretched the relaxation function.

Most detailed measurements and analyses were preformed on the $c_2$ and $c_3$ solutions. The scattering from solution $c_1$ was very weak thus requiring long accumulation time, during which some intensity fluctuations were intervening distorting the intensity correlation function. Nevertheless, the analysis of the relaxation data of $c_1$ (at 632.8 nm) showed that a rather good estimation of the “cluster” radius for this concentration is of about 1 nm. Figure 12.3 shows representative analysis examples of the solutions with concentrations $c_2$ and $c_3$. The best-fit curve (solid line through data points) was obtained with the aid of ILT (Eq. 12.2) and the resulting distribution of relaxation times $L(\ln \tau)$ is also shown as a dashed line. These data reveal that the sample $c_2$ is a monodispersed solution [single peak in $L(\ln \tau)$] while the denser sample ($c_3$) is polydispersed characterized by two main cluster populations. The analysis of the more dilute sample ($c_1$) studied in the present work showed that this solution is also monodispersed. These conclusions are supported by the analysis with stretched exponential functions. Indeed, the stretching exponent $\beta_{\text{KWW}}$, found after fitting with the aid of Eq. 12.4, is a measure of polydispersity; the lower the value of $\beta_{\text{KWW}}$ the greater the polydispersity. The magnitude of $\beta_{\text{KWW}}$ for solutions $c_2$ and $c_3$ was found to be 0.9 and 0.7, respectively. Although the difference between these two values is not drastic, the CONTIN analysis for all the accumulated time correlation
functions resulted systematically in a bimodal distribution of clusters in the dense $c_3$ dispersion and a monomodal distribution of the solution $c_2$.

![Intensity auto-correlation functions $g^{(2)}(t)-1$ for solutions $c_2$ and $c_3$ and their corresponding distribution of relaxation times $L(\ln \tau)$ obtained by the CONTIN analysis as described in the text.](image)

**Fig. 12.3** Intensity auto-correlation functions $g^{(2)}(t)-1$ for solutions $c_2$ and $c_3$ and their corresponding distribution of relaxation times $L(\ln \tau)$ obtained by the CONTIN analysis as described in the text.

The diffusive nature of the cluster motion we observe in As$_{33}$S$_{67}$/BA solutions can be verified by inspecting the wavevector- or $q$-dependence of the diffusion coefficients. The $q$-dependence can be obtained either by varying the scattering angle or the laser wavelength, in our case the second procedure was followed. Figure 12.4 illustrates the $q$-dependence of the solutions with concentrations $c_2$ and $c_3$. Within experimental error the data exhibit a $q$-independent behavior as is expected for diffusive processes.

The strong dependence of the energy gap on cluster size, as revealed by optical absorption studies, calls for an investigation of a possible “spectral dependence” of the
CHAPTER 12: Effect of cluster size of chalcogenide glass nanocolloidal solutions on the surface morphology of spin-coated amorphous films

304

Fig. 12.4 Wavevector dependence of the diffusion coefficient for solutions $c_2$ and $c_3$. The horizontal lines represent the mean values of $D$ at each concentration.

cluster size. It is well known that chalcogenide glasses exhibit a dazzling variety of photo-induced phenomena when illuminated by photons with energy near the band-gap of the glass [Elliott 1990, Boolchand 2001, Kolobov 2001, Kolobov 2003]. It would be thus interesting to check for possible photo-induced effects in solutions containing nanoparticles of chalcogenides in solutions. Photoinduced effects have also been reported in the supercooled liquid state of corresponding glasses [Kolobov 2003], though being of dynamic origin; i.e. after the removal of the stimulus (illumination), self-annealing processes restore equilibrium.

Recording time correlation function at various laser wavelengths and various power densities on the scattering volume the following observations emerged. (i) Changes in the diffusional motion of clusters and hence on cluster size were observed only for the higher concentration ($c_3$) used in the present work. (ii) When the illumination energy was far from the energy gap of the solution $c_3$, i.e. for laser wavelengths 632.8 and 671 nm no power dependence was observed. (iii) For light energy ($514.5$ nm = $2.41$ eV) approaching that of the band gap of $c_3$ (2.54 eV) significant photoinduced changes are observed. In particular, a systematic athermal
photo-aggregation phenomenon seems to take place with increasing the power density of the incident light as shown in Fig. 12.5. In particular, increasing the laser power by a factor of 2 and 4, the result is the increase of the hydrodynamic radius by ~11% and ~25%, respectively. These differences in hydrodynamic radii are beyond experimental error.

Fig. 12.5 Intensity auto-correlation functions $g^{(2)}(t)$-1 for solution $c_3$ and their corresponding distribution of hydrodynamic radii obtained for various power levels of the incident laser beam. The dashed vertical line is used as guide to reveal the shift of the cluster size distribution as a result of the athermal photo-aggregation process.

It could be claimed here that this is a thermal effect originating from laser radiation absorption. However, if this were true then heat induced effects would render the Brownian motion of the clusters faster, resulting in a higher diffusion coefficient of the suspended “clusters”; this should be reflected in a smaller hydrodynamic radius
according to Eq. 12.3. Since we observe the opposite trend, i.e. increase of \( R_h \) with increasing laser power, we can safely rule out that the observed effect is due to heat-induced effects. The cluster radii obtained using the procedure mentioned above are illustrated in Fig. 12.6. Photo-induced changes in cluster size are only observed at the highest concentration studied in this work.

Fig. 12.6 Spectral and concentration dependence of \( \text{As}_{33}\text{S}_{67} \) glass cluster size in butylamine solutions. The cluster size grows systematical with increasing concentration. The small filled circles at the bottom right side of the figure represent the small clusters present in solution \( c_3 \); see text for details.

AFM images of spin-coated As-S thin films with thicknesses 100 and 1700 nm prepared from solutions \( c_1 \) and \( c_2 \) are presented in Figs. 12.7(a,b) and Figs. 12.8(a,b), respectively. Preparation of films from the densest solution, \( c_3 \), was not of desired optical quality required for applications, due to high solution viscosity causing the macroscopic defects of films surface morphology. These figures illustrate the morphological details of the surface of as-deposited \( \text{As}_{33}\text{S}_{67} \) films revealing the apparent grainy morphology created most likely by evaporation of the solvent during film deposition process.
CHAPTER 12: Effect of cluster size of chalcogenide glass nanocolloidal solutions on the surface morphology of spin-coated amorphous films

Fig. 12.7 (a) AFM tapping mode image showing the surface morphology of as-deposited spin-coated As$_{33}$S$_{67}$ thin film (prepared from solution $c_1$) with thickness of 100 nm. Film surface reveals a grainy morphology as a result of the presence of solvent in thin film structure after its deposition. Typical grain sizes are of about 25 nm; (b) AFM tapping mode image showing the surface morphology of spin-coated As$_{33}$S$_{67}$ thin film with thickness of 100 nm stabilized at 90 °C for 1 hour. The grainy texture has considerably smoothed-out after solvent residua evaporation.

Film surfaces were scanned by AFM operating in the tapping mode where a tip is patting the atoms on top of the films with a specific frequency. This made it possible to reveal films local visco-elasticity by observing changes of that frequency. Such changes indicated the presence of solvent residua on surface of as-deposited thin films because solvent-rich regions exhibit higher deformability compared with solvent-poor regions.

Typical grain sizes (effective diameter) were of about 25 and 50 nm for films prepared from solutions $c_1$ and $c_2$, respectively. Evidently, a substantial smoothening of the grainy character of thin film surface morphology took place after film thermal stabilization in a vacuum oven at 90 °C and 5 Pa for 1 hour, see Figs. 12.7b, 12.8b. The evaporation of solvent during film stabilization process leads simultaneously to the increase of films roughness (at a length scale much smaller compared to the grain size) from 0.42 ± 0.2 nm to 2.02 ± 0.8 nm [Kohoutek 2007] for films prepared from $c_1$. 
Fig. 12.8 (a) AFM tapping mode image of the surface morphology of as-deposited spin-coated As$_{33}$S$_{67}$ film with thickness of 1700 nm (prepared from solution c$_2$) with typical grain sizes of about 50 nm; (b) AFM tapping mode image of the surface morphology of 1700 nm spin-coated As$_{33}$S$_{67}$ film stabilized at 90 °C for 1 hour. Cluster agglomeration is apparent at elevated temperatures.

solution and from $2.4 \pm 0.4$ nm to $5.3 \pm 0.8$ nm for films prepared from solution c$_2$.

This latter effect is attributed to surface “damage” during solvent evaporation. We consider that the grainy character of surface morphology of as-deposited spin-coated thin films is related to the agglomeration of chalcogenide clusters during solvent evaporation from the film structure at the time of film production.

Agglomeration of few nanometer sized chalcogenide clusters is reasonably expected in view of the concentration dependence of cluster size as revealed by DLS. In particular, during the first stages of film formation the continuously evaporating solvent leads to a progressively increasing concentration of the chalcogenide material and hence to increase of cluster size. At the end of the process (of free solvent evaporation) the cluster size, which is responsible for the grainy texture of the film surface, seems to have incorporated several hundreds of “clusters” present in the parent solution. This is apparent especially in case of films prepared from c$_2$ solution, see Figs. 12.8(a, b). The grainy texture of film surface smoothes-out considerably after thermal stabilization because of the decrease of solvent residua concentration and the
chapter 12: effect of cluster size of chalcogenide glass nanocolloidal solutions on the surface morphology of spin-coated amorphous films

redistribution of the chalcogenide material. The removal of solvent residua causes probably the increase of films roughness as reported in [Kohoutek 2007].

12.4 Conclusion remarks.

A relatively simple method for thin film fabrication of amorphous chalcogenides involving spin-coating from proper solutions has been used to fabricate As$_{33}$S$_{67}$ films. In this paper we focused on the quest of a possible relationship between grain morphology of as-deposited and thermally stabilized spin-coated As$_{33}$S$_{67}$ chalcogenide thin films and cluster size of the glass clusters in butylamine solutions. The grainy surface pattern was found to be related to the cluster size of the dissolved chalcogenide material in the parent solution.

Optical absorption spectroscopy was used to study the optical properties of solutions at various glass concentrations. The energy gap of the dispersed chalcogenide nanoparticles was found to depend inversely proportional on concentration. Optical absorption studies enabled us to choose the proper wavelengths for performing dynamic light scattering on the solutions in order to determine the cluster size distributions at various glass concentrations. DLS data analysis revealed an almost linear dependence between cluster size and concentration. Cluster hydrodynamic radii were found between 1 and 4.2 nm for the samples studied in the present work. For the denser solution a bimodal cluster distribution was observed. A very interesting athermal photo-aggregation process was revealed were the cluster size was sensitive to the laser power in a way opposite of what was expected from thermal effects, i.e. high laser power was found to enhance cluster aggregation. Atomic force microscopy was employed to investigate the grainy texture of the surface of as-deposited and thermally stabilized spin-coated films. Typical grain sizes were of about 25 and 50 nm for the films produced by a dilute and a moderately dense solution indicating that agglomeration of clusters during solvent evaporation from the film structure, at the time of film fabrication by the spin-coating procedure, takes place. The grainy pattern was found to smooth-out after film thermal stabilization.
References of Chapter 12:
Frumar M., Frumarova B., Wagner T. and Nemec P., in Ref. 5(a) pp. 23-44.
1). During the study of Sb$_x$Se$_{100-x}$, it was shown that glass formation in the Sb-Se binary system is possible for a wide composition range from pure Se up to the stoichiometric compound Sb$_2$Se$_3$. The experimental findings concerning this system are consistent with the phase separation that takes place in bulk, melt-quenched Sb-Se glasses over the composition range 4 < $x_{\text{Sb}}$ < 35. Indeed, the Raman spectra of Sb-Se bulk glasses exhibit unusual spectral features when compared with other structurally similar binary systems, such as As-S and As-Se glasses. Furthermore, the loss of fine structure in the $\rho(\tilde{v})$ function- in the well-annealed glasses is a rather reliable sign of phase separation in the scattering medium. The results of thermal studies also point to the outcome that bulk Sb-Se glasses are phase separated. The independence of $T_g$ on the Sb content for $x_{\text{Sb}} \geq 5$ is a clear indication that the extra Sb atoms are nor homogenously dispersed in the Se glass matrix. Therefore, the observed near-constant $T_g$ values correspond to the glass transition temperature of the Se-rich phase.
2). The present study of As$_x$Se$_{100-x}$ ($0 \leq x_{As} \leq 40$) binary system is the first Raman scattering investigation where polarization analysis was employed and reduced isotropic and anisotropic spectra were analyzed. The analysis showed that the addition of the trivalent As atoms induced chain crossing and the formation AsSe$_{3/2}$ pyramidal units. The pyramids are randomly or homogeneously dispersed in the structure for low As content increasing the rigidity of the glass.

- A qualitative analysis of the intermediate glass spectra ($5 \leq x_{As} \leq 35$) showed that the linear combination of the two limiting spectra is not a good model to describe the structure of the intermediate glass compositions. The difference between each experimental spectrum and the corresponding linear combination increased with increasing As content revealing structural correlations effects due the presence of As atoms and the generation of new structural units.

- The spectral features, i.e. position, width, intensity, of the spectra show an interesting dependence of $x_{As}$. All the above spectral parameters exhibit different trends at $x_{As}$ values exceeding $x_{As} = 15$. This behavior has been interpreted as a change from a stochastic to a non-stochastic building process of the structure. In particular, we proposed that at $x_{As}$ above that threshold the addition of As atoms leads to the creation of AsSe$_3$ pyramidal units which are bridged by a common Se atom.

- The presence of the quasi-tetrahedral (QT) unit, Se=AsSe$_{3/2}$ in the structure of binary As-Se glasses is a long-standing issue of this field. On the base of ab initio calculations presented in this work it was shown that If such molecules exist are present in the glass structure their concentration must be negligible.

- For a more quantitative analysis of the glass structure we used a set of Gaussian peaks to fit the complex, broad band profiles of the $R^{iso}$ and $R^{aniso}$ Raman spectra. A tentative assignment of various Gaussian peaks was attempted showed that the molecular model, which does not successfully describe the structure of the stoichiometric glass. Furthermore, the presence of an appreciable fraction of As-As bonds for the stoichiometric glass was found.
3). Analysis the resulting atomic configurations of the $\text{As}_x\text{Te}_{100-x}$ glasses revealed that homonuclear bonding is important over the whole glass forming region. In particular, As-As bonding is significant in the Te-rich region ($34 \geq x$) while Te-Te bonding is considerable in the As-rich region ($x \geq 50$), respectively. It has been shown that Te is predominantly twofold coordinated for $x \leq 50$ while As is threefold coordinated for all compositions investigated. It can be concluded that chemical ordering does not play an important role in the formation of short range order of As-Te glasses and – similarly to some other amorphous tellurides – (e.g. Ge$_2$Sb$_2$Te$_5$, GeSb$_2$Te$_4$, As$_{25}$Si$_{40}$Te$_{35}$) glassy As-Te alloys obey the ‘8-N’ rule for $x \leq 50$.

When compare the obtained structural information with physicochemical properties it was found that the total mean coordination number $<N>$ correlates qualitatively with thermal parameters, e.g. $T_g$ and $T_c-T_g$. $<N>$ as well as both $T_g$ and $T_c-T_g$ exhibit different slopes below and above the stoichiometric limit. The concentration dependence of the number of As-As bonds exhibits noticeable similarities with the corresponding dependence of the density and the optical energy gap. Finally, the number of Te-Te bonds seems to govern properties such as the conductivity and the mean polarizability of the system.

4). Raman scattering has been presumably the most valuable tool in elucidating the structure for these binary glasses in view of the variety of structural units present in their structure. The structure of the stoichiometric glass is composed of GeS$_4$ tetrahedral units bonded either via corner or edge sharing. As well, it has been found that the Raman peaks that are associated with the four vibrational modes dictated by the tetrahedral symmetry of the GeS$_4$ molecule. The highest frequency peak at 434 cm$^{-1}$ has been identified with the antisymmetric stretching vibrational mode of ES units. Moreover, three types of bonding around a reference GeS$_4$ tetrahedron. These types include four CS units, two CS and one ES unit, and two ES units. Using the areas determined by the fit, we find (assuming comparable polarizability matrix elements for these two species) that $\sim 28\%$ of the tetrahedra are arranged in ES bonding configuration.
The Raman spectra of Ge-rich glasses change appreciably even for few percent addition of Ge. New Raman bands were found and assign to different structural species, e.g. $\sim 258$ cm$^{-1}$ mode has been assigned to Ge-Ge bonding in ethane like units $S_3Ge$-$GeS_3$. We have shown that it is rather incorrect to assign the Raman at 238 cm$^{-1}$, which grows fast with the addition of Ge in the spectra of Ge-rich glasses, to the nanoscale phase separation of the glass structure to GeS-like distorted rocksalt octahedral units.

5). The structural studies on $(GeS_{1.5})_{100-x}(AgI)_x$ reveal that addition of AgI causes mild changes in the structure of the GeS$_{1.5}$ pointing to a non-network modifier role of the AgI additive. The interpretation of the Raman spectra of the AgI-doped glasses suggest a mild decrease of the ES units and the concomitant increase of complex $GeS_nI_{4-n}$ or $GeS_nGe_mI_{4-n-m}$ tetrahedra whose vibrations lie in the spectral range below 300 cm$^{-1}$. The presence of iodine atoms and their high chemical affinity for Ge atoms seems to be the incentive for the small but clearly seen structural changes of AgI-doped Ge-rich glasses. Weak peaks at the low energy part for the Raman spectra indicate the existence of $GeS_nGe_mI_{4-n-m}$ tetrahedral units decoupled from the glass network.

6). The structural studies carried out on $(AgI)_x (As_2S_3)_{100-x}$ glasses suggested that:

(a) The glasses with concentrations $x_{AgI} < 10$ are homogeneous and AgI is randomly dispersed in the As$_2S_3$ glass structure.

(b) The glasses with concentrations $10 < x_{AgI} < 20$ are microphase separated. Droplets sizes are of about 100 nm or less. These droplets, presumably rich in AgI, are in an amorphous state.

(c) The glasses with concentrations $x_{AgI} \geq 20$ are also microphase separated. Droplets sizes are of about 100 nm or less for $20 \leq x_{AgI} < 35$ whilst they grow enormously for $x_{AgI} \geq 35$. In both cases, these AgI-rich droplets are in crystalline state. The sizes of crystallites are very small for glass compositions near $x_{AgI} = 20$, while these crystallites grow progressively at higher AgI concentrations.
7). The analysis of the Raman spectra of Ag$_x$(As$_2$S$_3$)$_{100-x}$ glass forming system impy that. Ag atoms destroy parts of the pyramidal network of the base glass thus allowing the formation of cage-like realgar type molecules As$_4$S$_4$. Phase separation was detected only for the most heavily doped glass for $x_{Ag} = 25$. Considering findings of similar studied systems we conclude that the structure of the droplets is in the amorphous state since it is similar to that of the smithite-type glass.

8). The grainy surface pattern of thin amorphous As$_{33}$S$_{67}$ film prepared by spin-coating from butylamine solutions, was found to be related to the cluster size of the dissolved chalcogenide material in the parent solution. The energy gap of the dispersed chalcogenide nanoparticles was found to depend inversely proportional on concentration. DLS data analysis revealed an almost linear dependence between cluster size and concentration. Cluster hydrodynamic radii were found between 1 and 4.2 nm for the samples studied in the present work. For the denser solution a bimodal cluster distribution was observed. A very interesting athermal photo-aggregation process was revealed were the cluster size was sensitive to the laser power in a way opposite of what was expected from thermal effects, i.e. high laser power was found to enhance cluster aggregation. Typical grain sizes were of about 25 and 50 nm for the films produced by a dilute and a moderately dense solution indicating that agglomeration of clusters during solvent evaporation from the film structure, at the time of film fabrication by the spin-coating procedure, takes place. The grainy pattern was found to smooth-out after film thermal stabilization.
Publications


6. O. Kostadinova, S. Yannopoulos, Raman studies on $\text{As}_x\text{Se}_{100-x}$ (0 ≤ x ≤ 40 at% As) glassy system, *in preparation.*


8. I. Kaban, P. Jóvári, K. Kolev, O. Kostadinova, S. N. Yannopoulos, S. Boghosian, T. Petkova, W. Hoyer, Structural investigation of $(\text{AgI})_x(\text{As}_2\text{S}_3)_{100-x}$ glasses, *in preparation*