Evaluation Of The Photo-induced Structural Mechanisms In Chalcogenide

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EVALUATION OF THE PHOTO-INDUCED STRUCTURAL MECHANISMS IN CHALCOGENIDE GLASS MATERIALS

by

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Fall Term
2004
ABSTRACT

Chalcogenide glasses and their use in a wide range of optical, electronic and memory applications, has created a need for a more thorough understanding of material property variation as a function of composition and in geometries representative of actual devices. This study evaluates compositional dependencies and photo-induced structural mechanisms in As-S-Se chalcogenide glasses. An effective fabrication method for the reproducible processing of bulk chalcogenide materials has been demonstrated and an array of tools developed, for the systematic characterization of the resulting material’s physical and optical properties. The influence of compositional variation on the physical properties of 13 glasses within the As-S-Se system has been established. Key structural and optical differences have been observed and quantified between bulk glasses and their corresponding as-deposited films. The importance of annealing and aging of the film material and the impact on photosentivity and long term behavior important to subsequent device stability have been evaluated. Photo-induced structures have been created in the thin films using bandgap cw and sub-bandgap femtosecond laser sources and the exposure conditions and their influence on the post-exposure material properties, have been found to have different limitations and driving mechanisms. These mechanisms largely depend on both structural and/or electronic defects, whether initially present in the chalcogenide material or created upon exposure. These defect processes, largely studied previously in individual binary material systems, have now been shown to be consistently present, but varying in extent, across the ternary glass compositions and exposure conditions examined. We thus establish the varying photo-response of these defects as being the major reason for the optical variations observed.
Nonlinear optical material properties, as related to the multiphoton processes used in our exposure studies, have been modeled and a tentative explanation for their variation in the context of composition and method of evaluation is presented.
To my parents, for their never-ending support....

To baby Diane, I wish that Life will bring you its best...
ACKNOWLEDGMENTS

Time has passed since I came to CREOL in July 1999 and one of the most important lessons I kept learning is that you will never do everything by yourself. By looking at the table of contents, the reader will notice the extent of the experiments carried on in this study. Theoretical knowledge is one thing but a scientist can not exist without technical skills and the experience of others. I would never have been able to complete all of this work just by myself and I would like to truly acknowledge those who helped along the way.

First and foremost I would like to deeply thank my Ph.D. advisor, Dr. Kathleen Richardson, for providing me with the unique opportunity to join this amazing research center. Besides sharing her extensive knowledge, she gave me through the years the fantastic opportunity to interact with some amazingly interesting scientists, some of them whom became dear friends, and to attend multiple conferences in different parts of the world. For all this, Kathleen, you have my eternal gratitude.

I would also like to express my gratitude to my committee members for guiding me through these years and taking the time to review this extensive document. First, Dr. Real Vallée who made me feel part of the family at the COPL in Québec and welcomed me among the amazingly kind persons who work in this place. I will always keep this experience in my mind for it was such a fantastic combination of great learning and living. Martin, you opened to me your fantastic laser facility and your house with your wife and it did mean a lot to me. Your constant drive and passion for science will always impress me. Sudipta, I think I will remember you as my first professor at UCF and as a man constantly driven by curiosity and the will to
understand and educate others. May be one day on a soccer field… Dr. Christodoulides, it is an honor to include you on my committee. You provided a much needed bridge to the “nonlinear optics family” at CREOL.

Research needs money to be properly carried out, thus I am grateful to the National Science Foundation for providing the financial support to this study.

At this point I would also like to thank the great bunch of people who form(ed) the COPL. More specifically Jacques Laniel and Nicolas Hô for their constant support, their knowledge in optics and living a couple of months of my life in the cold (!) Québec winter, along with Marc Dauteil, Richard Piché and Gilles Paul-Hus for their help and patience whenever it was needed. I would not be complete without a special dedication to Alain Villeneuve who opened me first the doors of the COPL and followed my evolution even though I was not his student. You all have a very special place in my heart and you will not be forgotten.

The same can be said about Laurent Sarger and the CPMOH group at Bordeaux. Stéphane, Lionel and all of the technical staff, you’ve made my life so easy when I was there! I can’t wait for another round…

Another group that did a lot for me is the Laser Plasma Laboratory at CREOL: Arnaud, Joshua, Robert, Stanley and Tony “McGyver”. Thank you for your enthusiasm, the fun you brought during the long hours spent in the lab and the seriousness of your answers.

Dr. Alfons Schulte and his students, April and Yu, helped me beyond expectations with the Raman spectroscopy. Thank you for giving me some of your precious time!

I would also like to mention those who shared my daily life at CREOL, among them Courtney Lewis and Mark Wagenhauser for consistently giving me the means and support to keep going forward when my advisor was temporarily away. I also need to thank my
“workmates” of the GPCL for dealing with me and my jokes through the years: Clara, Kitty, Karima, Irene, Amy, Wendy, Maxime and Laeticia.

Friends have been made, a lot of them, and 5 years of a lifetime is not insignificant. Among the CREOL or REU students and the soccer fanatics, I will mention, without any order of preference, Waleed “the Professor” (thanks for so much, you are the real student of the year for as long as I’ve been here!!), Laurent, Mahesh, Bojan, Mircea, Ferenc, Bobby, Joachim, Tom, Rich, Chafik, Muzamil, Pierre, Sandeep and the Allemania Express team… and all those that I forget. The echo of our voices and the enormity of our arguments, while playing or watching soccer games in the conference rooms, is a measure of how much we all love life and each others. I am thankful to all of you for sharing your friendship and making everyday life a constant travel through the World cultures. I will miss you above everything else!

Another person who means a lot to me is my friend Hugues, who kept constant track of my life and my work in the United States. I am sure our paths will cross again, you are a good man. I would also like to thank Norbert Hiéramente for, on a warm summer night and dinner at the Ciron’s table, throwing on the table the idea to cross the Atlantic Ocean, and for putting me in touch with Hugues. You started it all… Many thanks also to Thierry Cardinal at the ICMCB for giving me the foundations on chalcogenide materials and answering so many questions.

“Merci” to my friends Nounours, Babichon, Cocoï and Maxime for making me feel like I never left them every time I come back home. I look forward to more celebrations!

Finally, I would like to thank my parents who not only gave me strong roots but also gave me wings to fly. Home was never far away and this diploma belongs to you as much as it does to me for everything you brought in… Merci pour tout!
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LIST OF ACRONYMS/ABBREVIATIONS

BE     Binding Energy
CB     Conduction Band
CN     Coordination Number
Ch     Chalcogen (atom)
ChG    Chalcogenide Glass
CON    Chemically Ordered Network
COPL   Centre d’Optique, Photonique et Lasers
CPMOH  Centre de Physique Moléculaire, Optique et Hertzienne
CPPM   Collinear Pump-Probe Method
CREOL  Center for Research and Education in Optics and Lasers
CRN    Covalent Random Network
CTE    Coefficient of Thermal Expansion
DSC    Differential Scanning Calorimetry
DTA    Differential Thermal Analysis
EXAFS  Extended X-ray Absorption Fine Structure
GPCL   Glass Processing and Characterization Laboratory
ICMCB  Institut de Chimie de la Matière Condensée de Bordeaux
LP     Lone-Pair (electrons)
LPL    Laser Plasma Laboratory
PB     Photo-bleaching
PD     Photo-darkening
PE     Photo-expansion
RBS    Rutherford Back Scattering
SNR    Signal-to-Noise ratio
TGA    Thermo-Gravimetric analysis
TMA    Thermo-Mechanical Analysis
VAP    Valence Alternation Pairs
VB     Valence Band
WDD    Wemple-DiDomenico
WRS    Waveguide-Raman Spectroscopy
XANES  X-ray Absorption Near-Edge Structure
XPS    X-ray Photoelectron Spectroscopy
XRD    X-Ray Diffraction
µTA    Micro-Thermal Analysis
CHAPTER ONE: MOTIVATION AND BACKGROUND

This chapter first describes the motivation behind this study and presents the questions which defined the guidelines for this work. An extensive background on chalcogenide glasses (ChG’s) covering their history, traditional processing techniques, general properties and applications will be presented. The various models proposed for photo-induced modifications in these materials will be comprehensively reviewed.

1.1 Motivation

Chalcogenide materials, including ChG’s have been extensively studied over the past 50 years. Most of the data published to date has focused on amorphous (a-) Se, amorphous or crystalline (c-) As$_2$S$_3$ or As$_2$Se$_3$. To our knowledge, no systematic study relating the variation in chemical compositional to corresponding physical property variation, which specifically examines such changes to linear and nonlinear optical properties, has been reported. The proposed study here will address these issues, specifically within the As-S-Se glass system.

Along with the growing interest in these materials for optoelectronic and telecommunication applications comes a need to understand any modification or variation in these properties resulting from their transformation from bulk material, to thin film form.
Specifically, this thesis aims to answer the following questions:

1) Can we reproducibly prepare and fabricate bulk and film materials with uniform physical properties?
   - Objective: define processing route requirements for optical quality starting (bulk) materials.

2) What is the compositional effect on the variation of physical properties within the As-S-Se system?
   - Objective: show how chemistry and resulting structure impact the physical and optical properties important to device applications.

3) What significant differences if any, exist between bulk glass samples and their corresponding as-deposited films?
   - Objective: quantify structural differences as well as corresponding property variation.

4) What is the compositional effect and that of the exposure conditions on resulting sensitivity in thin ChG films?
   - Objective: correlation of material/electronic structure with resulting induced index/physical property changes resulting from bandgap and sub-bandgap illumination, and exposure conditions which generate reversible, irreversible and ablative behaviors.

As will be reported here, the structure and bond arrangements of the ChG’s can be altered, sometimes reversibly, by various external factors such as thermal treatment, particle
beams, electrical or magnetic fields or light. Reported by De Neufville as early as 1973 in chalcogenides, the photo-darkening effect is a major process taking place in these compounds under the action of light which has yet to be interpreted conclusively.

Despite the development of numerous models since Street in 1977, the underlying structural or electronic phenomena taking place during photo-induced processes are still not well understood. As of today, no one model has been able to account for all modifications taking place in these materials. Although recent research on the subject has been abundant, most particularly in As$_2$S$_3$ glasses, these studies usually were focusing either on the bulk or the thin films but rarely proposing a systematic comparison between these materials.

We will first present a thorough background on chalcogenide materials and the photo-induced processes in chalcogenide glasses (ChG’s) reported to date. Next, we address the key questions defined above: we summarize the processes and techniques developed and results obtained to fabricate and characterize the bulk material and corresponding As-S-Se chalcogenide films. Lastly, we propose and discuss structural and optical (i.e. electronic) mechanisms believed to be taking place upon laser exposure of the chalcogenide materials. Included in the appendix is a listing of publications to date resulting from our work, and the different mathematical codes used in this study.
1.2. Historical review of chalcogenide development

1.2.1. History of chalcogenide glasses

It is difficult to define with accuracy when mankind first fabricated its own glass but some sources go back 10,000 years in time (1). It is also difficult to point in time when the field of chalcogenide glasses started. For the vast majority of time the vitreous glassy state was limited to oxygen compounds and their derivatives. Schulz-Sellack was the first to report data on oxygen-free glass in 1870 (2). Though vitreous selenium and arsenic selenide and sulfide were synthesized for the first time at the end of the 19th century, scientists were not attracted to these new materials. Vitreous selenium became of interest for the scientific community at the beginning of the 20th century when Wood (3) and Meier (4) reported the first research on the subject.

The rising of infrared (IR) optics in the 20th century lead to the need of new IR materials. Classical oxide glasses covered a transparency region from 3 µm to 5 µm while the heavy oxide materials helped to extend that region up to 8 µm. The interest for the chalcogens comes from the attempt of scientists to extend the IR transparency region in glasses past 8 µm.

The first works on ChG were attributed to Frerichs in the early 50’s on As$_2$S$_3$ glass (5, 6), and As$_2$Se$_3$ by Fraser (7) and Dewulf (8). Frerichs was also at the instigation of the development of selenium glasses and binary compounds with sulfur (6). Another important investigator of vitreous ChG around that time was Winter-Klein (9). At this point, two major research groups from Saint-Petersburg started the first developed research program on ChG: one was led by B.T.
Kolomiets and N.A. Goryunova from the “A.F. Joffe Physico-Technical Institute” who were reported to discover the first semiconducting glass (10), while the other group from the University of Saint-Petersburg was led by R.L. Myuller.

Another famous contributor to the knowledge on ChG is S.R. Ovshinsky who worked at Energy Conversion Devices in Michigan. His most famous discovery is the memory and switching effect in ChG (11, 12). This led to the development of non-crystalline ChG in various fields such as xerography or computer memories. Around the same period in the 1970’s, Sir N.F. Mott (a former Nobel Prize winner in Physics in 1977) and E.A. Davis developed the theory on the electronic processes in non-crystalline ChG (13). Several review books were published in the following years on glasses and with an interest on ChG: “The Chemistry of Glasses” by A. Paul in 1982, “The Physics of Amorphous Solids” by R. Zallen in 1983 or “Physics of Amorphous Materials” by S.R. Elliott in 1983. However, the first review entirely dedicated to ChG materials entitled “Chalcogenide Semiconducting Glasses” was published in 1983 by Z.U. Borisova who previously worked with Myuller in Saint-Petersburg. G.Z. Vinogradova from Moscow followed the next year with her monograph “Glass Formation and Phase Equilibrium in Chalcogenide Systems”. More recently, A.M. Andriesh dedicated a book to some specific applications of ChG entitled “Glassy Semiconductors in Photo-electric Systems for Optical Recording of Information”. Finally, M.A. Popescu gave a large and detailed account on the physical and technological aspects of chalcogenide systems in his 2001 book called “Non-Crystalline Chalcogenides”. Most recently a compendium of monographs on the subject of photo-induced processes in ChG entitled “Photo-induced Metastability in Amorphous Semiconductors” was compiled and edited by A. Kolobov (2003).
1.2.2. The chalcogens and their combinations

As previously mentioned, chalcogens are elements of the group VI-A of the Periodic Table and include sulfur, selenium and tellurium. Oxygen and polonium, which belong to the same group, do not enter in the chalcogen class. By extension, ChG are named for their association between these chalcogens with electropositive materials and organic radicals. The following table summarizes some physico-chemical data on the chalcogens.

Table 1-1: Summary of physico-chemical data for the chalcogens, adapted from (14).

<table>
<thead>
<tr>
<th>Property</th>
<th>Sulfur</th>
<th>Selenium</th>
<th>Tellurium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic mass</td>
<td>32.064</td>
<td>78.96</td>
<td>127.60</td>
</tr>
<tr>
<td>Electronegativity (Pauling)</td>
<td>2.5</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Electronic affinity (eV)</td>
<td>2.077</td>
<td>2.022</td>
<td>2</td>
</tr>
<tr>
<td>Ionization energy (eV)</td>
<td>10.360</td>
<td>9.752</td>
<td>9.009</td>
</tr>
<tr>
<td>Covalent radius (Å)</td>
<td>1.04</td>
<td>1.17</td>
<td>1.37</td>
</tr>
<tr>
<td>Ionic radius (Å)</td>
<td>1.82</td>
<td>1.93</td>
<td>2.21</td>
</tr>
<tr>
<td>Bonding Energy (kJ/mol)</td>
<td>266</td>
<td>184</td>
<td>168</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>112.8 (α)</td>
<td>217 (α)</td>
<td>429 (β)</td>
</tr>
<tr>
<td>Dissociation energy (kJ/mol)</td>
<td>421.33</td>
<td>305.2</td>
<td>259</td>
</tr>
<tr>
<td>Thermal conductivity (J/m.s.K)</td>
<td>0.272</td>
<td>0.237</td>
<td>5.85</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.069 (α)</td>
<td>4.82 (amorph.)</td>
<td>6.00 (amorph.)</td>
</tr>
</tbody>
</table>
1.2.2.1. Binary compounds

Chalcogens can form alloys together. Amorphous-Se-S, (15) Se-Te (16) and S-Te amorphous (17, 18) compounds were identified; however the scientific community seems to have, for the moment at least, left these glasses aside.

Many binary compounds can be synthesized by associating one of the ChG with another element of the periodic table. Among the most interesting elements are phosphorus, antimony, silicon, germanium and tin. A few other compounds based on heavy or light elements and alkali atoms are also under investigation.

Abrikosov et al. (19) reported in 1969 in their monograph the phase diagrams for the As-S and As-Se systems, the existence of As$_2$S$_2$ and As$_2$S$_3$ compounds for the first system, and AsSe and As$_2$Se$_3$ for the second system. As-S alloys can be formed with an As content up to 46%, while in As-Se this maximum content can be raised to almost 60%. Glasses with low As content can easily crystallize (e.g. for a content of 6% As the glass crystallizes at room temperature in one day, those in the range 5-16 weight % in a couple of days at 60ºC while it takes 30 days for As$_2$S$_3$ at 280ºC) (20). As-Se alloys can crystallize along the all composition range, however this has to be done under pressure and at elevated temperatures. This stability in bulk materials has stimulated activity in these materials, as well as our current interest in the ability to compositionally tailor bulk glasses, film or fiber with these systems for a range of applications.

The binary compounds that attract the most attention are the arsenic ChG’s in the system As$_2$S$_3$ and As$_2$Se$_3$. The typical As$_2$S$_3$ structure is usually pictured as an assembly of six AsS$_{3/2}$ pyramids (the As atom being the top of the pyramid while three S atoms form the base).
The well-known crystal configuration of As$_2$S$_3$ and As$_2$Se$_3$ is called “orpiment”. As described by Loudon (21), three out of the five valence electrons of each arsenic atoms form valence bonds with three adjacent ChG atoms in a hybrid state between sp$^3$ and s + 3p. Similarly, each chalcogen uses two of its six valence electrons to contribute to the valence bonds with arsenic. The remaining valence electrons of every species occupy non-bonding orbitals. Seen from a bigger angle, the orpiment structure is made of densely packed layers of interconnected 12 atom rings with Van der Waals forces in between the “puckered layers”. However, the building forces within the layers are hundred times stronger than the forces acting between layers. Note that the packing density is higher in As$_2$Se$_3$ than in As$_2$S$_3$.

Realgar (As$_4$Ch$_4$) is another structure beside orpiment in the crystalline form. Finally, the duranusite (As$_4$S) represents the last well-described crystalline compound that one can find in the As$_2$S$_3$ system. Z. Zohan et al., gave a thorough description of this structure (22).

1.2.2.2. Ternary compounds

The As-S-Se system that is of interest to us shows a very wide glass-forming region as shown in figure 1.1 (23).

Solid solutions can be formed all along the line As$_2$S$_3$-As$_2$Se$_3$ as proved via IR spectra and X-ray analysis by Velinov et al. (24). Crystallization has been shown to be difficult in this domain, especially along the S-Se line. The compounds obtained in the rest of the vitrification area show multiple compounds formed inside the final product (25). This system will be described in more detail in the following sections.
Figure 1.1 shows the typical glass forming region in the As-S-Se system according to a previous work (23).

![Diagram showing the glass-forming region in the As-S-Se system. The vitrification region is shadowed in grey.]

Figure 1.1: Glass-forming region in the As-S-Se system (23). The vitrification region is shadowed in grey.
1.3. Processing and purification of chalcogenide glasses

1.3.1. Fabrication techniques

1.3.1.1. Glasses and precipitates

Frerichs prepared As$_2$S$_3$ glass in 1953 (6) by distilling the technical-grade sulfide in a stream of H$_2$S after cooling the condensed liquid. Fraser, also in 1953, was able to form As$_2$Se$_3$ glass (7). The first method for the preparation of the As$_2$S$_3$ glass at the industrial scale was developed in 1957 by Glaze et al. (26) who were able to produce it on a kilogram scale.

The fastest growing interest in the next years led to the development of new processing techniques. The usual glass fabrication is done by weighing the respective elemental chemical compounds and placing them inside an ampoule, preferably high purity quartz. The different processing steps take place under vacuum in order to avoid poisoning by the volatile and highly toxic constituents and to protect ingredients from oxide formation. Sealed ampoules also avoid any atmospheric contamination, especially from the oxygen due to the high vapor pressure of the chalcogens and their ability to react easily with this compound. The ampoules are usually rotated or shaken following sealing (rotation of the ampoule or of the furnace) to promote the homogenization of the melt. Since the ChG network energy requires lower melting temperatures than for oxide glasses for example, the ampoule corrosion is low, if non-existent. The vacuum created in the ampoules also serves the purpose of avoiding high internal pressures during the melting phase. Quenching can take place either in the furnace by letting the oven cool down
after turning off the power, in air or in a cold liquid, usually water when more severe quenching is required. Due to the large thermal coefficients of expansion of these glasses, internal stress has to be dealt with by annealing below the glass transition temperature ($T_g$) followed by a slow cooling to room temperature.

1.3.1.2. Thin films

Many techniques have been successfully used to fabricate thin films of ChG, usually obtained from bulk glass targets. The classical processing is done by thermal evaporation under vacuum where amorphous pieces of bulk chalcogenide are placed in a heated crucible (27).

Alternatively, the flash evaporation method allows control of the composition by varying the crucible and substrate temperatures or the deposition rate. However, disordered features on the surface of the film can appear and imply a tight control of the previously mentioned parameters (28). High purity films can be obtained by chemical vapor deposition, which uses the decomposition processes under high temperature.

Laser (or electron) ablation uses high energy beams focused on a material. This energy transforms the material into a plasma that gets deposited on a substrate (29). This technique has the advantage to avoid contamination by the source (30), though the resulting films are sometime far away from structure than their parent material due to the aggressive nature of the process.

Finally, cathode sputtering involves an inert gas such as argon in a chamber under low pressure. After producing a gas discharge, ions are accelerated toward a target where molecules are sputtered onto a substrate. In this technique, the fractionation effect is much lower as compared to regular thermal evaporation techniques (31).
1.3.2. Impurities and purification

Small amounts of impurities are sometimes added to enhance the physical or optical properties of a melt. Into this category fall compounds such as metals (e.g. silver or copper), added to increase the conductivity of a melt for example.

However, impurities can also impair the stability and the homogeneity of a melt, in addition to the mechanical and optical properties mentioned above. ChG’s often exhibit high vapor pressures and their melts show high viscosities, which make them vulnerable to oxidation or hydrolysis. Oxygen is thus the primary contaminant in the case of ChG melts, since it reduces the optical transparency window of the final product. Sulfur is also known to show a variety of impurities, such as carbon or hydrogen. Seddon’s review (32) identified a large number of absorption bands of common impurities in chalcogenide glasses.

The ampoules used to contain the elemental starting materials during melting have to be of high purity and are usually made of silica. They have to be cleaned, sometimes by extreme means such as hydrofluoric acid, and baked before use to remove any surface contaminants.

The use of vacuum along the remaining fabrication steps is usually the best and easiest answer to this impurity problem. The high differential vapor pressure between the contaminants and the batch components is simply exploited by heating the system while under vacuum. An oxygen getter, such as magnesium (33), can also be placed inside the ampoule.
1.4. General properties of chalcogenide compounds in the systems As$_x$-S$_y$, As$_x$-Se$_y$ and As$_x$-S$_y$-Se$_z$

This section focuses on properties of amorphous ChG in the As-S, As-Se and As-S-Se systems. The properties relative to each chalcogen and the binary and ternary systems formed by these latest are extensively described by Popescu (34).

1.4.1. General structure

1.4.1.1. The glassy structure

Amorphous compounds were defined prior to the 1900’s as solids presenting a formless fracture surface known today as conchoidal structure (35). The rise of techniques such as X-ray Diffraction showed that these solids were also non-crystalline. The “amorphous” and “non-crystalline” terms are presently considered synonymous as opposed to “crystalline”. Any material that does not exhibit atoms arranged in a periodical pattern and a correspondingly featureless (i.e. peakless) XRD pattern is thus considered amorphous, “structurally” speaking.

These materials can also be classified according to their mechanical properties. Solids are considered as materials with viscosities exceeding $10^{14.6}$ poise, while fluids (including liquids and gases) have viscosities below this value. Among amorphous solids lies the class of “glasses”.
Zachariasen was the first to propose a geometrical model for the ideal glass in 1932 (36):
A definite range order is imposed when each and every atom fulfills the chemical valency requirement according to the 8-\(N\) rule. The latter states that, in most stable covalent glass matrices, an atom with \(N\) valence electrons is coordinated such that it would have a completely filled outer shell of electrons. This “geometrical” model was later the object of extensive reviews by Weyl and Marboe (37) or Rawson (38).

Morey defined in 1954 glasses as amorphous solids obtained from the melt, i.e. solidification of a liquid (39). Following this idea, Cohen and Turnbull developed the free volume model of the liquid state which implies that all liquids form an amorphous solid except for the intervention of crystallization (40). The same authors described extensively how to prevent crystallization, i.e. the greater the cooling rate, the smaller the sample volume hence the slower the crystallization rate, and developed numerous thermodynamics criteria (41), that formulate the problem in terms of experimental condition and macroscopic parameters (such as viscosity). Thus, the geometrical approach described earlier, which correlates the molecular constituents and structure to physical properties, can be considered in the end a complementary description to the kinetic approach.

A great deal of effort was further made in the 1970’s in order to establish a quantitative criterion for glass-forming. Stanworth quantitatively related the degree of spatial filling (\(f\)), calculated from molecular mass, crystal density and orbital atomic radii of glass components, to describe glass-forming ability in oxides (42).

Meanwhile, Philips established his theory on the calculation of sums of tensile and transverse stresses of covalent bonds for one atom to define the number of constraints (\(N_{co}\)). It establishes that the maximum mechanical stability in coordinate space is obtained, for a binary
alloy $A_xB_{1-x}$ with only short-range interactions, which supposedly leads to maximum glass-forming ability (43) when the short-range order defined by bending and stretching forces is sufficient to exhaust the local degrees of freedom. However, this criterion suffers from not taking into account long range interactions, ionicity and size effects and does not fit the class of tetrahedral glasses (44).

There exists no quantitative criterion that allows one to calculate coordination numbers necessary for glass-forming, describe the population of chemical bonds in glasses and connect them at the same time with their real properties. Feltz wrote on this subject: “we are dealing in the main with the qualitative rules. It must be noted that on the presently achieved level of theoretical development it is still necessary to be careful with the results of quantitative calculations even in the cases when they are in satisfactory concord with an experiment” (45). Many other theories have been developed by researchers over the years such as Dietzel (46), Baydakov and Blinov (47) but none of them showed a universal aspect or cannot be applied to multi-elements systems.

On the qualitative side, Dembovsky and Chechetkina tackled the glass-forming ability problem by studying the thermodynamical, kinetic and structure-chemical aspects through $T_g$, rates of cooling, energy barriers of crystals and so on (48).

Borisova et al. were among the first to establish that the magnitude of glass properties with components of different nature and composition coincide if the glasses have identical covalent or energy atomic coordination.

The largest majority of researchers agree on the following though: after cooling a liquid below its melting point it will either form a glass or crystallize. During the glass formation, the
viscosity, entropy, volume or internal energy change continuously, except in the vicinity of the glass transition temperature \( T_g \) where these changes are often rapid.

1.4.1.2. The chalcogenide glass structure

The ChG structure has been the object of extensive studies, considering both the bulk and thin film forms. Modeling a structure has proven difficult because of the great flexibility in the choice of the molecular units in the case of ChG. The vast majority of studies have been made on \( \text{As}_2\text{S}_3 \) and \( \text{As}_2\text{Se}_3 \) (as we will see later), which have been primarily the only alloys used in the As-S-Se system until recently.

Goriunova and Kolomiets pointed out the importance of covalent bonding in ChG as the most important property to guarantee stability of these glasses (49). As opposed to metallic bonding, covalent bonding ensures easier preparation of the glasses. Thus, the crosslinking initiated by the As atoms should reduce the freedom for disorder since the bonds are covalent.

Vaipolin and Porai-Koshits reported X-ray studies beginning of the 1960’s (50, 51) of vitreous \( \text{As}_2\text{S}_3 \) and \( \text{As}_2\text{Se}_3 \) and a number of binary glass compositions based on these two compounds. These glasses were shown to contain corrugated layers, which were deformed with increasing size of the chalcogens. At the same time, the arsenic atoms were shown to become octohedrally coordinated. The character of the bonds was also shown to become more ionic when at equimolecular compositions.

At the beginning of the 1980’s, Tanaka characterized ChG’s as a phase which is structurally rigid but possesses no long-range order. This, he attributes, was due to which their
optical, electrical and structural properties which were often smeared out in contrast to those of crystalline components, one of the reasons why scientists hesitated to enter the field of ChG’s.

At this point, we have to consider two well-known theories: the Covalent Random Network (CRN) and the Chemically Ordered Network (CON). The CRN and the CON models both satisfy the $8-N$ rule described previously and represent the distribution of bond types in a covalent network with multi elements.

In the CRN, the bonds are distributed between homopolar and heteropolar atomic pairs following a statistically random approach. This means that in the As–Se–S system, one would have to expect a statistical combination of homopolar (As–As, Se–Se, S–S) and heteropolar (As–Se, As–S, Se–S) bonds. However, this model would not support the layer-like molecular units which make up the crystals (1).

In contrast, the CON model supports the presence of low energy bonds. This way, As-rich glasses would exhibit As–As, As–Se, and As–S bonds; Se-rich glasses would have As–Se, As–S, and Se–Se bonds and S-rich glasses As–Se, As–S, and S–S bonds. The relative weight of each of the above units is expected to be proportionate to the overall composition of the glass itself (52). The bond statistics for these two models were calculated by Lucovský and Hayes (53). Many researchers have discussed both models in the case of ChG but in a recent study using x-ray absorption spectroscopy, Wang et al. showed that the As-S-Se system most likely follows the CON model (54).

The emergence of x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) as synchrotron radiation sources for x-ray absorption spectroscopic measurements has exposed researchers to a more thorough understanding of the electronic and structural properties of the amorphous materials, especially in a-As$_2$S$_3$ (52, 55, 56,
These two previous techniques are element-specific and allow one to investigate the short to medium range structure around the absorbing atom (58, 59).

Zachariasen’s two-dimensional representation of an A\textsubscript{2}B\textsubscript{3}-type glass (36) can be used for example as a representation for As\textsubscript{2}S\textsubscript{3} or As\textsubscript{2}Se\textsubscript{3}. The proposed structure consists of rings made of odd and even number of atoms. The stronger heteropolar bonds (As-S) are favored over homopolar bonds (S-S, As-As) and the bond lengths are within 1% the same as those found in crystals (1). The amorphous As\textsubscript{2}S\textsubscript{3} or As\textsubscript{2}Se\textsubscript{3} alloys are nowadays usually schematically represented by an AsCh\textsubscript{3} pyramid, the As atom being at the top and the three chalcogens at the base.

The singular properties of ChG are dependent on their compositions. The fact that, unlike a vast number of oxide glasses, ChG’s do not include the ionic component of the chemical bond, helped scientists to advance the fields examining the nature of glass structure and glass formation, especially in the simplest case of two elements systems with one chemical bond of one type. The nearest-neighbor coordination associated with covalent As-Ch (Ch being the chalcogen) bonds in ChG involve 3-fold coordinated As and 2-fold coordinated chalcogens. This has been shown by X-ray diffraction (60), Raman scattering (61) and nuclear quadrupole resonance studies (62). Less information on the second or third nearest-neighbor configuration is available though. It is known though that a small amount of homopolar bonds (As-As and S-S or Se-Se bonds) are produced due to the absence of long-range order beside the covalent As-Ch, and that a very low concentration (10\textsuperscript{18} cm\textsuperscript{-3}) of bonding defects appears(59, 63, 64, 65). These defects and their concentration in bulk and film materials will become important in our study.
A characteristic common to ChG is their electronic structure originating in the p-like lone pair electrons of the chalcogen. The sulfur atom, for example, has four outer p electrons, of which two are used for covalent bond formation with the neighboring arsenic p electrons. The two remaining p electrons form a so-called “lone pair” of electrons.

Note that there exists no essential difference in the band structure between crystalline and glassy \( \text{As}_2\text{S}_3 \). While the two filled bonding (\( \sigma \)) p-states lie at the bottom of the valence band, the filled lone pair (LP) p-states at the top of the valence band are separated from the empty \( \sigma^* \) states of the conduction band by the bandgap (66). These LP states are associated with the defect models of Kastner, Adler and Fritzsche (valence-alternation pair or VAP) and Mott and Street (charged dangling bonds) that we will cover in more details later on in this chapter.

DeNeufville and Rockstad showed (67) that one could use the average coordination number to characterize the connectivity of semiconducting glasses: binary and ternary materials having the same mean coordination number lie essentially on the same line if one plots their optical gap (\( E_g \)) as a function of their glass transition.

An interesting study was conducted by Know and Ban (68) on the distribution of the molecular composition in the vapor phase of an \( \text{As}_2\text{Se}_3 \) target, in the cases of evaporation by laser radiation and “explosive” vaporization (i.e. at \( T = 1000^\circ\text{C} \)). The formation of \( \text{As}_3\text{Se} \) and \( \text{As}_3\text{Se}_4 \) in the first case was related to the peculiarity of the short-range order in the solid.

Borisova (69) divided the multiple As-S-Se alloys her group fabricated in two groups: one containing the alloys presenting an excess in chalcogens and those presenting a small chalcogen amount. The group having a small amount of chalcogen exhibits structure units such as \( \text{As}_2\text{S}_{4/2} \), \( \text{As}_2\text{Se}_{4/2} \), \( \text{AsSe}_{3/2} \) and others which usually exhibit properties close to the As-S family.
The properties of As-S-Se compounds containing an excess of chalcogen (i.e. S or Se) are primarily determined by the structural-chemical singularities of the excess sulfur, as we will see in the next sub-paragraphs.

Previous studies on evaporated ChG films of As$_2$Se$_3$, As$_2$S$_3$, and GeS$_2$ showed significant concentrations of homopolar bonding in contrast to the almost totally heteropolar bonding in the corresponding bulk quenched glasses (59). Chen et al. obtained in 1980 a transmission electron micrograph of a domain wall network in a 600Å thick evaporated film of glassy As$_2$Se$_3$ (70). This micrograph exhibits hexagonal domains with diameters of 1µm, which were accounted to demonstrate the accumulation of strain energies from long range interactions and a subsequent strain-relief mechanism in such thin films (71). The presence of homopolar versus heteropolar bonds in bulk and films exposed to laser radiation will play an important role in our structural interpretation of photo-induced processes in these glasses as described subsequently. The photo-induced (PI) structural modifications of As$_2$S$_3$, As$_2$Se$_3$ and As-S-Se under illumination will be extensively discussed and reviewed in section (1.5).

1.4.2. Physico-mechanical properties

ChG are chemically stable in regular temperature and atmospheric conditions. However they can become unstable in alkali solutions as shown by Borisova (72).
Borisova reported the density and micro-hardness of more than 20 glasses in the As-S-Se system (73). As-S\(_x\)Se\(_y\) compounds with a total chalcogen amount \(1 \leq x + y \leq 2.5\) show a large number of structural units such as As\(_2\)S\(_{4/2}\), As\(_2\)Se\(_{4/2}\) and AsSe\(_{3/2}\). Increasing the chalcogen content of these glasses does reduce the micro-hardness. Note that alloys in the system As-S show systematically a lower hardness than their corresponding As-Se alloys. Low values of micro-hardness have also been linked to the blocking of the AsS\(_{5/2}\) structural units, which exhibit high hardness values due to the tetrahedral coordination of the S atoms, by the polymeric sulfur. Velinov et al. recently measured the micro-hardness along the As\(_2\)S\(_3\)-As\(_2\)Se\(_3\) composition line (24).

1.4.3. Thermal, electrical and magnetic properties

1.4.3.1. Thermal properties

In any ChG system, increasing the relative chalcogen atomic mass or its atomic content with respect to the other elements in the network, will diminish the average bond strength and thus reduce \(T_g\).

The expansion coefficient and \(T_g\) in the system As-S were reported by Tanaka et al. (74) for an As content between 28 and 40 atomic %. The differences in value for \(T_g\) found in the literature come from the various techniques used and the way the data are treated, and hence one has to be cautious when dealing with such results. This variation can be found for any type of
data, especially when it comes to results of thermal analyses. Andreichin also reports a thermal
diffusivity for As$_2$S$_3$ of 2.4x10$^{-3}$ cm$^2$/s (75).

In the As-Se system, the softening and melting ($T_m$) temperature of As$_2$Se$_3$ were obtained
from DTA measurements by Maijd (76) and equal to respectively 180°C and 202°C,
respectively. According to Thornberg and Johnson (77), $T_m$ was shown to depend strongly on
the heating rate while $T_g$ showed a slight dependency.

As-S-Se glasses exhibit low melting points and their $T_g$’s range from 35°C to 180°C as
reported by Borisova (73) (for more than 20 compositions) and Zhukov et al. (78). The
softening temperature along the As$_2$S$_3$-As$_2$Se$_3$ composition line is approximately constant (~
180°C) as shown by Velinov et al. (24). Crystallization for the same range of concentrations can
be successful over a 30 days period in a range of temperature 250-280°C

1.4.3.2. Electrical properties

For most amorphous semiconductors, the temperature dependence of the (d.c.) electrical
conductivity ($\sigma$) can be written for a large range of temperature as:

$$\sigma = \sigma_0 \exp\left(- \frac{E_a}{kT}\right)$$  \hspace{1cm} (1.1)

where $\sigma_0$ is a proportionality coefficient and $E_a$ is the activation energy. As-S alloys present a
very small $\sigma_0$ (~ 9 $\Omega^{-1}$ cm$^{-1}$) (79) as compared to other amorphous semiconductors (~ 10$^3$-10$^4$ $\Omega^{-1}$
Dielectric constants ($\varepsilon$) and permittivities were measured in both As-S and As-Se systems by Gutenev (80).

The electrical conductivity of a-As$_2$Se$_3$ as a function of temperature and dielectric constants along the As-Se line have been documented by Kitao (81). The activation was calculated to be equal to 1.0 5eV and 0.9 eV respectively above and below 200°C, value correlated by Iovu et al. (82). These latest also measured a conductivity of $3 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$.

It was shown that, by comparing the values of $-\log \sigma_{20\degree C}$ of As-S-Se compounds with those of As-S and As-Se, the electric conductivity of the As-S-Se alloys were very close to those of the As-S binary system, even in high selenium content glasses (69). Borisova reported a large set of electro-physical parameters (among which density, hardness, conductivity and activation energy) for As-S-Se glasses in her book (83).

1.4.4. Optical properties

Sulfides usually are transparent in the high wavelength range of the visible region where selenides or tellurides are completely opaque. However they all are highly transmissive in the near IR and mid-IR regions, specifically 12 µm, 15 µm and 20 µm for sulfides, selenides and tellurides, respectively (84). Bad homogeneity of a glass during fabrication can lead to the presence of striae with different densities, which will cause scattering and loss.
Because of the lack of long range order in ChG, their absorption band is radically changed when comparing the crystalline and amorphous states (85). Bishop showed in 1981 that impurities play a predominant role in determining the optically-induced properties of crystalline arsenic chalcogenides only (86). The optical absorption edge dependence on temperature was reported for both a-As$_2$S$_3$ and c-As$_2$S$_3$ (87) by Zakis and Fritzsche.

Tauc compared the absorption edge of a- and c-As$_2$S$_3$ (85) and showed that the high absorption ($\alpha > 10^4$ cm$^{-1}$) region was mostly associated with transitions from localized valence band states below $E_v$ to conduction band states above $E_c$ (delocalized), or vice-versa. For $1 \text{ cm}^{-1} < \alpha < 10^4$ cm$^{-1}$, the absorption was declared to be due to the presence of band tail states (a.k.a., the “Urbach Tail”) that extends into the gap. Wood and Tauc obtained for a-As$_2$S$_3$ a total concentration of band tail states of about $10^{20}$ cm$^{-3}$ in this latter region (88). The third region of the band ($\alpha < 1 \text{cm}^{-1}$) was found to be related to the preparation, purity and thermal history of the material.

Gutenev calculated the refractive indices ($n$) of multiple amorphous glasses in the system As$_x$S$_{1-x}$ (for an x range from 0.10 to 0.44) (80). According to Seddon (32), the refractive indices in the systems As-S and As-Se range from 2 to > 3, which gives rise to high Fresnel reflections at the interfaces with air (10% to more than 25%) and high Rayleigh scattering. Savage (84) has presented the refractive indices for multiple combinations of S, Se or Te with As, Ge, Sb and Si. He reports an index of $n = 2.395$ at $\lambda = 3 \mu\text{m}$ for As$_2$S$_3$ and a temperature coefficient of refractive index of $-0.0001 \text{°C}^{-1}$ in the range of 3-5 $\mu\text{m}$. Sanghera and Aggarwal (89) summarized many optical constants for As$_2$S$_3$ such as refractive index ($n = 2.415$ at $\lambda = 3 \mu\text{m}$), $dn/dt$, bulk and fiber transmission range and typical loss.
The optical gap of $\text{As}_2\text{Se}_3$ was determined to be $\sim 1.76$ eV (90, 91) and the photo-conductive gap (2.1 eV) was reported by Tanaka and Nakayama (92). Kitao (81) measured the refractive index for multiple $\text{As}_x\text{Se}_{1-x}$ glasses from $x = 0$ to 1. Studies on the refractive index of an $\text{AsSe}$ thin film (2 $\mu$m thick) as a function of the frequency of light were conducted by Grigorivici et al. (93).

Gutenev et al. also collected a large amount of data on the refractive indices $n$ of $\text{As-S-Se}$ amorphous glasses (94) and related their results to the predominantly covalent character of the chemical bonds. Henrion plotted the spectral dependence ($\sim$ from 1 to 3 $\mu$m) of the index of refraction for multiple pseudo-binary $\text{As-Ch}$ glasses (95) among the $\text{As}_2\text{Se}_3$-$\text{As}_2\text{S}_3$ series. The index was found to be between 2.5 and 2.7 over the complete range.

Simon and Borelli developed a localized model to understand the ChG vibrational spectrum (96, 97). This model assumed that all of the elements constituting the glass vibrate independently and are isolated from each other. Felty et al. used this model to interpret the reststrahlen bands of the amorphous system $\text{As}_2\text{S}_x\text{Se}_{3-x}$ (98) and assigned the bands at 300 and 215 cm$^{-1}$ to the As-S and As-Se bands, respectively.

The amorphous $\text{As}_2\text{Se}_3$ and $\text{As}_2\text{S}_3$ vibrational spectra were later detailed in more depth by Zallen et al. using Raman and infrared tools (99), and showed that the As atom vibrates in opposition to its three neighboring chalcogens while each chalcogen does the same, in relation to its two neighboring arsenic atoms. Lucovsky and Martin then proposed a schematic representation of the molecular order in a-$\text{As}_2\text{S}_3$ (60). Later Raman and IR spectra of ChG films showed obvious similarities between amorphous and crystalline states (100).
The recent advances in nonlinear optics have contributed to an increase in research on the ChG subject. Asobe et al., have focused their studies on the determination of nonlinear refractive index in As$_2$S$_3$ fibers (101) for switching applications (102). Bindra et al. (103) recently reported the observation of three-photon absorption in As$_2$S$_3$ at telecommunications wavelengths. $\chi^{(3)}$ was successfully measured by Kanbara and coworkers in As$_2$S$_3$ and an As-S-Se glass using degenerate four-wave mixing and third harmonic generation (104). Finally Smektala used the Z-scan method to characterize As$_2$S$_3$ and As$_2$Se$_3$ among other compounds (105), while studies by Cardinal et al. (106) or Richardson et al. (107) had previously reported nonlinear index for As$_2$S$_3$, As$_2$Se$_3$ and multiple As-S-Se glasses using the same technique.

1.5. Modifications in non-crystalline chalcogenide compounds

As explained previously, ChG alloys exhibit no long-range order, and hence, are intrinsically metastable. It is possible through a variety of means thus, to change the structure and bonds of these materials due to their structural flexibility. Chalcogen elements are only two-fold coordinated while the chalcogen atoms possess a lone pair of electrons, which can undergo light-induced reactions to produce structural defects of three-fold or single-coordinated atoms, as will be seen in this section. These photo-induced changes might be reversible or not, depending on the composition and the experimental parameters used to induce the change. One can thus change the properties of the starting material. Note that by “reversible” we mean that the photo-induced changes created into a material can be annealed out by heating to near $T_g$. 26
1.5.1. Types of photo-induced modifications

Using exposure under a specific wavelength of light, one can manipulate the lone-pair (LP) electrons which are characteristic of every chalcogen atom. This gives rise to two types of defects: either a single or a three-fold coordinated chalcogen species. The states related to these non-bonding electrons lie at the top of the valence band and can thus be preferentially excited by light of appropriate frequency.

The first accounts on significant structural or physical changes by light in ChG were published at the beginning of the 1970’s by Keneman (108), Berkes et al. (109), and Pearson and Bagley (110). Authors reported changes on density and decomposition (91), hardness (111), dissolution rate (112), crystallization (113), optical (114, 115, 116) and electrical properties (114, 116, 117). These photo-induced changes were observed for various complexities of compositions, i.e. from the chalcogen itself to binary, ternary and more complex compounds with various degrees of importance. As an example, Lyubin (118) observed a dramatic change in refractive index ($\Delta n = 0.7$) instead of the regular alteration ($\sim 0.1$) observed for these materials (119). No reason for this variation was mentioned.
1.5.2. Irreversible and reversible structural modification by light

1.5.2.1. Irreversible changes

Irreversible structural modification can be created in both amorphous and crystalline ChG compounds and have been shown to exist in unannealed films prepared either by vacuum evaporation or sputtering techniques (115).

Photo-vaporization is an irreversible transformation where a photo-oxidation reaction is followed by a thermal evaporation of the material. It was first shown in $\text{As}_2\text{S}_3$ by Janai in 1981 (120, 121). It is easy to understand that high energy sources, such as high power lasers, can create bubbles or other similar local evaporation defects in the material by heating the species several hundreds of degrees above the softening temperature thereby creating melting or evaporation, as shown by Feinleib (122).

Photo-crystallization was first observed by Dresner and Stringfellow (123) in a-Se. Crystals were formed in the irradiated region but could be erased by illumination in a different, nearby regime. Areas where the crystals were created showed different optical properties as compared to unexposed virgin region.

Among other transformations studied in these glasses is photo-induced anisotropy. This process results from the electronic excitation by photon absorption that allows bond switching in ChG semiconductors as explained by Tikhomirov (124). Kolobov described at the beginning of the 1990’s a new transformation called *athermal* photo-induced transformation in a-As-Se films (125). At this point two theories confront each other: the first one relies on the photon-induced intramolecular bond breaking that leads to a continuous random network (CRN), while the other
states that intermolecular bond breaking results in a disordered molecular glass. Photo-induced amorphization has also been observed in As$_2$S$_3$ by Frumar (126) and again related to an electronic process rather than a thermal process.

ChG films sometimes show variations in their thickness when exposed to light. Two physical changes can arise upon exposure: photo-contraction (thickness decrease) or photo-expansion (thickness increase). Hamanaka (127) showed that an As$_2$S$_3$ thin film could present an expansion of ~ 0.5% after illumination. This was also demonstrated by Kimura (128) and Mikhailov (129). Note, that it has also been shown that stress in ChG materials could be removed by illumination (130, 131). However, at this point the macroscopic phenomenon (132) cannot be explained and the photo-expansion mechanism is still speculative (114, 133). Finally, Hisakuni observed a so-called giant photo-expansion (134) in As$_2$S$_3$ and GeS$_2$ by illumination with a He-Ne laser (hv = 2.0 eV) for roughly 10 s. An expansion of 3 µm was observed for a 50 µm thick film, which was 10 times bigger than any other expansion observed in these materials.

Another modification shown by Hisakuni and Tanaka in an As$_2$S$_3$ material is the photo-induced softening (a.k.a. photo-induced glass transition or photo-induced fluidity) (135) where the illuminated region of an As$_2$S$_3$ peeled film sample becomes permanently fluid under irradiation by a He-Ne laser. This is proposed to be due to the two-fold coordinated ChG atoms (S here), which exhibit electro-atomic responses and make the glass behave as a soft semiconductor. This phenomenon is athermal. The Urbach tail light was also proposed to be responsible for the PI fluidity.
Krecmer et al. (136) were the first to observe reversible anisotropic volume change induced by polarized light on an As-S film. This showed that anisotropy extends to other material properties beside the optical tensor.

Finally, Saliminia et al. (137) reported the observation of a photo-refractive-like nonlinearity responsible for the formation of giant relief modulations in amorphous semiconductor glasses. The photo-induced softening of the matrix, formation of defects with enhanced polarizability, and their drift under the optical field gradient force was believed to be the origin of the mass transport.

1.5.2.2. Photo-chemical modifications

A number of irreversible transformations can be grouped as photo-chemical modifications. The first ones are photo-decomposition and photo-amplified oxidation where the chemical content of the glass is changed. Dissociation of As$_2$S$_3$ or As$_2$Se$_3$ can take place under electromagnetic radiation equal to $E_g$ as described by Berkes for the photolysis (109):

$$\text{As}_2\text{S}_3 \xrightleftharpoons{h\nu} 2\text{As} + 3\text{S}$$  \hspace{1cm} (1.2)

This photo-decomposition can occur for lasers with photon energy larger than the material bandgap (e.g. an argon laser). Amorphous sulfur can similarly transform into rhombic sulfur. This change can often be visually observed as a “photographic” effect in thin films and the densification is reversible by thermal treatment.
In the $\text{As}_2\text{Se}_3$ case, the decomposition takes place as follows:

$$\text{As}_2\text{Se}_3 \xrightarrow{hv} x\text{As} + \text{As}_{2-x}\text{Se}_3$$ (1.3)

with $0 < x < 2$. These steps might be followed by an oxidation of the arsenic in presence of moisture or oxygen:

The same happens for the $\text{As}_{2-x}\text{Se}_3$ compounds created in (1.3). The $\text{As}_2\text{O}_3$ crystals usually form at the surface of the exposed film. A depletion of arsenic is created in the film and $\text{S}_8$ rings can form before crystallizing. An optical darkening of the glass is then created as explained by Terao et al. (138). Other authors (139) claimed that in the case of $\text{As}_x\text{S}_x$ compounds the energy provided by the illumination was enough to isolate and release the As atoms before step (1.3) takes place.

Photo-diffusion in $\text{As}_2\text{S}_3$ was first shown by Kokado et al. using silver atoms (140). Wagner and Frumar (141) interpreted this photo-dissolution as a photo-enhanced diffusion in a diphasic system with an immiscibility gap. De Neufville and coworkers (116) interpreted the diffusion to be the result of a photo-enhanced oxidation for energy near the $E_g$.

Photo-polymerization is the last photo-chemical mechanism that we will describe in this short review. It translates into a red shift of the optical absorption band (142) and structural transformations in $\text{As}_2\text{S}_3$ and $\text{As}_2\text{Se}_3$ thin films under light illumination with a photon energy equal to $E_g$. During evaporation, $\text{As}_4\text{S}_4$ species are primarily created, along with $\text{As}_2\text{S}_4$, $\text{As}_4\text{S}_5$ and $\text{S}_2$ (143). These molecules impact the wafer during deposition and form a packing of multiple structural blocks, which upon annealing or illumination open and subsequently
polymerize. As a consequence, photo-polymerization takes place through the creation of non-equilibrium holes and electrons aside dangling bonds. Street (144) described the photo-polymerization process by formation of defect pairs $D^+$ and $D^-$ during the photon absorption that react with As-As bonds to obtain As-S or As-Se bonds. Mott et al. (145) explain the polymerization by electron-hole pairs, created by excitation of the non-bonding electrons of the ChG.

Onari et al. showed how to calculate this factor from an Arrhenius plot (146). The final result of this change in structure is an increase in density and refractive index of the film. Kolwicz (147) demonstrated that after prolonged illumination the properties of the film were almost similar to those of the bulks or annealed thin films.

Finally, photo-polymerization was proved to be the major contribution to photo-darkening during early stages of the irradiation of $\text{As}_2\text{S}_3$ by pulsed and cw ($\lambda = 514$ nm) laser (148) light.

1.5.2.3. Reversible modifications

Reversible photo-structural changes are defined as modifications induced by light in amorphous bulk (149) and thin films, which when annealed below $T_g$ (116) can be cancelled or reversed by thermal treatment. Note that reversible modifications do not apply to crystalline materials but only to disordered ones, due to the much higher photon energy necessary to induce structural changes in crystals.
The most important reversible phenomenon is known as photo-darkening (PD). As summarized by Ke. Tanaka (92), PD induces changes in density, hardness, softening temperature, dielectric, photo-electric and acoustic constants. Berkes (109) and de Neufville (116) were the first to highlight the PD process in As-S and As-Se alloys. When an amorphous (As$_2$S$_3$ for example) film is illuminated with light with photon energy close to $E_g$ (equal to 2.4 eV for As$_2$S$_3$) it results in a red shift (i.e. toward lower energies) of the absorption band edge and a decrease of the optical bandgap (150). Annealing the film near its softening temperature erases the “darkened” state and this process is often referred to as photo-bleaching (PB).

Photo-darkening can be observed in films thinner than 10-20 µm because it increases the absorption coefficient for the light of wavelength corresponding to the optical bandgap and thus the effective depth of light penetration in the film is decreased (151). This issue of illumination of thick samples and irradiation time (up to one week!) was also raised by Ohtsuka and Tanaka (152).

A consistent feature of amorphous alloys that show PD is the high concentration of at least one species with non-tetrahedral bonds, which allows for more freedom for steric arrangements as a result of the change in the atomic-scale interactions (153). Nakayama and Tanaka recently highlighted in As$_2$Se$_3$ the location at almost the same photon energy of the absorption edge of both the amorphous glass and the corresponding crystal (92). This means that the mobility edges in the amorphous As$_2$Se$_3$ are located at the band edge positions in the crystal. Hence this electronic resemblance induces a structural similarity and therefore the fact that the crystalline compound might be useful in the future in order to explain the PD process. Kuzukawa and coworkers (153) recently correlated the increase in thickness with the decrease in bandgap position in As$_2$S$_3$ and As$_2$Se$_3$ alloys for irradiation under PD experiment conditions.
The next figure shows the magnitude of the maximum reversible shift of the optical absorption edge ($\Delta E$) at various temperatures $T_i$ as a function of $T_i/T_g$ in various ChG and highlights the effects of substituting different Ch atoms.

![Graph showing the evolution of photo-darkening in Ch glasses (154).]

Figure 1.2: Evolution of photo-darkening in Ch glasses (154).

The significant structural differences between As-S and As-Se alloys certainly impact their PD properties. However, the structural basis of this process is not yet fully understood, though believed to be related to some polymerization mechanism.

Vleck and Frumar (155) along with Tanaka et al. (156) showed an increase of $\Delta E$ with the arsenic content in both S and Se-rich alloys. It was also noticed that in S-rich glasses no homogeneous phase existed when the As$_4$S$_4$ molecule was produced in significant quantity in the range $0.44 < x < 0.5$ for As$_x$S$_{1-x}$. A strong PD was recorded for the same range (157) but As$_4$S$_4$ was shown to play no role in the PD process (158). In As$_x$-Se$_{1-x}$ glasses, the optical gap shows a
continuous increase in $\Delta E$ as a function of the As concentration up to $x = 0.6$, after which is rapidly decreases (159). In $\text{As}_x\text{S}_{1-x}$ glasses, Malinovsky et al. showed a decrease of $\Delta E$ in S-rich compositions (160), accordingly to the results shown in the previous figure.

As described previously, photo-bleaching (PB) is the opposite effect of PD. The temperatures induced by the irradiation have to be slightly higher than for PD in order to obtain PB (161). An optical bleaching threshold temperature above which PB can be observed can then be defined for each composition. Lyubin remarkably described the modification of the transmission in an $\text{As}_2\text{Se}_3$ thin film under He-Ne illumination at various temperatures (162) and concluded that the value of the transmission after PB or PD was dependent of the illumination temperature, the wavelength and intensity of the light source.

Photo-induced anisotropy (PIA) was discovered in 1920 by Weigert (163). Both amorphous thin films (164) and bulk materials (165) are subject to this anisotropy upon illumination by light. This PIA can exist under different forms such as birefringence, dichroism, change in the intensity of the photo-luminescence or difference in the fine structure of the X-ray absorption edge for parallel or perpendicular polarizations. Note that the axis of the anisotropy can be rotated by changing the exposure light polarization. Optical anisotropy can be observed in annealed or photo-darkened glasses and can be erased by proper annealing.

Murayama showed in the case of $\alpha\text{-As}_2\text{S}_3$ that the absorption coefficient in the Urbach tail was higher in the perpendicular direction to the polarized beam than in the parallel direction (166), with irradiation using an unpolarized beam, giving the highest absorption value. Lyubin (167) and Lee (168) explained these differences by an oscillation dependent on the light intensity and on temperature. Kolobov and coworkers (169) pointed out that the sign of the PIA depended on the photon energy of the exciting light due to a change in the bond arrangement. Hajto et al.
(170) described a technique to eliminate the PIA by irradiation with an unpolarized beam without modifying the original PD. The resulting dichroism reaches a maximum for electrons with the highest probability of excitation from the states at the top of the valence band, originating from the orbitals of the LP. Thus the photons of high energy will excite the electrons from lower states and create PD without anisotropy, suggesting that PD is related to medium range structure while anisotropy is a particular form of reorganization linked to the polarization of the beam.

Fritzsche established that PIA was possible in ChG because these latest contain anisotropic entities (174). According to this, any event creating a structural change in the microscopic species will influence the nature of the local PIA, without necessarily creating a macroscopic anisotropy. Elliott and Tikhomirov (165) developed this concept into a two part microscopic mechanism: random creation of dipole moments inducing an optical irreversible scalar component and reorientation of structural units as a function of the electrical vector of the irradiated light causing a reversible vectorial component. Emelianova (172) explains this PIA using an electron-hole model and the creation of geminate pairs trapped by localized states.

Lyubin and Tikhomirov proved (173) that PIA could be also created in As$_2$S$_3$ with light of energy lower than the optical bandgap of the material and that an ellipticity of the beam was created by rotation of the polarization plane. Hajto and Ewen (174) showed that As$_2$S$_3$ exhibits a natural optical activity in addition to the PIA.

Among other reversible PI effects, an example of photo-induced birefringence in As$_2$S$_3$ and As$_2$Se$_3$ was shown by Jdanov et al. (175). Lyubin and Tikhomirov observed the existence of PI giotropy, i.e. PI circular birefringence in As$_2$S$_3$ (173) and this latter property was determined by spatial dispersion. They also showed PI scattering, as proved by the modification of the
1.5.3. Models for photo-induced processes

The photo-darkening (and its opposite, photo-bleaching) effect is obviously based on structural changes as we highlighted in the previous section. A number of models have been proposed since the first one in 1977 by Street. Some of them are based on the suggestion that bonds get broken and rearranged, while others propose that these bonds are left unchanged while various modifications of the coordination spheres (except for the first sphere) take place. As these models and the lack of a conclusive mechanism suitable for a range of chemical compositions is one of the bases of this study, we choose to review the various PI models, in chronological order.

The first model was proposed by R.A. Street in 1977 (144) and is based on the creation of electrically charged defects during covalent bonds breaking. An electron-hole pair is produced first after absorption of a photon, and a bonding state (exciton) is generated. The recombination of the exciton can take place either by direct recombination to the fundamental state or through the creation of a metastable pair $D^+D^-$. According to Street, the excitation of the self-trapped excitons increases the absorption which in turn creates the shift of the optical absorption edge. Applied to a-As$_2$S$_3$, this model anticipates the creation of valence alternation pairs (VAP) due to the eventual formation of homopolar bonds when the As-Ch bond breaks. Elliott (114) predicted
that a tetra-coordinated arsenic (\(\text{As}_4^+\)) species bonds with a single-coordinated Ch atom (\(\text{Ch}_1^-\)) to give an \(\text{As}_4^+\)-\(\text{Ch}_1^-\) pair accompanied by the creation of an As-As bond. The Street’s model, however, is not complete since it suggests the formation of a large amount of these over- and under-coordinated bonds, which is not the case.

The second model developed in 1980 by Tanaka for the As-S system (176), relies on the existence of localized defects whose density was determined in multiple studies (157, 175). A quasi-stable arrangement is created upon irradiation through an intermediate excited state while a thermal process will return the metastable state back to its fundamental configuration. A bond twisting mechanism can also take place to favor the process. A return to the fundamental state can be accomplished by heating the material at \(T_g\). This model could not work for stoichiometric germanium-Ch though, as the twisting of the bond is prevented for Ge due to its being tetra-coordinated and the absence of conjugated positions. Tanaka introduced the possibility of ChG trimers to allow his model to work, however such a configuration is so far, only a hypothesis.

Grigorivici developed his model in 1981 for \(\text{As}_x\text{Se}_x\) (\(x < 4\)) based on a photo-polymerization process (177). Starting from the existence of three states (a fundamental molecular state, an intermediate excited one and an excited metastable one), one can jump from one to another by means of phonon- and photon-assisted transitions. The energy of an absorbed photon helps to break the intramolecular bond in every molecule and a dimer is formed after reorientation of the atoms. Note that the intervention of a second photon is necessary when the system is in the intermediate state. This model fits successfully the PD, PB and thermal bleaching processes while giving a qualitative answer to micro-hardness or solubility changes. However, it does not detail the structural modifications taking place.
The same year (1981), Kolobov et al. developed a theory that represents the various configurational states of specific isomers (178). This implies that interatomic distances in rings or chains of ChG elements are shorter than between the molecular units. Bonds can be broken then created under light irradiation between different chains or rings, without implying a change in bond types. As explained by Kolobov et al. (178), when adding additional As to As$_2$Se$_3$ the arsenic atom is introduced in the structure with a free bond, allowing further bonding and distortion. Under light irradiation further bond breaking and formation is possible along with an increase in rigidity of the network. The induced bonds get stretched thus creating a reduction in energy to ionize the atom. This explains the optical shift toward lower energies and the PD. The problem of this model lies in the fact that it cannot explain the volume expansion linked to PD.

Kolobov recently developed a nanometer scale mechanism for the reversible photo-structural changes in amorphous chalcogenides. After photo-excitation, one LP electron is left in the LP orbital while the other LP electron goes into the anti-bonding state. A bond might then be created between chains forming a C$_3^0$ pair (where C represents the chalcogen, the superscript is the charge and the subscript is the coordination number) instead of the previous C$_2^+$. -C$_2^0$. The bond corresponding to the C$_3^0$ pair can then return to its initial state or other bonds can break, which will form VAPs. Any creation of defects will induce displacements of the atoms of the network. The consequent repulsive interaction between LP electrons result in the shift of the top of the valence band to higher energy thus resulting in a decrease in the optical gap.

Malinovski established a model in 1982 and in the following years with his coworkers (179, 180). They proposed that the heating taking place during the illumination induces PI structural changes. Their assumption is based on non-radiative recombination of the photo-
excited carriers through multiphotonic transition. However, it seems that the temperature
dependence of the PD between 100 and 300K contradicts the model.

Popescu in 1985 tried to simulate the structural changes taking place during PD in a-
As$_2$Se$_3$ (181). This model is primarily structural and does not introduce the anisotropic centers
developed by other models. He explained the variation of the intermediate range structure and of
the homopolar bond content in the material. However, some verification related to photo-
structural phenomena still have to be established according to the author himself.

Elliott in 1986 proposed the so-called “unified model” (182), which is based on the
breaking of inter- and intramolecular bonds. This latter process would occur be due to the
creation of self-trapped excitons and bond switching, while the breaking of the weak
intermolecular bonds follows the creation of a hole in the LP orbital of a chalcogen that would
lead to a shift away of the same chalcogen and its neighbor. This model has the advantage that it
explains the intermediate range structural modifications confirmed in experiments by Yang (56).
However the content of As-As bonds given by Elliott’s model is too small as compared to those
observed in the literature.

The LPS model was developed in 1989 by Lee, Paessler and Sayers (183) and is based on
experimental results showing that the PI structural modifications involve specific local atomic
configuration. In the model, the main cluster S'(As'S$_2$)$_2$ is centered on a S atom, placed in
between two pyramidal As$_2$S$_3$ units. The As atoms at the extremity of the cluster are bound with
S atoms to form an 11 atom configuration. Upon absorption of a photon, one LP electron of the
central sulfur atom transfers as exciton or to a conduction band state, which weakens the $\pi$
character of the bond and enhances the $p$ character. By rapid thermal processes, the original $\pi$-
type bond can be transformed into a $p$-type one. The obtained structure is then believed to be symbolic of the PD. In the end, an anisotropic sulfur center with helicoidal surrounding structures arises.

Fritzsche presented in 1993 (184) a model describing the multiple features of the PI changes for both reversible and irreversible changes. He claims, according to the data accumulated through the years by the scientific community, that the PI transformations affect all the atoms and not only just specific sites as proposed previously. Starting from the habitual electron-hole pair formation, he proposed that the recombination process induces shifts in atomic configurations and spatial positions. The PD is explained by interactions of LP electrons.

Shimakawa’s layered model describes both PD and volume expansion observed in a-$\text{As}_2\text{S}_3\text{Se}$. Shimakawa et al. (185) proposed a short-range arrangement made of a stack of layers similarly to crystals. In this model, photons are absorbed upon illumination and the absorbing layers get negatively charged, creating a repulsive Coulomb force between layers, thus weakening Van der Waals force, increasing the interlayer distance and producing volume expansion. This also explains the increase in distance between two As atoms and in the valence angle of S atoms (56). Only the slip motion of the layers is described to be related to PD.

Finally, Meherun-Nessa et al. have recently (186) proposed that the fundamental optical absorption in amorphous ChG could be explained by considering the fractals, which Zallen (187) described as dominating most of the physical properties in amorphous semiconductors. They described the concept of density of electronic states on fractals and showed that disorder was influencing the nature of the density of these states.
1.5.4. Models for photo-induced anisotropy

Despite some authors claiming that the PIA mechanism is still vague, several models have been proposed to explain this process.

Grigorivici et al. proposed a model with VAP states (188) similar to the isotropic transformations taking place in PD, the only difference being that PD preferentially induces the orientation of covalent bonds.

Popescu’s model involved computerized structural simulations (181). This model uses a layered As-Se structure. Polymerization takes place under illumination, two As-As bonds get broken and the center As₄S₄ molecule is inserted in the network. In case of polarized light, the center molecule results in a different final orientation.

The LPS model based on 11 atoms already presented is similar to the previous one and involves a twisting of the molecule where the bond angle \( \theta_{\text{As-S-As}} \) increases and As-S distance remains constant. The structure of the As-Ch is determined by the bonds between the AsS₃ pyramids and the position of the chalcogens is defined by the dihedral angles As-S. Two environments (bridge and helix) can exist around S atoms. The helicoidal configuration leads to a twisting of the two AsS₃ pyramids on each part of the bridging atom while the bridge configuration leads to a symmetrical oscillation of the bridging atom without twisting.

Fritzche proposed (189) that a cumulative effect will reduce the absorption for the polarization direction of the incident light and enhance the absorption along the other
perpendicular directions, thus creating anisotropy. In case of non-polarized light, the increase in absorption takes place along the direction of incidence of the non-polarized beam.

Tikhomirov and Elliott (165) explained PIA using the concept of intimate VAP’s (IVAP’s), similar to previously mentioned D⁺D⁻ and C⁺⁺C⁻⁻ pairs, which also justify the coexistence of diamagnetism and pinning of the Fermi level in the gap of the ChG. The idea of Tikhomirov is to relate the PI structural changes to the PI charge transfer between positively and negatively charged atoms of the IVAP’s, this transfer inducing changes of the micro-anisotropy and chirality of the IVAP’s and their neighbors with polarization of light. This explains also the PI-gyrotropy (190) (dichroism and birefringence mentioned earlier) induced by circular polarized light in ChG. As a conclusion, PIA is explained by Tikhomirov as the result of bond flipping at IVAP’s.

Finally, Fritzsche wrote (191) that ChG become optically anisotropic because they contain some entities which are optically anisotropic. Any hole-electron pair recombination will change the nature of the original anisotropy. The absence of electron-hole pair diffusion and the geminate nature separates recombination events contributing to anisotropy from those leading to isotropic changes. Hence the dependence on temperature or photon energy of anisotropic and isotropic PI changes is different.
1.5.5. Other photo-induced modifications

UV exposure was found to alter considerably the mechanical strength of As$_2$Se$_3$ fibers (192). A large PD was created by various UV irradiations ($\lambda = 193$ nm, 248 nm and 308 nm) by Barasch et al. (193) and the spectral composition of the radiation was found to influence only the efficiency of the reaction, thus highlighting the athermal character of the phenomenon. Hayashi et al. also observed the shift of the absorption band edge toward lower energies using UV exposure on ChG and showed that the creation of inner core holes in the As 3d shell was responsible for the high rate of PD induced by UV (194).

1.6. Applications of chalcogenide glasses

The range of applications for ChG is as large as the number of compositions studied through the decades. The main properties the As-S-Se ChG possess that most influence their use are their wide IR transparency window (up to 12 $\mu$m), their photo-sensitivity, their recently discovered high nonlinearities and their convenient processing. Once again, we will focus here on As-S-Se based materials.

Discovered by Ovshinsky in 1959 (195) and quickly applied as soon as 1962 by Pearson (196) or Eaton (197) to the As-Ch compounds, the switching behavior in amorphous alloys is a major application of ChG’s. The actual devices employed today are 6 orders of magnitude faster
than the first ChG switch. Another device is the thermo-switch, based on As-Ch compounds doped with silicon.

Xerography is also historically one of the first applications of Ch materials in the industry. Many compositions are used for xerography, As$_2$Se$_3$ and As$_2$S$_3$-based films being often the materials of choice. Chalcogenide compounds can also be found in integrated radiographic systems based on As-Se materials among which one has been implemented in the Montreal General Hospital in Canada (198), photo-thermal (199) recording, bubbles recording (200), holography and information storage in As$_2$S$_3$ films (201). Gratings have also been largely taking advantage of materials such as As$_2$S$_3$ as the abundant literature on the subject shows (202, 203).

Summaries of the different chalcogenide materials for high diffraction efficiency applications along with their maximum resolution and diffraction efficiency were published by Keneman (108) and Ovshinsky (204). Recently, Teteris et al. reported the change in diffraction efficiency in a-As$_2$S$_3$ as a function of aging, recording light intensity, temperature or substrate (205, 206).

In the recent years, emphasis has been placed on acousto-optical devices (207) and optical media (208) or photonic bandgap structures (209). The telecommunication field expansion gave rise to extensive research on optical As$_2$S$_3$ fibers (210) and thin films eventually doped with erbium (211) for use in the IR ($\lambda = 0.8$-$12 \mu$m). These fibers find their passive applications in IR imaging (212), laser power delivery (213), thermal imaging (214) and fiber multiplexing (215). Sanghera recently published a detailed review on the topic (216).

Amorphous As$_2$S$_3$ has shown multiple promises for future passive applications such as microlenses (217), arrays for CCD or imaging systems (218). Eisenberg recently showed the
possibility of 3D plane-convex shaping of these microlenses (219), while Saitoh et al. directly wrote lenses on the face end of As$_2$S$_3$ fibers (220).

Finally, the fast development of the nonlinear optics field associated to the recently shown encouraging nonlinear properties of some As-S-Se glasses (106, 221, 222) and fibers (223) should open even more widely the fields of applications of these materials.
CHAPTER TWO: EXPERIMENTAL TECHNIQUES

This chapter is dedicated to the fabrication and characterization techniques utilized for the bulk glasses and their corresponding thin films, prepared and used in this study. A short theory background will be presented in each case along with the reasons for using each particular technique. Where we have published details of such measurements, a reference to that publication is included. The experimental setups will also be described.

2.1. Processing

2.1.1. Bulk glass fabrication

Bulk glasses were prepared following a conventional melt quenching technique, similar to those presented in the previous chapter or suggested by Kokorinova (224) in an evacuated silica ampoule.

Two “generations” of glasses were fabricated. The first and second “generations” were processed respectively in 1.3 cm and 2.5 cm (i.e. 1 inch) diameter ampoules. The reason for this change was due to the notably improved (as measured) better homogeneity of the second generation of bulk materials and the interest in preparing larger batches at once (up to 50 grams in the latter case versus a maximum of 12 grams in the former). The process was the same.
throughout with the exception of a pump change that allowed better vacuum in the line for the second generation of materials. Additional details can be found in papers previously published or submitted (225, 226).

High purity raw chemicals from Cerac (As 99.9995%, S 99.999% and Se 99.999%) were used to obtain the desired quantity of glass. The As-S-Se ternary diagram presented below summarizes the compositions studied. Those used in the present study are numbered as shown for future reference.

![Figure 2.1: Compositions studied in the ternary diagram As-S-Se. The shaded area represents the glass forming region according to Hvorostenko (227).](image)

In order to avoid any poisoning or contamination of the resultant material, elementary starting materials were weighed and placed in a high purity silica tube (G.E. materials from QSI Inc.) in a dry box under nitrogen atmosphere. An oxygen getter (an helicoidal piece of magnesium) was eventually used to “grab” surface oxide released during heat treatment to purify
starting materials. The silica tube was thermally pretreated overnight at 900°C in a Lindberg furnace to remove surface moisture and any other contaminants. The tube with its batch was evacuated using a turbo pump (ATH-30C from Alcatel) down to $10^{-6}-10^{-7}$ Torr. A treatment of 4h at 105°C was applied to the tube containing the raw materials. The distillation of the raw materials was performed in a Mellen four-zone furnace at first, but purity studies showed that this step could be avoided with the turbo pump without affecting the purity of the glasses. A methane-oxygen torch was used to seal the tube, which was then placed in a rocking furnace and homogenized overnight at a melting temperature of ~ 900°C. The tube was air-quenched around 500-550°C (depending on the composition) after being removed from the furnace. Annealing was performed in a high purity silica tube placed inside the same furnace used for melting. An argon flow was connected on one end, while a thermocouple and a gas exit were placed on the other end. The cold glass sample was removed from the primary ampoule and placed in a non-reactive boat in the middle of the tube. The sample was heated up at a rate of $2^\circ$C/min up to 40°C below its $T_g$. The temperature was then left stable for at least 6 hours and the furnace was cooled down at a rate of ~ 1°C/min down to room temperature. Bulk specimens were then cut, ground and polished for further characterization with aluminum slurries and grinding (GRIT 1200 and 900) and polishing pads from Buehler. Small pieces were kept for thermal analysis or XRD characterization; the polished discs were used for optical measurements (FT-IR, absorption, etc.) and the remaining glass was sent to the Centre d’Optique, Photonique et Lasers (COPL) in Québec, Canada for thin film fabrication.
2.1.2. Thin film fabrication

Fabrication techniques have been previously described in section (1.3.1.2) (27-31). The fabrication of our thin films was done at the COPL in Québec in a clean room environment. The glasses were deposited onto a silicon substrate by classical thermal evaporation. The process took place in a glass bell jar under a vacuum pressure of $10^{-7}$ Torr. The substrate was rotated on the top of the bell jar for better homogeneity, and was unheated. The bulk glass was broken in small pieces and put in a boat at the bottom of the bell. Up to three substrates can be placed in the jar at the same time. The rate of evaporation was kept constant between 20-30Å/s and permanently controlled by the operator while monitored with a crystal thickness monitor. The typical thicknesses deposited range from 600 nm to 2.5 µm depending on the future application. The samples were then consistently annealed in a furnace 40°C below $T_g$.

2.1.3. Fabrication of structures in thin films

A number of techniques such as photo-lithography, laser beam exposure or ion implantation have been developed in the past to create structures in a ChG thin film or on its surface. Hunsperger gives a good review of these in his book (228). We will limit ourselves to those of interest for our study, namely photo-lithography and laser irradiation.
2.1.3.1. Waveguide fabrication by chemical etching

The first technique used was chemical etching. The principle is to first deposit a photoresist layer on top of the freshly deposited thin film and harden the resist through a heat process. A UV lamp ($\lambda = 320$ nm) is used to expose the sample through a specially designed mask which incorporates the desired features (vertical lines in our case) and the film is then “developed” by chemical means, in the exposed zones. The final result in our case was a channel waveguide.

Figure 2.2: SEM picture (side view) of a multilayer ChG film. Photoresist ridges are still observable on the top of the film (229).
Deposition process parameters have been thoroughly investigated in the past in order to obtain ridge waveguides with specified dimensions. Further technical details are available elsewhere (229). These optimized parameters were used in all subsequent deposition of ChG films produced for later evaluation.

2.1.3.2. Structure fabrication by Ar$^+$ laser irradiation

The fabrication of waveguides and other structures in materials using laser sources has been the object of many studies in the recent years. Due in part to the absorption band location in our materials (between 500 nm and 750 nm), we chose two exposure lines: one located at 514 nm (argon ion laser) and one at 785 nm (Ti:Sapphire laser), in order to observe eventual differences in the fabrication processes. The main differences between these two laser sources will be discussed further.
Simple structures such as waveguides have been fabricated in ChG materials in the past using Ar\(^+\) exposure (229). Saliminia et al. demonstrated the fabrication of a Bragg grating with near As\(_2\)S\(_3\)-bandgap illumination using two interfering beams at 514 nm in a multi-layer ChG waveguide (27).

The irradiations by Ar\(^+\) laser (\(\lambda = 514\) nm) were performed at the COPL in Québec. The purpose of these experiments was to fabricate photo-induced features in ChG bulk glasses and their corresponding thin films and to characterize the resulting film property changes as a function of exposure dose. Four glass compositions of interest were identified (As\(_2\)S\(_3\), As\(_{40}\)S\(_{30}\)Se\(_{30}\), As\(_2\)Se\(_3\) and As\(_{24}\)S\(_{38}\)Se\(_{38}\)). The goal of our study was to observe the variations in properties with respect to the bulk materials, understand the compositional effect on the resulting material photo-sensitivity for bulk glasses and films and finally assess the exposure condition (polarization, intensity or dose) influence on the properties for each composition. Identified chunks of the bulk target materials described previously were used for the thermal deposition of 1.5 \(\mu\)m-thick thin films on glass substrates and oxidized silicon wafers. Polished discs of the same four bulk glasses were included in the study for parallel irradiation on the glass surface.

In order to avoid lengthy exposure on a multitude of samples, we designed an “all in one” sample that would allow regions for multiple exposure conditions, polarization states, and spot/line geometries on a single sample. A schematic of the designs are presented on the next page.

A threshold value of \(\sim 85\) J/cm\(^2\) for As\(_2\)S\(_3\), past which no significant further refractive index increase could be observed, was calculated using previous results from our collaborators (230) to determine the maximum dose for our study. Laser parameters were fixed such that the threshold value would correspond to a 10 min irradiation time and additional illumination
periods below and above this threshold were selected. In the end the irradiation dose was set to cover a range between 0 and 127 J/cm\(^2\) for all four compositions.

Multiple irradiated spots, square areas and waveguides were then created for different polarizations of the beam both in thin films and bulk samples with the argon laser source (\(\lambda = 514\) nm). Note that the laser intensity and polarization of the beam were tuned using a half-wave and a quarter-wave plate, respectively.

Figure 2.4: Schematic of the first test sample for “in-situ” measurements.
Figure 2.5: Schematic of the second test sample for “in-situ” measurements.

The spots on both wafers had the same characteristics to allow one to accurately conduct a comparison of the thermal conductivity between two wafers of the same glass composition. Indeed, as of today we can only measure relative conductivities and no absolute conductivity with the probes we have. One paper (231) has reported absolute measurements but the probe was specially designed and is not available commercially. The spots were created through squared apertures (2.4mm x 2.9mm) at selected energies. The thin films were created through a mask with designed lines on it. The length of the waveguides was ~ 2 inches.

The following characterizations were performed:

- Refractive index characterization and absorption spectroscopy on bulk materials and films deposited on glass substrates,
- Waveguide-Raman spectroscopy and micro-thermal analysis on 2D-waveguides.
All of the resulting samples were stored in the dark to avoid any crystallization or any other light induced modifications or contamination.

2.1.3.3. Waveguide fabrication by fs laser source

Laser-induced breakdown in dielectrics has been extensively studied and the “long pulse” ($\tau_p > 10\text{ps}$) versus “short pulse” regimes ($\tau_p < 10\text{ps}$) have been well documented (232). Short pulses have the advantage of creating no heat transfer to the material lattice and the structures created are localized. Multi-photon absorption, tunneling ionization and impact ionization can be involved and both physical ablation and refractive index modeling can be achieved. Other advantages of femtosecond laser writing lie in the sharp intensity-dependent threshold which permits modification to occur only near the beam focus, and high spatial resolution that can exceed the diffraction limit. The deep penetration of a near-IR beam within these IR-transparent media also allows for writing of 3D-structures in a wide variety of glasses (233-236). While initially working intensities could be achieved with kilohertz repetition rates with microjoule energies (237), recent studies have shown advantages such as faster processing speed when using MHz repetition rates with lower pulse energies using femtosecond laser oscillators (235, 236).

Efimov et al. wrote waveguides in an As$_2$S$_3$ thin film in a prior collaboration with our group at CREOL using a train of femtosecond (fs) pulses at 840 nm i.e. below the bandgap of the material (238). Meneghini and Villeneuve (239) showed the possibility of photo-modifying As$_2$S$_3$ by interfering two beams of light at $\lambda = 800$ nm. More recently, our group focused its efforts with the Laser Plasma Laboratory (LPL) at CREOL (Dr. Martin Richardson) on the As$_2$S$_3$
material (240). In this study we expanded our field of knowledge to the same four compositions used in parallel with Ar\(^+\) exposition.

A femtosecond (fs) laser oscillator developed at CREOL by the LPL was used for 2-D waveguide fabrication. The source was a fs (44 fs) Ti:Sapphire laser (\(\lambda = 785\) nm) with a repetition rate of 27 MHz. The measured energy per pulse was 20nJ. The Gaussian laser beam was focused with a Schwartzschild microscope (15x objective, working distance 24 mm) onto the sample. The laser intensity was tuned with a variable metallic neutral-density filter placed before the microscope objective. The sample was placed on a 3-D motorized stage to allow for precise motion control.

Deposition conditions of the ChG films were identical to those reported for the Ar\(^+\) irradiation experiments. The ChG compositions of interest were again As\(_2\)S\(_3\), As\(_{40}\)S\(_{30}\)Se\(_{30}\), As\(_2\)Se\(_3\) and As\(_{24}\)S\(_{38}\)Se\(_{38}\). In order to obtain photo-induced waveguides of good quality in these films, we first assessed the threshold between ablation and photo-induced writing in the four materials mentioned above by writing spots and increasing the laser intensity at the same time until ablation was observed. The second step consisted of fabricating irradiated squares, made of multiple photo-induced lines scanned along the whole area, with a total surface of 1 mm\(^2\) and a jump between written “lines” of 5 \(\mu\)m. In the last step, we fabricated 2D-waveguides in the thin films deposited on oxidized silicon wafers with the same or similar laser intensities used to write the irradiated squares. These waveguides were 2.0 cm to 2.5 cm long after writing due to the limitation of the translation stage and 1.0 cm to 1.5 cm long after cleaving.
Various optical experiments were then performed. The results of these are presented in the next chapter. Structural changes were assessed using waveguide-Raman spectroscopy according to the method described later on in this chapter.

Physical changes at the surface of the samples were observed using white-light interferometry with a Zygo instrument (New View 5000) which also highlighted the optical phase changes of the different features. From these measured phase change data, induced index changes imparted in the films following laser exposure, could be determined.

2.2. Homogeneity and Purity assessment

Except for the sulfur-rich compounds, ChG present an absorption edge located around 800 nm making them opaque for IR radiations in the visible range. The presence of physical defects in the glass (such as striae, flaws, crystal phases, inclusions or bubbles deriving from bad melting practice) has been assessed using techniques other than the simple “naked eye”. We present in this section various techniques typically employed in this study to determine the homogeneity and the purity of our melts.
2.2.1. Homogeneity

The last step of processing ends as explained previously, by a melting phase in a rocking furnace. This rocking has to be stopped before quenching of the melt to a solid. As a consequence, a gradient of concentration with the various species (As, S or Se) can be created in the bulks thus leading to a sample with non-homogeneous physical and optical properties.

A homogeneity study was undertaken to assess the effect of compositional variation on the absorption edge position and other properties in our glasses as a function of position within the melt (boule) and between melts. Such movement of the edge had been shown in previous studies in our group (106, 241) to accompany chemical (As/S/Se concentration) variation.

We fabricated a series of As$_{24}$S$_{38}$Se$_{38}$ glass samples with varying melt parameters (e.g. batch size, distillation, quenching temperature, annealing) and measured the density, $T_g$, linear index and Raman ratio of these compositions, accordingly to the procedures that will be described in the next paragraphs. More details on the resulting, optimized melting parameters and specificities of this study can be found in a previous paper (225).

2.2.2. X-Ray Diffraction (XRD)

XRD was discovered by Max Von Laue in 1912 and immediately applied to structure determination in 1913 by W.L. Bragg and his father W.H. Bragg. XRD is presently the most widely used technique to detect the presence of a crystalline phase in glasses. X-rays energies
range from 200 eV to 1 MeV in the electromagnetic spectrum, in between ultraviolet radiation
and γ-rays.

X-ray diffraction is a combined effect of scattering and interference (243). Scattering is a
process of absorption and reemission of an electromagnetic radiation. According to this, an x-
ray photon is absorbed by an atom and another photon is emitted with the same energy (elastic
scattering). If the scattered waves are in phase they interfere constructively and form diffracted
beams with specific directions. The well-known Bragg’s law associates the wavelength of the x-
rays to the spacing between atomic planes and can be expressed as:

$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$  \hspace{1cm} (2.1)

where $d_{hkl}$ is the interplanar spacing (factor of the structure), $\lambda$ is the wavelength and $\theta_{hkl}$ is the
angle between the atomic plane and the incident and diffracted waves.

Bragg’s law is used for indexing diffraction patterns and assessing the crystal structure of
the material for example.

A RIGAKU X-Ray diffractometer was used at CREOL to confirm the absence of
crystallinity in the different glasses prepared. An electron beam with very high velocity is
generated by a heated tungsten filament cathode with a high negative potential and directed onto
a water-cooled copper anode at ground potential. The loss of energy of the electrons at the
impact with the anode is displayed by X-rays with energy of ~ 8 keV and wavelength of 1.542 Å.
Only a small percentage (usually less than 1%) of the beam is converted into X-rays, the rest
being dissipated as heat in the water-cooled copper anode (242).
The ChG samples examined by XRD were ground into a fine powder with a pestle and a mortar, then deposited on double-sided tape, which was itself placed on an aluminum holder. This resulting sample was then inserted in the characterization chamber. Data acquisition was made with Data Scan 3.1 and analyzed with Jade 3.1 (from Materials Data Inc.) software in the 2θ range from 10° to 80°. Step size was set to 0.04° and a scanning speed of 2.4°/min was employed.

2.2.3. Energy Dispersive X-Ray Spectroscopy (EDS)

EDS is a spectroscopic technique that allows qualitative and quantitative determinations of the elements present in a sampled volume with a typical lateral resolution of ~ 1 µm and sensitivity of ~ 1 atomic percent.

An electron beam focused by an electronic microscope interacts with the atoms of a sample. As the electron beam displaces electrons in the sample, detection equipment converts the electrons scattered by the electron beam to into a microscopic image.

An electron from an outer atomic shell of the atom drops into the vacancy created in the inner shell by the beam, allowing the atom to return to its normal state. The difference in energy between the vacant shell and the shell contributing the electron is lost under the form of element specific X-rays. A semiconductor material is used to detect the X-rays and an energy dispersive spectrometer discriminates among X-ray energies.
The experimental graph often mentions the different shells (K, L, M) involved in addition to the element name. These characteristic lines are related to the Bohr model of the atom. Figure 2.6 shows a schematic of the origin of some characteristic lines.

![Diagram of electron transitions in an atom producing characteristic X-rays](image)

Figure 2.6: Electron transitions in an atom producing characteristic X-rays. Adapted from Suryanaryana (242).

In EDS, data is collected for all energies at once, and is displayed as a histogram of electronic counts versus x-ray energy. As a consequence, the analysis is both qualitative (for elements with atomic numbers between that of beryllium to uranium) and quantitative without any need of standards. The minimum detection limits is typically from 0.1 weight percent to a few percent and is dependent on the element and matrix.

The equipment employed in this study was a JEOL 6400 Scanning Electron Microscope (SEM) with Kevax, located at the Materials Characterization Facility (MCF) at the University of Central Florida. This equipment allows magnification in excess of 200,000 times for high accelerating voltage.
The samples were typically glass chunks in order to evaluate the composition both inside and at the surface of the sample. The glass pieces were placed on a holder by double sided tape. A thin coating (10 nm) of Pd/Au was first deposited on top of the chunks in a vacuum chamber for detection purpose since some of the ChG have very low conductivities. The acceleration voltage and the acquisition time were set at respectively 20 keV and 60 seconds. The KLM peaks of As, S and Se were obtained and the integration was performed by the software. The typical sensitivity is less than 1% atomic content.

2.2.4. Fourier-Transform Infrared (FT-IR) spectroscopy

FT-IR combines the advantage of IR spectroscopy and Fourier-Transform to allow the identification of functional groups and the detection of presence of impurities.

When a molecule absorbs specific frequencies of IR radiation, vibrations or rotations of the functional groups are created and an absorbance spectrum regrouping the absorbed frequencies can be observed. This spectrum is specific to each molecule, which allows an experimenter to know with precision the functional groups forming the sample. In addition, the radiation absorbed is proportional to the concentration of each compound. This electronic process is combined with Fourier Transform, named after Jean-Baptiste Joseph Fourier (a French mathematician), which converts time-based signals (described as series of sinusoidal terms) into the frequency domain.
The Fourier-Transform of a complex function \( g \) of two independent variables \( (x \text{ and } y) \) can be represented by \( \mathbb{F}\{g\} \) as defined by Goodman (243):

\[
\mathbb{F}\{g\} = \int\int_{-\infty}^{\infty} g(x, y) \exp[-j2\pi(f_x x + f_y y)]dxdy \tag{2.2}
\]

where \( f_x \) and \( f_y \) are two independent variables referred to as frequencies. Accordingly, the inverse Fourier-Transform of a function \( G(f_x, f_y) \) is represented as:

\[
\mathbb{F}^{-1}\{G\} = \int\int_{-\infty}^{\infty} G(x, y) \exp[j2\pi(f_x x + f_y y)]df_x df_y \tag{2.3}
\]

The locations of extrinsic and intrinsic absorption bands (S-H, Se-H, C-S, As-O, Se-O, S-OH, etc…) in the ChG spectra in the range 5000-500 cm\(^{-1}\) has been extremely well summarized by Kokorina (244) and Seddon (32).

The IR beam used in FT-IR is split into two components in an interferometer, one component traveling to a mirror placed at a fixed distance and the other one to a moving mirror, thus creating constructive and destructive interferences. The resulting interference pattern (a.k.a. interferogram) is a time-based function that is translated as a function of frequency after Fourier-Transform. This is the spectra obtained which is nothing less but a pattern of the absorbed frequencies.

We used the FT-IR spectrometry to assess the purity of our sample, i.e. verify that no oxygen, hydrogen or carbon-based bonds had been created with the elements (i.e. As, S or Se) of
the batch. The equipment was a Mattson Infinity 60MI spectrometer with a 0.50 cm\(^{-1}\) resolution and equipped with a KBr beamsplitter (7000-350 cm\(^{-1}\)) at the National Center for Forensic Science (Orlando, Florida). The system is entirely automated and controlled by computer (Winfirst 3.57 by Mattson Inst.). Glass polished discs were placed on a double-sided tape bonded to the sample holder. Nitrogen gas was used to equilibrate the atmosphere in the sample compartment. A background was first acquired and automatically subtracted from the data. Each spectrum and background was the result of 32 successive scans with a forward velocity set at 10 kHz and a reverse velocity at 25 kHz.

2.2.5. X-Ray Photoelectron Spectroscopy (XPS)

XPS allows elemental, chemical oxidation state and bonding information while providing contamination analysis.

The external photoeffect (where electrons are ejected from an irradiated matter) was discovered by Hertz in 1887 from which Einstein postulated his quantum theory of light. The first use of photoelectron spectroscopy as a technique to determine the electronic structure of a material accounts around the 1940’s.
In the XPS process, photons with a given energy $h\nu$ are absorbed and cause the emission of an electron above the Fermi level $\phi$ with an energy:

$$E_{kin} = h\nu - E_i - \Phi$$  \hspace{1cm} (2.4)

where $E_i$ is the binding energy of the electronic level that was excited by absorption of the photon. An electron energy analyzer is typically used to measure the energy distribution. The photoelectron emitted has an energy characteristic of the atom involved and the total photocurrent is directly proportional to the concentration of the atomic species involved in the near surface region of the sample (245). Note that any binding energy shift due to chemical bond formation involving a change in the electronic charge is resolved by XPS. Hence XPS is a useful technique to determine the environment of an atom. The source used is typically a metal-target x-ray tube or a synchrotron radiation source.

We used XPS first to assess the magnitude of eventual oxidation (or other contaminants) in our glass and secondly to obtain information on the local chemical bonding of the As and chalcogen elements. The method has already proved valuable on many materials and specifically in our case on As-Se glasses (246).

As described by Seal et al. (247) a PHI 5400 ESCA was used to study the bulk and film samples under a vacuum of $10^{-9}$ Torr. A Mg-K$_\alpha$ x-ray source was used for the analysis. Survey scans were recorded between 0 to 1000 eV. More details are available in the publications referenced above.
2.3. Density measurement

Density refers to the mass contained within a unit volume under specified conditions and is usually given in kg/m$^3$. Density of the bulk glasses was measured by the Archimedes (or buoyancy) method. Archimedes' Principle states that the apparent weight of an object immersed in a liquid decreases by an amount equal to the weight of the volume of the liquid that it displaces.

The apparatus consisted of a beaker filled with diethyl terephtalate put on top of a Mettler AE 163 analytical balance. A bridge was clamped to the balance pan and a sample sinker/holder was placed on the same bridge. A thermometer was placed in the liquid. The principle is to measure the weight of the sample in the air ($m_A$) first, then place the sample on the sinker part and plunge it in the beaker in such a way that the sample is covered with at least 10 mm of liquid. After making sure that no bubbles were trapped in between the glass and the sinker, the weight of the sample is measured in the liquid ($m_L$). The density of the diethyl ($\rho_D$) is obtained from a calibrated table knowing its temperature. Thus the density of the glass $\rho_g$ is calculated using:

$$\rho_g = \rho_D \cdot \left( \frac{m_A}{m_A - m_L} \right)$$

(2.5)
Each sample was weighed five times and the average density was recorded, along with error bars representative of the first standard deviation. The accuracy on the measurements was ±0.002 g/cm³.

### 2.4. Hardness testing

One of the most important changes in a glass due to a structure modification is the micro-hardness. This property has been shown to depend linearly on the concentration of atoms (224). Hardness is a measure of the amount of force required to plastically deform a material. It can be measured using multiple methods and are usually given in Knoop or Vickers numbers.

In the Knoop method a pyramidal diamond-shaped head is pressed into the sample with a given load (248). From the dimensions of the indentation and the load value one can calculate the hardness of the material. These values range from 2000 for hard materials such as sapphire or 7000 for a diamond down to 4 for a soft material. The Vickers hardness should be reported following (as an example) 700 HV/0.2 and as a number only i.e. without the kg/mm² unit, which means in this case a Vickers hardness of 700 was obtained using a 0.2 kgf force. Vickers hardness can also be reported in MPa units (multiply Hᵥ in kg/mm² by 9.807).
The Vickers method uses a different indentation head with a square base and an angle of 136 degrees between opposite faces. The Vickers hardness of a test piece is calculated by dividing the indenter load ($L$) by the area of the indentation ($d^2$).

$$H_v = \sin \frac{136^\circ}{2} \times \frac{L}{d^2} = 1.8544 \times \frac{L}{d^2} \text{ (in kg/mm}^2)$$

(2.6)

Other hardness values such as Moh or Rockwell are more specific and rarely used and are not as appropriate for brittle solids such as glass. Unfortunately there is no simple calculation method to convert the different hardness between them but conversion tables or charts are available for this purpose.

This study employed a DUH-202 dynamic ultra micro hardness tester (from Shimadzu). The technique consists of applying a load to a test piece to create an indentation. The surface area is then calculated through measurement of the length of the diagonal lines of the created indentation, after the removal of the load and following the method mentioned previously.

All of our experiments were carried on bulk glass samples with a thickness ranging from 1.5 mm to 2 mm. The same procedure was applied to the different ChG compositions as follows: After the diamond indenter found the surface of a sample, a predetermined constant loading rate of 7.1 g/sec was electromagnetically applied until reaching the final value of $P = 200$ grams, which is the highest allowed by the equipment. The indenter was left in place for an additional period of 15 seconds before it was lifted off the sample surface. The indentation diagonals were then measured using the eyepiece and a 50x objective. The Vickers hardness was then calculated by the dedicated software using the diagonal length information. Finally, five
indentations were performed for each sample. The results provided represent the average of these five measurements per composition along with the standard deviation (note that the dynamic hardness is automatically calculated during the experiment).

The annual calibration of the indenter was performed before these experiments were carried out and the measurement accuracy on the calibration sample ($H_v = 700$) was found to be $\pm 7$, which is better than the 3% set by the manufacturer.

2.5. Thermal analysis

Thermal characteristics of glasses are one of their most important properties since they are a representation of their processing history and can be linked to other properties. As an example, Phillips (43), Tanaka (259) or Sreeram (250) developed models to relate $T_g$ of chalcogenide or other materials such as polymers to various physical or optical properties.

Among the multiple thermal characterization tools developed, Differential Scanning Calorimetry (DSC) and Micro-Thermal Analysis ($\mu$TA) are viable measurement techniques and have now become widely known and used tools.

By heating a material, one can observe the multiple and successive processes taking place inside the sample. The glass transition temperature ($T_g$) is the temperature at which there is a change in the rate of change of the volume of a glass on cooling or heating. It is the temperature below which the glass is a solid and above which the glass is a liquid. The value of $T_g$ depends
on the cooling or heating rate. $T_g$ is usually specified by differential thermal or calorimetric techniques (249).

2.5.1. Differential Thermal Analysis (DTA) and Scanning Calorimetry (DSC)

DSC and DTA are usually employed for bulk materials since these techniques require a sample with a mass of typically tens of milligrams and a roughly cubical shape with a volume of a couple of mm$^3$.

DTA is one of the oldest and most used thermal characterization techniques due mainly to its simplicity of operation (251). The principle of this technique is to subject the sample of interest and a reference to the same heating program and to measure the difference in temperature ($\Delta T$) between the two materials. If an endothermic event occurs in the sample, $\Delta T$ is no longer equal to zero and a variation in the signal is observed. The same applies to an exothermic event but the signal will then be observed going in the opposite direction.

In a typical DSC experiment, a sample and a reference are both subject to a linear heating ramp. The calorimeter typically records the temperature difference between the sample and the reference and then converts the information into the heat flow that goes into and out of the sample. The supplied energy difference is recorded as a function of the temperature. Thermal events appear as deviations from the baseline. Thus DSC measures temperatures and heat flows associated with thermal transitions in a material. In the case of a glass, one can measure the glass transition temperature ($T_g$), crystallization temperature ($T_X$) and melting temperature ($T_m$).
Other events such as oxidation or decomposition might also be eventually observed. Additional information such as heat capacity, melting enthalpy or apparent activation energy can also be calculated from DSC patterns.

Note that in both cases it is important to mention how the endothermic events are represented, considering that by convention an endothermic (and thus an exothermic one) event in DTA is represented in the opposite way of the DSC convention.

In our study, we will only report the data obtained with DSC since the equipment is more accurate than the DTA in the low temperatures where the $T_g$ of our materials lie. A comparison of data between the two was conducted though and a word will be given on the results.

DTA studies were performed using a Simultaneous TGA-DTA (Model SDT 2960, TA Instruments, New Castle, DE) and a DSC (Model DSC Cell 2920 also from TA Instruments) to obtain glass transition temperatures ($T_g$). Pieces of glass weighing around 30 mg were placed in aluminum pans of high thermal conductivity to ensure an adequate differential temperature signal during a thermal event. The pans were sealed to prevent contamination of the furnace by volatilization of glass components. Both reference and the sample pans were subjected to a heating ramp of 15°C/min from room temperature to 250 °C maximum under a nitrogen purge gas of 96 ml/min in each experiment. The temperature difference ($\Delta T$) and the heat flow (W/g) were recorded respectively in the case of the TGA-DTA and DSC. $T_g$ was measured three times for each sample using the minimum of the first derivative of either the temperature difference curve ($°C/°C$) or the first derivative of the heat flow (W/g/°C). The average of these two measurements and resulting standard deviation were reported for each sample.
TGA stands for thermal gravimetric analyzer. Since the aluminum pans were sealed this part of the equipment was only used to ensure that there was no weight loss during the experiment that would have been immediately related to a leak in the pans.

2.5.2. Thermo-Mechanical Analysis (TMA)

The TMA system used in this study (TA Instruments, model 2940) was used to assess the modifications in glass sample properties resulting from changes in four experimental parameters: temperature, force, atmosphere and time. This technique allows one to measure the melting and softening points, tensile and compression modulus, glass transition and expansion coefficient of a solid, film, fiber or powder form. Note that the DTA and DSC techniques are more sensitive to determine the $T_g$ of a glass as these tools measure actual heat flow, whereas TMA is quantifying specimen distortion and movement.

While some prior data has been obtained in the glass system of interest here in prior work in our laboratory (252), the study did not include many of the compositions of interest to our effort. We were thus interested in measuring the coefficient of thermal expansion (CTE) of our bulk glasses. When a material is subject to a heating cycle, its dimensions change and usually increase with the temperature. The CTE of a glass is defined before ($\alpha$) and after ($\beta$) its $T_g$. $\alpha$ is also called the linear coefficient of thermal expansion while $\beta$ is referred to as the coefficient of volume expansion (248). $\alpha$ is a measure of the proportional change in length of a given sample
for a temperature change of 1 degree and is given either in $K^{-1}$ or $°C^{-1}$ depending on the units, according to the following relationship:

$$\alpha = \frac{1}{L} \frac{\Delta L}{\Delta T}$$

(2.7)

where $L$ is the original length, $\Delta L$ is the variation in length and $\Delta T$ is the change in temperature. $\alpha$ is typically related to the structure and type of bonding in the solid.

A Thermomechanical Analyzer (model 2940, TA Instruments) was used to evaluate the CTE for our glasses. The typical procedure consists of placing the polished glass in the system’s furnace chamber while a penetration probe sits on top of the sample. Liquid nitrogen is poured in the container surrounding the oven to decrease the temperature. Once the temperature has reached a stable plateau, a thermal ramp is applied (usually from 5°C/min to 10°C/min) and the dimension change is recorded as a function of temperature. The coefficient $\alpha$ is easily calculated from the slope of the $\Delta L/T$ curve.

The samples required for this technique must possess two polished parallel faces with a maximum thickness of 1 inch. No minimum value is indicated; however a consequent thickness is needed to minimize the error on the measurement. We used samples with thickness ranging from 3 to 4 mm. The heating ramp was set at 5°C/min due to the lower $T_g$ of these glasses. The starting temperature was established to be around -20°C using liquid nitrogen in the cylinder surrounding the furnace chamber to allow sufficient time to the sample to equilibrate. The final temperature was set at 20°C above the respective $T_g$ of each glass composition. The linear coefficient of thermal expansion $\alpha$ was calculated from 25°C to the inflexion point of the TMA
curve corresponding to the onset of the $T_g$ of the glass material. By using standard references we estimated the sensitivity of the expansion probe to be ± 0.3 µm in the temperature range where the calculation of the linear coefficient of expansion $\alpha$ was performed. This translates to a calculated error of ± 0.01 x $10^{-5}$/°C.

2.5.3. Micro-Thermal Analysis (µTA)

Micro-Thermal Analysis and the science and tools developed to evaluate material changes in small volumes is the result of a joint effort between TA Instruments, M. Redding (Loughborough University, UK), H. Pollock and A. Hammiche (Lancaster University, UK), Thermomicroscopes (California, USA) and Linkam Scientific Instruments Ltd. (UK). The instrument is the product of an evolution through various analytical techniques.

The Atomic Force Microscopy (AFM) developed by Binning et al. (253) has been considerably improved through the last decade. In particular, the development of thermal probes gave rise to scanning thermal microscopy (SThM) and localized thermal analysis (LTA). SThM provides surface thermal conductivity mapping and sub-surface imaging (254), which can also be performed by modulated thermal differential scanning calorimetry (MT-DSC) (255). LTA allows one to observe and measure thermal events such as melting, glass transition and recrystallization within small volumes of materials (a few mm$^3$) as reported by Hammiche et al. (256).
Micro-thermal analysis has become in the last decade a widely used analytical tool for films or aggregates of variety of materials such as biological, semiconductor and polymer samples (257). To the best of our knowledge, few papers have been published in the domain of AFM on chalcogenide glasses (258) however none of them reported SThM or LTA measurements on such materials.

A Micro-Thermal Analyzer system (µTA™ 2990 from TA Instruments) equipped with an Explorer Head was used at CREOL. The thermal probe element consisted of a 5 µm diameter Platinum/Rhodium (90%/10%) thermal resistor from ThermoMicroscopes (Model 1615-00). The nominal resistance of the probe is 2.10 ohms and the temperature coefficient of resistance is 0.00165K. The thermal probe response was calibrated with biphenyl, anisic acid and polyethylene terephthalate samples with known melting temperatures (± 0.1°C). The temperature calibration was checked daily to ensure proper measurements and a standard deviation of ± 1°C over a period of 2 weeks was obtained. Figure 2.7 shows the typical response curves (i.e. sensor position, power and derivative of the power) obtained for the PET calibration sample.
Figure 2.7: Typical μTA curves for PET calibration sample.

As thermal analysis of bulk materials is routine using either DSC or DTA tools, μTA was determined to be a suitable technique for obtaining similar information on films of glasses in our study which could not be evaluated via DSC or DTA. In the present study, samples (either bulk glass or thin films) of As$_2$S$_3$ material were analyzed using μTA. The goal was to compare properties for bulk and film materials when measured at identical conditions. We first scanned the samples over a 100 microns x 100 microns area. Since small defects (up to a couple of microns in diameter) were observed after each local thermal analysis on a thin film, we chose to continuously relocate the next test on a different area of the sample to avoid cumulative or interfering thermal effects from a previous analysis. The same procedure was used for the bulk
glasses; however the defects created were observed to be much smaller in diameter. The cooling ramp was set at the same value as the heating ramp (either 0.01°C/sec, 5°C/sec or 15°C/sec). The thermal probe was automatically cleaned by heating it at 400°C in the air after every run.

A total of five points were randomly selected on the surface of each bulk material and their average calculated to obtain the transition temperature for a heating rate of 15°C/sec. Note that only three compositions were characterized with this technique (As₂S₃, As₄₀S₃₀Se₃₀, As₂Se₃).

Multiple (eight) locations were chosen on an irradiated As₂S₃ thin film in order to highlight different thermal response of the exposed glass as compared to non-exposed regions as a function of exposure dose on the surface of the film. The thermal conductivity profile of the film for a constant temperature of the probe was also recorded. Note that the localized thermal analysis for the irradiated film is based on only one run since a second run gives a different result due to the previously described thermally damage associated with the measurement.

Finally, the transition temperature values obtained for an As₂S₃ thin film for different exposure conditions at different locations around the focal position of the lens were obtained in collaboration with TA Instruments.

2.5.4. Thermal conductivity

Thermal conductivity maps of 2-D regions can be generated using the µTA™ 2990. The thermal probe is heated by a current flowing through it, and the power required to maintain the tip at a specified constant temperature (or average temperature if the modulation is turned on) is
recorded while the probe is scanned across the specimen. An image based on the contrast in apparent thermal conductivity is thus constructed. Topographic information is still recorded via the tip displacement/optical lever feedback circuit. Modulation of the signal is made possible through temperature amplitude (from 0.001°C to 100°C) and frequency settings (2 kHz to 100 kHz). Additional details on the technique and its application toward polymers, semiconductors, biological and pharmaceuticals materials can be found in Price’s paper (259).

This tool was used in our study to identify and quantify thermal conductivity variations in photo-induced materials, more specifically those exposed under Ar⁺ and Ti:Sapphire light as mentioned in previous paragraphs. Samples were characterized at constant scanning speed of 100 µm/sec over a surface of 100 µm x 100 µm. The temperature was first set constant at \( T = (T_g - 20^\circ C) \) and then decreased in 10°C steps while observing changes in surface thermal conductivity. The signal was then modulated using various frequencies to scan along the depth of the sample, using the same temperature procedure mentioned above in order to obtain the best frequency-temperature set which gave the best resolution.

2.6. Refractive index

Optical glasses suitable for applications in the IR region should have a high transparency in this spectral range. In addition and according to Lloyd, their refractive indices must be high and as independent of temperature as possible (260). However such indices thereby required
specific anti-reflection coatings to mitigate the corresponding high Fresnel losses that scale with index.

The refractive index of a substance is the ratio of the speed of light in a vacuum to the speed of light in that substance. In a material, the photons are absorbed and reemitted by the molecules, which slows down the speed of a light wave. This retardation is represented in Maxwell’s equations by having the parameters $\mu$, $\varepsilon$ and $\sigma$ depart from their free-space values (261). The refractive index can be written as:

$$n = \left(\frac{\varepsilon\mu}{\varepsilon_0\mu_0}\right)^{1/2} \quad (2.8)$$

From Maxwell equations, the complex refractive index related to the complex dielectric constant can be also resolved into real and imaginary components as:

$$\hat{n} = n - ik \quad (2.9)$$

It is customary to define $n$ as the refractive index and $k$ as the extinction coefficient or absorption index. This index is function of the wavelength, so that two beams with different colors (or frequencies) travel at different speeds.
2.6.1. Bulk glasses

Classical methods to measure the refractive index of bulk glasses usually include using an Abbe’s refractometer or an ellipsometer.

In the case of an Abbe’s refractometer one needs a prism with higher index than the material of interest. Since our glasses present refractive indices of up to \( n = 2.8 \) or even above, no suitable material that could be used as a prism conveniently exists and thus this tool is not used for these materials. Thus we identified and compared three alternate, commonly employed methods to evaluate the refractive index.

2.6.1.1. Absorption spectroscopy methods

Following the absorption measurements, the sample absorbance, transmittance and reflection coefficient, \( R \), were recorded with the same equipment and a scan rate of 6 nm/min with a data interval of 0.01 nm around the region of interest (usually 1550 nm) ± 1 nm for calculation of the linear index.

Refractive index was then calculated based on the Fresnel equation with single surface loss, \( R \) determined from the absorption data. The error in index calculation was determined to be equal to ± 0.01 (225). While this method offers limited accuracy, it is straightforward and results can be readily obtained from absorption measurements, thus allowing the user to get a broad idea of the effective refractive index.

A simple Mathlab code was developed to calculate the refractive index and absorption coefficient of bulk materials. One can express the transmission \( T(\lambda) \) of a bulk material over a
wavelength range as a function of the thickness $L$ of the material, the refractive index $n(\lambda)$ and the absorption coefficient $\alpha(\lambda)$ as follows (262):

$$
T(\lambda) = \frac{16n^2(\lambda) \times \exp[-\alpha(\lambda) \times L]}{[n(\lambda) + 1]^4 - [n(\lambda) - 1]^4 \times \exp[-2 \cdot \alpha(\lambda) \times L]} 
$$  \hspace{1cm} (2.10)

Since the refractive index and absorption coefficient are only functions of wavelength, if one can record $T_1(\lambda)$ and $T_2(\lambda)$ for two samples with different thicknesses $L_1$ and $L_2$ one can back-calculate the refractive index $n(\lambda)$ and the absorption coefficient $\alpha(\lambda)$.

2.6.1.2. Ellipsometry

Ellipsometry is a well-established non-destructive optical method that allows precise determination of the thickness and the optical properties of a thin film. It measures the change in polarization of a light reflected from the surface of a sample. The measured values are expressed as $\Psi$ and $\Delta$. These values are related to the ratio of Fresnel reflection coefficients $Rp$ and $Rs$ for p and s-polarized light.

This ratio can be expressed as:

$$
\tan \Psi \cdot \exp(i\Delta) = \frac{Rp}{Rs} 
$$  \hspace{1cm} (2.11)
Both s- and p-directions are perpendicular to the direction of propagation, however s-direction is defined as parallel to the sample surface while the p-direction is contained in the plane of incidence. One can note that the phase information is contained in Δ. A linearly polarized input beam will be converted upon reflection into an elliptically polarized beam. For any angle of incidence greater than 0° and less than 90°, p-polarized light and s-polarized will be reflected differently. An extensive review on ellipsometry was recently published by Vedam (263).

We used an UVISEL Spectroscopic Phase Modulated Ellipsometer (SPME) from Jobin-Yvon at the COPL to measure the refractive index and thickness of thin bulk samples (less than 1 mm-thick). The wavelength scanning range was 300 nm to 1700 nm. The optical coefficients described above were measured and converted by the software into refractive index and extinction coefficient. These data curves were then fitted with the embedded software using Sellmeier’s model. The precision on the measurement of the refractive index according to the manufacturer is equal to 0.001.

2.6.2. Thin films

It is difficult and often cumbersome to accurately determine optical and other physical properties of thin film specimens. As a key aspect of our study aimed to quantify exposure induced property changes in bulk and film specimens, multiple experimental and analytical tools were used to cross calibrate absolute starting values of \( n_0 \) to be able to establish meaningful
resultant $\Delta n$ values for use in our study. The ellipsometry method described previously was also used for thin film samples, specifically the samples used for argon ion laser irradiation experiments, performed on freshly deposited materials made at the COPL prior to and following exposure to quantify induced index change with dose.

2.6.2.1. Grating coupling method

The refractive indices of thin films were determined first at the COPL in Québec (264) by the mean of a grating coupling experiment. The measurements were performed around $\lambda = 1.5 \, \mu m$ for both annealed and non-annealed glasses for eight As-S-Se compositions (those numbered 1 to 7 and the 12th). The glass films were deposited by the same evaporation technique described earlier on a silica grating for a thickness of ~ 2.5 $\mu m$ in order to allow the propagation of up to 5 modes at the wavelength of operation. By focusing the beam inside the grating the refractive index could be calculated. Only the TE polarization was used for determination of the index.

2.6.2.2. Swanepoel’s method

Another technique that one can use to measure the refractive index of a thin film is based on the acquisition of the transmittance spectrum using a classical spectrometer. By using the interference fringes obtained, it has been shown by Swanepoel (265) that one can estimate the refractive index and thickness of a thin film. Gonzalez-Leal (266) and Petkov (267) used this method on some As-S-Se compositions. The same technique was used on our films and compared to the previous ones. Since this method relies heavily on computational calculations
on the experimental data, it is strongly suggested that one refers to the provided references instead of extensively describing the algorithm used.

The acquisition conditions of the transmittance spectra are the same as those described earlier for the absorption spectra using the same Cary 500 spectrometer, the only difference being that the samples are thin films instead of bulk glasses. It might be worth mentioning that these films were deposited on a transparent glass substrate and placed perpendicularly with respect to the spectrometer beam.

One can then fit the refractive index dispersion curve using Sellmeier’s coefficients \((A, B\) and \(\lambda_0)\) for a transparent material:

\[
n^2(\lambda) = A + B \cdot \frac{\lambda^2}{\lambda^2 - \lambda_0^2}
\]  

(2.12)

The data obtained can also be described using the Wemple-DiDomenico (WDD) relation (268).

\[
n^2(\hbar \nu) = 1 + \frac{E_o \cdot E_d}{E_o^2 - (\hbar \nu)^2}
\]  

(2.13)

where \(E_o\) is the oscillator energy and \(E_d\) is the dispersion energy. These two parameters can be easily obtained by plotting \((n^2-1)^{-1}\) versus \((\hbar \nu)^2\).
It is interesting to note that the refractive index at long wavelengths $n_\infty$ can be expressed as a function of $E_o$ and $E_d$:

$$n_\infty = \sqrt{1 + \frac{E_d}{E_o}}$$  \hspace{1cm} (2.14)

Finally, the refractive index follows the well-known Lorentz-Lorenz formula:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\varepsilon_0} \sum_j N_j \alpha_{p,j}$$  \hspace{1cm} (2.15)

where $\varepsilon_0$ is the vacuum permittivity and $N_j$ is the number of polarizable units of type $j$ per volume unit, with polarizability $\alpha_{p,j}$.

As we will demonstrate in the discussion part, these parameters ($E_o, E_d, N_j$) will be employed in future assessment of pre- and post-exposure material properties.

2.6.2.3. Interferometry microscopy

As structures written in thin films included a large number of waveguides, we felt the need to develop a quick technique to estimate the refractive index of these multiple photo-induced zones. The principle of this method is to relate the deformation of the interference fringes from the surface of a sample, acquired by white light interferometry (Zygo), to an index
variation between the non-exposed and exposed regions of the sample. A complete set of interference fringes is shown in figure 2.8 along with an expended region for an As$_2$S$_3$ sample.

As observed on the expended region, the deviation of the fringe is larger on the left-hand side of the picture as compared to the right-hand side. Each “spike” corresponds to a phase difference of the light path induced by the presence of a waveguide. The exposure intensity is decreasing from the left to the right.

Figure 2.8: Interference fringes set (top) and expended region (bottom) acquired by white light interferometry.
Using the known refractive index of the non-exposed sample, we thus express $\Delta n$ as:

$$\Delta n = n \cdot \frac{\Delta d}{d}$$  \hspace{1cm} (2.16)

where $n$ and $d$ are respectively the known refractive index and thickness of the sample and $\Delta d$ is the measured deviation.

### 2.6.2.4. “n and k” technique

During the course of this study, a parallel evaluation of the thickness and optical constants of non-exposed $\text{As}_2\text{S}_3$ and $\text{As}_2\text{Se}_3$ thin films was performed by Filmetrics, Inc. as part of our argon ion laser exposure experiments. The purpose was to collect information on the optical parameters of a same sample and assess the variation between different measurement methods.

The instrument used was a commercial desktop “n and k” (model F20) system. The scanning range was from $\lambda = 400 \text{ nm}$ to $1100 \text{ nm}$ and the illumination source was a regulated tungsten-halogen lamp. The scanned area was $500 \mu\text{m}^2$. Spectral analysis of reflectance from the top and bottom of the thin-film provided thickness, refractive index, and extinction coefficient.
2.7. Absorption/Transmission spectroscopy

It is crucial to determine the absorption characteristics of a glass, especially when it comes to optical materials in order to evaluate their potential application. When light is incident on a dielectric boundary, some of the energy is reflected, some is absorbed and the rest is transmitted. The optical absorption of a glass varies with thickness and wavelength and is a function of its physical and chemical structure (248).

The absorption coefficient ($\alpha$) measures the spatial decrease in intensity of a propagating beam due to progressive conversion of the beam into different forms of energy or matter (269).

The extinction (or absorption) coefficient ($\alpha_e$) translates the decrease in beam intensity due to all contributing processes and appears in the famous Lambert-Beer or Bouguer Law:

$$I(x) = I(0) \exp(-\alpha_e x) \quad (2.17)$$

or

$$\frac{dI(x)}{dI(0)} = -\alpha \cdot dx \quad (2.18)$$

where $I(x)$ is the beam intensity after it has traveled a distance $x$ in the medium and $I(0)$ is the initial intensity. The absorption coefficient has a unit of inverse length (cm$^{-1}$) and shows a strong dependence on temperature, wavelength, etc. The theory of electromagnetic waves relates $\alpha$ to the complex permittivity $\varepsilon$ and permeability $\mu$ of the medium.
As mentioned previously, light is either reflected, transmitted or absorbed. This can be written in the following relationship:

\[ A + R + T = 1 \]  

(2.19)

where \( A \) is the total fraction of incident light absorbed by the sample, \( R \) represents the surface reflections and \( T \) the fraction transmitted.

This technique was used in the present study to observe the shift in the absorption band-edge of every bulk and film specimen evaluated. Absorption spectroscopy was also used as a tool to assess the eventual existence of unwanted species (mainly water absorption) in the range of the spectrophotometer, and to quantify exposure induced changes in absorption with dose.

The spectroscopy study was performed at CREOL using a Varian Cary 500 Scan analyzer and Scan 2.00 software. Bulk sample thicknesses were between 0.8 mm and 3.3 mm. After recording the baseline to remove the background signal, absorbance was systematically observed between 200 nm and 3300 nm (double beam mode with a signal bandwidth of 2 nm). The data interval was set to 1 nm with a scan rate of 600 nm/min. The absorbance was eventually recorded a second time around the absorption band ± 100 nm with a smaller data interval and scan rate to obtain a more detailed curve and thus allow a more accurate calculation of the bandgap of the samples.

Thin films were studied by acquiring the %\( T \) (transmission) instead of the absorption as was the case for bulk glasses. Typical interferences fringes were observed and the signal was used to calculate the refractive index dispersion curves using Swanepoel’s technique as mentioned in the previous section. The technique allowed additionally for calculation of the
deposited thin film thickness, optical absorbance and absorption coefficient. The absorption coefficient of ChG is known to change rapidly for photon energies close to their bandgap and can be divided in three regions (267).

For high absorption coefficient ($\alpha \geq 10^4 \text{ cm}^{-1}$) Tauc’s power law (270) states that:

$$\alpha h \nu = B(h \nu - E_g)^2$$

(2.20)

where B is the slope of the Tauc edge that depends on the width of the localized states in the bandgap, which are attributed to the homopolar bonds in the ChG. This relationship allows us to estimate the values of the optical bandgap $E_g$.

For weak absorption ($10^1 \text{ cm}^{-1} < \alpha < 10^4 \text{ cm}^{-1}$) the absorption coefficient follows the Urbach exponential relation (271):

$$\alpha = \alpha_e \times \exp(h \nu)/E_e$$

(2.21)

where $E_e$ is the Urbach energy. $E_e$ is thought to provide information as to the extent of disorder or randomness in the amorphous ChG. Absorption in this region is related to the transitions between extended states in one band and the localized states in the exponential tail of the other band, hence disorder here refers more towards that of electronic states within the material as compared to irregularity in atomic arrangement.
Finally, the extinction coefficient ($\kappa$) can be easily assessed from $\alpha$ following:

$$\kappa = \frac{\alpha \lambda}{4\pi}$$

(2.22)

2.8. Raman spectroscopy

Raman scattering is the scattering of light by optical-mode lattice vibration. The oscillation of the molecule during nuclear vibration is quite slow compared to the very rapid oscillation of a light wave passing by. The molecules are thus affected by the very rapid oscillating electric field of light. Since the electronic cloud follows the nuclei, we find fluctuations in shape of the electronic cloud that surrounds the molecule from both the nuclear vibrations and the light wave (272).

The sum of these two perturbing effects can be summarized as the summation of waves. The slow oscillation of the electronic cloud is added to the rapid one of the light waves. The light beam perturbs the electronic cloud and induces an instantaneous dipole moment with a frequency equal to the perturbating light radiation. Smekal in 1925 had concluded that the conservation of energy must hold for such an inelastic collision. A simple picture of the principle of emission and excitation is given in the figure 2.9.
The levels of vibrations are represented by $v_0$ (ground state), $v_1$, $v_2$ etc. The difference in energy $\Delta E$ between two states is what is directly observed in the IR spectrum and by the Raman shift in frequency from the Rayleigh line as shown in figure 2.9. Note that the molecule is first excited to a very high energy state ("virtual state" on the figure). Three cases are then possible: return of the molecule to the ground state with emission of a photon of energy $h v_0$ (Rayleigh scattering), relaxation to a higher energy level than the ground state with emission of a photon of energy $h(v_0 - v_1)$, and finally relaxation to the ground state after being excited from a higher energy level which creates the emission of a photon of energy $h(v_0 + v_1)$. The last two cases correspond to Raman scattering.
The equipment needed to observe Raman scattering is simple. The emission and scattering from the sample are usually collected with a lens and focused into a monochromator. Gases, liquids and solids can be observed. The main problem of this technique comes from the fluorescence background, when stray light is superimposed on the signal at frequencies close to the Rayleigh line.

We used “Micro-Raman spectroscopy” to assess variation in bonding of bulk glasses. The setup consisted of a Coherent Innova 300 Argon laser to excite a titanium-sapphire crystal. The micro-Raman configuration was achieved by employing 180° backscattering geometry. The 840 nm excitation wavelength was focused onto the sample via a 40X microscope objective. The backscattered light was collected from the sample, focused into the spectrometer, and analyzed with a back-illuminated thinned HR640 Jobin Yvon CCD detector mounted on the exit port of a single grating spectrograph. The Rayleigh line was suppressed with a CdTe bandgap filter. The high resolution was determined by the size of the slits at the input of our spectrometer. The
typical depth resolution of the system is around $1.5 \, \mu m$. A fixed 50 mW output power of the 840 nm excitation was chosen after the monochromator, to ensure no photo-structural damage of the samples during the analysis. The Raman spectra were collected in the region $200-500 \, \text{cm}^{-1}$.

Thin films were characterized using both micro-Raman and waveguide-Raman spectroscopy (WRS) (273, 274) configurations. The waveguide-Raman configuration is shown in the next figure. The apparatus is the same as for micro-Raman. In waveguide-Raman, however, the beam is directly coupled inside the waveguide and the scattering is collected at $90^\circ$ from the top surface of the film. The advantage of this technique is a greater sampling area which gives a higher SNR and the elimination of the Raman signal superposition from the substrate in thin films.

![Waveguide Raman setup](image)

**Figure 2.11:** Waveguide Raman setup (275).
2.9. Nonlinear optical properties

To this point, we have described tools used to assess material modification due to the linear interaction of the exposure light. However as our study employs high intensity interactions, we must consider the nonlinear optical response as well.

A simplified definition of nonlinear optics is the study of the interaction of intense laser light with matter. Since the second harmonic generation experiment by Franken et al. in 1961 (276), interest in this field has grown continuously to cover nowadays a “spectrum” ranging from fundamental theory with the interaction of light with matter, to applications such as optical switching or frequency conversion (277).

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. “Nonlinear” means that these optical phenomena occur when the response of a material system to an applied optical field depends in a nonlinear manner upon the strength of the optical field. Whereas in the case of linear optics the polarization depends linearly upon the electric field strength in a manner that can be described by:

\[ \tilde{P}(t) = \chi^{(1)} \tilde{E}(t) \]  \hspace{1cm} (2.23)

where \( \chi^{(1)} \) is the linear susceptibility.
The nonlinear optical response can often be described by expressing the polarization as a power series in the field strength:

\[
\vec{P}(t) = \chi^{(1)} \vec{E}(t) + \chi^{(2)} \vec{E}^2(t) + \chi^{(3)} \vec{E}^3(t) + \ldots \tag{2.24}
\]

where \(\chi^{(2)}\) and \(\chi^{(3)}\) are respectively the second- and third-order nonlinear optical susceptibilities.

The refractive index can be written as:

\[
n = n_0 + \bar{n}_2 \langle \vec{E}^2 \rangle \tag{2.25}
\]

or

\[
n = n_0 + n_2 I \tag{2.26}
\]

where the angular brackets around the \(\vec{E}^2\) quantity represent a time average, \(n_0\) is the usual refractive index and \(\bar{n}_2\) is the second-order index of refraction giving the rate at which the refractive index increases with increasing optical intensity. Equation (2.26) is representative of the Kerr effect, which is the refractive index change of a material by an amount proportional to the square of the strength of an applied static field.

The linear and nonlinear refractive indices are related to the linear and nonlinear susceptibilities by:

\[
n_0 = \left(1 + 4\pi \chi^{(1)} \right)^{1/2} \tag{2.27}
\]

\[
n_2 = \frac{12\pi^2}{n_0 c} \frac{\chi^{(3)}}{\bar{n}_2} = \frac{4\pi}{n_0 c} \frac{\chi^{(3)}}{\bar{n}_2} \tag{2.28}
\]
Consequently, by Kramers-Kronig relationship, the absorption can be expressed in the same way by:

\[ \alpha = \alpha_0 + \alpha_2 I + \alpha_3 I^2 \]  

(2.29)

where \( \alpha_0 \), \( \alpha_2 \) and \( \alpha_3 \) stand respectively for the linear, two photon and three photon absorption.

A very well-known method to measure the nonlinear refractive index is the Z-scan technique. These aspects are described in detail in referenced works (278), with key issues (only) summarized here.

2.9.1. Nonlinear index models

Boling, Glass and Owyoung developed an expression for \( n_2 \) based on a semi-classical model of the simple harmonic oscillator. Details of the mathematical derivations are provided elsewhere (279). Based on Clausius-Mossotti relationship, they demonstrated that \( n_2 \) could be related to the Abbe number \( \nu_d \) and the refractive index \( n_d \):

\[ n_2(10^{13} \text{ esu}) = 68 \cdot (n_d - 1) \cdot (n_d^2 + 2)^2 / \nu_d \left[ 1.517 + \frac{\left( n_d^2 + 2 \right) \cdot (n_d + 1) \cdot \nu_d}{6 \cdot n_d} \right]^{\frac{1}{2}} \]  

(2.30)
The Abbe number can be expressed as:

\[ \nu_d = \frac{n_d - 1}{n_f - n_c} \quad (2.31) \]

where \( n_d, n_f \) and \( n_c \) are the linear refractive indices at respectively \( \lambda_f = 486.13 \text{ nm}, \lambda_d = 587.56 \text{ nm} \) and \( \lambda_c = 656.27 \text{ nm} \). The authors also generated a simpler formula that fitted the experimental data better than any of the derived expressions:

\[ n_z (10^{13} \text{ esu}) = 391 \cdot \frac{(n_d - 1)}{\nu_d^5} \quad (2.32) \]

However, since most of our data were fitted with Wemple-DiDomenico formula it is interesting to express Boling’s formula as a function of the oscillator energy \( E_o \) and the dispersion energy \( E_d \) following the approach employed in Petkov’s work (280):

\[ n_z = \sqrt{3} \cdot gS (n^2 + 2)^{1.5} \cdot (n^2 - 1)^2 \cdot \frac{\hbar^2 e^2}{12nmE_dE_o^2} \quad (2.33) \]

where \( n \) is the linear index at long wavelengths, \( \hbar \) is Planck’s constant divided by \( 2\pi \), \( g \) is the anharmonicity parameter, \( S \) is the oscillator strength and \( e \) and \( m \) are respectively the charge and mass of the electron. Boling in his work mentions that the best results for a number of oxides and fluorides glasses were obtained with \( gS = 3 \).
2.9.2. Z-Scan

Developed by Sheik-Bahae et al. (278), the Z-scan technique is a simple and popular experimental technique to measure intensity dependent nonlinear susceptibilities of materials. In this method, the sample is translated in the z-direction along the axis of a focused Gaussian beam, and the far field intensity is measured as function of sample position. Analysis of the intensity versus sample position Z-scan curve, predicated on a local response, gives the real and imaginary parts of the third order susceptibility.

In this technique the optical effects can be measured by translating a sample in and out of the focal region of an incident laser beam. Consequently increases and decreases in the maximum intensity incident on the sample produces wavefront distortions created by nonlinear optical effects in the sample being observed. The Z-scan is obtained by moving the sample along a well-defined, focused laser beam, and thereby varying the light intensity in the sample. By varying the aperture in front of the detector, one makes the Z-scan transmittance more or less sensitive to either the real or imaginary parts of the nonlinear response of the material, i.e., nonlinear refractive index and nonlinear absorption, respectively.

We used the Z-scan technique at CREOL in collaboration with Dr. Van Stryland’s group. The source was an OPO (\(\lambda = 1.55\) nm; 100 fs; repetition rate 1 kHz). The beam size was measured to be 35\(\mu\)m and the energy at the sample equals 10-20 nJ. The irradiance was 3 GW/cm\(^2\).
The very high sensitivity of the z-scan setup with regards to the optical flatness of the sample was a major issue and a second polishing had to be undertaken to improve the surface quality. Nine compositions could be measured out of the thirteen that compose our diagram. This technique and the data obtained will be further discussed in the results section.

2.9.3. Collinear Pump-Probe method (CPPM)

A different approach to measuring nonlinearities in glass materials was developed by Martin, Bousquet, Canioni and Sarger (281, 282). CPPM is used to study ultrafast dynamics in condensed media and provides a transient absorption signal which exhibits an oscillatory behavior versus pump probe delay. The pump beam perturbs the sample and creates a change in the refractive index of the material through the Kerr effect. The probe beam is used to observe
the modifications taking place. A detailed description and analysis for this particular technique has been written by Santran (283).

Our experiment took place at the Centre de Physique Moléculaire, Optique et Hertzienne (CPMOH) at the Université Bordeaux I (Bordeaux, France) among Laurent Sarger’s group. Figure 2.13 is a schematic of the CPPM technique.

![Schematic of the collinear pump-probe experiment. The arrows and circles represent the beams polarizations.](image)

Figure 2.13: Schematic of the collinear pump-probe experiment. The arrows and circles represent the beams polarizations.

The laser source was an OPAL delivering linearly polarized pulses of 100 fs around $\lambda = 1.504 \mu m$ with an output power of 150 mW at 80 MHz. The beam waist was measured to equal 30.5 $\mu m$ at the sample with an average power of 60 mW and 250 mW (two sets of experiments
were performed). Compositions 1 to 11 were characterized along with SiO$_2$ and Si reference samples.

In this pump probe experiment, the pump and probe beams are orthogonally polarized and focused onto the sample. The probe intensity is affected by the pump induced nonlinearity of the material and an energy transfer takes place between the two beams, creating nonlinear fringes which depend on the diagonal tensors of the third-order nonlinear optical susceptibility. Analysis of the signal intensity as a function of the delay (created by a vibrating pot) between the pump and the probe allows one to characterize completely the $\chi^{(3)}$ of the material. The accuracy on the measurements was limited by the all laser parameters and estimated to be 10%.
CHAPTER THREE: RESULTS

This chapter summarizes the data acquired in the course of this study. It will be divided into three main parts: physical properties, optical properties and structural characterization. Additional data or details relating to these measurements and their interpretation can be obtained in the published mentioned references of our work.

3.1. Physical properties

In this first section, we report the data acquired for the physical properties of the bulk materials such as density, hardness, thermal properties, etc... These results will be used to assess the effective and required homogeneity of our materials and describe the influence of the composition on the physical properties of the bulk glasses. We also account for thermal measurements made on bulk materials and thin films using the various thermal characterization tools described in the previous section, the purpose being to identify a suitable technique to compare some of the physical properties of both types of materials and observe photo-induced structures written in the thickness of the thin films.
3.1.1. Homogeneity and purity

3.1.1.1. Homogeneity study (bulk materials)

The homogeneity study on composition As$_{24}$S$_{38}$Se$_{38}$ was reported in a previous paper (225). A summary of the results is presented below and one is invited to refer to the article for more details on the data.

The effects of batch size, quenching temperature, annealing and distillation on the physical and optical properties of As$_{24}$S$_{38}$Se$_{38}$ glasses were investigated. No significant change in $T_g$ or $\rho$ (less than 2%) over the range of melt process parameters chosen was observed. Measurements of refractive index showed some differences within boules (~3.5% or less) with variation largest for those samples cooled/quenched from well above $T_g$. For most properties examined, no appreciable change was observed for samples undergoing purification, over the range of melt volumes examined. Samples within the study exhibited good structural uniformity as evidenced by the similarity in Raman peak areas, which depends on bonding and chemical uniformity. All glasses exhibited good within slice optical homogeneity as characterized by their UV edge position overlap. Within-boule variation was largest for samples slow cooled from the melt where melt segregation was believed to occur.
3.1.1.2. Purity of bulk glasses

Figure 3.1 shows a typical EDS spectrum for composition As$_{40}$S$_{30}$Se$_{30}$.

![EDS spectrum for the As$_{40}$S$_{30}$Se$_{30}$ composition](image)

The data were collected over three regions for each of the compositions (numbered 1 to 13) indicated in the ternary diagram, and the average resulting composition in atomic percent of the three measurements is reported in Table 3-1.

Table 3-1 shows very small variations in the actual bulk glass composition as measured by EDS with respect to the batched target compositions. Except for a couple of samples, the general trend observed is a small but consistent loss in sulfur. This can be visually observed under the form of small pale yellow patches on the melting tube walls for S-rich compositions after quenching.
Table 3-1: Experimental composition as measured with EDS (226).

<table>
<thead>
<tr>
<th>Composition (Target)</th>
<th>Composition (Actual)</th>
<th>Composition (Target)</th>
<th>Composition (Actual)</th>
<th>Composition (Target)</th>
<th>Composition (Actual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$<em>{40}$S$</em>{60}$</td>
<td>As$<em>{40.78}$S$</em>{59.22}$</td>
<td>As$<em>{24}$S$</em>{76}$</td>
<td>As$<em>{24.57}$S$</em>{75.43}$</td>
<td>As$<em>{40}$S$</em>{30}$Se$_{30}$</td>
<td>As$<em>{40.46}$S$</em>{29.05}$Se$_{30.5}$</td>
</tr>
<tr>
<td>As$<em>{40}$S$</em>{45}$Se$_{15}$</td>
<td>As$<em>{40.56}$S$</em>{43.80}$Se$_{15.64}$</td>
<td>As$<em>{24}$S$</em>{37}$Se$_{19}$</td>
<td>As$<em>{24.69}$S$</em>{56.18}$Se$_{19.1}$</td>
<td>As$<em>{40}$S$</em>{10}$Se$_{45}$</td>
<td>As$<em>{40.18}$S$</em>{59.82}$</td>
</tr>
<tr>
<td>As$<em>{40}$S$</em>{30}$Se$_{30}$</td>
<td>As$<em>{40.46}$S$</em>{29.05}$Se$_{30.49}$</td>
<td>As$<em>{24}$S$</em>{38}$Se$_{38}$</td>
<td>As$<em>{24.91}$S$</em>{37.41}$Se$_{37.7}$</td>
<td>As$<em>{40}$S$</em>{15}$Se$_{45}$</td>
<td>As$<em>{40.53}$S$</em>{13.90}$Se$_{45.48}$</td>
</tr>
<tr>
<td>As$<em>{40}$S$</em>{15}$Se$_{45}$</td>
<td>As$<em>{40.52}$S$</em>{13.90}$Se$_{45.48}$</td>
<td>As$<em>{24}$S$</em>{10}$Se$_{57}$</td>
<td>As$<em>{24.04}$S$</em>{18.46}$Se$_{57.5}$</td>
<td>As$<em>{40}$S$</em>{60}$</td>
<td>As$<em>{40.18}$S$</em>{59.82}$</td>
</tr>
</tbody>
</table>

Note that such compositional report is rarely published thus making it difficult to compare to other works. As to sample purity, no contamination was observed on any samples, either at the surface or inside the bulk glasses, despite the fact that the accelerating energy used was high enough to resolve at least 0.01 percent in oxygen (or other) trace species.

Figure 3.2 shows the FT-IR spectra for two samples. The contaminated specimen shows bands clearly corresponding to a previous contamination of the sulfur. As reported in the first chapter, sulfur is known to be a “dirty” element that requires subtle purification and handling to avoid further contamination. The clean spectrum is flat all the way to 5000 cm$^{-1}$ and starts to get consistently noisy up to 7000 cm$^{-1}$.
Figure 3.2: FT-IR spectra of a clean and a contaminated As-S bulk sample (226).

These data along with the EDS measurements will be reported in a series of papers that will cover the aspects of processing, purification and physical and optical characterizations that we developed in the past years (226, 284). EDS requires a significant though simple sample preparation and the method requires roughly 2 to 3 hours for a set of samples (maximum of 6 per set) while the FT-IR method is faster (~ 1 minute per sample for sample preparation plus data acquisition) which is why we chose to use FT-IR as a regular contamination detection technique.
for single batches, while EDS was reserved for occasional larger set of batches corresponding to specific studies.

Another way to gauge relative purity of glasses is XRD. The next figure regroups the XRD spectra acquired for compositions 1 to 5.

![XRD Spectra](image)

**Figure 3.3**: Evolution of the amorphous peaks of compositions 1-5 as obtained by XRD. The dotted lines highlight the shift of the center position of the second peak (226).

Typical amorphous “peaks” are shown while no crystalline phase was observed as evidenced by the lack of sharp narrow peaks. One can observe a shift of the three peaks (as shown on the figure by the dotted lines). XRD data are in accordance with previous reports (285, 286, 24), suggesting that it is very difficult to obtain crystal particles unless a very specific
and constant thermal treatment is applied for periods ranging from a week to a month depending on the composition.

XPS was used to evaluate oxide contamination and stability of glasses to oxidation (287). A survey spectrum taken from this publication illustrates XPS spectra for both As$_2$S$_3$ and As$_2$O$_3$.

![XPS Survey Spectra](image)

Figure 3.4: XPS Survey Spectra of: (1) Bulk polished As$_2$S$_3$ as prepared in laboratory; (2) 99.99 % pure powder As$_2$O$_3$ (Alfa chemicals) (287).

As can be seen, a small O 1s peak is detected in the As$_2$S$_3$ spectra prior to any subsequent heating. This source of oxygen was confirmed to come from surface contamination in the XPS instrument and not from the processing or melting steps of the glass, which further validate our purification process steps.
3.1.2. Physico-thermal analysis

3.1.2.1. Density of bulk glasses

As part of our effort to develop a table of physical data on bulk glasses, density values were calculated and are reported in table 3-2 along with other physico-thermal properties. Density is observed as varying linearly with sulfur or selenium content. The isostructural substitution of Se for S results in a large density modification. However, while the same linear variation is observed for a change in As content, this latest seems to have a less significant impact on the varying density. Figure 3.9 in section 3.2.1.3 shows $T_g$ as a function of density. These results (and additional data on hardness) have been summarized elsewhere for other glasses in the As-S-Se system by our group (107). We will comment on this in the next chapter.

3.1.2.2. Hardness measurements

The following figures show the Vickers hardness variation versus selenium content and coordination number. Hardness seems to be fairly constant for the $\text{As}_{40}\text{S}_x\text{Se}_{60-x}$ series while increasing linearly with decreasing S content for the $\text{As}_{24}\text{S}_y\text{Se}_{76-y}$ series. Analytical results of the linear fit are presented in figures 3.5 to 3.7.
Figure 3.5: Vickers hardness versus selenium content for $\text{As}_{40}\text{S}_x\text{Se}_{60-x}$ with $0 \leq x \leq 60$.

Figure 3.6: Vickers hardness versus selenium content for $\text{As}_{24}\text{S}_y\text{Se}_{76-y}$ with $0 \leq y \leq 76$. 
Table 3-2 summarizes these data. Glassy ChG’s from the As$_{24}$S$_{y}$Se$_{76-y}$ series show however, a much more significant change (from $H = 77$ to 100) as compared to the As$_{40}$S$_{x}$Se$_{60-x}$ series (from $H = 129$ to 135).

Hardness is also increasing with increasing As content (from 18 mol % to 40 mol %) for the S/Se = 1 series. As shown in the following figure the relationship between hardness and the coordination number $<r>$ is almost linear ($R = 0.99614$, where $R = 1$ would indicate a perfect linear relationship between the two variables). The coordination number of a ChG composition is simply the average of the weighted coordination number of the constituents composing the glass.

![Figure 3.7: Hardness versus coordination number for As$_x$S$_{(100-x)/2}$Se$_{(100-x)/2}$ with 18 $\leq x \leq$ 40. The glass compositions are numbered.](image-url)

$$y = -548.35 + 283.82x$$

$R = 0.99614$
Hardness clearly increases with increasing CN.

3.1.2.3. DTA & DSC

$T_g$ of the glass was measured for all compositions. The results between DTA and DSC showed a typical and constant difference of $3^\circ$C. As mentioned in the experimental chapter, our DSC equipment is designed for better accuracy at low temperatures hence the DSC was designated as our equipment of choice for these measurements.

A typical DSC response curve is shown in figure 3.8 for As$_{40}$S$_{60}$.

Figure 3.8: Typical DSC signal (heat flow and its derivative) for a-As$_2$S$_3$ bulk sample.
The data for all compositions are reported in table 3.2.

Table 3-2: Summary of physico-thermal data for bulk glasses compositions 1-12 (226, 284).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm(^3)) ± 0.01</th>
<th>(T_g) (°C) ± 2</th>
<th>CTE (x10(^{-5}/)°C) ± 0.01</th>
<th>Bandgap (eV) ± 0.02</th>
<th>Hardness (kg/mm(^2)) ± 7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.17</td>
<td>211</td>
<td>2.09</td>
<td>2.33</td>
<td>129</td>
</tr>
<tr>
<td>2</td>
<td>3.53</td>
<td>206</td>
<td>2.23</td>
<td>2.14</td>
<td>129.7</td>
</tr>
<tr>
<td>3</td>
<td>3.86</td>
<td>202</td>
<td>2.32</td>
<td>1.99</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>4.20</td>
<td>198</td>
<td>2.39</td>
<td>1.90</td>
<td>133.7</td>
</tr>
<tr>
<td>5</td>
<td>4.53</td>
<td>193</td>
<td>2.47</td>
<td>1.78</td>
<td>135</td>
</tr>
<tr>
<td>6</td>
<td>3.70</td>
<td>154</td>
<td>2.87</td>
<td>2.01</td>
<td>114</td>
</tr>
<tr>
<td>7</td>
<td>3.61</td>
<td>131</td>
<td>2.27</td>
<td>2.02</td>
<td>86.8</td>
</tr>
<tr>
<td>8</td>
<td>2.67</td>
<td>147</td>
<td>2.61</td>
<td>2.55</td>
<td>76.6</td>
</tr>
<tr>
<td>9</td>
<td>3.11</td>
<td>137</td>
<td>3.44</td>
<td>2.16</td>
<td>77.7</td>
</tr>
<tr>
<td>10</td>
<td>4.05</td>
<td>122</td>
<td>3.56</td>
<td>1.94</td>
<td>95.4</td>
</tr>
<tr>
<td>11</td>
<td>4.46</td>
<td>116</td>
<td>3.32</td>
<td>1.87</td>
<td>99.63</td>
</tr>
<tr>
<td>12</td>
<td>3.51</td>
<td>115</td>
<td>3.96</td>
<td>2.04</td>
<td>70.2</td>
</tr>
</tbody>
</table>
The isostructural substitution of Se for S resulted in small $T_g$ change while the variation in As concentration, e.g. along the $[S]/[Se]=1$ line, creates a significant change in $T_g$.

The vertical and horizontal dotted lines in figure 3.9 correspond respectively to the $[S]/[Se]=1$ and constant As concentration lines and are used to highlight an eventual variation in the data. The deviation on multiple measurements performed on a same composition was smaller than 0.2%, which accounts for the excellent accuracy and repeatability of the system.

![Figure 3.9: Glass transition temperature as a function of density for some ChG (226).](image)

Note that glasses with very low $T_g$ are not of interest due to the structural changes that might take place at device working temperatures, which would induce an annealing of the glass.
Finally, one can observe the excellent relationship between the thermal and physical properties (as shown on the previous figure) of these compositions.

3.1.2.4. TMA

The following figures show the CTE variation versus selenium content and coordination number.

Figure 3.10: CTE ($\alpha$) versus selenium content in bulk glasses. The glass compositions are numbered.
CTE increases clearly with Se content for the $\text{As}_{40}S_x\text{Se}_{60-x}$ and $\text{As}_{24}S_y\text{Se}_{76-y}$ series. The CTE also decreases with a linear behavior for increasing coordination number. Analytical results of the linear fits are presented in the figures.

![Graph showing CTE (α) versus coordination number in bulk glasses. The glass compositions are numbered.](image)

Figure 3.11: CTE (α) versus coordination number in bulk glasses. The glass compositions are numbered.

### 3.1.2.5. Micro-Thermal Analysis

As described earlier, $\mu$TA was used as a convenient tool to evaluate and compare the thermal properties of bulk glasses versus thin films since DTA or DSC could not be applied to films. The other purpose was to observe the changes in thermal conductivity taking place in the thin films upon exposure, if any.
When the thermal probe in contact with the surface of the sample is heated, the material starts expanding first then collapses when the melting temperature is reached. The maximum of the sharp peak in the derivative of the power represents $T_m$, as can be observed in the PET calibration figure (figure 2.7) presented in the previous chapter. The average of three measurements made on a calibration PET sample was 245°C for a reported theoretical temperature of 244.92°C. At higher temperature, around 340°C, one could also observe a sharp peak corresponding to the decomposition of the sample. The same thermal events are observed in figure 3.12 for the a-As$_2$S$_3$ bulk sample and a heating rate of 15°C/sec.

![Figure 3.12: μTA response for a-As$_2$S$_3$ bulk sample.](image)

Figure 3.12: μTA response for a-As$_2$S$_3$ bulk sample.
The average $T_m$ of this sample was determined using the maximum of the first derivative of the power (W/°C), found to be equal to 304°C. Average transition temperature values for As$_{40}$S$_{30}$Se$_{30}$ and As$_2$Se$_3$ were similarly found to be 289°C and 278°C, respectively. The standard deviation observed for the bulk samples was ±1°C. The signal obtained for a heating rate of 0.01°C/sec was too noisy to extract any significant information. $T_g$ values were determined with the onset of the sensor position curve (figure 3.13), since the signal was too small to be observed on the power or its derivative signals. Values found are much smaller than for the DSC ones as shown in Table 3-3 and the standard deviation was very large (5 to 6°C) due to the very fast heating ramp used in this technique as compared to that used in DSC (10°C/min).

![Graph showing sensor deflection and glass transition](image)

Figure 3.13: Sensor deflection (zoom) showing the characteristic glass transition for an As$_2$S$_3$ bulk sample.
Table 3-3: Average of transition temperatures for bulk samples as determined by DSC or μTA. The standard deviation indicated here for the two first columns corresponds to the manufacturer specifications.

<table>
<thead>
<tr>
<th>Bulk Composition</th>
<th>$T_g$ (°C) DSC</th>
<th>$T_m$ (°C) μTA</th>
<th>$T_g$ (°C) μTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>± 2°C</td>
<td>± 2°C</td>
<td>± 5-6°C</td>
</tr>
<tr>
<td>As$<em>{40}$S$</em>{60}$</td>
<td>210</td>
<td>304</td>
<td>188</td>
</tr>
<tr>
<td>As$<em>{40}$S$</em>{30}$Se$_{30}$</td>
<td>201</td>
<td>292</td>
<td>174</td>
</tr>
<tr>
<td>As$<em>{40}$Se$</em>{60}$</td>
<td>194</td>
<td>283</td>
<td>164</td>
</tr>
</tbody>
</table>

Note that the samples were cut and that $T_m$ values measured in the center of the material were found in agreement with the measurements operated at the surface of the sample.

The thermal conductivity measurements prior- and past-irradiation allowed the observation of the photo-induced structures which showed higher thermal conductivity versus the non-exposed regions. However, it was not possible to quantify the extent of these changes because the small measured variation was in the error bars of the technique.

3.2. Optical properties

This section is divided between the linear and nonlinear optical properties of our materials. As mentioned in the previous chapter, we identified and compared several alternate and commonly employed methods to evaluate the linear refractive index, absorption and optical
bandgap of our bulk glasses and thin films. These results will be used in the next chapter to
demonstrate first the influence of composition on the optical properties of bulk materials, then
the differences between bulk glasses and as-deposited thin films, and finally the consequences of
thin films exposure at different wavelengths (\( \lambda = 514 \) nm and 785 nm). The nonlinear properties
\((n_2 \text{ or } \chi^{(3)})\) as measured or modeled accordingly to different theories will also be reported at the
end of this section.

3.2.1. Bulk glasses optical properties

We present the refractive index and absorption results for bulk glasses as obtained by
spectroscopy (Fresnel loss), calculation (Matlab) and ellipsometry.

3.2.1.1. Spectroscopy (Fresnel loss and Matlab calculation)

Figure 3.14 shows a plot of the refractive index as a function of the coordination number
of the glass as determined by calculation of the Fresnel loss.
As discussed earlier, the method employed has the inconvenience of exhibiting a limited accuracy (± 0.01).

The shift of the absorption edge with composition variation was measured and is shown in the figures 3.15 to 3.17 along with the absorption change as a function of wavelength. All spectra were aligned at “absorption = 0” to give a better idea of the spectral shift.

The bandgap was calculated from the intersection of the tangent to the absorption band with the horizontal axis and reported in table 3-2 in the previous section along with $T_g$ and density data for more commodity.
Figure 3.15: Absorption spectra of $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$ series with $x = 0, 15, 30, 45$ and $60$ (compositions 1 to 5) (288).

Figure 3.16: Absorption spectra of the $\text{As}_{24}\text{S}_{76-x}\text{Se}_x$ series with $x = 0, 19, 38, 57$ and $76$ (288).
A significant red shift is observed with each Se content increase from one composition to the next for the series As$_{40}$S$_{60-x}$Se$_x$ and As$_{24}$S$_{76-x}$Se$_x$. However, as presented in the next figure, decreasing the As content induces only a small blue shift. Note that for wavelength above 2000 nm the Se-rich compositions (5 and 11) showed a slight increase in absorbance.

Figure 3.17: Absorption spectra of the [S]/[Se]=1 series (compositions 3, 6, 7, 12 and 13) (288).

We used a Matlab code to ascertain the refractive index and absorption measurements from the spectroscopy method. Shown next is the typical data calculated from the transmission spectra of two As$_{40}$S$_{45}$Se$_{15}$ bulk samples with different thicknesses. The refractive index dispersion curve was fitted with Sellmeier’s model and the coefficients were found to be $A = 5.34$, $B = 1.12$ and $\lambda_0 = 397.5$ nm. When calculated at 1.5 $\mu$m, $n_0 = 2.558$ and compared to the value found with the Fresnel loss method ($n_0 \sim 2.48$) we find a difference of $\sim 0.08$. This method
was only used on the first series of samples and the average deviation with the Fresnel method is \(\sim 0.12\).

![Graph showing refractive index vs. wavelength with model fit and Matlab calculated data](image)

**Figure 3.18:** As\(_{40}\)S\(_{45}\)Se\(_{15}\) refractive index as calculated with Matlab and fitted with Sellmeier’s model.

Absorption was also calculated using the Matlab code and is shown in the following figure for composition As\(_{40}\)S\(_{45}\)Se\(_{15}\). The extinction coefficient was calculated using equation (2.22) and is also plotted in figure 3.19.
3.2.1.2. Ellipsometry

The ellipsometry technique was used on the bulk samples and the thin films at the COPL to observe eventual differences between these materials. We report first the data on bulk samples here. The measurements were carried on thin polished discs (1 mm or less). The next table shows the Sellmeier’s coefficients for these bulk glasses as calculated from the ellipsometer embedded software. As a reminder, these bulk glasses were used for thermal depositions of all the thin films exposed.
Table 3-4: Sellmeier coefficients calculated by ellipsometry for bulk glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>A</th>
<th>B</th>
<th>$\lambda_0$</th>
<th>$n_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(nm)</td>
<td></td>
<td>(1.5 µm)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.75</td>
<td>0.34</td>
<td>429.5</td>
<td>2.474</td>
</tr>
<tr>
<td>2</td>
<td>4.3</td>
<td>2.3</td>
<td>350.1</td>
<td>2.595</td>
</tr>
<tr>
<td>3</td>
<td>4.81</td>
<td>2.36</td>
<td>406</td>
<td>2.712</td>
</tr>
<tr>
<td>4</td>
<td>4.91</td>
<td>2.64</td>
<td>423.6</td>
<td>2.79</td>
</tr>
<tr>
<td>5</td>
<td>4.01</td>
<td>3.88</td>
<td>450</td>
<td>2.876</td>
</tr>
<tr>
<td>6</td>
<td>2.263</td>
<td>4.02</td>
<td>350.2</td>
<td>2.552</td>
</tr>
<tr>
<td>7</td>
<td>5.66</td>
<td>0.39</td>
<td>540.2</td>
<td>2.472</td>
</tr>
<tr>
<td>8</td>
<td>4.47</td>
<td>0.56</td>
<td>386.8</td>
<td>2.253</td>
</tr>
<tr>
<td>9</td>
<td>3.01</td>
<td>2.64</td>
<td>289.8</td>
<td>2.397</td>
</tr>
<tr>
<td>10</td>
<td>4.72</td>
<td>1.77</td>
<td>412.1</td>
<td>2.577</td>
</tr>
<tr>
<td>11</td>
<td>4.16</td>
<td>2.93</td>
<td>361.7</td>
<td>2.697</td>
</tr>
<tr>
<td>12</td>
<td>4.37</td>
<td>1.31</td>
<td>299.1</td>
<td>2.393</td>
</tr>
</tbody>
</table>

When compared to the Fresnel loss method, the calculated values at 1.5 µm showed a consistently higher refractive index of ~ 0.1. Values of the refractive index of As$_{40}$S$_{45}$Se$_{15}$ were calculated at 1 µm, 1.5 µm and 2 µm and compared to those obtained with the Matlab code; the ellipsometer gave higher values by respectively 0.048, 0.036 and 0.032. As a reminder the error on the ellipsometry measurement is reported to be 0.001 whereas the computation method accuracy is estimated to be 0.007. This shows that the calculation method can be considered as an interesting tool for rapid refractive index estimation, even though it requires two samples of different thickness and is less accurate (as expected) than an ellipsometer.

Note that the ellipsometry data for thin films will be presented in the next section even though they were acquired at the same time as the bulk glasses.
3.2.2. Thin films optical properties

We used three main techniques to characterize the optical properties of the thin films: grating coupling method, ellipsometry and Swanepoel’s method. The data acquired will be used first to compare the optical properties of the bulk materials, as presented previously, to those of the thin films, and then to observe the variations, if any, upon exposure at 514 nm and 785 nm.

3.2.2.1. Non-exposed films by grating coupling method

The refractive indices obtained for compositions 1 to 8 deposited on the gratings are reported in the figures below. These compositions were the same as those used for calculation of the bulk glasses using the Fresnel loss method. The experiment was performed by Jacques Laniel (264) at the COPL in Québec and we present in figures 3.20 and 3.21 some of the data that show the influence of annealing on the samples.
Figure 3.20: Refractive index for annealed and non-annealed compositions 1 to 5 (264).

Figure 3.21: Refractive index for annealed and non-annealed compositions with varying arsenic content (264).
The precision on the value of the thin film refractive index was ± 0.003. The refractive index increases almost linearly from glass composition 1 (n = 2.4) to glass composition 5 (n = 2.8) for increasing Se content. The annealing is observed to cause an increase of the refractive index of about 2%. For a decreasing As content and constant ratio [S]/[Se] = 1 the refractive index decreases almost linearly from n = 2.55 to 2.38.

3.2.2.2. Ellipsometry (514 nm exposure)

As mentioned previously, the ellipsometry data on thin films were acquired along with the bulk samples at the COPL. The data presented here correspond to non-exposed and exposed films past 514 nm exposure.

Figure 3.22 is typical of the evolution of the refractive index dispersion for thin film upon exposure at 514 nm. These data were used as the conclusive unexposed n₀ value (at a given wavelength) from which induced indices (Δn) were determined. The refractive index is observed to increase with increasing exposure time. The data for the corresponding bulk material is provided for comparison and the thin films consistently exhibited smaller n₀ as compared to the bulk glasses.
Figure 3.22: Refractive index versus wavelength for As$_2$Se$_3$ for varying exposure times.

Figure 3.23 shows $\Delta n$ versus exposure dose for all compositions. As mentioned previously, $n_0$ increases with increasing exposure and all compositions show saturation in the $\Delta n$ for the highest deposited energies. As$_2$Se$_3$ shows a unique “giant” $\Delta n$ of $\sim 0.3$ which we will discuss in the next chapter. The observed $\Delta n$ for all compositions is higher with increasing Se content. Higher Se-content materials show a higher $\Delta n$ upon exposure for a given deposited “dose”. The inserted window allows one to better observe the saturation effect of the $\Delta n$ variation for all compositions (except As$_2$Se$_3$).
Figure 3.23: Photo-induced $\Delta n$ versus fluence for all compositions at 514 nm. The small figure is an expended view of part of the main figure.

Note that the same experiment was performed while switching the argon laser beam from linear to circular polarization. No significant difference in $\Delta n$ was observed upon this change in polarization.

3.2.2.3. Swanepoel’s method (785 nm exposure)

The next figure shows the linear refractive index dispersion curves as obtained through Swanepoel’s calculation and using a Sellmeier’s model for the four studied compositions in the 785 nm experiment. For the sake of comparison, we included the dispersion curves calculated by ellipsometry for the samples of the 514 nm experiment. Hence the solid lines represent the as-deposited non-irradiated samples for the 785 nm exposure experiment, while the dashed lines
correspond to the as-deposited non-irradiated samples for the subsequent 514 nm exposure experiments.

![Refractive index vs Wavelength graph](image)

**Figure 3.24**: Non-exposed thin films prior to (dashed lines) 514 nm and (solid lines) 785 nm exposure.

From these data, “starting” $n_0$ values were determined against which subsequent post-exposure measurements were compared to determine induced ($\Delta n$) index. Interestingly we observe slight changes between the refractive index dispersions of the annealed as-deposited thin films. As a reminder, the deposition processes were performed a couple of months apart, however the starting target bulk materials were from an identical melt. For comparison purposes, the deviation calculated between thin films of the same composition at $\lambda = 1.5 \, \mu m$ is $\sim 0.03$ for compositions $\text{As}_2\text{S}_3$, $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ and $\text{As}_{24}\text{S}_{38}\text{Se}_{38}$, while equal to $\sim 0.08$ for $\text{As}_2\text{Se}_3$. We thus attribute these changes mostly to the lower accuracy of the Swanepoel’s model, as
compared to the ellipsometry technique, in the high absorption region of the materials. Another justification for the larger variation observed for the \( \text{As}_2\text{Se}_3 \) material is a rare bulk material flaw.

Table 3-5: \( n_0 \) at various wavelength and \( E_g \) upon exposure at 514 nm and 785 nm. Fluence values are provided for the exposed samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( \lambda ); fluence (Exp.)</th>
<th>( n_0 ) (1 ( \mu )m)</th>
<th>( n_0 ) (1.5 ( \mu )m)</th>
<th>( n_0 ) (2 ( \mu )m)</th>
<th>( E_g ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{As}_2\text{S}_3 )</td>
<td>514 nm ; 125 J/cm(^2)</td>
<td>2.337</td>
<td>2.398</td>
<td>2.317</td>
<td>2.366</td>
</tr>
<tr>
<td></td>
<td>785 nm ; 1800 J/cm(^2)</td>
<td>2.358</td>
<td>2.431</td>
<td>2.346</td>
<td>2.416</td>
</tr>
<tr>
<td>( \text{As}<em>{40}\text{S}</em>{30}\text{Se}_{30} )</td>
<td>514 nm ; 125 J/cm(^2)</td>
<td>2.608</td>
<td>2.715</td>
<td>2.57</td>
<td>2.622</td>
</tr>
<tr>
<td></td>
<td>785 nm ; 1400 J/cm(^2)</td>
<td>2.548</td>
<td>2.682</td>
<td>2.536</td>
<td>2.667</td>
</tr>
<tr>
<td>( \text{As}_2\text{Se}_3 )</td>
<td>514 nm ; 125 J/cm(^2)</td>
<td>2.962</td>
<td>3.432</td>
<td>2.657</td>
<td>2.971</td>
</tr>
<tr>
<td></td>
<td>785 nm ; 300 J/cm(^2)</td>
<td>2.768</td>
<td>2.855</td>
<td>2.744</td>
<td>2.830</td>
</tr>
<tr>
<td>( \text{As}<em>{24}\text{S}</em>{38}\text{Se}_{38} )</td>
<td>514 nm ; 125 J/cm(^2)</td>
<td>2.313</td>
<td>2.416</td>
<td>2.291</td>
<td>2.354</td>
</tr>
<tr>
<td></td>
<td>785 nm ; 1320 J/cm(^2)</td>
<td>2.268</td>
<td>2.354</td>
<td>2.263</td>
<td>2.350</td>
</tr>
</tbody>
</table>

Table 3.5 summarizes comparable optical properties (refractive index and bandgap values) for thin films, as measured or calculated using equation (2.12). for 785 nm exposure and using ellipsometry following 514 nm irradiation. We present the data for the thin films non-
exposed and those that were irradiated with the highest dose to show the highest variations. Additional data are available elsewhere (284) or will be shown in figures presented in this section.

The refractive index was increasing for all compositions with increasing intensity or dose upon 785 nm exposure as shown in the next figure. All of the compositions exhibit an exponential-like trend, even though As$_2$Se$_3$ behavior is more subtle.

Figure 3.25: $\Delta n$ versus fluence for all compositions for 785 nm exposure.

Table 3-6 regroups the calculated parameters $E_{vo}$, $E_{db}$, $E_{ig}$, $E_{ev}$, the average bond lengths $d_{av}$, and the number of polarizable units $N$ for the four compositions studied under 785 nm exposure as calculated from the equations presented in sections 2.6.2.2 and 2.7. Values in italic are for the exposed thin film.
Table 3-6: Calculated optical parameters for as-deposited and exposed ($\lambda = 785$ nm) compositions. Values in italic correspond to irradiated samples and the illumination fluence is specified for each composition.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fluence</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$E_e$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$d_{av}$ (Å)</th>
<th>$N$ (x10$^{21}$/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_2$S$_3$</td>
<td>1800 J/cm$^2$</td>
<td>6.21</td>
<td>27.5</td>
<td>0.093</td>
<td>2.24</td>
<td>2.28</td>
<td>4.65</td>
</tr>
<tr>
<td>As$<em>{40}$S$</em>{30}$Se$_{30}$</td>
<td>5.95</td>
<td>27.8</td>
<td>0.090</td>
<td>2.10</td>
<td>2.32</td>
<td>4.86</td>
<td></td>
</tr>
<tr>
<td>As$_2$Se$_3$</td>
<td>1400 J/cm$^2$</td>
<td>5.49</td>
<td>29.6</td>
<td>0.081</td>
<td>1.91</td>
<td>2.34</td>
<td>4.6</td>
</tr>
<tr>
<td>As$<em>{24}$S$</em>{38}$Se$_{38}$</td>
<td>5.31</td>
<td>30.1</td>
<td>0.079</td>
<td>1.87</td>
<td>2.40</td>
<td>4.75</td>
<td></td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>300 J/cm$^2$</td>
<td>5.01</td>
<td>31.6</td>
<td>0.074</td>
<td>1.71</td>
<td>2.45</td>
<td>4.23</td>
</tr>
<tr>
<td>As$<em>{24}$S$</em>{38}$Se$_{38}$</td>
<td>4.82</td>
<td>32.7</td>
<td>0.071</td>
<td>1.68</td>
<td>2.89</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>1320 J/cm$^2$</td>
<td>7.5</td>
<td>30.6</td>
<td>0.122</td>
<td>1.9</td>
<td>2.40</td>
<td>5.82</td>
</tr>
<tr>
<td>As$<em>{24}$S$</em>{38}$Se$_{38}$</td>
<td>7.27</td>
<td>32.1</td>
<td>0.107</td>
<td>1.82</td>
<td>2.42</td>
<td>6.01</td>
<td></td>
</tr>
</tbody>
</table>

Due to the amount of data presented in this table, we will discuss their evolutions and significations in section 4.4. Finally, note that the As$_2$S$_3$, As$_{40}$S$_{30}$Se$_{30}$, As$_2$Se$_3$ and As$_{24}$S$_{38}$Se$_{38}$ ablation thresholds were estimated (for 785 nm exposure) as 33, 26, 9 and 18 GW/cm$^2$ with an error of 5%.

3.2.2.4. “n and k” method

The data obtained from Filmetrics Inc. quantified the refractive indices at $\lambda = 632.8$ nm and 550 nm for both As$_2$S$_3$ and As$_2$Se$_3$ compositions. The variation between these data and those obtained for these wavelengths for the non-exposed thin films measured by ellipsometry or
Swanepoel’s technique was ~ 0.04 higher for the As$_2$S$_3$ composition and 0.05 smaller for the As$_2$Se$_3$ composition. The error on the measurement is ± 0.001.

3.2.3. Nonlinear optical properties

We identified several methods to evaluate the nonlinear response of our bulk materials and thin films. The nonlinear properties ($n_2$ or $\chi^{(3)}$) were either experimentally measured or modeled (or both) according to different theories for bulk materials and thin films.

3.2.3.1. Z-scan results

The data obtained by z-scan at CREOL in collaboration with Van Stryland et al. were in accordance with the data obtained for the compositions 1 to 7 by Cardinal (106). These data are presented in the next figure.

It is observed that the nonlinearity increases with Se content. Values for glasses 10 and 11 could not be estimated with the z-scan technique and compositions 5 also presented some problems of “stability” during the experiment. Here we mean that exposure conditions during the measurement were such that we expect that some of the measurement-induced photo-structural modifications to our samples are occurring during testing. This is discussed for other samples with larger Se content, shortly. Note that the silica reference sample had a nonlinearity measured as $n_2 = 2.6 \times 10^{-16}$ cm$^2$/GW. The error on the measurement is estimated at ± 10%.
Figure 3.26: Nonlinear refractive index measured by z-scan method. Values for compositions 10 and 11 are estimates (288).

3.2.3.2. Pump-Probe experiment results

Table 3.7 presents the ratio between the nonlinear susceptibilities of the different compositions studied and the $\chi^{(3)}$ of the silica reference glass, for both regimes (60 mW and 250 mW).
Table 3-7: $\chi^{(3)}_{\text{ChG}}/\chi^{(3)}_{\text{SiO}_2}$ for compositions 1-12 as measured by CPPM.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\chi^{(3)}<em>{\text{ChG}}/\chi^{(3)}</em>{\text{SiO}_2}$</th>
<th>$\chi^{(3)}<em>{\text{ChG}}/\chi^{(3)}</em>{\text{SiO}_2}$</th>
<th>Composition</th>
<th>$\chi^{(3)}<em>{\text{ChG}}/\chi^{(3)}</em>{\text{SiO}_2}$</th>
<th>$\chi^{(3)}<em>{\text{ChG}}/\chi^{(3)}</em>{\text{SiO}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60mW</td>
<td>250mW</td>
<td>250mW</td>
<td>60mW</td>
<td>250mW</td>
<td>250mW</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>35</td>
<td>7</td>
<td>108</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>111</td>
<td>59</td>
<td>8</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>195</td>
<td>70</td>
<td>9</td>
<td>88</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>66</td>
<td>58</td>
<td>10</td>
<td>68</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>66</td>
<td>60</td>
<td>11</td>
<td>36</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>125</td>
<td>65</td>
<td>12</td>
<td>86</td>
<td>38</td>
</tr>
</tbody>
</table>

Significant fluctuations in the signal were observed at 250 mW for Se-rich materials.

Each reported value is the average of 3 measurements per sample. The error on the reported data is 20% and 10% for the experiments performed at 250 mW and 60 mW, respectively.

The nonlinear susceptibility is decreasing with decreasing As content / decreasing $n_0$.

The trend in the other results will be developed in the discussion chapter. Note that the variation for both $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$ and $\text{As}_{24}\text{S}_{76-x}\text{Se}_x$ series exhibit a “roof” effect, which translates into minima for $\text{As}_x\text{S}_y$ and $\text{As}_x\text{Se}_y$ glasses and maxima for S/Se = 1 (i.e. glasses $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ and $\text{As}_{24}\text{S}_{38}\text{Se}_{38}$ among their respective series).
3.2.3.3. Boling’s nonlinear models

Table 3.8 summarizes the results of the three Boling’s models presented in section 2.9.1 for compositions As$_2$S$_3$, As$_2$Se$_3$, As$_{40}$S$_{30}$Se$_{30}$ and As$_{24}$S$_{38}$Se$_{38}$. We included the results from the Z-scan and CPPM experiments (converted into $n_2$, in esu units) for comparison. The optical parameters needed for calculation were extracted from the thin films obtained prior or past 785 nm-exposure. The results in italic correspond to exposed samples. The Roman numerals (I), (II) and (III) correspond to formulas (2.30), (2.32) and (2.33), respectively.

Table 3-8: Calculated and experimental $n_2$ ($\times 10^{-13}$ esu) for multiple As-S-Se compositions.

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_2$ (I)</th>
<th>$n_2$ (II)</th>
<th>$n_2$ (III)</th>
<th>$n_2$ (exp) Z-scan</th>
<th>$n_2$ (exp) CPPM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>± 20%</td>
<td>± 20%</td>
<td>± 20%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>70</td>
<td>18</td>
<td>47</td>
<td>46</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>21</td>
<td>61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>As$<em>{40}$S$</em>{30}$Se$_{30}$</td>
<td>156</td>
<td>29</td>
<td>90</td>
<td>72</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>194</td>
<td>33</td>
<td>128</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>As$_2$Se$_3$</td>
<td>298</td>
<td>43</td>
<td>171</td>
<td>217</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>52</td>
<td>203</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>As$<em>{24}$S$</em>{38}$Se$_{38}$</td>
<td>31</td>
<td>10</td>
<td>23</td>
<td>250</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td>11</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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Photo-induced samples are thus predicted to consistently exhibit a higher \( n_2 \) than the non-exposed materials. All of the calculated \( n_2 \) increase for increasing Se content (and increasing \( n_0 \)) as do the Z-scan experimental results, however the CPPM data shows the opposite for the \( \text{As}_{40}\text{S}_{30}\text{Se}_{30} \)-to-\( \text{As}_2\text{S}_3 \) transition. It is also predicted by the models that \( n_2 \) would decrease for decreasing As content (and decreasing \( n_0 \)). Whereas the CPPM experimental results follow the same behavior, the nonlinearity as measured by Z-scan is shown to increase. These results will be extensively discussed in the next chapter.

### 3.3. Structural characterization

This section describes key data acquired by Raman spectroscopy for bulk glasses and thin films. These results will be used to highlight compositional effects and the resulting structural changes in bulk materials. The effects of deposition, annealing and aging are reported for thin films along with resulting photo-induced structural modifications. Much of the Raman data included in this section has been previously published as a result of our ongoing evaluation of these materials and are relevant to structural modification interpretation.
3.3.1. Raman spectroscopy on bulk glasses

Figure 3.27 shows data obtained for compositions 1, 2, 3, 6, 7 and 12 (106) to highlight the trends in structure modification as a function of the isostructural substitution of sulfur by selenium (compositions 1, 2 and 3), and as a function of the substitution of arsenic by chalcogen elements (compositions 3, 6, 7 and 12).

![Raman spectroscopy of selected ChG (106).](image)

**Figure 3.27:** Raman spectroscopy of selected ChG (106).
The primary Raman bands for typical homopolar bonds (S-S, Se-Se) and heteropolar bonds (As-S or As-Se) expected to be found in these glasses are labeled in the diagram. Deconvolution of the different peaks with the respective frequencies of each species was also performed in great details in a different study (289).

3.3.2. Raman spectroscopy on thin films: annealing and aging

Raman spectra of a waveguide, a fiber, a crystal and bulk (all made of As$_2$S$_3$) were collected and are shown in figure 3.28.

![Figure 3.28: Comparison of Raman spectra for As$_2$S$_3$ bulk, fiber, waveguide and crystal (290).](image-url)
One can observe the shoulder that we are familiar with for the bulk and the fiber. The crystal exhibits a typical pattern while the waveguide exhibits sharp peaks in the low frequencies and around 350 cm\(^{-1}\) and 370 cm\(^{-1}\).

We also present Raman spectra that were collected after deposition prior- and post-annealing, and photo-induced by an argon ion laser at \(\lambda = 514\) nm. The peaks of the non-annealed sample are observed to be sharper than those on the annealed spectrum. Sharpness decreases further upon exposition.

![Normalized Raman Intensity](image1)

Figure 3.29: Variation in WRS (excited at 840 nm) for fresh, annealed and photo-structurally modified As\(_2\)S\(_3\) single layers (exposure \(\lambda=514.5\) nm) (290).

Figures 3.30 and 3.31 show the Raman spectra of two thin films that were irradiated respectively 5 months and 3 years prior to measurement.
Figure 3.30: Raman spectra of a 5 months-old film for different positions on the sample (290).

The expanded inset of the frequency range 200-250 cm\(^{-1}\) in figure 3.30 shows the As-As bands. The “peak” signal corresponds to the irradiated region of the grating while the “valley” one lies in between two exposed regions. The non-irradiated region was chosen outside the exposed area. The “fresh” film shows sharp features while the “old” signal in figure 3.31 resembles to a bulk one.
3.3.3. Raman spectroscopy on laser-exposed thin films

WRS was also performed on the waveguides created upon irradiation with the argon laser (through a mask) and the Ti:sapphire laser (by focusing the beam inside the thin film and moving the sample along one direction). Figure 3.32 shows a comparison of the non-exposed four compositions prior to exposure at $\lambda = 514$ nm. Note that the films were 2 months old at the time of the experiment. No crystal phase was detected by XRD. Apart from $\text{As}_{40}\text{Se}_{60}$, all films show a certain amount of sharp features related to $\text{As}_4\text{S}_4$ & As-As units present.
Figures 3.33 and 3.34 show the evolution of the bands with increased exposure at 514 nm for As$_2$S$_3$ and As$_2$Se$_3$. One can observe that the peaks marked by the colored bands for As$_2$S$_3$ decrease, while no observable changes are observed in As$_2$Se$_3$. 
Figure 3.33: Evolution of As$_2$S$_3$ WRS upon exposition at $\lambda = 514$ nm.

Figure 3.34: Evolution of As$_2$Se$_3$ WRS upon exposition at $\lambda = 514$ nm.

Raman spectra 3.35 and 3.36 were acquired prior- and past-exposure at 785 nm. A clear difference between the as-deposited and exposed thin films is observable. The Raman spectra of
exposed As$_2$Se$_3$ regions do not show noticeable variations. Significant changes appear at low frequencies for the As$_2$S$_3$ sample. Subtle changes were observed for As$_{40}$S$_{30}$Se$_{30}$ and As$_{24}$S$_{38}$Se$_{38}$ compositions in the shoulder of the main bands.

Figure 3.35: Evolution of As$_2$S$_3$ WRS upon exposition at $\lambda = 785$ nm

Figure 3.36: Evolution of As$_2$Se$_3$ WRS upon exposition at $\lambda = 785$ nm.
CHAPTER FOUR: DISCUSSION

This chapter summarizes the discussion related to the results presented in chapter three. Interpretations of findings have been divided into four sections:

- Fabrication technique and uniformity of bulk materials
- Compositional effect and its influence on physical, optical and structural properties in bulk glasses
- Identification of properties variations between bulk glasses and as-deposited thin films
- Influence of glass composition and exposition conditions on the final properties of irradiated thin films

Whereby the results presented and how they provide valid answers to the questions defined as the objectives of this study (pages 1 and 2) are specifically addressed.
4.1. Fabrication technique and batch reproducibility

Could we reproducibly prepare and fabricate bulk and film materials with uniform physical properties?

In this section we approach the problem of fabricating reliable homogeneous and uniform bulk glasses which provide the basis for this whole study, as well as identifying proper techniques to ensure the purity and “quality control” for consistent results.

Following our homogeneity study on the \( \text{As}_2\text{S}_{38}\text{Se}_{38} \) bulk material (225), the range of sample preparation parameters employed clearly illustrated that bulk glass specimens with suitable optical and structural uniformity could be successfully fabricated for use as starting materials for thin film processing.

This is first illustrated through the non-significant deviation observed on some of the physical properties of ChG in our homogeneity study (225). In addition, the small atomic percent deviation in glass composition observed in our compositional EDS study, as reported in Table 3-1, confirms the result. As a point of comparison, Petkov reported a similar maximum deviation of roughly 2% atomic percent in a recent work on chalcogenides (280).

Furthermore, the consistent absence of contamination as shown either by EDS, FT-IR, or XPS confirms that our bulk material fabrication process is adequate and qualifies for high purity optical glasses in the As-S-Se system. These findings confirm our ability to make reproducible material of defined composition with repeatable process-defined property uniformity.
Lastly, additional techniques such as absorption spectroscopy and DSC were also used to assess batch repeatability and uniformity, as they allowed one to regularly characterize every sample fabricated. The rare samples exhibiting significant physical or optical properties deviations were discarded and consistently related to contaminated raw materials or operator error.

4.2. Compositional effects in bulk glasses

What would be the compositional effect on the physical properties within the As-S-Se system?

As observed in Table 3-2 and the specific figures shown in chapter 3, all of the physico-thermal and optical properties of the As-S-Se system show systematic property variations. We will first comment on the data obtained in this study (as compared to literature data when available).

Density was found to be consistent with previous data reported for As$_2$S$_3$ (85, 106, 292) and As$_2$Se$_3$ (106, 293), and this reinforced the fact that the packing density is higher in As$_2$Se$_3$ than in As$_2$S$_3$. The variation in density observed can be considered as linear with substitution of S atoms for Se atoms. The same behavior is apparent as a function of As (or total Ch) content. The slight drift observed for some points in figure 3.9 is related to the small variation in composition as reported in table 3-1 by EDS.
The $T_g$ values obtained for bulk glasses were found to be consistent with a previous study on similar glasses (106) and varying as one might expect with sulfur or selenium content. The data obtained for $T_g$ and density clearly follow a partial molar density model. Thus the data for compositions 1 to 5 can be predicted with an estimated accuracy better than 1% (106) by using:

$$
(T_g, \rho)_{\text{As}_{(x+y/2)}S_xSe_y} = [x\text{As}_2S_3 \cdot (T_g, \rho)_{\text{As}_2S_3}] + [y\text{As}_2Se_3 \cdot (T_g, \rho)_{\text{As}_2Se_3}]
$$

(4.1)

The same type of relationship can obviously be applied to compositions 7 to 11. The micro-hardness results obtained for stoichiometric materials ($\text{As}_{40}S_{60-x}Se_x$ series) exhibit higher hardness than that observed for the As-deficient $\text{As}_{24}S_{76-y}Se_y$ series as observed in figures 3.5 and 3.6. The larger concentration of chalcogen-chalcogen / homopolar bonds (S-S, S-Se and Se-Se) in As-deficient materials, as shown by our Raman spectroscopy data (figure 3.27), is related to the lack of As atoms available to satisfy those needed to form $\text{As}(S,Se)_3$ units. These latter units theoretically form the entire structure of the stoichiometric glasses $\text{As}_2\text{Ch}_3$. As mentioned in section 1.4.1.2, materials with high S or Se content tend to form preferably rings or chains with weak Van der Waals forces bonding the molecular units. The As atoms play here a cross-linking role between the molecular units (As is 3 coordinated while the chalcogens are only 2 coordinated) and thus strengthen the whole unit (the chalcogen rings are opened by the arsenic atoms and a layer-like structure with strong interlayer covalent bonds is formed with a higher degree of interconnectivity and order than in the As poor materials). This strengthened unit provides a higher resistance to crack initiation. As a consequence the bulk materials from the $\text{As}_{24}S_ySe_{76-y}$ series show a weaker hardness as compared to the $\text{As}_{40}S_xSe_{60-x}$ series due to a lesser extent of connectivity within the mixed layer/chain network.
Networks presenting chains of elemental S or Se \((r = 2)\) tend to be mechanically floppy because the number of nearest neighbors bonding constraints per atom (equal to 2) is smaller than the degrees of freedom per atom (equal to 3) (294). The mean-field theory developed by Philips and Thorpe (295-297) founds that the critical value of \(\langle r \rangle\) is \(\langle r_c \rangle = 2.40\) below which there are \(5/2[\langle r_c \rangle - \langle r \rangle]\) floppy modes per atom. At \(\langle r_c \rangle = 2.40\) the mean-field theory predicts that the number of constraints per atom is equal to the degree of freedom per atom, thus establishing the onset of rigidity. As a consequence under-coordinated networks for \(\langle r \rangle < 2.40\) (such as the As\(_{24}\)S\(_y\)Se\(_{76-y}\) series) show polymer-like structures with stiff regions immersed in a matrix exhibiting localized softness due to these floppy modes. This was confirmed later on by Varshneya (298) for binary ChG materials with varying \(\langle r \rangle\).

Varshneya and Swiler also mentioned the linear relationship between hardness and average coordination number \(\langle r \rangle\) for a number of chalcogenide compositions (299). According to this and Philips’s critical value of \(\langle r \rangle\), the stoichiometric compositions of series As\(_{40}\)S\(_x\)Se\(_{60-x}\) should theoretically exhibit the highest micro-hardness (and also for other properties as we will mention) among our materials since they present the highest connectivity between As and ChG’s atoms, thus the stiffest structure. Indeed, our data (figure 3.7) prove the validity of this concept. Also, following Varshneya and Swiler’s findings mentioned previously, ChG materials with equal \(\langle r \rangle\) should theoretically present a similar hardness which is also the case here. The slight change observed is well contained in the error bars of the measurement for As\(_{40}\)S\(_x\)Se\(_{60-x}\) and can certainly be attributed to the subtle changes existing between As-S and As-Se bonds.

However, as shown in figure 3.6, constant hardness does not seem to be valid anymore for the As\(_{24}\)S\(_y\)Se\(_{76-y}\) series despite the glass materials having the same \(\langle r \rangle\). The same phenomenon was observed by Feng et al. (294), but for \(\langle r \rangle > 2.40\). In our study, micro-
hardness is shown to be increasing with Se content. This could be an indication that the materials presenting the characteristics of being both As-poor and Se-rich have more densely packed layers as compared to the S-rich glasses.

If we now consider coefficient of thermal expansion (CTE) data obtained by TMA, we observe that the value found for As$_2$S$_3$ is similar to what one can find in the literature (300). As observed for the hardness data, the change in CTE for the As$_{40}$S$_x$Se$_{60-x}$ series is rather small while more significant for the As$_{24}$S$_{76-y}$Se$_y$ series. As it is known, the thermal expansion of glass material is caused by changes in lengths of relatively weak intermolecular forces between the existing structural units. This manifests in our data in terms of the relatively high values of the CTE, which is related to the structure and type of bonding in the solid. By comparing the two series or observing the change in CTE (figure 3.11) and $T_g$ (figure 3.9) with coordination number, the values of $T_g$ increase while those of the CTE decrease by increasing the content of units with $<_r> = 2.4$ (those from the As$_{40}$S$_{60-x}$Se$_x$ series), which shows that those structural units contribute to the strength of glassy skeleton and enhance the stability of the glass by increasing the connectivity. These results are consistent with those observed for the hardness of our materials. Thus one expects that higher values of glass transition temperature $T_g$ implies a higher degree of interconnection of structural elements in the network. Thermal stability is thus higher for the compositions of the As$_{40}$S$_{60-x}$Se$_x$ series as compared to the As-deficient series. Note also that the chemical bonds inside structural units of As$_2$S$_3$, As$_2$Se$_3$ or similarly coordinated samples are of covalent type, which are much stronger than intermolecular bonds between structural units. These bonds are almost not influenced by the expansion which means that the variation in the interatomic distance within the structural units involved make only a small portion in the value of the CTE.
As a consequence the physico-thermal data summarized in Table 3-2, namely $T_g$, CTE, micro-hardness and density, provide a comprehensive summary of the network structures present in the stoichiometric and As-deficient glasses examined here. These results are supported by the Raman spectroscopy and XPS data which form the basis of other theses outside of this study (301) confirm the existence of homopolar bonds for ChG-rich compositions, thus weakening the overall network and impacting the physico-thermal properties mentioned previously.

We proved that structural changes were likely according to the variations observed in CTE, micro-hardness, density and $T_g$. Indeed, looking at the Raman data in figure 3.24, two major bands are apparent respectively between 200 and 300 cm$^{-1}$ and 300-400 cm$^{-1}$. The first one increases with increasing Se content while the second one decreases for compositions 1 to 3. The first band was actually observed to show two features centered at 230 and 240 cm$^{-1}$. The second one corresponds to the anti-symmetric stretching vibration of As-S-As in the pyramidal AsS$_{3/2}$ unit (107). By decreasing the As content in compositions 6, 7 and 12 a narrow band seems to appear to become patent for composition 12. Note also the shoulder between 450 and 500 cm$^{-1}$ for the same As content decrease.

The results for compositions 1, 2 and 3 were found to be in agreement with a previous work by Freitas (274). Other studies (302-304) had attributed the bands at 230 cm$^{-1}$ and 345 cm$^{-1}$ respectively to the antisymmetric stretching vibrations As-Se-As in As$_2$Se$_3$ and As-S-As in As$_2$S$_3$.

Note that the Raman spectra of As$_2$S$_3$ and As$_2$Se$_3$ are quite simple and the two bands around 342 cm$^{-1}$ and 227 cm$^{-1}$ were shown to represent the majority of structures present in the glass, i.e. pyramidal AsS$_3$ and AsSe$_3$ (305, 306). Thus one might think that the As$_{40}$S$_{60-x}$Se$_x$ compositions (1 to 5) are weighted two-phase structures. In addition, the variation observed at
230 and 240 cm\(^{-1}\) was also reported by the same authors, this latest being characteristic of pyramidal As\(_n\)Se\(_{n-3}\) units (307).

The two main bands at 255 cm\(^{-1}\) and the one between 450 and 500 cm\(^{-1}\) are respectively attributed to Se-Se and S-S homopolar bonds vibrations. All this is in agreement with the CON structural model introduced in section (1.3.1.2.), which expects that arsenic rich glasses would exhibit As–As, As–Se, and As–S bonds; selenium rich glasses would have As–Se, As–S, and Se–Se bonds and sulfur rich glasses As–Se, As–S, and S–S bonds.

Some additional interesting observations can be made: the S\(_8\) rings extensively described (138, 308) are responsible for bands at 434 and 474 cm\(^{-1}\) (stretching mode). More importantly, the increase in intensity of the homopolar and heteropolar bonds bands at the expense of the pyramidal bonds signal and the higher relative intensity weight of the Se-Se bands as compared to the S-S ones is a sign that the Se atoms are progressively leaving the pyramidal units to form long chains while S atoms remain in these pyramids. Bands located below 200 cm\(^{-1}\) contain a significant number of defects such as As\(_4\)S(Se)\(_4\), S(Se), As-As and As\(_4\) molecular fragments (309). These phenomena are not explained by the CON model. Finally, by looking closely at the Se-Se and S-S bands, one can observe that more molecular sub-units are present in the binary compounds As\(_2\)S\(_3\) and As\(_2\)Se\(_3\) than in the ternary glasses for a ratio [S]/[Se]=1 and decreasing [As].

As shown by Protasova et al. (310), the As-S-As configuration in S-rich glasses tends to become As-S-S for increasing S content while the same behavior is observed for Se-rich glasses through creation of As-Se-Se bonds. As discussed previously through Raman results, the increase in Se content leads to the replacement of the Se atoms by S atoms around the arsenic while Se-Se bonds get formed. To be complete on the structural subject, a recent study in our
group (289) combining EXAFS, XPS and Raman spectroscopy on all 13 compositions showed that in As$_{40}$S$_{60-x}$Se$_x$ glasses, the main structures were mixed AsCh$_3$ pyramidal units. XPS confirmed the gradual change of As environments for varying chalcogen contents and also proved the existence (in very limited amount) of homopolar ChG bonds in the stoichiometric binary compositions (namely As$_2$S$_3$ and As$_2$Se$_3$). For chalcogen-rich As-S-Se glasses, Raman results show that the structure is composed of chalcogen chain fragments cross-linked by pyramidal AsCh$_3$ units.

If we now consider the resulting optical data for the bulk and film and as it relates to subsequent discussion of photo-induced changes to these properties, the bandgap values obtained for As$_2$S$_3$ and As$_2$Se$_3$ (see Table 3-2) are different by $\pm$ 0.2eV as compared to those found in the literature (87, 90, 91) but similar to one of our previous study (106). Since the previously mentioned properties (density, $T_g$, etc.) are in agreement with the literature, this can be explained by the method of calculation used in the different techniques. In addition, drawing a tangential line is obviously very subjective depending on what part of the edge one chooses to draw his line from. According to Tauc (85), the region of small absorbance located at higher wavelength after the band edge is related to the preparation and purity of the materials thus confirming the quality of our processing. The substitution of sulfur by selenium atoms induces a significant red shift of the absorption edge as shown in figures 3.12 and 3.13. The substitution of As atoms by chalcogens had however little effect on the linear absorption as shown in figure 3.14. As seen with other properties, the red shift of the absorption edge can be linked to the continuous substitution of S atoms by Se atoms, at least for the compositions with constant As content (i.e. series As$_{40}$S$_{60-x}$Se$_x$ and As$_{24}$S$_{76-y}$Se$_y$). Interestingly a blue shift occurs in the series where the ratio As/Ch is changed (i.e. compositions 3-6-7-12). At the same time this blue shift is very
small as compared to the large red shifts observed for the other series, thus supporting the
formation that Se-Se and S-Se bonds that counteract the decrease of the cation/anion ratio as
discussed previously in (106).

Considering now first the refractive indices as obtained by Fresnel loss, despite the
limited accuracy we found surprisingly good values compared to those of the literature for As$_2$S$_3$
(32, 84, 106), As$_2$Se$_3$ (93, 106) and the compositions 2, 3 and 4, which were previously studied
in our group (106). However the range of reported refractive indices for As$_2$S$_3$, for example, is
wide (from 2.34 to 2.44) but most of the community usually stands for $n_0 \sim 2.4$. As mentioned in
chapter 3, the data obtained using the Matlab code and the ellipsometer exhibit higher values
versus the Fresnel method. These data are however more closely connected to the change in
composition (up to $\sim 2\%$ loss in sulfur and increase in the relative As concentration) observed
using EDS. A higher As content is reported as increasing the refractive index of the As-S-Se
glasses, at least in the glass forming region of our composition range, thus explaining the slightly
higher refractive index observed for our compositions when compared to the rest of the
literature. As a consequence we strongly believe that the Matlab analysis and ellipsometer
techniques shown produce results closer to the compositional reality of our materials as could be
expected from the ellipsometric accuracy. Hence index based on ellipsometry technique will be
used as the basis for our effort.

As mentioned previously, the refractive index follows the Lorentz-Lorenz formula
(equation 2.15) (311). The number of polarizable units, important chemical and optical entities
in the photo-modification process, can be expressed as the sum of contributions of the As, S and
Se atoms. If we consider series of materials with a constant As content such as in our study
(either [As] = 40\% or 24\%), we can thus plot $(n^2 - 1/n^2 + 2)$ versus Se or S content and expect a
linear relationship. Figure 4.1 was created with the data obtained by ellipsometry, with \( n_0 \) chosen at 1550 nm:

Figure 4.1: \( \frac{n^2 - 1}{n^2 + 2} \) versus Se content for bulk glasses.

These results show that not only the refractive index of Se-rich materials is higher than S-rich materials, as predicted by Lorentz-Lorenz relationship (since bigger Se atoms have higher polarizability than S atoms), but the number of polarizable units present in our bulk glasses are directly related to Se content. Hence, one might intuitively predict high Se content materials to have systematically larger photo-response than other glasses in our study.

The same index behavior could have been inferred from the density measurements, as the same monotonic trends observed here are seen in density data summarized in section 3.1.2.3.
The classical model for an oscillating electron, which shows that the refractive index is linearly dependent of the density of electron present in the material, can also explain this behavior. Additionally, the red-shift of the absorption edge seen in our experiments further supports this increase of the refractive index via the Kramers-Kronig relation. Regarding the absorption edge that was shown to be quasi-invariant for [S]/[Se] =1 glasses with decreasing As content, as there is a measured change in the refractive index and it could not be explained by the bandgap measurements, this again gives strong evidence as to the network’s responsibility for the observed variation.

As a conclusion, we observed that the change in composition, either by Se for S substitution or As for Ch replacement, impacted the different physico-thermal and optical properties, which were found to be similar to the literature when provided (specifically for As$_2$S$_3$ and As$_2$Se$_3$). These variations have been quantified and the eventual structural changes taking place have been identified by Raman spectroscopy and supported by XPS. The refractive index was shown to be strongly related to the high polarizability of Se atoms and the structural changes taking place in the glass matrix upon increase of the chalcogen content.
4.3. From bulk glass to thin film

What significant differences if any, exist between bulk glass samples and their corresponding as-deposited films?

The discussion in this section will cover the data obtained on thin films as obtained by micro-thermal analysis, Raman spectroscopy, XPS and linear refractive indices. To understand how material in device geometry might be expected to vary from that observed in bulk materials, such an investigation on property variation was undertaken.

As measured by Laniel with our materials and using the grating-coupling method (265), observed a decrease in the refractive index of deposited thin films versus bulk materials and a constant increase of the $n_0$ of these same thin films upon annealing. These results are consistent with the expected lower density configuration of atoms found in films and fiber whose structures condense at much higher cooling rates than bulk materials. The same behavior was observed in samples prepared for the irradiation experiments and measured in our study using the Swanepoel’s technique. Since these data were acquired in the scope of the photo-induced study, we will limit ourselves to results seen in our study.

The observed change in refractive index indicates that a change in the structure of the material took place upon thermal evaporation of the bulk materials. As shown by Knox and Ban (68), analysis of the vapor phase upon evaporation of As$_2$Se$_3$ leads to a broad range of molecular species, from chains of various sizes to As$_x$Se$_y$ molecular units with various x and y coefficients.
One can thus expect the creation of a different structural matrix (as compared to the initial bulk glass arrangement) upon condensation of the vapor phase on a substrate.

Our Raman figure (3.28) shows indeed quite different spectra for bulk glasses compared to as-deposited and annealed thin films. The most pronounced variation is seen for As$_2$S$_3$ and to a lesser extent in other ternary glasses. The features observed on the waveguide spectra for As$_2$S$_3$ are quite interesting. Consider first the as-deposited thin film, the main band previously discussed at 345 cm$^{-1}$ is observed in all spectra. The sharp features are related to the presence of As$_4$S$_4$ units in the as-deposited film as previously observed in various studies (312). One can observe a difference in the peaks between the annealed and unannealed films (figure 3.29). This is believed to be due to a film polymerization which reduces the As$_4$S$_4$ molecular units content and also the number of homopolar (reduction of the As-As band at 235 cm$^{-1}$ and S-S band above 400 cm$^{-1}$) bonds during As-S bond recombination. The shape of the annealed film is evolving towards a bulk-shaped spectrum.

Looking at figure 3.30 where micro-Raman spectra of As$_2$S$_3$ gratings examined structural signatures in the grating peaks and valleys, one can observe first a shift toward lower frequencies of both the valley and peak regions as compared with the non-exposed area, which is a sign of more rigid As-As bonds. The peak intensity signal is also lower than the two other ones, meaning that the homopolar bond content has been decreased which confirms this effect previously observed in figure 3.29.

Examining the spectra for the aged films, one can observe for the old film that the sharp molecular features observable on the fresh film have disappeared. The majority of the Raman spectrum now looks similar to that of the bulk glass, however this is a sign that the homopolar
bonds largely re-configure back to “normal” As-S bonds but do not totally disappear since we can still see some As-As bands in the low wavenumber region of spectra.

Leadbetter et al. work by diffraction studies (312) or El-Ocker et al. (313) by optical characterization of As$_2$Se$_3$ also observed defects classified as homopolar bonds. Apling et al. observed the creation of As-As bonds in As$_2$S$_3$ films while Kosek and coworkers quantified (129) these As-As bonds as representing up to a third of all the species (among the As$_4$Ch$_4$ units), this As-As content decreasing upon annealing and further illumination. According to recent Raman studies on As$_{40}$S$_{20}$Se$_{20}$, AsS(Se)$_{3/2}$ pyramidal units form the backbone of the glass with numerous As$_4$S(Se)$_4$, S(Se), As-As and As$_4$ molecular fragments (309). The existence of molecular fragments of As$_4$S(Se)$_4$, S–S, and Se–Se in the film structure was found to be responsible for this. Hence these studies support our current findings.

It is also worth mentioning that a physical relief was observed with a rounding of the morphology for an old grating aged more than 3 years. This grating had been sitting on a shelf exposed to room temperature and laboratory light. The optical properties were measured and a huge loss in first order diffraction efficiency (drop by 70%) was observed along with a decrease in the $\Delta n$ formed initially (314). Hence it is correct to mention that aging plays the role of a slow, room temperature annealing process made possible by the proximity of the glass’ T$_g$ to room temperature. This issue has to be taken into account in further experiments and can be characterized by Raman spectroscopy as shown. Particularly, pre-aging of the material following exposition and prior to exposure should minimize this problem of post-writing relaxation.

We can conclude that the change in refractive index is obviously linked to the creation of different molecular features in our thin films upon thermal deposition and annealing, as observed.
using Raman spectroscopy. XPS was also used to characterize deposited ChG films (264) and the signal obtained was different from the bulk materials. The changes observed were related to an increase in Se-Se bonds and change in the surrounding configurations of the As and Se atoms, thus giving even more credibility to our findings.

To confirm these proposed structural arguments, we also tried to compare the $T_g$ of the bulk materials to their corresponding thin films. As mentioned in the experimental section, the first step was to compare the data acquired by DSC and μTA on bulk materials and see how they compare. A direct relationship between the data was difficult to establish for heating rates of 15°C/sec or 5°C/sec versus the typical 10°C/min rates used in DSC. While $T_g$ was clearly marked by a sharp peak with the DSC method, it was not possible to detect the same signal using the power signal of the μTA. The opposite is also true for $T_m$ since we need to avoid melting of our materials in the DSC equipment. However, the data acquired either for $T_g$ (DSC) or $T_m$ (μTA) is in excellent agreement with previous studies (106) and the well-known melting temperature for As$_2$S$_3$ (307°C). We would like to point out that a small peak could be constantly observed around the $T_g$ value on the μTA derivative of the power signal for a smaller heating rate of 1°C/sec, however, this was not practical to use as a marked “property value” due to the lack of resolution for this peak, and hence we used $T_m$ as our material structure parameter.

Hammiche et al. used the sensor position trace to determine the glass transition, recrystallization and melt temperatures of a PET sample (257). We used this same technique to observe $T_g$ values of the bulk glasses but the resulting accuracy among multiple measurements on the same sample was not found to be very good (up to ±6°C). However, we noticed that the
sensor curve also gave smaller $T_m$ values (up to 20°C) than those obtained with the power signal, which explains these very low $T_g$ values as compared to those obtained by DSC.

At this point, we conclude that these two techniques are clearly complementary despite the shifted information they provide (due to very different heating ramps) and that the accuracy of the power signal ($\mu$TA) on bulks is excellent.

As noticed previously, the excellent accuracy of the technique allows us to evaluate the increase in $T_m$ and relate this to a change in structure taking place upon film formation. We compared bulk glass results to data obtained on films firstly during the evaporation process and secondly as modified during the irradiation process.

Even though it was not possible to measure all of the same physico-thermal properties of these materials as we did for the bulk materials, we can confidently expect that they will exhibit differences in these other properties since we showed in the previous section that they were all intimately connected.

As a conclusion, molecular changes were observed and identified upon deposition of the bulk materials via thermal evaporation into thin films. XPS confirmed a change in surrounding around the As, S and Se atoms. These variations were shown to impact in a certain extent optical and physical properties such as refractive index or thermal transition events.
4.4. Composition and exposure influence on photo-induced properties in thin films

*What is the compositional effect and that of the exposure conditions on resulting sensitivity in thin ChG films?*

In this section we discuss the compositional influence observed on the subsequent properties of the exposed samples. The effect of exposure conditions (wavelength, intensity, dose or others) will also be described.

The starting as-deposited and annealed thin films exhibit similar refractive index dispersion curves prior to exposure as seen in figure 3.24. The significant deviation displayed by As\(_2\)Se\(_3\) between the two depositions is attributed to what seems to be a rare flaw in the bulk material chunk used rather than to the deposition process, or operator error in setting deposition parameters. A higher than expected Se concentration seems to be the reason according to the high refractive index value of the film sample fabricated for 514 nm exposure. Note that the same spectral behavior was observed all over the deposited film area. Laser exposure of the films resulted in a variety of property changes, including induced absorption, index changes and in some instances topographic photo-expansion.

The photo-expansion observed in both experiments is dependent on the beam intensity and the laser source used. Material deformation was observed to be higher using the argon laser (up to 150 nm in As\(_2\)Se\(_3\)) as compared to the fs source (up to 25 nm in As\(_2\)Se\(_3\)). A thermal effect might be envisioned as the sole reason for photo-expansion, i.e. if the temperature gets higher than the T\(_g\) of the glass then the material will flow. This is not precisely believed to be the case.
Krecmer et al. (316) postulated a mechanism of light-induced bond-twisting motion involving the two-fold coordinated ChG atoms. The transition of the LP’s from the VB to localized states at the CB edge would cause a change in the repulsive interaction between the excited LP orbitals of the excited ChG and those of its neighbors. The recombination time for photo-excited carriers in localized states being much longer than for extended states, local structural rearrangement could take place before recombination occurs. Non-radiative recombination is also more likely for carriers trapped in localized states as discussed by Stuchlik (317) and the energy liberated by these encourages additional local structural changes such as bond breaking. In addition, since ChG atoms exhibit the intrinsic anisotropy of the p-like electron orbitals, this means that only the atoms having favorable orientations with respect to the electric field vector of linearly-polarized light will absorb photons and participate in structural changes. This would explain the photo-expansion observed and fit perfectly our theory, which states that some of the LP’s at the top of the VB are delocalized upon photon illumination into localized states just below the CB, thus narrowing the bandgap of the material, which as a note would also be favored by the creation of new defect (localized) states in the bandgap. In addition, bandgap illumination is supposed to facilitate the rupture of a fraction of As-S bonds leading to the creation of As-As bonds (318) as we also previously observed (275). Since As-As bonds are slightly longer than As-S bonds (respectively 0.259 nm versus 0.221 nm), those perpendicular to the substrate plane can contribute to further photo-expansion. Bandgap illumination has been reported to lead to so-called “giant-photo-expansion” (several hundreds of nanometers for a film of a couple of microns (127) and up to 3 \( \mu \)m for a thick film of 20 \( \mu \)m (134)) thus the highest photo-expansion observed for bandgap exposure in this study is not surprising considering the extensive time of our exposures.
The refractive index changes upon illumination by both laser sources show that Se-rich materials exhibit a consistent higher $n_0$ variation for a given exposure energy or intensity as compared to the S-rich $\text{As}_2\text{S}_3$. The sample with high Ch content ($\text{As}_{24}\text{S}_{38}\text{Se}_{38}$) also shows in both experiments a steeper “response” than the $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ material. As previously discussed for the bulk materials, we believe this can be related to the highest polarizability of the Se atoms versus S atoms as described earlier by the Lorentz-Lorenz equation. Since we consider that the polarizability values and the arsenic content remain unchanged, then $(n^2-1)(n^2+2)$ should be a linear function versus $N_{\text{Se}}$ (number density of Se). As we can not accurately measure the density of our films, $(n^2-1)(n^2+2)$ is plotted versus Se content in figure 4.2. In the case of thin films, this gives us, using $n_0$ of the thin films calculated at 1.5 $\mu$m and irradiated at 785 nm.

![Figure 4.2: Refractive index versus Se content for non-exposed and (highest) exposed thin films using Lorentz-Lorenz relationship.](image)
Estimates of density from RBS would thus allow figure 4.2 to be redrawn while normalizing versus effective density.

According to figure 4.2, this means that a higher number of polarizable units is present upon exposure in all of the materials leading to the increase in refractive index of the material.

Interestingly, the photo-induced changes created by cw exposure show a saturation effect as can be deduced from the plateau observed for the change in refractive index of the materials (figure 3.23). This has been previously observed by Vallée et al. (230) in the case of the formation of Bragg gratings at the same wavelength. We identify this saturation to the depletion upon exposure of defects, which will be discussed at the end of this section, that we think are responsible for the observed increase in $\Delta n$. As mentioned in section 3.2.2.2, no significant difference in $\Delta n$ was observed upon changing the polarization of the argon laser beam, which means that mechanisms responsible for photo-darkening effects are different from those driving photo-anisotropy. On the other hand, the extent of femtosecond-induced changes appears to be limited by the material threshold for ablation. Two regimes appear to be present in this case: an initial change up to what can be determined as a threshold energy or intensity after which the increase in refractive index becomes much accelerated and pronounced. Since the photon energy of the laser source is well below the bandgap of the material, this suggests that the mechanisms responsible for the $\Delta n$ rely on nonlinear optical processes as was also previously observed by Zoubir et al. (240). Contribution of the $\chi^{(3)}$ of these materials would thus “kick in” at a given intensity, contributing to the increase of the refractive index.
The behavior observed in this latter case was fitted accordingly to a model developed for optical ablation by high-power ultrashort pulses (319), based on the generation of free-electrons through multiphoton ionization. The electron rate-equation is as follows:

\[ \frac{\partial n_e}{\partial t} = \alpha \cdot I(t) \cdot n_e + \sigma_k \cdot I(t)^k \]  

\(4.2\)

where \(n_e\) is the electron density, \(\alpha\) is the avalanche coefficient, \(I(t)\) is the time-dependent intensity of the laser, and \(\sigma_k\) is the \(k\)-photon absorption cross section. According to Kaiser et al. (320), the first term on the right hand side of the equation which represents the avalanche ionization can be ignored for pulse durations smaller than 150 fs. This was proved valid in an earlier work on \(\text{As}_2\text{S}_3\) (240). The \(\text{As}_2\text{S}_3\) two-photon absorption cross-section value was calculated by Tanaka (321). According to the references above, the electron density is expected to increase with the laser intensity until it reaches a critical value prior to ablation. Our intensities were selected as close from ablation as possible, as can be compared in the figure below and on the materials ablation threshold mentioned earlier in this document in section 3.2.1.5. Equation (4.2) thus becomes:

\[ \frac{\partial n_e}{\partial t} = \sigma_k \cdot I(t)^k \cdot \frac{N_0 - n_e}{N_0} \]  

\(4.3\)

where \(N_0\) is the depletion parameter which corresponds to the maximum number of bonds (not polarizable units) available to participate to the photo-chemical reaction. The next figure shows
the photo-induced $\Delta n$ and electron density versus pulse intensity for the femtosecond exposure of As$_2$S$_3$:

![Graph](image)

**Figure 4.3**: Photo-induced $\Delta n$ (squares) and electron density ($n_e$, dotted line) versus pulse intensity for As$_2$S$_3$.

The depletion parameter was found to be $N_0 \sim 2 \times 10^{18} \text{ cm}^{-3}$ which is in good accordance with the number of available atoms in the matrix in the order of $10^{21}-10^{22} \text{ cm}^{-3}$ depending on the composition considered. This model thus predicts the generation of additional free electrons upon exposure, which are considered in our theory as playing a major role particularly on the nonlinear optical properties of our materials by increasing the overall polarizability of the sample as discussed in section 4.2. While the two-photon absorption cross-section was not readily available in the literature for the others compositions, the trend observed in the photo-induced $\Delta n$ versus intensity for these materials is similar to As$_2$S$_3$, hence the same behavior is expected for
As₄₀S₃₀Se₃₀ and As₂₄S₃₈Se₃₈. Note that the behavior of the As₂Se₃ sample upon femtosecond illumination is almost linear (figure 3.25) as one should expect since the photons energy (1.58eV) is close if not similar to the bandgap energy of the material.

The increase in dispersion energies upon illumination or increasing Se content, as calculated using Wemple-DiDomenico model (equation 2.20), can be linked to an increase in the arsenic coordination. Indeed, the dispersion energy can be expressed as:

\[ E_d = \beta \cdot N_c \cdot Z_a \cdot N_e \]  \hspace{1cm} (4.4)

where \( \beta \) is a constant, depending on the ionic or covalent character of the material (in our case \( \beta = 0.37 \)), \( N_c \) is the cation coordination number, \( Z_a \) is the anion valence and \( N_e \) is the number of valence electrons per anion. Since \( Z_a, \beta \) and \( N_e \) are constant along the As₂S₃-As₂Se₃ compositional line, the cation coordination number has to increase if \( E_d \) increases thus confirming that a structural rearrangement is taking place and leads to refractive index increase. As stated by Wemple (322) As atoms form bonding As-ChG bridges between interlayers thus contributing to an increase in the As effective coordination, leading to \( N_c > 3 \) which is our case.

As a conclusion the interaction between layers increases from As₂S₃ to As₂Se₃ thus one can expect an increase in overall hardness which we observed in bulk materials (table 3.2). Georgiev reported along the same idea an increase in \( N_c \) (323) due to the existence of 4-fold coordinated As thus supporting our findings, while Sanghera noticed an increase in compactness thus hardness.
Finally, the dispersion energy can also be expressed as:

\[ E_d = f \cdot Z_a \cdot N_e \times \left[ N_a d^3 \right] \]  

(4.5)

where \( f \) is the oscillator strength, \( Z_a \) and \( N_e \) are the same parameters previously defined for equation (4.4), \( N_a \) is the number of polarizable units and \( d \) is the average bond length. As we discussed previously, the average bond length is expected to increase upon irradiation.

Estimating the number of polarizable units with the density and molar mass of the different compositions helps us to back-calculate the average bond length of these materials (table 3.6). These values are close from what one might expect for unexposed As\(_2\)S\(_3\) and As\(_2\)Se\(_3\) (324). The resulting post-exposure increase in bond length is another proof of the deformation of the glassy network upon irradiation, and the evidence to support the mechanism of bond distortion (lengthening) as was well as breaking-reformation.

The large oscillator energy \( E_o \) decrease for decreasing Se content is explained by the much lower As-Se (96 kJ.mol\(^{-1}\)) bond energy as compared to As-S (379 kJ.mol\(^{-1}\)). The \( E_o \) increase from As\(_{40}\)S\(_{30}\)Se\(_{30}\) to As\(_{24}\)S\(_{38}\)Se\(_{38}\) is also linked to the highest content in homopolar bonds found in As\(_{24}\)S\(_{38}\)Se\(_{38}\) and their higher energies (As-As, S-S and Se-Se respectively 382, 425.3 and 332.6 kJ.mol\(^{-1}\) (266)) as compared to the heteropolar ones found in As\(_{40}\)S\(_{30}\)Se\(_{30}\).

While inducing changes in structure, index and polarizable units, the examined absorption coefficient is observed to increase upon exposure for all of the materials. No definitive conclusions versus composition variation could be drawn from the obtained results on the four compositions studied.
The Urbach absorption region, weak absorption region, was investigated according to equation (2.21). The Urbach energy is reported to be a figure of the disorder in amorphous ChG materials and to be connected with the width of the extended tails (267). The transitions of the electrons upon illumination from the defect states forming the top of the VB to the CB (or band-edge) led in our case to a reduction of the Urbach energy and a reordering of the original electronic defects configurations. The Tauc parameter B (equation 2.20) in the high absorption region depends on the width of the localized states in bandgap and is attributed to defects/wrong bonds in ChG (280). According to Mott and Davis, it is connected to the creation of these localized states at the edges of the VB and CB. We observe an increase in this parameter upon increasing exposure which means that new defect states are effectively created. The bandgap is in turn reduced which goes along with the creation of new states. Since the oscillator energy is related to the optical bandgap $E_g$ ($E_o \sim 2.5 E_g$), the structural reasons (large differences in bonding energies) proposed earlier for decreasing $E_o$ also contribute to the decrease in $E_g$. In addition, the creation of localized states as previously suggested in the bandgap upon illumination further contributes to this decrease.

As observed in a previous study (290) and illustrated in this document (figure 3.29) the exposure at 514 nm further polymerizes the network and modify the As-As bonds distribution (as seen by the change for the band 235 cm$^{-1}$), while a photo-expansion of the film is observed. This is equally observed in this set of exposure at 514 nm as shown for the As$_2$S$_3$ sample (figure 3.33), which goes along with the variations in optical properties as discussed above.

As we have discussed already in this document, Ch atoms and group IV atoms form chemical bonds between like atoms. The energies of these bonds (reminder: As-As, S-S and Se-Se are respectively 382, 425.3 and 332.6 kJ.mol$^{-1}$) are close from some of the heteropolar bonds,
especially As-S (379 kJ.mol\(^{-1}\) while As-Se is 96 kJ.mol\(^{-1}\)). This enables the change of coordination of individual atoms (325, 326) as we just discussed in our study for As atoms. Hence the energies needed for optically-induced or enhanced reactions such as the photolytic reaction presented here (327):

\[
2|M - C| \leftarrow \frac{h\nu, I_1, T_i}{h\nu_1, I_1} \rightarrow |M - M| + |C - C|
\]  

(4.6)

where \(M\) represents As in our case and \(C\) would be the Ch atom, are much lower than in oxides. \(h\nu\) and \(I\) represent the energy and intensity of the irradiation light and \(T\) is the temperature, the coefficient \(i = 1\) or \(2\) depending on the direction of the reaction. According to Frumar, \(h\nu_1 > h\nu_2\) and \(I_1 > I_2\) shift the reaction to the right while annealing shifts it to the left. Hence as an example, in the As-S system the reaction would be interpreted as:

\[
2(As_2S_3)_n \leftrightarrow nAs_4S_4 + nS_2
\]  

(4.7)

with \(n > 1\). As we observed on the Raman spectra (figures 3.29 and 3.33) following 514 nm exposure, the reaction is favored in the backward direction thus creating homogenization and polymerization of the network. Note that we have identified in the previous sections the location of S-S units in our Raman spectra between 450-500 cm\(^{-1}\) and As\(_4\)S\(_4\) bands located below 200 cm\(^{-1}\). Frumar et al. also calculated precise locations of As\(_4\)S\(_4\) at 145, 168, 190, 214, 223 and 361 cm\(^{-1}\) (327). However the As\(_2\)Se\(_3\) sample does not seem to show any kind of variation (figure 3.34). It might be worth at this point to explore the Boson peak region for further understanding but
material limitation did not allow us to do so. These experiments are under way in the work of Dr. Alfons Schulte. Photo-induced As$_2$S$_3$ thin films at 785 nm are shown by Raman spectroscopy in figure 3.35 to undergo creation of homopolar bonds, thus suggesting that reaction (4.7) is favored in the forward direction. This is in agreement with Frumar’s assumption that increasing the intensity (from mW/cm$^2$ for 514 nm exposure to GW/cm$^2$ for 785 nm exposure) favors the creation of homopolar bonds. This also happens because the thin film had time to relax after deposition for roughly 2-3 months with the 785 nm exposure experiments having been delayed; thus the “starting” glass films exhibited a more bulk-like structure as shown on figure 3.35. The creation of homopolar bonds goes along with changes in properties and creation of defects observed as previously discussed.

These optical and structural changes suggest notable changes in linear properties that could impact nonlinear properties. To assess the link between the previously discussed linear properties of our materials and their nonlinear properties, we employed two evaluation techniques to assess $n_2$ or $\chi^{(3)}$ behavior in our bulk and film materials. Measurements of $n_2$ in films proved to be impossible within our study thus results discussed are limited to those measured in bulk specimens. However the $n_2$ or $\chi^{(3)}$ of the thin films were estimated through different models.

Discussed here are results of measurement of the nonlinear properties for our As-S-Se glasses as characterized through Z-scan and collinear pump-probe method (CPPM). As stated earlier, results acquired by Z-scan were in good accordance with a prior work from Cardinal et al. (106) in our group and the experiment conditions used to carry out the measurements were similar.
We related the increasing nonlinearity to:

(1) the iterative influence of Se substitution for sulfur in stoichiometric compositions (glass compositions 1 to 5) and the impact on the refractive index and polarizability with increased Se content,

(2) the existence of multi-atom Se chains and lone-pairs of electrons, thus creating large clouds of highly polarizable entities.

Indeed, our Raman (figure 3.27) and XPS spectra (247) show that homopolar Se-Se bonds concentration increases with increasing Se and ChG content, while the data acquired by Z-scan show equally an increase in nonlinearity along the same lines.

By simply plotting $n_2$ (Z-scan) versus the number of selenium LP, we obtain figure 4.4:

Figure 4.4: Nonlinear refractive index of bulk glasses (Z-scan) versus Se LP concentration.
In a different work, Quémard et al. (328) proved similarly that the nonlinearity is seen to increase with increasing Se-chain lengths in ChG, even though this trend reached a maximum for chains of extended lengths at very high Se content (~ 80 atomic %). The authors suggested that the concentration of electron LP was the dominant factor in achieving large nonlinearities but that the variation of $n_2$ was not proportional to the LP concentration. The LP dominant factor was confirmed by Harbold et al. for the most polarizable constituent (Se) in As–S–Se glasses (329).

Lenz et al. (330) were able to measure for $\text{As}_2\text{Se}_3$ a $n_2$ roughly 500 times higher than silica at 1.55 $\mu$m with a 1 kHz optical parametric amplifier and peak intensity lower than 1 GW/cm$^2$ (versus 3 G W/cm$^2$ in our case), mentioning the existence of two-photon absorption for this material, which is not surprising considering the wavelength of operation and the bandgap of the material. Indeed, when the frequency of the incident light is close from one-half of the frequency of the material resonance, the magnitude of the nonlinear index of refraction gets two-photon resonantly enhanced and accompanied by two-photon absorption (TPA). These effects are much more pronounced in $\text{As}_2\text{Se}_3$ than in $\text{As}_2\text{S}_3$, as originally discussed in our 1998 paper on the subject (107).

As stated previously, measuring the nonlinearities of compositions with high Se content and acquiring a good signal proved difficult and irreproducible. The Z-scan samples could not be observed under a microscope to observe any structural change in the bulk part since they are completely black (only $\text{As}_2\text{S}_3$ and $\text{As}_{24}\text{S}_{76}$ are “transparent”). However we believe that the high repetition rate of the laser source is a non-negligible factor and that for Se-rich materials (and to a lesser extent for Ch-rich materials) structural modifications at this repetition rate and energies might take place thus deforming the “lens” created by the sample, changing the shape of the
beam and making constant measurements quite difficult. This issue, we believe, was addressed using the CPPM technique. Indeed we observed in the first CPPM experiment (at 250 mW) that high intensities would lead to a consistent increase in the signal and for Se-rich materials to the appearance of fumes, meaning we were burning the sample. By significantly reducing the pump intensity we were able to get a clean signal constant over a period of ~ 1-2 minutes.

However, the As$_{24}$S$_{76-y}$Se$_y$ materials exhibit a higher nonlinearity when compared to their As$_{40}$S$_{60-x}$Se$_x$ counterparts i.e. for decreasing As content. This is consistent with the increasing nonlinearity seen previously along the [S/Se] = 1 compositional line (up to composition 7), which is somewhat surprising at first look.

To the extent of our knowledge and considering Boling’s models presented in chapter 2, the nonlinear refractive index tends to increase with increasing linear refractive index. Results for Boling’s model are shown in table 3.8 even though the calculations were performed for thin films. Boling’s theory indeed agreed with the trend observed for the As$_{40}$S$_{60-x}$Se$_x$ and As$_{24}$S$_{76-y}$Se$_y$ series where the $n_2$ increases simultaneously with the Se content and $n_0$. However, theory and experimental data go the opposite way for decreasing As content along the [S/Se] = 1 line. This is also in disagreement with the Miller's rules from which an estimation of the nonlinear susceptibility is: $\chi^{(3)} \sim [\chi^{(1)}]^4 \times 10^{10}$ esu (331). We can relate the nonlinear susceptibility of a material to the $E_o$ and $E_d$ parameters calculated through the WDD relationship. As we know, we can express the refractive index $n$ and polarizability $P$ to the electric field $E$ as follows:

\begin{align*}
  n &= n_0 + n_z \langle E \rangle^2 \quad (4.8) \\
  P &= \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 \quad (4.9)
\end{align*}
According to (332) we can express the linear susceptibility as:

\[ \chi^{(1)} = \frac{n^2 - 1}{4 \cdot \pi} \]  

(4.10)

Using WDD formula (2.20) into the previous equation leads to:

\[ \chi^{(1)} = \frac{E_y E_0}{4 \pi (E_0^2 - (h\nu)^2)} \]  

(4.11)

Since the ChG are considered as optically isotropic, \( \chi^{(2)} \) is zero. As we just mentioned, Miller’s Rule states that:

\[ \chi^{(3)} = A \cdot (\chi^{(1)})^4 \]  

(4.12)

with A being a constant. Using the two previous equations, we thus obtain:

\[ \chi^{(3)} = A \cdot \left[ \frac{E_y E_0}{4 \pi (E_0^2 - (h\nu)^2)} \right]^4 \]  

(4.13)
At long wavelength (i.e. $h \nu \rightarrow 0$) $n = n_\infty$ and equation (4.13) reduces into:

$$
\chi^{(3)} = \frac{A}{(4\pi)^d} \frac{E_d^4}{E_0^4} = \frac{A}{(4\pi)^d} \left(n_e^2 - 1\right)^d
$$

(4.14)

$A$ was determined from 97 experimentally-obtained values (332) and equals $\sim 1.7 \times 10^{-10}$ (if $\chi^{(3)}$ in esu units) thus:

$$
\chi^{(3)} = 6.82 \times 10^{-15} \frac{E_d^4}{E_0^4} = 6.82 \times 10^{-15} \left(n_e^2 - 1\right)^d
$$

(4.15)

As we observed so far, exposure creates a change in refractive index and structural properties of our ChG materials, thus leading to variations in $E_d$ and $E_0$. Using equation (4.13) we can thus predict the spectral dependence of $\chi^{(3)}$ for the different compositions as shown in figure 4.5. The solid lines are for non-exposed thin films while the dotted lines represent thin films after exposure.
Figure 4.5: Spectral dependence of $\chi^{(3)}$ for the different thin films non-exposed (solid lines) and exposed (dotted lines) as calculated by equation (4.13).

This confirms that higher refractive index along with the subsequent variations in $E_d$ and $E_o$ lead to higher third-order susceptibilities. It is believed that the fast component of $n_2$ and $\chi^{(3)}$ are mostly electronic (333). This means that the electronic contribution is more important in our Se-rich materials. However As$_{24}$S$_{38}$Se$_{38}$ shows the smallest $\chi^{(3)}$ as observed with CPPM, and despite a $n_2$ value 400 times higher than that of SiO$_2$ as seen in the Z-scan measurements. This confirms that additional contributions are needed to explain the high nonlinearity behavior of As$_{24}$S$_{38}$Se$_{38}$. Interestingly, Kang et al. (334) estimated the nuclear contribution in Ge-Ga-S glasses to $\sim 12\%$, however no data is available on glasses in our system.
It is interesting to note that Boling stated in his paper (279) that “the more extended the polarizable bond, the less appropriate the application of the Lorentz-Lorenz expression for the local field correction” in his model. The high polarizability of the extended Se chains might thus be the reason for the behavior observed and the deviation observed between the Z-scan measurements and the Boling’s models. Related to this, Harbold et al. studied the nonlinearity behavior of many ChG compositions including As$_2$S$_3$, As$_{40}$S$_{30}$Se$_{30}$ and As$_2$Se$_3$ (329) and observed the same monotonic behavior for S for Se substitution in constant As content glasses. However, by studying the nonlinear behavior of Ge-As-S-Se materials (335), where the energy gap remains constant whatever the variation in Se content, they found that in absence of bandgap modification there was no systematic increase of $n_2$ versus increased Se and LP concentration. They observed that $n_2$ increases as the bandgap narrows in the selenide and sulfoselenide glass systems thus coming to the conclusion that the general trend in the nonlinearity is accounted for by the normalized photon energy and not just the concentration of LP pairs.

To date we have studied and accounted for the mechanisms involved in increasing nonlinearity to be obviously dominated by the linear refractive index, according to the traditional models, and believe that lone-pairs of electrons play a factor in large nonlinearities. However there definitely seem to be a consensus for additional mechanism(s) taking place.

Note that the CPPM method gave lower nonlinearity values than the Z-scan technique. According to the inventors of this technique, the CPPM technique should only account for electronic nonlinearity. These low values correspond more to some of the Boling’s models, especially the low values found for As$_{24}$S$_{38}$Se$_{38}$ and are a further statement for other possible contributions. However the “roof effect” observed ($n_2$ increases from S-rich materials up to S/Se = 1, then decreases for Se-rich materials) is still not understood.
As introduced in chapter 2, the Ti:Sapphire laser source in the configuration that we used (sub-100 fs pulses) is known to involve electronic processes and specifically avoids the thermal effects that might be encountered with longer pulses when interacting with materials. We also know that $\Delta n = n_2 \cdot I$ and thus by back-calculating $n_2$ from the $\Delta n$ data that we report in both experiments, we should get a plot of $n_2$ versus $I$ that accounts only for electronic contributions in the case of the femtosecond exposure experiment, while accounting for total (electronic, thermal and nuclear) contributions for the argon experiment. Since the argon experiment was performed with a constant average power at the sample for most of the compositions, we could not present all of the data versus intensity (we controlled time of exposure and hence the integrated “dose”), otherwise most of the $\Delta n$ at 514 nm exposure would have had the same intensity. Following the same idea though, we calculated an “$n_2$” equal to the ratio of the $\Delta n$ by the fluence (in J/cm$^2$). Figure 4.6 shows the results of such calculations for As$_2$S$_3$. 

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The argon experiment curve was fitted and extended to account for the threshold whereby no further significant refractive change is expected according to (230) and is shown as a black dotted line on the graph. Note that this would correspond to a maximum $\Delta n \sim 0.1 - 0.12$, which are the highest values reported in $\text{As}_2\text{S}_3$ in the literature, thus the fitting is considered as good. As a consequence one can see that thermal and nuclear contributions obviously play a role in the processes taking place during the argon exposure. We conclude at this point that thermal processes, and to a lesser extent nuclear processes must take part in the increase of the nonlinear index. The magnitude of the contributions of each however requires further study and will be the source of further investigation.
The defects mentioned along this discussion were shown to be a major factor in the evolution of the previously mentioned properties. Additional information on these defects is needed. Defects can be classified, according to Popescu (336), into point defects (such as dangling bonds or quasi-vacancies), chemical defects (wrong bonds, impurities) or electronic-structural defects (VAP’s, quasi-molecular defects). Frumar (327) also mentions that over- or under-coordinated defects increase the densities of the localized states in the band-tails. This goes along with our thinking that higher densities of states reduce the bandgap and lead to its shift.

At this point and considering our results, we have observed coordination number variations which translate into electronic defects hence we can expect the creation of VAP’s in our network. The theory on these VAP’s has been presented in chapter I. The changes in bond configurations as observed through Raman spectroscopy can lead to some “wrong” bonds or homopolar bonds which create units of highly polarizable electron clouds. In addition, the numerous lone-pairs corresponding to the non-bonding orbitals and located at the top of the VB can be used for formation of new bonds with different geometry than the starting entities. Additional free electrons were shown to be generated through the free electron model for increasing pulse intensity. At this point in time it is not possible to estimate with exactitude the energy levels of all of these new states corresponding to the multiple defects with respect to the positions of the VB and CB, however what is certain is that we have shown that they do exist and get incorporated in the bandgap.

As previously mentioned in this section, the difference in molecular species found in the vapor phase following various evaporation techniques, as shown by Knox and Ban (68), will in turn lead to differences in the as-deposited thin film structure upon condensation of these same
species on the substrate. Hence, following our discussion on the major role played by specific thin film structural entities on the resulting photo-induced optical properties, we also predict that different film deposition techniques will contribute to dissimilarities in thin film photo-sensitivity upon exposure.

Finally, we were able with the µTA technique to observe and correlate small structural changes due to different exposure conditions at 514 nm with variations in the transition temperature as shown by the irradiated film experiment (337). However we are not able at this point to quantify the absolute thermal conductivity of the regions studied. This is due to the fact that the equipment only provides a thermal conductivity variation.

According to our results and as we have consistently shown across this chapter, we relate in the end the creation of defects to the creation of localized states in the bandgap with the consequent effects extensively described. Note that the pre-existing states have been observed to be displaced from the VB to the edge of the CB. The high nonlinear optical properties of some of the materials have been related to this increasing number of free electrons through the increase of the electronic contribution. The differences observed with the experimental data are related to the presence of defects. The change in structure in the network as predicated by Raman spectroscopy, XPS and through the calculation of different optical parameters has been proven to play also a significant role on the variation of the properties of our photo-induced materials.
4.5. Devices considerations

As shown in this study, the photo-induced properties of As-S-Se chalcogenide materials combined with their demonstrated capability of being fabricated with low loss (338) (e.g. ~ 0.1 dB/cm in As$_2$S$_3$) makes them attractive for fabrication of waveguides or other structures. Such performance, the flexibility to engineer structure-property of the desired glass, and the compatibility with existing on-chip planar fabrication methodologies, makes use of ChG materials promising for use in integrated optics applications. It has been discussed in general in this thesis, and in more detail in (339) that through the use of short-pulsed femtosecond laser sources, it is possible to write at a specific depth in the bulk glass material; here, one is limited only by the working distance of the focusing microscope, thus opening the possibility to create waveguide arrays or 3-D structures in a bulk glass.

The transparency of ChG’s in the IR region combined with their highly nonlinear optical properties can be used for all-optical switching applications at telecom wavelengths, providing that they exhibit low 2 photon-absorption at the wavelength of operation and $E_g > 2h\nu$. Since $E_g$ is related to the dispersion energy ($E_o$) and we have shown that the highest nonlinearity is expected for large $E_d$ and small $E_o$ values, this allows one to narrow the choice of candidate materials to those with specific $E_o$ values. The range of materials becomes obviously larger as the wavelength of operation increases.

At the same time, one has to make sure that the $T_g$ of these materials is high enough to avoid structural (and thus optical) modifications upon operation in a regular device environment; such in-service performance expectation would eliminate for example, low $T_g$ glass materials 7
to 13 in our study from typical device applications. This issue can be resolved by either doping these ChG’s to enhance their thermal-mechanical stability (through small additions of higher coordination species such as Ge), or through a focused aging process whereby structural relaxation in moderate $T_g$ films are relieved following deposition and prior to further modification, hence stabilizing the material from large physical property variations. As shown herein for the glasses studied, long term structural relaxation, while modifying the glass network to a more bulk-like configuration, does not result in dramatic change to material photosensitivity. This means that aged glasses can still be written to induce optical or other structural changes. Thus, aging of the film material prior to device fabrication can, from our standpoint, result in stable, robust devices.

Lastly, note that the low phonon energy of these materials can facilitate many mid-IR transitions for rare-earth ions, which are usually not present in materials with higher phonon energies (340). This for most ChG’s requires modest amounts of Ga for example, to enhance solubility of rare earth ions in the host matrix. While not discussed in detail in the context of this study, doping these materials has been proven efficient for active applications such as fibers and optical switching as mentioned in section 1.6. We have also shown (341) that ion implantation of these glasses can result in doped local regions which sustain emission. Such creation of active regions, coupled with gratings which selectively filter resonance wavelength (i.e. form the mirrors of a cavity) would allow active on-chip functionality. Hence, further utilization of these glasses in applications where multi-functionality is required (i.e., spatially separated regions of local index change, doping with rare earth, and optical filtering via a grating) could be realized in a single material. This is unique to ChG’s and provides additional impetus to other researchers, to continue in efforts to understand the full possibilities in these versatile materials.
Providing that the long time stability of these structures can be controlled as shown in our prior aging results and additional processing steps do not adversely impact key chemical and optical properties of the glass, further enhancements in the knowledge of material properties and performance should lead towards chalcogenide materials with optimum optical and structural properties for the engineering and production of effective active and passive devices.
CHAPTER FIVE: CONCLUSIONS AND PERSPECTIVES

We demonstrated that we have put in place an effective fabrication setup for the reproducible processing of bulk ChG materials at CREOL. Compositional homogeneity and impurity issues have been resolved and we have developed an array of tools (EDS, FT-IR, XRD, XPS) allowing for detection of any contamination. The effects of batch size, quenching temperature, annealing and distillation on the physical and optical properties of ChG were investigated. Hence we are confident that bulk glasses are uniform and homogeneous as well as reproducible from batch to batch. The latter is especially important as it is essential when the materials serve as targets for film deposition.

This consistency in processing can be observed in the different physico-thermal properties (density and $T_g$) measured. We have also developed a fundamental understanding of the physico-thermal and optical properties of the bulk materials and their evolution with respect to changes in composition and have constituted what can be considered a databank for the thirteen compositions studied. The properties obtained for the well-studied compositions ($\text{As}_2\text{S}_3$ and $\text{As}_2\text{Se}_3$) have been observed to be in accordance with numerous previous studies lending validity to the current processing and characterization techniques. Structural modifications in the bulk glasses were assessed using both Raman and XPS techniques. The main bands on the Raman spectra have been attributed to different entities (homopolar or heteropolar bonds). The appearance of defects and homopolar bonds has been shown in the bulk glass for stoichiometric ($\text{As}_{40}\text{S(Se)}_{60}$) undergoing Se for S substitution and the change in chemical environment of the same S,Se and As atoms described by XPS in both bulk glass and films. This latter technique
explained the measurable bandgap shift that one could expect by such chemical environment changes.

The nonlinear properties of the bulk glass were investigated by z-scan and collinear pump-probe technique. Z-scan allowed us to obtain reproducible results to those obtained on a subset of glasses measured by our group previously while the pump-probe opened questions to the contribution of electronic, thermal or nuclear processes in our materials. The influence of defects such as lone-electron pairs has been highlighted. This provided a basis to compare the properties of the bulk glass to those of the thin films.

The changes in refractive index, bandgap and thermal properties from the bulk materials to their corresponding thin film have been evaluated and linked to molecular rearrangement. The thin film structure has been clearly identified as being different from the bulk with an increase in homopolar bonds resulting from condensation of molecular species known to be present in the vapor phase of deposition. The annealing effect on the film has been characterized by a polymerization-like mechanism, which opens these molecular fragments, reduces their homopolar bonds content and increases the network nature of the film structure. This can be seen in changes to the glass’ Raman spectrum, as a loss in sharp peaks distinctive of the film. Long term (3 year) aging studies has shown the evolution of a totally bulk glass-like spectrum. XPS confirmed a change in surrounding around the As, S and Se atoms. These variations were shown to impact in a certain extent optical and physical properties such as refractive index or thermal transition events.

The Micro-Thermal Analysis (µTA) technique has been shown to be a complementary tool to DSC for thin films analysis. The accuracy and repeatability of the µTA power signal on both bulk glasses and films was found to be excellent. The change in properties, preliminary
observed in the refractive index section, between bulk glass and thin films was also noticed and quantified when measuring the thermal properties by \( \mu \text{TA} \).

Femtosecond and cw laser sources were used to create photo-induced structures in thin films. Variations in the optical properties were limited by saturation effects in the case of cw exposition and material ablation threshold for pulsed irradiation. Both irradiations experiments lead to similar ending optical and structural properties changes but through much different intensity and energy requirements. In particular, the pulsed exposure is believed to exhibit two distinct working regimes, linear first and then nonlinear upon energy threshold crossing.

The materials composition was found to impact in some extent the optical and structural properties. Photo-expansion was observed in both experiments and related to deposited energy. The increase in refractive index (as calculated by different techniques) and absorption were quantified and the selenium and polarizable units’ contents influences were raised. These variations were also partially linked to single and multiphoton processes respectively for cw and femtosecond irradiations using a free electron model. The oscillator and dispersion energies were calculated using Wemple-DiDomenico model and their increase upon illumination related to an increase in the arsenic coordination, greater interlayers interaction and increase in compactness of the network. The changes in bonding energies due to structural rearrangement upon exposure or increased selenium content were also found to play a role in the variations of the oscillator energy.

The Urbach and Tauc absorption regions were investigated. The transitions of the electrons from the defect states, forming the top of the valence band, to the conduction band lead to a reduction of the Urbach energy and a reordering of the original electronic defects configurations. The bandgap was observed to decrease upon irradiation and was explained by
the creation and expansion of new localized states at the edges of both valence and conduction bands according to the Tauc parameter.

Photo-induced thin films have been proved to undergo creation of homopolar bonds while the structure of the relaxed non-exposed regions was shown to exhibit close to bulk-like shapes thus validating our previous observations. These defects were shown to be a major factor in the evolution of the previously mentioned properties. Different deposition techniques leading to variations in the starting molecular species in thin films are thus predicted to impact their photo-sensitivity upon laser exposure.

The nonlinear refractive indices of the thin films were estimated using different Boling’s models based on sole electronic contribution. The major influence of lone-pairs of electrons and defects was reiterated. Electronic contributions were considered to be the major factor in the femtosecond experiment while thermal and nuclear processes were suggested to take place as well in the cw study.

It has been shown that the $\mu$TA technique is able to resolve and correlate small structural changes due to different exposure conditions with variations in the transition temperature as shown by the irradiated film experiment. While thermal conductivity variations could be observed, no absolute quantification was possible due to hardware limitation.
As a conclusion, this study provided numerous and detailed answers to each and every questions that initiated this work, through careful measurements and methodical analysis of the physical, optical and structural properties and their variations in the part of ternary diagram covered by our chalcogenide materials:

- Could we reproducibly prepare and fabricate bulk and film materials with uniform physical properties?
- What would be the compositional effect on the physical properties within the As-S-Se system?
- What significant differences if any, exist between bulk glass samples and their corresponding as-deposited films?
- What is the compositional effect and that of the exposure conditions on resulting sensitivity in thin ChG films?

As it is often the case in science, these questions lead the path to new ones and invite to a further understanding in a number of domains. In particular, our study calls for a deeper analysis of the nonlinear phenomena taking place and their quantified contributions. Development of a specific thermal probe would help to quantify the thermal conductivity variations observed and get a further understanding of phonons processes. At the same time, additional techniques such as NMR, EXAFS or NQR would provide even more intimate details on the atoms immediate neighborhood and the effective electronic energy positions of the defect states present in the glass. Structural understanding would also be worth extended to the medium range order through investigation of the boson peak region. In-situ measurements of the glass structure
evolution through Raman spectroscopy performed at the same time as laser manufacturing have been planned. This would lead the way in structural understanding, not only for our chalcogenide materials but additionally for any glass that might be susceptible to be engineered through femtosecond laser irradiation. The knowledge accumulated through the processing and understanding of these chalcogenide materials are vital for the necessary long term stability of envisioned device applications.
APPENDIX: MATLAB CODE FOR REFRACTIVE INDEX CALCULATION
We present the Matlab code developed to calculate $n_0$ and $\alpha$ of bulk glass materials using the data from visible/NIR spectroscopy (Cary500).

clear;

A = xlsread('Book2.xls');
lmda=A(:,1);
T1=A(:,2);
T2=A(:,3);

% T1(1325:1390)=0;
% T2(1320:1390)=0;

L1=0.624;
L2=0.223;
Np=1320;
for index=1:Np

no=2.4;
o1=1.1;
TL1=T1(index)/10;
TL2=T2(index)/10;

n=no;
alpha = (-.5/L1)*log(-8*n.^2./(n-1).^4 + sqrt((8*n.^2./(n-1).^4).^2 + TL1.*((n+1)./(n-1)).^4));
f1 = TL2 - 16*n.^2.*exp(-alpha*L1)./((n+1).^4 - ((n-1).^4).*exp(-2*alpha*L2));

n=no1;
alpha = (-.5/L1)*log(-8*n.^2./(n-1).^4 + sqrt((8*n.^2./(n-1).^4).^2 + TL1.*((n+1)./(n-1)).^4));
f2 = TL2 - 16*n.^2.*exp(-alpha*L1)./((n+1).^4 - ((n-1).^4).*exp(-2*alpha*L2));

n2=no;
counter=0;
error=1;

while (abs(error)>1e-4)

    n = no - f1*(n-no)/(f2-f1);
    error=n-n2
end

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alpha = (-.5/L1)*log(-8*n.^2./(n-1).^4 + sqrt((8*n.^2./(n-1).^4).^2 + TL1.*((n+1)./(n-1)).^4));
f2 = TL2 - 16*n.^2.*exp(-alpha*L1)./(n+1).^4 - ((n-1).^4).*exp(-2*alpha*L2));
n2=n;
counter=counter+1;
if (counter>100)
    display('no convergance');
    break;
end

n_e(index)=n;
alpha_e(index) = (-.5/L1)*log(-8*n.^2./(n-1).^4 + sqrt((8*n.^2./(n-1).^4).^2 + TL1.*((n+1)./(n-1)).^4));
end
figure (1)
subplot(3,1,1),plot(lmda(1:Np),n_e);
subplot(3,1,2),plot(lmda(1:Np),alpha_e);
subplot(3,1,3),plot(lmda,T1,lmda,T2);

id=fopen('data.txt','w');
fprintf(id,'%f %f %f ',[lmda(1:Np); n_e; alpha_e]);
fclose(id);

The following picture is a captured screen of the data window obtained upon calculation showing, from top to bottom, the refractive index, absorption and transmission plots.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Details</th>
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