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Optimization of processing parameters for As2Se3 glass for low loss, high strength fibers

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OPTIMIZATION OF PROCESSING PARAMETERS FOR $\text{As}_2\text{Se}_3$
GLASS FOR LOW LOSS, HIGH STRENGTH

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Baptiste Giroire
August 2012

Accepted by:
Dr. Kathleen Richardson, Committee Chair
Dr. Vincent Blouin
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ABSTRACT

Chalcogenide glasses have been widely studied due to their extraordinary transparency in the infrared (IR) region from 0.5 to 20 µm. This transparency combined with excellent thermo-mechanical properties, makes them ideal candidate for infrared optics including IR fiber optic applications. However, such non-oxide glasses generally exhibit low mechanical strength, as compared to their oxide counterpart, which are based on covalently bonded metal-oxygen species. In addition to mechanical robustness, low optical loss (hence low impurity content) is required for most IR optical materials, including the one in this study, amorphous arsenic tri-selenide, As₂Se₃. In this effort, As₂Se₃ glass was investigated and the impact of the glass purity on material physical properties quantified. Properties evaluated includes chemical composition, structure, thermal, optical and mechanical properties.

There are many sources of optical loss in chalcogenide glasses, physical defects, heterogeneous phase(s), and oxide, hydroxide or hydride-containing species. These extrinsic impurities generally come from poor melting profiles, sample preparation or quality/purity of the raw materials. Reduction of intrinsic losses due of the material has also been explored. It was found that an impurity content of 0.1 ppb has to be reached to yield a total reduction of the band at 4.57 µm. Various methods, such as thermal treatment of the raw material or the addition of impurity-getters in the melt followed by distillation were performed in our lab, to achieve different level of purity in the glass specimens. The role of glass purity on these attributes was compared. The relationship between impurity concentration and mechanical properties of arsenic selenide glass, both in bulk and fiber forms has been investigated. The concentration of oxide-containing impurities embedded in the glassy matrix appeared to have a strong impact on the microhardness of the resulting material. A reduction of ~60% of
the water, oxides and hydroxides content resulted in an increase of 200 MPa of the hardness of the glass system. Moreover, it has been demonstrated that the increase of the hydride (Se-H) content in the material would yield a lower microhardness of the glass. These observations have been correlated with the impact of the impurity concentration on the glass network connectivity. A material with weaker glass connectivity would exhibit smaller resistance to crack initiation. The evolution of the properties and homogeneity of the glass from small batch to preform and the effect of the drawing process have been studied. The results of the processing-related variables on final glass quality will be discussed.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENT</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>CHAPTER I: INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.0 Motivation of the project</td>
<td>1</td>
</tr>
<tr>
<td>2.0 Glasses</td>
<td>2</td>
</tr>
<tr>
<td>2.1 Fundamentals of chalcogenide glass formation</td>
<td>2</td>
</tr>
<tr>
<td>2.2 Attributes of optical fiber</td>
<td>4</td>
</tr>
<tr>
<td>2.2.1 Unclad fibers</td>
<td>4</td>
</tr>
<tr>
<td>2.2.2 Core-clad fibers</td>
<td>7</td>
</tr>
<tr>
<td>3.0 Glass system studied Binary As_{40}Se_{60}, arsenic triselenide</td>
<td>8</td>
</tr>
<tr>
<td>4.0 Purification methods</td>
<td>10</td>
</tr>
<tr>
<td>4.1 Definition of impurities vs defects</td>
<td>10</td>
</tr>
<tr>
<td>4.2 Surface oxide removal via thermal treatment</td>
<td>13</td>
</tr>
<tr>
<td>4.3 Distillation (Mg, AlCl_{3})</td>
<td>15</td>
</tr>
<tr>
<td>5.0 Summary – objective of the study and organization of the thesis</td>
<td>16</td>
</tr>
<tr>
<td>6.0 References</td>
<td>17</td>
</tr>
<tr>
<td>CHAPTER II: LITERATURE REVIEW</td>
<td>20</td>
</tr>
<tr>
<td>1.0 Purification of chalcogenides glasses</td>
<td>20</td>
</tr>
<tr>
<td>1.1 Impurities in chalcogenide glasses</td>
<td>20</td>
</tr>
</tbody>
</table>
1.0 Sample preparation ........................................................................................................... 41
  1.1 Bulk chalcogenide glass synthesis ............................................................................... 41
    1.1.1 Conventional melting protocol: unpurified “reference” materials .................. 41
    1.1.2 Purification setup ................................................................................................. 44
    1.1.3 Preform preparation ............................................................................................. 49
  1.2 Fiber drawing .............................................................................................................. 49
    1.2.1 Unclad arsenic selenide fibers ........................................................................... 49
2.0 Property measurements ................................................................................................. 52
  2.1 Bulk properties ........................................................................................................... 52
    2.1.1 Physical properties: density .............................................................................. 53
    2.1.2 Thermal properties ............................................................................................. 54
    2.1.3 Structural properties .......................................................................................... 55
    2.1.4 Optical properties ............................................................................................... 63
    2.1.5 Mechanical properties ....................................................................................... 66
    2.1.6 Homogeneity assessment of glass preform ....................................................... 67
  2.2 Fiber properties ......................................................................................................... 68
    2.2.1 Optical properties ............................................................................................... 68
    2.2.2 Mechanical properties ....................................................................................... 70
    2.2.3 Thermal properties ............................................................................................. 75
    2.2.4 Physical properties: Density ............................................................................... 75
3.0 Summary ....................................................................................................................... 76
4.0 References ..................................................................................................................... 77

CHAPTER IV: RESULTS AND DISCUSSION ........................................................................... 79

1.0 Evolution of the properties from bulk to preform (5 slices) ........................................... 79
1.1 Density analysis ........................................................................................................ 79
1.2 Structural homogeneity of the preform ..................................................................... 81
  1.2.1 Raman spectroscopy .......................................................................................... 81
  1.2.2 Energy dispersive X-Ray spectroscopy ............................................................ 82
1.3 Vickers microhardness .............................................................................................. 83
1.4 Fourier transform infrared spectroscopy ..................................................................... 84

2.0 Characterization of the bulk glass properties ............................................................ 86
  2.1 Thermal properties .................................................................................................. 86
  2.2 Microhardness analysis .......................................................................................... 88
    2.2.1 Load independent hardness .......................................................................... 88
    2.2.2 Effect of purification on hardness ................................................................ 90
  2.3 Optical properties .................................................................................................. 92
    2.3.1 Fourier Transform Infrared spectroscopy ...................................................... 92
    2.3.2 Ultraviolet-Visible spectroscopy, bandgap calculation .................................. 97
    2.3.3 Raman spectroscopy ...................................................................................... 100
  2.4 Physical properties: density ................................................................................ 101

3.0 Characterization of unclad fibers ............................................................................ 102
  3.1 Physical properties: density ................................................................................ 102
  3.2 Thermal properties ................................................................................................ 103
  3.3 Structural properties .............................................................................................. 105
    3.3.1 X-Ray diffraction ......................................................................................... 105
    3.3.2 Raman spectroscopy ...................................................................................... 105
  3.4 Mechanical properties ............................................................................................ 107
    3.4.1 Vickers microhardness .................................................................................. 107
    3.4.2 Tensile testing ................................................................................................ 110
LIST OF TABLES

Table I-1 Properties of As$_2$Se$_3$ glass .......................................................... 9
Table I-2 Impurities present in chalcogenide glasses ........................................ 11
Table I-3 Lowest concentration of impurity found in literature for common unclad uncoated chalcogenide fiber ......................................................... 12
Table I-4 Bond energy of impurities in chalcogenide glasses .............................. 14
Table II-1 Frequency and intensity of the absorption bands of impurities in FTIR spectroscopy ................................................................. 22
Table II-2 Optimal loss impurity concentration ................................................... 28
Table II-3 Bond energy of bridging impurities present in arsenic selenide glasses ........................................................................................................ 37
Table III-1 Denomination of all sample characterized ........................................... 48
Table IV-1 Atomic composition results of an unpurified sample of As$_2$Se$_3$ with a cartoon representation of a sliced preform on the right ......................................................... 83
Table IV-2 Effect of the purification method used, on thermal properties of As$_2$Se$_3$ ................................................................................................. 87
Table IV-3 Effect of the purification method on the absorption coefficient of impurity bands of As$_2$Se$_3$ glass ......................................................... 97
Table IV-4 Bandgap energy in function of the sample purity .................................. 99
Table IV-5 Effect of purification on density of As$_2$Se$_3$ glass .............................. 101
Table IV-6 Effect of diameter and purification of the glass on the density of As$_2$Se$_3$ fibers ....................................................................................... 102
Table IV-7 Effect of diameter and purification of the glass on the thermal properties of As$_2$Se$_3$ fibers ............................................................. 104
Table IV-8 Effect of the fiber drawing on the hardness of As₂Se₃ glass system ............................................................. 107

Table IV-9 Weibull parameters of the unclad, as-drawn fibers.................................................. 114

Table IV-10 Change in bond energy induced by the proposed mechanism........................................... 122
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>Effect of the temperature on the enthalpy of a glass forming melt.</td>
<td>3</td>
</tr>
<tr>
<td>I-2</td>
<td>Schematic representation of the fiber draw tower.</td>
<td>5</td>
</tr>
<tr>
<td>I-3</td>
<td>Viscosity curve of different silica type of glass.</td>
<td>6</td>
</tr>
<tr>
<td>I-4</td>
<td>Schematic representation of the double crucible fiber drawing technique.</td>
<td>7</td>
</tr>
<tr>
<td>I-5</td>
<td>Infrared photography of a) Striae observed in a cross section of a chalcogenide glass rod; b) Bubble in a core-clad chalcogenide fiber.</td>
<td>11</td>
</tr>
<tr>
<td>II-1</td>
<td>Schematic of a two-zone furnace where $T_1 &gt; T_2$.</td>
<td>25</td>
</tr>
<tr>
<td>II-2</td>
<td>Schematic of a core-clad optical fiber.</td>
<td>36</td>
</tr>
<tr>
<td>II-3</td>
<td>Effect of impurities on the glass network connectivity.</td>
<td>37</td>
</tr>
<tr>
<td>III-1</td>
<td>a) Flow chart of the glass making process b) Time/Temperature profile of the conventional melting protocol.</td>
<td>43</td>
</tr>
<tr>
<td>III-2</td>
<td>Schematic representation of the oxide volatilization via thermal treatment setup. a) Treatment of raw precursors. b) Combination of the purified materials.</td>
<td>44</td>
</tr>
<tr>
<td>III-3</td>
<td>Schematic of the dynamic vacuum setup.</td>
<td>46</td>
</tr>
<tr>
<td>III-4</td>
<td>Glass distillation process. a) Four-zone furnace setup b) Resulting tube after distillation.</td>
<td>46</td>
</tr>
<tr>
<td>III-5</td>
<td>Hydride removal setup.</td>
<td>48</td>
</tr>
<tr>
<td>III-6</td>
<td>Optical fiber draw tower at AMRL.</td>
<td>50</td>
</tr>
<tr>
<td>III-7</td>
<td>Viscosity curve for $\text{As}<em>x\text{Se}</em>{100-x}$ glass family with $\text{As}_2\text{Se}_3$ at the rightmost.</td>
<td>51</td>
</tr>
<tr>
<td>III-8</td>
<td>a) First drop of a drawn preform b) Bent $\text{As}_2\text{Se}_3$ uncoated fiber.</td>
<td>52</td>
</tr>
<tr>
<td>III-9</td>
<td>Schematic of balance used to measure density of bulk glass.</td>
<td>53</td>
</tr>
</tbody>
</table>
Figure III-10 Schematic representation of an incident X-Ray beam on a crystal surface
Figure III-11 Typical XRD pattern of silica glass
Figure III-12 XRD of crystalline nanotubes of selenium
Figure III-13 Picture of the inside of the sample chamber
Figure III-14 Schematic of an electron microscope and electron interactions with materials
Figure III-15 Bohr representation of an atomic structure
Figure III-16 Schematic representation of a Raman spectrometer
Figure III-17 Schematic representation of the ellipsometer set up
Figure III-18 Schematic of the geometry of Vickers indenter
Figure III-19 Picture of a) Unpurified $\text{As}_2\text{Se}_3$ preform b) Sliced unpurified $\text{As}_2\text{Se}_3$ glass
Figure III-20 Optical loss for fiber measurement setup
Figure III-21 Picture of the Bending tester built at GCPL
Figure III-22 Schematic representation of the two-point bend tester
Figure III-23 Pictures of a 250 µm $\text{As}_2\text{Se}_3$ fiber clamped a) before the tensile test b) after the experiment
Figure IV-1 Density variation in $\text{As}_2\text{Se}_3$ preform
Figure IV-2 Raman spectroscopy of unpurified 40 g preform of $\text{As}_2\text{Se}_3$
Figure IV-3 EDX spectra of a slice of a $\text{As}_2\text{Se}_3$ preform
Figure IV-4 Vickers hardness measurement of $\text{As}_2\text{Se}_3$ preform
Figure IV-5 FTIR spectra of 4 slices of a 40 g $\text{As}_2\text{Se}_3$ batch
Figure IV-6 Typical DSC curve of an $\text{As}_2\text{Se}_3$ glass
Figure IV-7 Hardness versus force load
Figure IV-8 Pictures of indentations made using the Shimadzu DUH-211S a) 200mN load, b) 350 mN load: cracks can be observed
Figure IV-9 a) Vickers microhardness of As$_2$Se$_3$ sample prepared with different purification methods b) Water and hydroxide content as a function of the purification method

Figure IV-10 Effect of thermal treatment on the purity of As$_2$Se$_3$ glass

Figure IV-11 Effect of impurity-getter on FTIR spectra of As$_2$Se$_3$ glass

Figure IV-12 Zoom in the FTIR curve a) 2.5 - 4 µm b) 4 - 6.5 µm c) 12 - 18 µm

Figure IV-13 UV-Vis spectra of unpurified As$_2$Se$_3$ glass

Figure IV-14 Raman spectra of all bulk As$_2$Se$_3$ glass prepared in the bulk form

Figure IV-15 a) Raman spectroscopy of thermally purified As$_2$Se$_3$ fibers of different diameters b) Zoom on the 200-300 cm$^{-1}$ region

Figure IV-16 Comparison of Raman spectra of As$_2$Se$_3$ in fiber and bulk form

Figure IV-17 Effect of the diameter size on the Vickers microhardness of As$_2$Se$_3$ fibers

Figure IV-18 Effect of the purity of the fiber on its Vickers Microhardness

Figure IV-19 Stress-strain curve of unpurified and thermally (oxide volatilization) purified As$_2$Se$_3$ fibers

Figure IV-20 Evolution of the Weibull distribution for bending stress at failure of As$_2$Se$_3$ fibers as a function of the purity

Figure IV-21 a) Vickers microhardness as purification method b) Water and hydroxide content as a function of the purification method c) Se-H bond content as a function of the purification method

Figure IV-22 Molecular representation of As$_2$Se$_3$ glass network. a) Effect of the removal of molecular water on the glass network. b) Effect of the removal of OH on the glass network connectivity
Figure IV-23 Effect of the creation of a Se-H bond on the glass network connectivity ................................................................. 119
Figure IV-24 Dimerization of aluminum chloride upon heating .......................................................... 121
Figure IV-25 Reaction mechanism between aluminum-chloride and water impurity present in the glass matrix ......................................................... 121
Figure IV-26 Effect of the reaction between the glass and HCl on the Se-H band ................................................................. 123
Figure IV-27 Structure of As$_2$Se$_3$ glass a) in the bulk form b) in the fiber form ................................................................. 125
CHAPTER I: INTRODUCTION

1.0 Motivation of the project

Chalcogenide glasses are non-oxide glasses, which exhibit an extraordinary transparency in the infrared (IR) wavelength region from 0.5 to 20 \( \mu \)m. They are attractive materials for IR applications and fiber optics. They are promising for fabrication of laser power delivery, chemical sensor system or high-speed switches [1]. The development of such systems requires the melting and fabrication of stable low-loss fiber. The uniformity of a fiber is defined by the homogeneity of the thermal, physical, mechanical and optical properties throughout the whole fiber. Transparency and optical loss of the resulting fibers of such glasses are impurity-sensitive properties. High purity fibers exhibit better optical transmission in the mid IR wavelength, defined as the spectral window that spans the 2-12 \( \mu \)m range in the IR spectrum. Homogeneity of the bulk glass is a key step in achieving low loss fibers. Inhomogeneities in composition and/or structure and defects, induce scattering of the light and increase the overall loss. While it has been shown by others that some of the extrinsic sources of loss can be reduced, the main drawback of chalcogenide glass fiber is often their relatively poor mechanical properties. Drawing a high strength fiber means a good resistance to crack initiation and propagation (Vickers hardness) as well as high bending resistance, which are directly related to the fiber application. Indeed, the fibers would be bundled in a spring-shaped wire; therefore a high bending stress is required. In the proposed effort, a common optical glass, arsenic triselenide \( (\text{As}_2\text{Se}_3) \) will be examined. Comparison of ‘standard’ glass material processed with reagent grade elemental starting materials (referred as unpurified material) will be made to glasses fabricated using purified raw materials.
The impact of the purification steps on glass properties, specifically optical, mechanical and physical properties (glass stability against crystallization during fiber drawing), will be quantified. This evaluation of bulk glass and the properties of As$_2$Se$_3$ glass fibers will be compared. By assessing the impact of purification on these important bulk glass and glass fiber characteristics, their potential for use in applications that demand higher strength will be determined.

In this thesis the following key questions will be investigated and answered:

1) Effect of the purification method on the properties of the glass.

2) Effect of drawing on the properties of the fiber.

3) Determine a correlation between the mechanical properties and the purity of the bulk/fiber.

4) Determine the effect of the purification technique on the structure of the glass network.

2.0 Glasses

2.1 Fundamentals of chalcogenide glass formation

Generally, a glass is defined as a supercooled liquid. However, glasses can be formed without proceeding through a melt (vapor deposition, sol-gel). Glasses of various chemical nature can be synthesized: metallic, organic and inorganic glasses [12]. A correct definition of a glass has to take into account the fact that glasses do not exhibit a long-range atomic arrangement and do exhibit a time-dependent glass transformation behavior [12]. The temperature range over which this latter property exists is known as the glass transformation range ($T_g$). It can be explained in terms of
change in enthalpy during the glass formation. A plot of enthalpy (related to volume) as a function of temperature plot is shown Figure I-1 [12].

![Diagram of enthalpy vs temperature](image)

**Figure I-1 Effect of the temperature on the enthalpy of a glass forming melt**

[Taken from reference 12]

If a melt is cooled at a slow rate, the enthalpy decreases linearly with temperature following the liquidus, and at $T = T_m$ an abrupt decrease occurs without going through the supercooled region. This rapid change in volume (enthalpy) corresponds in the formation of crystals, creating a fully crystalline structure, which exhibits long-range order and periodic atomic arrangement. The change in enthalpy is due to a phase change from the liquid state to the solid crystal phase. When the cooling rate is faster the liquid reaches the supercooled liquid state. The liquid continues to rearrange as the temperature decreases, but no rapid, discontinuous, change in enthalpy is observed. The liquid viscosity increases as the temperature decreases until a point is reached where the atoms cannot rearrange to the equilibrium liquid-like structure. The enthalpy begins to deviate from the equilibrium line, following a curve of a decreased slope. Eventually the viscosity of the supercooled liquid is such that the atoms cannot rearrange and this leads to the formation of an amorphous solid with
no long-range order. The slope-changing region is called the transformation range; this temperature range corresponds to the transformation from a frozen liquid to a glass. The supercooled liquid line and the glass line intercept at a point called the fictive temperature, $T_f$. Since the glass transition is dependent on the cooling rate, a glass that is cooled slower will have a lower $T_f$ and its structure would be closer to the crystal structure than a faster cooled melt.

Chalcogenide glasses are mainly composed of chalcogenide (group VI) elements: sulfur, selenium, and tellurium. No oxygen atoms are present in these systems, which is the reason why they are also called non-oxide glasses. Indeed oxygen atoms tend to increase the opacity of the glass for wavelengths higher than 12 $\mu$m, as they are included in it. Other elements from groups IV and V are added in chalcogenide glasses, such as Germanium, Arsenic, Antimony and Tin.

2.2 Attributes of optical fibers

The first optical fibers were developed in the 50’s and were only able to carry detectable light on a few meters [10]. Nowadays, very low loss can be achieved on silica fiber: < 0.16 dB/km (at 1.55 $\mu$m) in mass production fibers [22]. In this effort we have examined unclad fiber and core-clad fibers, which are discussed below.

2.2.1 Unclad fibers

Optical fibers are drawn using a drawing tower. A schematic representation of the fiber tower is shown in Figure I-2. The tower is composed of a single zone furnace, a diameter controller, a tension meter and a drum to ease the collect of the fiber.
Generally, a coating cup as well as an UV curving oven is introduced in the setup to deposit a polymer coating at the surface of the fiber. This additional layer aids in reduction of crack formation due to post-drawn handling.

Once the glass preform has been made, the preform is loaded into a fiber drawing tower. The fiber is then heated up to its drawing temperature that is determined from its viscosity curve as seen in Figure I-3. Typically, fiber drawing takes place in the temperature range that corresponds to a viscosity of around $\log \eta = 5$ Pa.s, as depicted in the figure by the red box in Figure I-3.
The drawing temperature may vary from the temperature corresponding to $\log \eta = 5$ Pa.s, depending on the material composition and the thermal history of the material. When the bottom part of the preform is heated up for a few minutes, the first drop falls down due to gravity and is collected by an operator and attached to a take-up drum. The drum mechanism pulls fiber at a rate of 10-20 m/s and very long segment of fiber can be drawn from one preform. The diameter of the resulting fiber can be changed by modifying the feeding parameter and by adjusting the drawing temperature.

Addition of coating on the fiber surface prevents the creation of flaws and hence, prevents optical loss and breaking of the fiber under tensile or bending stress.
2.2.2 Core-clad fiber

The double crucible method of optical fiber manufacture was developed in 1980 by James D. Tichmarsh [13]. In this technique, two concentric crucibles are filled with molten core and cladding glasses as seen in Figure I-4. Fibers are drawn from the outfall of the nozzles at the bottom of the brushings. If the brushings geometry (alignment, curvature, size) is the same and the drawing is performed under the same temperature conditions, then the ratio of core to cladding diameter will only be a function of the melt levels.

![Figure I-4 Schematic representation of the double crucible fiber drawing technique](image)

The constant core-clad ratio can be obtained in a continuous process. The materials are selected so that $n_1 > n_2$, to confine the light in the core of the resulting fiber. This technique allows one to make fibers with lower optical loss and better mechanical properties [13]. Indeed, the total internal reflection phenomenon occurs when light enters a medium with a refractive index $n_1$ and then hits the interface with a second medium of a refractive index $n_2$ (with $n_1 > n_2$). The light must enter the core of the fiber with an angle smaller than a “critical angle” defined as the maximum angle the light can enter the core without going through the interface. If this condition is
satisfied, the light will then bounce off the interface and will indefinitely remain in the core material of the fiber.

This critical angle is dependent in the refractive indices of the core and cladding material and is defined by this equation [10]:

$$\theta_c = \arcsin\left(\frac{n_2}{n_1}\right)$$  \hspace{1cm} (1)

Changing the cladding and/or the core materials can hence modulate the critical angle.

3.0 Glass system studied: Binary As$_{40}$Se$_{60}$, arsenic triselenide

Amorphous As$_{40}$Se$_{60}$, also called stoichiometric arsenic triselenide (As$_2$Se$_3$), is a system that has been widely studied [1], [2], [16]. Pure amorphous selenium consists of a mixture of Se$_8$ rings and chain structures, which are composed of covalent bonded Se chains [6]. Intra-molecular bonding is covalent but only Van de Waals forces exist between the Se$_8$ rings and the Se chains. Addition of arsenic polymerizes the structure by forming three bonds with Se, acting as a cross-linking agent between molecular units [5]. As the arsenic content is increased the Se$_8$ rings tend to open and disappear from the structure. When arsenic is added, a layer-like structure is formed with a molecular unit composed of an arsenic atom sitting on the top of an AsSe$_3$ pyramidal structure. The nature of the bonds in the layers is covalent whereas the interlayers of the structure are weak Van der Waals forces. A transition from a cross-linked chain-like network to a three dimensional system occurs in the stoichiometric compound As$_2$Se$_3$. 
In the present study, only As$_2$Se$_3$ glasses are examined, in their “standard” reagent grade form (unpurified) or following various types of purification discussed in section 1.4 below. While minor levels of impurities or defects in a glass do not largely influence physical properties, optical properties are very sensitive to physical defects and/or chemical impurities. Hence, the following properties, determined to be important to optical fibers needed for high strength applications will be examined. Table I-1 summarizes the thermal, mechanical, optical and physical main properties of As$_{40}$Se$_{60}$ glass in bulk form, and in fiber form, as determined by a literature search, which will be investigated in this study. However, the temperature of maximum rate of nucleation and growth and the effect of the purification methods on these properties will not be studied. Notation has been made to any purification processes that have been carried out on the materials.

Table I-1 Properties of As$_2$Se$_3$ glass

<table>
<thead>
<tr>
<th>Property</th>
<th>Literature Bulk</th>
<th>Literature Fiber</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (±0.02 g/cm$^3$)</td>
<td>4.62</td>
<td>4.58</td>
<td>[7], [17]</td>
</tr>
<tr>
<td>CTE (±150 ppm/K)</td>
<td>21.28</td>
<td>N/A</td>
<td>[7], [16]</td>
</tr>
<tr>
<td>$T_g$ (±3 °C)</td>
<td>193</td>
<td>170</td>
<td>[1], [14]</td>
</tr>
<tr>
<td>$T_x$ (±3 °C)</td>
<td>373</td>
<td>273</td>
<td>[14], [16]</td>
</tr>
<tr>
<td>$T_m$ (±3 °C)</td>
<td>380</td>
<td>370</td>
<td>[14], [16]</td>
</tr>
<tr>
<td>$\Delta T = T_x - T_g$ (°C)</td>
<td>170</td>
<td>128</td>
<td>[14], [16]</td>
</tr>
<tr>
<td>$T$ ($W_{\text{max}}$) (°C)</td>
<td>210</td>
<td>N/A</td>
<td>[8]</td>
</tr>
<tr>
<td>$T$ ($V_{\text{max}}$) (°C)</td>
<td>245</td>
<td>N/A</td>
<td>[8]</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.79</td>
<td>2.79</td>
<td>[1], [4]</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>1.51</td>
<td>N/A</td>
<td>[1]</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>1.40 ± .05 (200mN)</td>
<td>1.54 (100mN)</td>
<td>[17]</td>
</tr>
</tbody>
</table>
Glasses materials are not in an equilibrium state, their structures continue to relax and evolve with time. As$_2$Se$_3$ is known to be a material that forms glass readily, to be stable to crystallization and its large $\Delta T = T_x - T_g$ allows one to conveniently draw fiber.

4.0 Purification methods

Purification of optical glass involves the use of chemical or physical processes or mechanisms to remove impurities present in elemental starting materials used in the glass melting process.

4.1 Definition of impurities versus defects

There are two main sources of optical losses in chalcogenide glasses: physical defects and impurities.

Scattering of a light radiation can be induced by bridging and non-bringing impurities [14]. Such impurities are found in chalcogenide glasses. Non-bridging impurities are compounds dissolved in the glass matrix. Impurities present in the raw materials remain in the material to generate single bonds with the glass matrix. Finally, heterogeneous inclusions are also incorporated in the glass during the reaction between the melt and its environment. The nature of the different impurities can be seen in Table I-2.
Table I-2 Impurities present in chalcogenide glasses

<table>
<thead>
<tr>
<th>Bridging / Non-bridging impurities</th>
<th>Embedded into glass network</th>
<th>Stable dissolved compounds</th>
<th>Heterogeneous inclusions</th>
</tr>
</thead>
</table>

Physical defects on the other hands do not require the presence of external specie to be present in the glass. Micro-segregation and crystallization can induce the formation of nano-phase and nano-crystal of a secondary phase that act as scattering center, which deviate light radiations and hence loss of signal in an optical material. Extensive corrugated inhomogeneities also called striaes and bubbles are reported as physical defects, (picture of these inhomogeneities are shown Figure I-5). The scattering is due to slight changes in the refractive index of the material throughout the length of the material due to slight change of composition.

![Figure I-5 Infrared photography of a) Striaes observed in a cross section of a chalcogenide glass rod, b) Bubble in a core-clad chalcogenide fiber [taken from reference 21]](image)

The presence of both impurities and physical defects can induce important loss of transmission in the glass. Impurities in the matrix absorb and/or scatter light of particular wavelength under their vibration modes. The dispersed energy is hence lost and radiates out of the material.
Previous studies discussed the impact (and the benefits) of the glass purity on the optical loss of chalcogenide glass fiber [14], [18]. However, studies of the effect of the impurity concentration on thermal, physical and mechanical properties of the glass are not as common. It has been reported that the density of chalcogenide glasses was decreasing with increasing purity of the material [19]. Thermal properties can also be affected by the purity of the material. The thermal stability of the glass is decreased due to changes in both $T_g$ and $T_x$ of the glass. Unfortunately purity of the glass tends to increase $T_g$ and decrease the onset of the crystallization event so that $\Delta T = T_x - T_g$ is decreased, which can be problematic for shaping application such as molding or fiber drawing. It has been determined that the mechanical properties of glass were to be correlated with the network connectivity and hence the purity of the glass [27]. Removing bridging impurities can be a key factor to that extent.

Table I-3 summarizes the lowest impurity concentration level found in the most common chalcogenide glasses [15].

<table>
<thead>
<tr>
<th>Impurity</th>
<th>As$_2$S$_3$</th>
<th>As$<em>2$S$</em>{1.5}$S$_{1.5}$</th>
<th>As$_2$Se$_2$Te</th>
<th>Ge$<em>{25}$Sb$</em>{16}$S$_{65}$</th>
<th>As$_2$Se$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.05</td>
<td>0.2</td>
<td>0.02</td>
<td>0.13</td>
<td>0.1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.001</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon</td>
<td>&lt;0.2</td>
<td>&lt;0.02</td>
<td>0.6</td>
<td>&lt;5</td>
<td>0.5</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.1</td>
<td>&lt;0.4</td>
<td>0.05</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Metals (Mg, Al, Mn, Ni)</td>
<td>0.001</td>
<td>&lt;0.2</td>
<td>0.02</td>
<td>&lt;0.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Different techniques were used to determine the concentration of each impurity. The lowest impurity concentrations were obtained from sample treated with multiple glass distillation processes combined with the use of impurity getters. The glass this study will focus (As$_2$Se$_3$) on is not the one where the lowest concentrations were yielded. From these observations, the use of impurity getters and glass distillation has been selected as the key purification technique that we will focus on in this study.

Described below are two primary methods used to yield high purity chalcogenide glasses.

4.2 Surface oxide removal via thermal treatment

A primary step in obtaining a high purity glass is to use a dynamic vacuum/heat treatment technique to reduce the oxygen content of the glass. Individual high purity (5 or 6 N) raw elements are heat treated while under vacuum to remove the surface oxides present. This process allows the reduction of surface oxides traces present on the raw materials such as As$_2$O$_3$, SeO$_2$, Se$_2$O$_3$ (for arsenic selenide glasses). Table I-4 reports the bond energy of the most common impurities present in arsenic selenide glasses [20].
Table I-4 Bond energy of impurities in chalcogenide glasses [taken from reference 20]

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Type of bond</th>
<th>Bond energy (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₂O₃</td>
<td>As-O</td>
<td>481 (± 8)</td>
</tr>
<tr>
<td>Se₂O₃</td>
<td>Se-O</td>
<td>464.8 (± 21.3)</td>
</tr>
<tr>
<td>TeO₃</td>
<td>Te-O</td>
<td>376.1 (± 20.9)</td>
</tr>
<tr>
<td>SeO₃, SeO₂</td>
<td>Se-O</td>
<td>464.8 (± 21.3)</td>
</tr>
<tr>
<td>GeO₂</td>
<td>Ge-O</td>
<td>659.4 (± 12.6)</td>
</tr>
</tbody>
</table>

Different energies are required to remove each impurity from the system. Typically, moisture and molecular water can be removed at 100 °C under vacuum but traces of oxides remain in the glass. Additional treatments at higher temperature allow the bond breaking of the metal-oxygen/chalcogen-oxygen bond at the surface of the raw material without melting the material. Oxygen (or hydroxide) atom (molecule) can then recombine into molecular water or O₂ and be removed from the system via dynamic vacuum. The formation of O₂ or water is favored since the oxygen-oxygen bond energy is higher than the metal-oxygen energies.

Different level of purity can be reached depending on the time and temperature profile. A precise knowledge of the vaporization temperature of every element in the glass is necessary before conducting this kind of experiment: a slight change in composition can have a dramatic effect on the refractive index of the glass.

Thermal treatment is a good method to remove part of the impurities but it only affects the surface of the raw materials. Therefore, new purification techniques have to be performed in order to decrease the optical loss of chalcogenide glasses.
Chemical purification has been widely explored in the past 20 years to improve the glass purity for optical applications.

4.3 Distillation (Mg, AlCl₃)

In order to achieve higher purity in the glass preform chemical purification has to be performed. Magnesium, aluminum, zirconium, and copper are the most common materials used as oxygen getter in chalcogenide glass [2]. The getter is included with the raw elements in a distillation chamber. Upon heating, the getter reacts and combines with the oxide present in the bulk glass. The distillation process is carried out at a temperature where the chalcogenide glass is distilled but the metal and oxides are not. A very small amount of getter is necessary to perform a distillation, usually less than 1 weight %. The precursor materials and the oxygen getter are disposed together in a necked tube and put in a two-zone furnace. The temperature is set so that the first zone is at a higher temperature than the melting temperature of the precursors, which will afterwards vaporize and get condensed to the cooler zone. The difference of temperature between the two zones is the driving force of the distillation. The oxygen impurities that were collected by the magnesium remain trapped in the first zone [2].

Chemical purification of glass implies the addition of a reagent in the glass batch, which reacts selectively with impurities during the melting. Only small amounts of these getters have to be added. The added material should have a very small influence on the transparency of the resulting glass. This approach aims to change the chemical form of the impurity to a compound that can be extracted from the melt afterwards. Vacuum-distillation of the melt is necessary in order to remove the newly-formed impurity species. The distillate is then homogenized by melting. Several
getters can be chosen to get different purity result. Furthermore, the combination of multiple getters can be realized for some composition to obtain higher level of purity in the glass.

5.0 Summary - objective of the study and organization of the thesis

In this chapter, the background of glass science, fiber processing and purification methods to yield high purity chalcogenide glasses have been presented. The principal characteristics of the material studied as well as the nature of the impurities and defects to be removed were introduced. The effects of the impurities and physical defects on the different physical properties that will be studied in depth in this thesis were discussed.

In this thesis the following key questions will be investigated and answered:

1) Effect of the purification method on the properties of the glass.

2) Effect of drawing on the properties of the fiber.

3) Determine a correlation between the mechanical properties and the purity of the bulk/fiber.

4) Determine the effect of the purification technique on the structure of the glass network.
6.0 References


CHAPTER II: LITERATURE REVIEW

This chapter discusses about the methods and techniques used in the community to obtain high purity glasses. This chapter also summarizes and quantifies the state of the art for low optical loss fibers. The conventional methods to measure the mechanical properties of glass in both bulk and fiber form are also reviewed.

1.0 Purification of chalcogenide glass

In this section, the determination of the presence of impurities in non-oxide glasses and the conventional method used to yield high purity non-oxide glasses are reviewed. The state of the art for \( \text{As}_2\text{S}_3 \) and \( \text{As}_2\text{Se}_3 \) is also presented.

1.1 Impurities in chalcogenide glasses

As introduced in chapter I section 1, chalcogenide glasses are transparent materials in the near- to mid-infrared (MIR) region from 2-20 \( \mu \text{m} \). A conventional synthesis of chalcogenide glasses does not yield an ideal transparency. Therefore, further additional treatments have to be performed in order to obtain high purity chalcogenide glasses and subsequently low-loss fibers. Chalcogenide glasses include a wide range of compositions and they can be binary or multicomponent systems. They always contain a chalcogen species, selenium, sulfur or tellurium in addition to elements from groups IV-VI of the periodic table of the elements.

Since different precursors are present in chalcogenide glass systems, this implies that it is necessary to consider different purification methods for the various chemical species present. Physical and/or chemical purification techniques are performed to
remove traces of impurities that can impact physical properties or of importance in the present study, optical properties of the resulting glass.

Physical impurities, which involve the presence of nano-crystal and/or nano-drops of a secondary glass phase, can induce scattering of the transmission [1]. The phase separation process is driven by the thermodynamics and different separation can be identified: spinodal decomposition or nucleation and growth of droplets in a matrix. Phase separations modify the other properties of the resulting material such as density or mechanical properties [12]. Extensive corrugated inhomogeneities, called striaes, can also be observed. These phenomena are present due to a poor control of the temperature profile during the glass making process. The losses induced by the presence of these inhomogeneities increased as the bulk glass is drawn into a fiber. Presence of various sizes of bubbles in the glass bulk is also recorded to scatter IR transmission. Bubbles are formed during melting and remain in the glass when quenching temperature or quenching time is not adequate. Chalcogenide-chalcogenide (Se-Se, S-S bonds) and metal-metal bonds such as As-As or Sb-Sb homo-bonds are also responsible for optical loss in the glass matrix. These can exhibit absorption bands that can be similar to the one of an impurity.

However, losses in the IR transmission in the chalcogenide glasses mainly come from the presence of oxygen, hydrogen and carbon related species at the glass surface and in the glass matrix. In addition losses due to silica traces coming from the tube can be present. These impurities are included as bridging or non-bridging atoms in the glass bulk. Hetero-phase solutions are found when substances are not soluble like carbons at the low temperature used (lower than 1000 °C) in the chalcogenide glass melt.
1.2 Detection of impurities

The common way to determine the presence of impurities in glass system is the Fourier transform infrared spectroscopy (FTIR).

For the glass we are interested in (As$_2$Se$_3$, As$_2$S$_3$ and related compositions), the main impurities were observed using FTIR (see chapter III), and are presented in the Table II-1 [23], [24]. The intensity of the peaks is described by using « s » for strong, « m » for medium and « w » for weak.

Table II.1 Frequency and intensity of the absorption bands of impurities in FTIR spectroscopy [Taken from reference 21,22]

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Bond</th>
<th>Position (µm) and intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_2$O$_3$</td>
<td>As-O</td>
<td>7.50, 7.90 s, 9.10, 9.50 w, 10.20, 10.40, 12.50 s, 14.10</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Si-O</td>
<td>9.00 m, 9.27 m, 9.40 m</td>
</tr>
<tr>
<td>SeO$_2$</td>
<td>Se-O</td>
<td>10.00 s, 10.70, 13.96 s, 16.00</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>C-S</td>
<td>4.94, 7.60</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>H-S</td>
<td>2.00-2.10, 4.01 s, 3.70 m, 2.54 w</td>
</tr>
<tr>
<td>H$_2$Se</td>
<td>H-Se</td>
<td>3.53 w, 4.12 m, 4.45 m, 4.50-4.70, 5.57 s, 7.17, 7.80 15.90</td>
</tr>
<tr>
<td>OH group</td>
<td>O-H</td>
<td>2.24 m, 2.78 m, 2.84 s, 2.93 s</td>
</tr>
<tr>
<td>Carbonate</td>
<td>C-H</td>
<td>3.41 m, 3.50 m</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>O-H</td>
<td>2.32 m, 6.30 s</td>
</tr>
</tbody>
</table>

Physical defects and extensive corrugated inhomogeneities (also called striaes) presence can be detected in the glass bulk before opening the quartz tube using an infrared camera. These absorption bands will be used as characteristic points in the following FTIR analysis of glass produced in this thesis. The vibrational absorption of the various impurities will generate absorption bands in the resulting FTIR spectra.
1.3 Purification of chalcogenide glasses

As stated previously, chalcogenide glasses can be made from multiple precursors, hence purification techniques have to be adapted to the composition and the nature of impurities and the predicted nature of impurities. Moreover, the selected purification method used can be adapted to the quality of the final product desired. Indeed, highly pure chalcogenide glasses fabrication requires multiple steps of purification [25], which can be costly and time consuming. Moreover, it was shown that the defects should be less than $10^2$-$10^3$ per cm$^3$ to avoid scattering.

1.3.1 Physical defect removal

The presence of defects is most often due to an inadequate heating or conditioning profile of the melt, or physical inhomogeneities added with the batch that do not melt (for example, carbon). The presence of such defects is either due to a wrong melting temperature or quenching profile [1]. If the melting temperature is too low or is not held long enough a partial quantity of high melting temperature precursors, usually germanium, can remain in solid form in the melt and will scatter light. Bubbles can be trapped in the glass during the quenching step of the glass making. When the melt is cooled too fast, bubbles will not be able to escape the solution before the viscosity reaches a critical value. Crystallization is also sensitive to the cooling of the glass. In some glass system the growth and nucleation curves overlap-region is large and, if the melt remains in this temperature region, crystals will grow and will be present in the glass matrix. Bubbles and crystals scatter light and induce significant optical loss. Remelting the glass is the only way to remove these impurities.
1.3.2 Surface oxide removal

A non-negligible concentration of oxides impurities remaining in the final product is coming from contamination of raw materials during storage. Big pieces of raw elements are used to lower the surface and hence lower the concentration of surface oxides. But additional treatments are required to reduce the surface oxides concentration. A quick thermal treatment under vacuum removes the surfaces oxides traces such as \( \text{As}_2\text{O}_3, \text{SeO}_2, \text{TeO}_2 \), etc. Different level of purity can be reached with such treatment; individual element treatment yields better purity since the difference in purification temperature between the starting materials can be important (i.e. germanium and sulfur). Arsenic is purified at 300 °C for 2 hours and selenium at 250 °C for 2 hours [26]. The key driving force for this mechanism is the difference of pressure vapor between the surface oxide \( \text{As}_2\text{O}_3, \text{SeO}_2 \) and the metal. The greater vapor pressure of \( \text{As}_2\text{O}_3, \text{SeO}_2 \) over those of the metals (As, Se) [27] allows the removal of the oxide species. If selenium is heated at higher temperature, significant vapor loss can be observed. A good knowledge of the precursors is required in order to optimize the process.

1.3.3 Oxide removal

A chemical distillation process is used to remove the remaining oxides in the glass. Oxygen containing impurities are removed by melting the glass with addition of an oxygen getter [2]. The use of oxygen getter during a distillation process has shown to significantly reduce the optical losses at different wavelength. Typical oxygen getters used are aluminum, magnesium and copper. The main impurities removed using this method are arsenic oxides, water, and hydroxides but also silica coming from the tube walls. All precursors are included in the distillation chamber
with the oxygen getter. Residual oxides in the precursors are trapped by the getter and form a surface oxide layer. The raw materials and the getter were contained in a sealed ampoule. The distillation is performed in a two-zone furnace by varying the temperature gradient.

![Figure II-1 Schematic of a two-zone furnace where $T_1 > T_2$](image)

The temperature profile is set so that the batch melt in the segment containing the oxygen getter, then vaporize and distill to the second colder segment. The segment containing the oxygen getter combined with the impurities is removed from the system with a methane-oxygen torch and the remaining segment is used to melt the glass.

1.3.4 Hydride removal

A similar technique has been developed to remove the hydride in the glass. Tellurium tetrachloride is the usual compound selected as a hydrogen getter. Other
compounds such as AsCl₃ or SeCl₂ can be used. However, they are not solid under ambient conditions (20°C and atmospheric pressure). This process involves the creation of reactive chlorine atmosphere [28]. The high purity hydrogen getter is added to the batch and a dynamic distillation of the precursors was run in a two-zone furnace. The hydrogen chloride produced is eliminated during dynamic distillation. The segment containing the distillated purified precursors was sealed apart from the other segment using a methane-oxygen torch. The distillated is then melted to form the glass using the conventional melting technique.

In chalcogenide glasses the hydrogen impurities are mainly coming from selenium and sulfur therefore when the temperature rises during melting the following reaction occurs:

$$\text{TeCl}_4 + 4\text{HX} \rightarrow 4\text{HCl} + \text{Te}_{\text{(glass)}} + 4\text{X}_{\text{(glass)}}$$

(2)

With X being Se or S. Tellurium in the glassy state remains in the final glass network but present the advantage of not reducing the optical property of the final material.

1.4 Purification of As₂Se₃: state of the art.

1.4.1 Optimum loss: intrinsic loss of the glass

Investigation on the minimal loss achievable has been made in chalcogenide glasses, especially for As₂Se₃ and As₂S₃. Different studies reporting the intrinsic loss of glass estimated from the “weak absorption tail” allowed the determination of the ideal glass transmission window. It is done by extrapolation from comparing the optical absorption to the photon energy of glass. Therefore, the content of impurity leading to the optimal intrinsic optical loss can be calculated [3]. This content is calculated from the extinction coefficient of the impurity group concerned. The
extinction coefficient is a quantitative measure for estimation of the impurity effect on optical loss in glasses. It is determined from the absorbance of the material.

Knowing that the absorbance is defined by:

\[ A = \log \left( \frac{I}{I_0} \right) \]  

(3)

and that:

\[ I = I_0 e^{-x\alpha} \]  

(4)

The relationship between the absorption coefficient and the absorbance of the material can then be described by the following equation:

\[ \alpha = \frac{\ln(10^A)}{-x} \]  

(5)

with \( A \) being the absorbance of the material (at a specific wavelength), \( I_0 \) the source signal, \( I \) the measured intensity transmitted through a layer of material, \( x \) is the thickness of the sample in cm and \( \alpha \) the absorption coefficient of the material in cm\(^{-1}\).

Table II-2 presents the calculated concentration of impurities in both As\(_2\)Se\(_3\) and As\(_2\)S\(_3\) glasses to generate band-less spectra.
Table II-2 Optimal loss impurity concentration [taken from reference 22]

<table>
<thead>
<tr>
<th>Impurity compound</th>
<th>Glass</th>
<th>Calculated content of impurity leading to the optimum loss. (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH</td>
<td>As$_2$S$_3$</td>
<td>0.3</td>
</tr>
<tr>
<td>SeH</td>
<td>As$_2$Se$_3$</td>
<td>0.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>As$_2$S$_3$</td>
<td>0.05</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>As$_2$S$_3$</td>
<td>0.2</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>As$_2$Se$_3$</td>
<td>100</td>
</tr>
<tr>
<td>Se-O</td>
<td>As$_2$Se$_3$</td>
<td>2000</td>
</tr>
</tbody>
</table>

From this table we can see that hydrogen-containing species are the one that require the lowest concentration, hence the better purification.

1.4.2 State of the art in purified, chalcogenide glasses

As As$_2$Se$_3$ is chemically and structurally similar to As$_2$S$_3$, arsenic-sulfide data are included for comparison. However, As$_2$S$_3$ will not be examined in this study.

1.4.2.1 Arsenic-sulfide

Best loss reported for optical fibers are usually specific on a single wavelength: the minimal loss of the transmission window for a specific glass system.

Churbanov et al. recorded the yielding of very high purity arsenic sulfide that involves the use of arsenic monosulfide (As$_4$S$_4$) as the source of arsenic, the “ultra-purification” of initial substance from oxygen, high vacuum loading of the components, control of the melting temperature (no overheating), low cooling rate
from the melt to the glass. The use of arsenic monosulfide lowers the concentration of oxides imported to the melt from the raw material as compared to the use of pure arsenic. The control of the melting temperature has proven to be very important, indeed melting at 950°C instead of 800°C increase the defects concentration by a factor of 97. The precursors were purified by a series of chemical distillation methods to lower the oxide and hydride concentration. The content of impurity containing OH groups obtained was 0.5-1 ppb, SH groups 100-150 ppb, CO₂ 0.5-1 ppb, silicon 200 ppb. The minimum optical losses in the whole transparency region were recorded to be 12 dB/km at 3 µm and 14 dB/km at 4.8 µm. Twenty year before in 1984, that best lost recorded was 94 dB/km at 3 µm. [6]

1.4.2.2 As₂Se₃

Arsenic selenide (As₂Se₃) glasses purification relies more on the Se purification since the higher transparency region (4-5 µm) of this system correspond to the wavelength where Se-H band are mainly absorbing (4.57 µm).

Nguyen et al. recorded the preparation of a high purity arsenic selenide glass. The elemental precursors were thermally purified to remove the oxide layers. A primary sublimation/distillation treatment in a two-zone furnace was performed using 10 ppm of aluminum in the batch to remove the oxides containing impurities as well as high melting temperature elements such as carbon or silicon. High purity tellurium tetrachloride was prepared in a two-step process. Addition of 0.1 wt.% of TeCl₄ to the purified batch followed by a remelt at 750°C for 24 hours allowed the reaction to occur between hydrogen containing impurities and TeCl₄. The glass was then subsequently distilled under vacuum at 550°C for 15 hours to eliminate gaseous
byproducts (HCl) formed during the reaction with TeCl₄. The distillate was then remelted a 750°C for 24 hours, followed by a quench at 400°C. The glass was then draw into fiber and optical loss where characterized using a cutback technique. A significant reduction of the intensity Se-H (at 4.57 µm) absorption band from 10 dB/m to 0.2 dB/m is observed. The calculated concentration of H-Se impurities was estimated to be 0.18 ppm.

Since very low optical loss are recorded only at a specific wavelength for each composition, it is possible to purposely form a new impurity to reduce the content of another one that absorbs in the minimal loss of the transmission region of the glass. Churbanov et al. synthesized arsenic selenide glasses with 5% of arsenic sulfide implemented in the batch. The final composition was (As₂Se₃)₀.₉₅(As₂S₃)₀.₀₅. The addition of sulfur in the melt reduces the intensity of the Se-H at 4.57 µm band to almost full transparency. This is due to the higher bond energy between hydrogen and sulfur than between selenium and hydrogen. The minimal loss observed in this system is 0.7 dB/m at 5.5 µm.

These example shows that there is still room for improvement in purification of chalcogenide glasses (180 times the theoretical level for As₂Se₃ [24]).

2.0 Mechanical properties of chalcogenide glass

In this section, a review on the mechanical properties of non-oxide glass (hardness, bending, tensile) is presented for bulk glass and fiber.
2.1 Hardness of bulk glass

Hardness (H) is a measure of the ability of a material to resist permanent plastic deformation. A hardness test involves indenting the material with an object like a ball or a diamond tip under a static load, and then the measurement of the area of the indentation region that remains after the load is withdrawn. A global equation for hardness measured this way is:

\[ H = \frac{L}{A} \]  

(6)

Where \( L \) (in N) is the applied load and \( A \) the resulting area (in mm\(^2\)), of the indentation. Hardness can be seen as the surface resistance to crack initiation of a material. The mechanical hardness, and therefore strength of material decreases as the flaw or scratch concentration increase, hence handling of the surface (scratches and also post-fabrication annealing that impacts near-surface density) can also impact measured hardness. Hardness is also load dependent, and measurements of glass hardness, must be made in a load regime whereby all energy is transferred to the material to yield an indentation (only), and not to generate new cracks. Crack formation at loads above a material-specific threshold yields erroneous hardness results, as part of the indentation energy no longer goes exclusively to crack formation but is rather translated to crack propagation. Therefore, an appropriate indentation load must be determined for each sample, and these indentation conditions should be defined when reporting hardness data [17].

Chalcogenide glasses usually exhibit low strength and hardness compared to oxide glasses such as silica. Soda-lime-silicate glasses generally have hardness around 5 GPa, whereas hardness of bulk pieces of chalcogenide glasses usually sits around 1.5 GPa (As\(_2\)Se\(_3\)). Generally, a number of 15 tests are done to average the hardness value.
In the arsenic selenide glass family, it was found that the hardness was increasing with increasing content of arsenic up to 40%. Arsenic is responsible for cross-linking between selenium chains in arsenic selenide. Therefore, the hardness of the glass increases as the arsenic increase. When the arsenic content goes higher than 40% As-As bonds are formed, which decreases the continuity of the polymer structure and hence the material becomes less packed. Low loads have to be used to avoid micro cracking at the glass surface.

2.2 Mechanical properties of fibers

2.2.1 Hardness

Measure of hardness is made using the same method as for the bulk glass. Particular attention is put on the position of the fiber. The measurement is made on the top part of the fiber (tangent to the diameter). The fiber is held straight so that no motion of the fiber is allowed during the experiment. The hardness of fresh fibers (as drawn) has been shown [17] in prior studies to be low and was shown to significantly increase while aging. Arsenic-selenide fibers are drawn under a continuous stress, which causes an orientation of the As-Se bond in the structure. Chalcogenide glasses exhibit low $T_g$. Hence, slow relaxation can still occur at room temperature for such glasses. The observed increase of the micro hardness with time has to be correlated with the increase of the density with time. Relaxation in the glass corresponds to a structural rearrangement of the strained bonds into relaxed (stronger) bonds. Therefore, the number of strained bonds in the glass matrix is decreased. When the indenter load is applied, it is averaged over a larger number of stronger bonds resulting in more resistance to crack initiation and hence an increased hardness.
2.2.2 Flexural, bending strength

Strength testing in bending is made using a two-point fiber bending technique, as shown Figure III-21. The fiber is mounted between two steel bars on the bend tester. The motion of one bar towards the other induces the bending of the fiber into a small elliptical shape. Eventually the large tension created at the apex of the fiber is such that it causes the fiber to break. The distance between the two bars is recorded when failure occurs, and the breaking stress can be calculated from this distance and the fiber diameter. Matthewson [29] derived the maximum tensile stress occurring at the surface of the fiber prior to breaking as:

$$\sigma_{max} = 1.198 \frac{E r}{D-r}$$ (7)

Where $E$ is the Young modulus of the fiber measured independently by tensile testing, $D$ is the minimum distance between the two moving bars that suspend the fiber under test, and $r$ the diameter of the fiber tested. An average of 10-15 tests have to be performed to get reliable data. All segment of fiber tested have to be inspected to determine the presence of flaws.

The bending strength of arsenic selenide fibers degrades rapidly, and in a few weeks the strength of the aged fibers can drop by as much as 60% of the as-drawn value. This observed phenomenon is primarily due to degradation of the surface of the fiber during storage, which generates weaker points at the surface. The failure under bending stress starts from the surface of the fiber; therefore, a lower surface quality will induce a decrease in the strength at failure [29].
2.2.3 Sources of loss in fibers

There exist many different sources of transmission loss in optical fibers due to absorption, Rayleigh scattering or bending of the fiber. While well studied in silica [30], it is not as well studied in chalcogenide glasses.

Any impurity remaining in the glass network of the preform will be present in the resulting fiber. These impurities can absorb part of the optical energy generating loss in the output signal. The most common impurities present in chalcogenides glasses are hydroxides, oxides, hydrides and water. Each remaining impurity will absorb optical energy at its specific vibrational energy and induce loss at a specific wavelength. Hence, effort on the removal of certain impurities can be targeted for a specific application.

One of the main sources of optical loss in fibers is Rayleigh scattering of light due to slight changes in local refractive index [32]. Fluctuation in the glass composition and different cooling rate of the material when the supercooled liquid is brought down to low temperatures are generating these changes in refractive index. Such fluctuations are increased when the batch size of the material is increased.

The last source of optical loss in fibers to take into account is loss due to bending. Two types of bending loss are reported: microbends and macrobends. Microbends are small microscopic bends happening when the fiber is cabled whereas macrobends are bends having a larger radius of curvature compared to the fiber diameter. Microbends losses are induced by discontinuities or imperfections in the fiber. Improper and uneven coating of the fiber increases the microbend loss. Macrobend losses are important when the fiber curvature is less than a few centimeters. The light propagating to the inner side of the bend travels a shorter distance than the one the outer side. The phase of the light wave is not maintained,
and this causes some of the light to be converted into higher-order modes, which then are radiated out of the fiber. Fibers with bigger diameter will be less affected by this type of loss.

3.0 Correlation between strength and optical properties of chalcogenide glasses

In this section, the correlation between strength and optical loss of chalcogenide glass fiber is discussed.

3.1 Core-clad fiber

The main technique used to yield high transparency chalcogenide fibers with both high hardness and bending strength value is to draw core-clad fiber using the double crucible drawing method. The outer thin part of the fiber (cladding) is designed so that its refractive index is lower than the one of the core to contain the light inside the core of the glass (see Figure II-2).
Figure II-2: Schematic of a core-clad optical fiber

The clad improves the bending strength of the fiber and also absorbs mechanical damages without decreasing the transmission of the core of the fiber [14]. The lifetime (time of use before failure) of the fiber is hence increased [32].

3.2 Effect of purity to mechanical properties

It is expected that the presence of the impurity decreases the network connectivity in chalcogenide glasses. The presence of oxides in the glass system breaks down the network decreasing the hardness of the material. An As-Se bond is broken to be replaced by either a Se-OH or As-OH bond as shown in Figure II-3.
The presence of bridging impurities in the melt has the effect of breaking the network. The glass matrix is hence depolymerized and the network connectivity decreases. Although stronger bonds are generated by the introduction of such impurities in the glass matrix (see Table III-3) [20], the network connectivity has more impact on the resulting hardness.

**Table II-3 Bond energy (at room temperature) of bridging impurities present in arsenic selenide glasses**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (kJ.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-O</td>
<td>481</td>
</tr>
<tr>
<td>Se-O</td>
<td>464.8</td>
</tr>
<tr>
<td>As-H</td>
<td>274</td>
</tr>
<tr>
<td>Se-H</td>
<td>314.47</td>
</tr>
<tr>
<td>As-Se</td>
<td>96</td>
</tr>
</tbody>
</table>
It has been demonstrated that the amount of arsenic in the $\text{As}_x\text{Se}_{100-x}$ greatly influences the hardness of the material [17]. The change in hardness with arsenic content can be as high as 0.9 GPa (for a load of 10 g). The arsenic acts as a cross linking agent between the Se chain and therefore reinforces the network connectivity in the glass (see chapter I section 1). The higher the arsenic content (up to stoichiometric $x = 40\%$) in the material, the higher the hardness is [17].

The evolution of the impurity concentration of fibers with aging has been studied. A decrease of transparency of arsenic-chalcogenide fibers is observed with increasing storage time of the fibers in air. It was shown by Shyraev et al. that an increase in the optical loss of $\text{As}_{35}\text{S}_{65}$ (coated with the commercial polymer F-420) from 200 to 400 dB/km could be observed after storage of 1 month in air. This variation in loss could be up to 220% for this fiber. The maximum variation in the fiber bending strength was recorded to be 60% for an $\text{As}_{40}\text{S}_{60}$ fiber stored in air for 3 years.

These changes are due to nucleation and propagation of cracks over time (during storage) at the surface of the fiber. Therefore, the mechanical strength of unclad fibers dropped more drastically than the one of core-clad fibers [29].

4.0 Summary

In this chapter, the literature review has been done on the methods used to purify chalcogenide glasses. The determination and assignment of impurity in non-oxide glasses as well as the present state of the art in term of impurity concentration in low optical loss fibers and the effect of the purification on the optical losses has been reviewed. A discussion of methods developed to assess mechanical properties of both bulk glass and fibers were presented, and the impact of fiber drawing on
resulting structure and possible differences from structural arrangements in bulk glasses defined.

These prior literature findings provide the background related to the present effort, which consist in examining the effect of the purity on the mechanical properties as well as the effect of the purification on the properties of the glass

5.0 References


CHAPTER III: EXPERIMENTAL PROCEDURE

Chapter 3 discusses the methods used to synthesized and prepared the desired glass sample and the techniques used to determine their thermal, optical, physical and mechanical properties as well as their homogeneity in both bulk and fiber forms.

1.0 Sample preparation

1.1 Bulk chalcogenide glass synthesis

This section discusses the methods employed to synthesize chalcogenide glasses in our laboratory. Additionally the methods developed to yield low oxide and low hydride content in non-oxide glasses are described.

1.1.1 Conventional melting protocol: unpurified ‘reference’ materials

Arsenic selenide glasses prepared by standard processing batching, melting and quenching routes in sealed quartz ampoules using as-received raw materials [11], served as the “reference” materials for the present study. These reference materials served as the starting benchmark for further study where glass-processing methods were modified to include purification processes. These initial reference glasses were prepared in 10 g batches. The composition studied was As$_{40}$Se$_{60}$.

The reference glasses were produced from high purity raw materials: As 99.999% (Cerac) and Se 99.999% (Alfa-Aesar). The pure elements were weighed and batched into a 10 mm inner diameter quartz ampoule in a nitrogen-purged glove box so that no air (oxygen) can enter the system during batching. The ampoule was then sealed using a methane-oxygen torch. The ampoule was then heated overnight (16
hours or more) at 2.5 K/min to peak the melting temperature of 700 °C. A rocking furnace was used to increase the homogeneity of the melt via rocking. The temperature of the furnace was then slowly brought down to 550 °C and the position of the furnace was set vertical to allow the removal of any remaining bubble from the melt. Once the temperature was reached, the sample was air-quenched to room temperature. The glass was subsequently put back in a furnace subsequently for overnight annealing below the glass transition temperature (i.e. at 160 °C) to avoid cracking of the glass ingot. A pictorial representation of the whole glass-making process is shown Figure III-1a. A schematic of the melting cycle (draw one with time/temperature with ramp rates, soaks and cooling rates) is shown in Figure III-1b.
Once removed from the fused quartz ampoule, the ingot was then cut and polished and inspected visually for defects or bubbles, and then subjected to further characterization.
1.1.2 Purification setup

1.1.2.1 Surface oxides volatilization via thermal treatment

A specific setup was designed and constructed to perform the surface oxide removal as seen in Figure III-2.

This setup, designed and constructed by Dr. Sylvain Danto and our group members, is composed of three different silica tubes connected to a vacuum pump. While contact of the chalcogenide glass ingredients with the silica tube in the purification line may introduce trace amounts of oxide to the post-treated materials, the contact time is limited and the relative diffusion rate of oxide into these species, is believe to be small. Arsenic and selenium were inserted in two different tubes (A and B) and were then heat-treated separately using a mini-tube furnace, which enveloped the bottom of the tube. Each elemental raw material is heated up separately under dynamic vacuum (both valves in the schematic, open) to extract any oxide vapor coming off during the thermal oxide volatilization process. The time and temperature
of such treatment varied by element. Arsenic was processed at 300 °C for 2 hours and selenium at 250 °C for 2 hours. After heat treatment, both purified elements were combined into a singular reaction tube (tube A in Figure III-2 b) without breaking the vacuum by rotating them from their downward position thanks to a rotation free junction. Both post-processed elements will be contained in a single tube (A in the scheme). Once the materials were in the same quartz tube, it was sealed and the glass was synthesized using the conventional melting process shown in Figure III-1b.

As will be discussed in more detail in the results section, surface oxide removal used in this procedure was not able to fully remove all impurities, as even after thermal treatment, some traces of residual oxide and hydride were still found in the processed chalcogenide glasses. This suggests that other purification steps or methods would still be required to remove oxides and hydrides from the glass to obtain the ultimate, intrinsic loss levels reported in Table II-2 [3]. As the goal of this thesis was to evaluate the role of purification on mechanical properties of arsenic triselenide glass and fibers and not development of an ultra-pure processing technology, the present levels of impurities were considered sufficient for the study.

1.1.2.2 Oxide removal

In this study, in addition to the surface oxide route discussed above, alternative methods were examined to remove additional oxide, water, and hydrides. To achieve these goals, distillation was performed using AlCl₃ as a getter. The material was batched with the raw unpurified elements in a silica ampoule. The amount of getter added was 0.24 wt.% The materials were brought up to 250 °C under dynamic vacuum to allow the selenium to melt and start the reaction with the chlorine coming
from the getter to generate HCl, which then was vacuumed out from the reacting batch as shown on Figure III-3.

The materials were then inserted in a bend tube to perform glass distillation on a three-zone furnace as shown on Figure III-4.
In this experiment the glass is placed between the two hot ends of the furnace at 750 °C. The cold ends are divided in two-zones so that the gradient of temperature forces the glass to redeposit in the bottom of the tube.

The overall objective of this method is to remove both oxides and hydride from the glass matrix via chemical reaction. The expected chemical reactions between the getter and the impurities are described in equation (8) and (9) (with M being the glass matrix).

\[
2\text{Al}^{3+} + \text{As}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2 \text{As-M} \quad (8)
\]

\[
\text{Cl}^- + \text{H-Se} \rightarrow \text{HCl} + \text{Se-M} \quad (9)
\]

These chemical reactions present the advantage of generating two new species that can be individually removed from the glass. The alumina (\(\text{Al}_2\text{O}_3\)) formed from the reaction between \(\text{Al}^{3+}\) and the oxides exhibits a high melting point of 2015 °C [44]. Therefore a distillation process under the melting point can remove the alumina from the glass network. Moreover HCl is known to be volatile above room temperature; hence, it can be removed via a dynamic vacuum extraction.

1.1.2.3 Hydrides removal

A chemical technique was designed to specifically target the removal of the hydride remaining in the distillate glass. \(\text{AlCl}_3\) was dissolved inside a covered beaker by a hydrochloridric acid solution. The glass was either crushed into a fine powder or kept in the polished disk and added to the solution. Experiments were made with and without and the \(\text{AlCl}_3\) in the solution since chlorine ions are also present in the raw hydrochloridric acid solution. The setup is presented Figure III-5.
The solution was then heated up and stirred overnight under a fume hood. The powder was then dried out, and was then batched and melted using the conventional route of making glass.

Table III-1 shows the denomination that will be used to describe the level of purity in the glass sample.

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>Purification level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>Unpurified</td>
</tr>
<tr>
<td>Oxide volatilization</td>
<td>After surface oxide volatilization via thermal treatment</td>
</tr>
<tr>
<td>AlCl$_3$ in the melt</td>
<td>Glass processed with the getter remaining in the matrix</td>
</tr>
<tr>
<td>After H distillation</td>
<td>Glass with the getter in the melt after the dynamic vacuum step</td>
</tr>
<tr>
<td>After glass distillation</td>
<td>Sample after the full process of the glass distillation</td>
</tr>
<tr>
<td>Hydride removal</td>
<td>Sample after the HCl solution treatment</td>
</tr>
</tbody>
</table>
1.1.3 Preform preparation

Preforms for this studied are defined as rods of chalcogenide glass (purified or reference compositions) that were subsequently drawn into fibers using the fiber draw facility within AMRL. Rod preforms were prepared using the same method as discussed above, keeping the batch size constant at 35 g. A particular attention was focused on the quench of the glass. It was slowly brought down to quenching temperature; the furnace was shaken in order to minimize the opportunity for bubble formation. Trapped bubbles in the rod preform could be translated into drawn fiber, so the objective was to minimize the presence of such physical defect formation. The purification techniques discussed in section 1.1.2 were applied to the rod preforms for comparison with the reference preform. The temperature profile used is shown in Fig. III-1b.

1.2 Fiber drawing

In this section, the technique used to draw As$_2$Se$_3$ fiber in the fiber draw facilities located at COMSET/AMRL is presented.

1.2.1 Unclad arsenic selenide fibers

Arsenic selenide fibers were prepared using the draw tower in AMRL shown in Figure III-6. Fibers were drawn from 35-40 g rod preforms, which did not have any secondary glass cladding layer. While ultimate (absolute) strength data on drawn fiber would require the use of an overcladding layer (glass or polymer) to minimize the formation/presence of handling-induced flaws that could compromise surface quality, the objective of the current study was to evaluate qualitative variations, rather than absolute values. As strength measurements were not performed and only fiber
hardness, tensile stress and bending stress measurements were used to assess mechanical properties of the drawn fibers, the direct access to the as-drawn glass surface was of interest. It would allow rapid measurement of post-drawn fiber (immediately after drawing) without having to strip a polymer-overclad layer from the glass surface [43].

The diameter of the drawn preform, determined by the inner diameter of the silica tube used in the glass making process, always remained 10 mm. The length of the preform was between 8 and 11 cm.

![Figure III-6 Optical fiber draw tower at AMRL](image)

The preform is clamped at its upper part and inserted in the drawing chamber. The sample was then brought down to the single heating zone furnace. The drawing tower is composed of a controlled atmosphere furnace (filled with helium gas), to prevent the hot preform to react with oxygen and reduce the resulting quality of the fibers. A CCD camera was present to monitor the fiber diameter as it was drawn. For safety matter, a (vented) dry nitrogen flow was passed over the preform to prevent release from any potentially hazardous vapors coming off the preform surface during the drawing.
The furnace was first preheated close to the $T_g$ of the glass at 200 °C with a rate of 7 °C/min and was then set at the fiber drawing temperature region of 300 °C, as seen on Figure III-7 [9]. The ramp rate was 10 °C/min to avoid nucleation and/or crystallization of the sample during the temperature increase. From the viscosity curve, the first drop was supposed to come off around 320 °C and drawn at 325 °C. After a few tries, the drop was received when the temperature was changed to 335 °C. Fibers of different diameter size were collected from changing the feed. The diameter of the arsenic selenide fibers was initially set for 250 µm and then brought down to 200 and 150 µm by changing the feed. Fibers of 100 µm diameter were obtained when the temperature was raised to 350 °C.

![Figure III-7 Viscosity curve for As$_x$Se$_{100-x}$ glass family with As$_2$Se$_3$ at the rightmost [taken from reference 9]](image)

Unpurified as well as purified fibers were drawn using the same setup. Approximately 50-60 meters of fibers were collected for every sample. Figure III-8 shows pictures of the first drop of the preform along with a picture of a 250 µm fiber.
As seen on the picture above, the surface of the drawn preform remained shiny, with a glassy aspect. A special care was taken in storing the fibers since studies have shown that aging induced change in the fibers properties. All fibers were stored in ambient air (laboratory) at room temperature (around 21 °C), attached vertically on a cardboard.

2.0 Property measurements

2.1 Bulk properties

In this section, the techniques used to determine the physical, thermal, mechanical, structural, for bulk glass are presented.
2.1.1 Physical property: density

Density is defined as the mass of a substance per unit of volume. The units of density are conventionally g/cm\(^3\). The density of bulk glass materials was determined by the Archimedes’ method using a liquid of known density as a function of temperature. A representation of the apparatus is shown Figure III-10. The measurements were made on polished samples. The measurements were performed inside a glove box to improve the accuracy and repeatability of the result. The accuracy was 0.05 g/cm\(^3\).

A diethyl phthalate solution was used for these experiments. The bulk glass was first weighed in air and then once submerged in the liquid. The density of the glass can then be calculated from these two values:

\[
P_{\text{liq}} = P_{\text{air}} + P_{\text{Archimedes}}
\]

With:
\( \tilde{P}_{\text{liq}} \) : weight of the bulk glass submerged in diethyl phthalate

\( \tilde{P}_{\text{air}} \) : weight of the bulk glass in air

\( F_{\text{Archimedes}} \) : Archimedes’ forces

The previous equation can then be written:

\[
B \times g = A \times g - V \times \rho_0 \times g \quad \text{with} \quad V = \frac{A}{\rho_{\text{sample}}} \quad (11)
\]

And therefore,

\[
\rho_{\text{Sample}} = \rho_0 \frac{A}{A-B} \quad (12)
\]

With:

- \( \rho_{\text{Sample}} \) : density of the glass bulk sample (in g/cm\(^3\))
- \( \rho_0 \) : density of the diethyl phthalate liquid at a given temperature (in g/cm\(^3\))
- \( A \) : weight in the sample in air (in g)
- \( B \) : weight of the sample submerged in diethyl phthalate (in g)

2.1.2 Thermal properties

Differential scanning calorimeter (DSC) experiments were performed on the prepared sample. In a DSC experiment, the calorimeter records the difference in temperature between the sample and the reference. The apparatus measures the amount of heat required to keep the sample and reference at the same temperature throughout the experiment. This supplied energy difference is recorded as a function of temperature. Therefore, DSC measures the change in heat flow with temperature and is a convenient way to identify thermal transitions in the material. In glassy
materials, it is possible to determine the glass temperature transition \((T_g)\), the crystallization temperature \((T_x)\) and the melting temperature \((T_m)\) from a DSC measurement. In this study, the thermal properties of the glasses were determined using a DSC 2920 of TA instruments. The sample and reference were hermetically sealed in alumina pan. The weight of the sample was around 30 mg (+/- 5 mg), and the pan used as the reference was empty. The heating rate was 10 K/min to peak at 500 °C. The glass transition temperature was determined at the inflection point of the endotherm, the first derivative of the DSC profile. The crystallization temperature was taken at maximum of the endothermic peak of the crystallization. The accuracy of these measurement was estimated to be +/- 2 °C. The stability of the glass against crystallization is determined by the difference between the glass transition and the crystallization temperature. If \(T_x - T_g > 100 \, ^\circ C\) the glass is stable, if not it is considered unstable. This parameter is important in regard to fiber drawing.

2.1.3 Structural properties

2.1.3.1 X-ray diffraction

X-ray diffraction (XRD) is mostly used to determine the structure of crystalline materials. Their crystallographic properties and the chemical composition infer on the resulting XRD spectrum. In glass science XRD is utilized to check if crystals are present in the glass matrix after annealing.

An X-Ray beam is an electromagnetic radiation with wavelength of the same order of magnitude as the bond distance in solids (5-25 nm). Therefore, an X-ray beam will be scattered by a crystal when the beam hits the crystal. XRD relies on the
diffraction of X-Ray beam on a set of parallel planes with a d-spacing as shown below [35]:

An impinging X-ray interacts with the electron cloud of atoms in the crystalline structure. In specific direction, an important intensity can be observed due to constructive interference of the different waves. As shown in the figure above, a maximum refracted intensity occurs when the diffracted wave is in phase with the incident wave. Constructive interference will be observed for X-Rays that are reflected at a particular angle from the lattice. Bragg’s law gives the angles for constructive and destructive interference from scattering a crystal lattice [36]:

\[ n\lambda = 2d_{hkl} \sin(\theta) \]  

Where \( \lambda \) is the incident wavelength of the X-Ray beam, \( d_{hkl} \) is the distance between two atomic planes of the crystal lattice; \( n \) is an integer and \( \theta \) the incident
angle of the X-Ray beam. Bragg’s law implies that the unit cell size infer on the angle of maximum intensity of the diffracted beam.

XRD patterns are displayed in intensity (arbitrary units) as a function of $2\theta$ (in degrees). The XRD pattern of a glass material shows major difference with the one of a crystal sample as can be seen in the following Figures III-11,12 [38] [36].

![Figure III-11 Typical XRD pattern of silica glass](Taken from reference 38)

![Figure III-12 XRD of crystalline nanotubes of selenium](Taken from reference 36)

As seen above XRD patterns of glass do not exhibit sharp peaks at various and specific $2\theta$ values but only one broad peak centered at a unique $2\theta$ value.

In this study, XRD patterns were collected using a Shimadzu XD-3A instrument with a Cu K$_{\alpha}$ X-ray source at 1.5418 Å. The samples were scanned from $2\theta = 5$ to $80^\circ$ with a step size of 0.02°. Samples were optically polished and mounted on an aluminum sample holder for measurement. The thickness of the sample was adjusted to fit the system requirement (~2 mm).
2.1.3.2 Energy dispersive X-Ray spectroscopy

Energy dispersive spectroscopy (EDS) or electron dispersive X-ray is a technique used to investigate the elemental composition and chemical characterization of a sample. This instrument is usually coupled with a scanning electron microscope (SEM) that can also be used to generate high magnification pictures. SEM picture are generated via an electron beam. This electron beam is created by a cathode and is then focused by magnetic lenses.

Energy dispersive X-Ray spectroscopy can be used to obtain quantitative elemental analysis about a very specific location within the area of interest of a sample. EDX can provide rapid qualitative or quantitative analysis of the elemental composition within a depth of 2 µm. Figure III-13 shows a picture of the inside of the SEM chamber used.

![Figure III-13 Picture of the inside of the SEM sample chamber](image)

In an SEM experiment, an electron beam is directed towards the surface of a sample. When the electrons interact with the sample, different phenomena occur. The image is produced from the detection of a variety of signals. The Figure III-14
shows the different interactions between the electron and the sample in a SEM experiment.

![Schematic of an electron microscope and electron interactions with materials](image)

The information is coming from three different sources during a SEM scan. The secondary electrons, the backscattered electrons and the X-Ray generated are the signals combined to generate the final image.

The secondary electrons are coming from the surface atoms of the sample. The detection of these electrons produces a good quality image of the surface. The sample morphology is responsible for the contrast of the resulting image. The small diameter of the electron beam induces a high-resolution image.

Backscattered electrons are high-energy electrons coming from the beams that are reflected back by interaction with the material. Heavy elements (high atomic number) backscatter electrons more easily than the lighter one (lower atomic number) which creates a contrast in the resulting picture. Lighter elements will appear brighter in the image. Backscattered electrons are used to detect variation of composition between different areas of the sample.
A beam electron can interact with an inner shell electron of the material. The energy of the incoming electron ejects the electron generating a hole. The ejected electron is called an Auger electron. This hole is then filled by a higher energy valence electron. This operation is paired with the emission of a X-Ray. The emitted X-Ray energy is characteristic of the element atomic structure. In the following figure, a Bohr representation an atom is shown Figure III-15.

![Bohr representation of an atomic structure](image)

Figure III-15 Bohr representation of an atomic structure

In an EDX experiment, all electrons are collected at the same moment. An EDX spectrum displays the electronic counts versus X-Ray energy. Therefore, this technique provides a quantitative and qualitative analysis. The minimum detection limit is usually 0.1 wt% but it can be higher depending on the elements. Very light elements with few electrons such as hydrogen, helium and lithium cannot be detected using this method. Samples have to be polished since rough samples yield less accuracy because the X-Rays are then generated in all directions.
Experiments were carried out using a SEM/EDS SU 6600 on polished samples. The accuracy of the measurement was estimated to be around one atomic percent. A magnification of a 1000 was used and the energy of the incoming electron was 20 keV. Copper was used as a standard to set the EDX up.

2.1.3.3 Raman spectroscopy

Raman spectroscopy is a technique used for structural analysis of condensed matter [36]. This technique allows the study of vibrational, rotational and other low frequency modes in a material. Raman spectroscopy is a non-destructive method where the incident monochromatic light is scattered by an optical lattice vibration. The laser light is interacting with molecular vibrational mode and phonons resulting in a change in energy in the laser photons. This shift in energy provides information on the vibrational modes of the material. This shift in energy is produced due to the Raman effect occurring when a laser interacts with the electron cloud and the bonds of a molecule. The incident photons excite the molecule from the ground state to a virtual energy state. When a molecule is excited, it can return to its ground state energy by emitting a photon of the same energy ($h\nu_0$) as the incident light. This phenomenon is called Rayleigh scattering and these photons do not concern Raman spectroscopy. Or the relaxation of the molecule can induce the production of a new photon of different (rotational and/or vibrational) energy. The mismatch in energy between the original and excited state creates a shift in the photon frequency corresponding to the Raman scattering.

If the new photon exhibits a higher energy $h(\nu_1 - \nu_0)$ than the ground state then the emitted photon will be shifted to a lower energy. This shift is identified as a Stokes
shift. If the new photon exhibits a lower energy $h(\nu_0+\nu_1)$ than the ground state then the emitted photon will be shifted to a higher energy. This shift is identified as an anti-Stokes shift [35].

![Schematic representation of a Raman spectrometer](image)

Figure III-16 Schematic representation of a Raman spectrometer
[Taken from reference 39]

Above is the representation of a Raman spectrometer [39]. The emission and scattering from the sample are collected from the sample with a lens and focused into a monochromator. Raman spectroscopy can be used on gas, liquid and solid sample.

A Sentarra micro Raman system from Bruker Optik was used to realize the Raman spectra measurements using a 785 nm excitation with a 1mW power beam. The laser was focused on a polished and clean surface with a microscope objective. A backscattering geometry was used to collect the Raman signal, which was then analyzed via a CDD detector.
2.1.4. Optical properties

2.1.4.1 Fourier transform Infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a straightforward method to detect the presence of impurities and the identification of functional groups in a chalcogenide glass. The absorption of specific IR radiation by a molecule results in vibrational or rotational excitation of the functional groups. A spectrum displaying the absorbed frequencies can be observed. Each spectrum is specific to a molecule, which makes this technique ideal for the detection of impurities. Moreover, the radiation absorbed is proportional to the concentration of the corresponding compound. Since the main impurities in chalcogenide glasses are water, hydrogen and oxygen containing species, the experiment is usually run under a nitrogen atmosphere to avoid the contribution from the environment. A 25 minutes purge was realized before analyzing every sample. Sample prepared for FTIR were 2 mm thick disks (+/-1 mm) and were optically polished. The quality of the polishing was verified using a white light interferometer.

2.1.4.2 Refractive index

In optics, the refractive index “n” is a measure of how light propagates through a substance. Different methods are used to measure the index of refraction of a material depending on the shape of the material or their density variation. The refractive index of a glass sample is of great interest for applications such as optical fibers for use in the IR region

The technique of ellipsometry was designed by Paul Drude in 1887. It was used to measure the dielectric properties of materials such as semiconductors or metals.
Ellipsometry is a very sensitive technique that can be used to measure optical properties from layers thinner than the wavelength of interest. This method can probe the complex refractive index or dielectric function tensor. Figure III-18 describes the set up of a typical ellipsometer.

![Schematic representation of the ellipsometer set up](image)

The instrument relies on the fact that the reflection at a dielectric interface depends on the polarization of the light while the transmission of light through transparent layer changes the phase of the incoming wave depending on the refractive index of the material.

As shown in the Figure III-17, an incident light beam is polarized with finite component $E_p$ and $E_s$ in the parallel and perpendicular direction to the incident plane of the light. The reflected beam will be attenuated due to interaction between the polarized beam and the material. Moreover, the phase will also be shifted according the Fresnel equations:

$$\frac{R_s}{E_s} = -\frac{\sin(i-r)}{\sin(i+r)} \quad \& \quad \frac{R_p}{E_p} = -\frac{\tan(i-r)}{\tan(i+r)}$$

(14)
The ratio between the parallel and the perpendicular component can be obtained by combining the 2 previous equations:

\[ \frac{R_p}{R_s} = -\frac{\cos(i+r)}{\cos(i-r)} \]  

(15)

where \( i \) is the angle of incidence, \( r \) is the angle of refraction, \( R_s \) is the reflected perpendicular component, \( R_p \) is the reflected parallel component, \( E_s \) is the incident perpendicular component and \( E_p \) is the incident parallel component.

The more common way the general equation of ellipsometry is found is the following:

\[ \rho = \frac{R_p}{R_s} = \tan(\psi)e^{i\Delta} \]  

(16)

where \( \tan(\psi) \) is the amplitude ratio upon reflection and \( \Delta \) is the face shift.

The analyzer can be used to measure the ellipse of polarization of the reflected light. The dielectric function can be extrapolated from this measurement.

The instrument used in this study, a M44TM spectroscopic ellipsometer (from J.A. Woolam Co. Inc.), is more adapted for gross refractive index measurement. It incorporates a variable angle stage allowing adjustment of the incident angle. The instrument operates on a rotating polarizer principle, in which the polarization of incoming light is varied, and reflected intensity is recorded with a grating coupled CCD over a wavelength range of 600 to 1100 nm. Ellipsometric data was recorded at a 75-degree angle of incidence on optically polished disk of approximately 2 mm in thickness. The precision on the measurement of the refractive index according to the manufacturer of the M44TM is estimated to ±0.02. The precision on the measure is too low for optical application.
2.1.5 Mechanical properties

2.1.5.1 Vickers microhardness

Hardness is a measure of the resistance of a material to permanent plastic deformation usually by penetration [42]. There are multiple methods to measure hardness such as Brinell method, Knoop method, Rockwell method, and Vickers method. The usual method to determine hardness is to measure the depth or area of an indentation left by an indenter of a specific shape when a specific force is applied for a specific time [17]. Microhardness (Knoop and Vickers methods) usually refers to static indentation made with low loads (less than 1 kgf). The surface tested requires an optical polishing. The smaller the load used the higher the surface quality required. In our case, a Shimadzu DUH-211S microhardness tester was available. The Vickers method uses a diamond tip with a square base and an angle of 136 degrees between opposite triangular faces as shown in Figure III-18 below.

![Schematic of the geometry of Vickers indenter](Taken from reference 40)
Vickers test presents the advantage of being less sensitive to the surface quality than Knoop method and the indenter can penetrate twice as deep as Knoop method.

Loads of 50, 100, 150, 200 and 250 mN were used with a speed of 1.0 mN/sec and the force was held 20 seconds to determine the load-free indentation region. The values obtained are the average of 5 tests. The diagonal length of the indentation was measured after the test was done using the apparatus and the microhardness value was subsequently calculated. Errors for microhardness (H\textsubscript{v}) were around +/−2%. To minimize the error on the study, 10 to 15 measurements were performed all over the surface of the optically polished disk. The measurements were done on the flat part of the disk, corresponding to the inside of the material (not the outside surface). Moreover, the measurements were made from two different glasses synthesized using the exact same purification method.

2.1.6 Homogeneity assessment of glass preform

Preforms were synthesized using the same purification technique as the 10 g batches described in section 1.1.1 of chapter III. The 35 to 40 g preform were sliced into 2 mm (± 0.5 mm) thick samples, as seen on Figure III-19 to detect and quantify the effect of the batch size on the glass properties and homogeneity.
All properties were measured on slices taken from the bottom to top of the as-melted ingot, with a minimum of five slices used to evaluate the homogeneity of the various glass properties of interest within the melt.

2.2 Fiber properties

In this section, the techniques used to determine the physical, thermal, mechanical, structural, for As$_2$Se$_3$ fibers are presented.

2.2.1 Optical properties

2.2.1.1 Fourier Transform Infrared spectroscopy

The optical loss of the fiber prepared will be monitored using the cutback technique. Determining the fiber attenuation coefficient required transmitting light of known wavelength through a fiber and measuring the changes over distances. The cutback
method, involves coupling the fiber to the laser source and measuring the output power at the far end of the fiber as shown in Figure III-20.

After cutting the fiber, the new output power is then measured and the optical loss attenuation coefficient can be obtained from:

\[
\text{Attenuation coefficient (dB/km)} = \frac{\text{Power (end)} - \text{Power (source) (dB)}}{\text{length of fiber (km)}} \quad (17)
\]

The attenuation coefficient is usually expressed in dB/km or dB/m. Two different laser sources were available at Clemson University: 1.32 and 1.523 \( \mu \text{m} \). The measurements were done on approximately 50 cm long fibers.

There are multiple sources of errors for the fiber optical loss measurement. Both ends of the fiber have to be perfectly squared to reduce scattering of the light source. Moreover external stress or change in stress induce on the fiber during the measurement can create additional loss. In this study, the fibers were taped down to prevent any movement during the test.
2.2.1.2 Refractive index

In optics, the refractive index “n” is a measure of how light propagates through a substance. Different methods are used to measure the index of a refraction of a material depending on the shape of the material or their variations in phase. The refractive index of a fiber sample is of great interest for applications such as optical fibers for use in the IR region. The same technique (ellipsometry) will be used to determine the fibers refractive indices.

2.2.1.3 Raman spectroscopy

Raman spectroscopy was performed on both the external surface of the fiber and its cross section to identify change in bond energy induced by the drawing. A scan over the cross-section was done to identify changes in the structure. Moreover, the effect of the diameter size of the fiber on the bond energy was studied.

2.2.2 Mechanical properties

2.2.2.1 Vickers microhardness measurement

Hardness measurement using the Vickers indentation method was done using the Shimadzu DUH-211S microhardness tester, as discussed in section 2.1.5.1 in this chapter. Measurements were done all along the surface of the bare fiber, with the first measurements made in a clearly flaw-free region (as seen through the microscope on the indenter) near the center of the fiber diameter. All different diameter sizes of fibers were tested. As noted in the earlier part of this chapter, rather than subjecting coated fibers to stripping prior to hardness testing, bare fibers were drawn and immediately measured in areas that were visibly free from flaws, in order
to avoid compromising the hardness measurement. Subsequent measurements as a function of aging time in ambient air (laboratory, 21 °C) environment were made to evaluate if any aging-related change in hardness could be observed due to sub-$T_g$ relaxation of the as-drawn fiber structure. Such changes had been previously observed in chalcogenide glasses [17].

2.2.2.2 Bending test

A two-point bending tester, shown in Figure III-21, has been used in our group to investigate the prepared fibers. This apparatus was originally a 10 cm-long drill press vise that consists of 2 parallel plates. One of the plates was fixed to the base; the other is connected to a translational stage. Small grooves (see right picture of Figure III-21) were present between the plate and the base so that the fiber could be held properly.
The translational plate was controlled by the vice. A precise control of the distance between the two plates at failure was possible when the translation speed was slow. The precision of the measure was about 0.1 mm. Figure III-22 shows a schematic representation of the bend tester.

![Figure III-22 Schematic representation of the two-point bend tester](image)

The translational force applied by the faceplate to the fiber eventually provokes the failure of the fiber. At fracture the stress of the fiber can be described by:

\[
\sigma = 1.198 \frac{E}{D-d} \frac{2r}{D-d} \quad (18)
\]

Where:

- \( r \) (in m) is the actual radius of the fiber
- \( d \) (in m) is the overall diameter of the fiber including coating (generally \(2r \neq d\))
- \( D \) (in m) is the distance between the 2 faceplates at fracture
$E$ (in Pa) is the tensile stress of the fiber. A very good control on the translation of the stage was possible. The error on the translation and the final $D$ value was estimated to be less than 0.2 mm.

2.2.2.3 Tensile tests

Tensile measurement is a fundamental test in fiber science. In this experiment, a sample is subjected to an uniaxial tension until failure. Various properties can be directly measured from the tensile test from ultimate tensile (maximum stress before necking) test to the maximum elongation. Different properties can be extrapolated from a tensile test: Young’s modulus ($E$), Poisson’s ratio or yield strength. In this study we will focus on the determination of the Young’s modulus of the fiber as a function of the purity and the fiber diameter. The Young’s modulus corresponds to the ratio of the stress (in Pa) to strain (dimensionless). This modulus can be determined from the linear portion of the stress-strain curve using the following equation [31]:

$$E = \frac{\text{stress}}{\text{strain}} = \frac{\sigma}{\varepsilon} = \frac{FL_0}{\Delta L A_0} \quad (19)$$

where:

- $\sigma$ is the stain (in Pa)
- $\varepsilon$ is the strain (dimensionless)
- $F$ is the force applied to the fiber under tension (in N)
- $L_0$ is the length of the object before the tension is applied (in m)
- $A_0$ is the area of the cross section of the fiber before the force is applied (m$^2$)
- $\Delta L$ is the change in the length of the fiber due to the experiment (in m)
Figure III-23 shows a picture of the setup with a clamped 250 $\mu$m diameter $\text{As}_2\text{Se}_3$ fiber.

![Figure III-23 Pictures of a 250 $\mu$m diameter $\text{As}_2\text{Se}_3$ fiber clamped a) before the tensile test b) after the experiment.]

The fibers were clamped to maintain the fiber in a vertical position as seen on the picture above. The tension stress was then applied to the fiber. The fiber being particularly brittle, a particular care had to be taken on the clamping part to avoid breaking the fiber before starting the experiment. Moreover, the measurements were only accounted when the breaking of the fiber occurred in the middle of the fiber as seen on Figure III-23 b.

Tensile measurements were performed in within the MSE facilities at Clemson University, with the help of Jae Lowe. The instrument used was an Instom model 1125 tester. Expected sources of error in this measurement include the positioning
of the fiber on both clamps, the length of the fiber tested and fiber slipping within the clamps during the test. A particular attention was put on the fiber the test and only fiber were the breaking point was right in between the two clamps were taken into account. Under these conditions, no slipping was detected (looking at the traces left on the paper holding the fiber).

2.2.3 Thermal properties

Thermal properties of all fibers were investigated using the differential scanning calorimeter (see section 2.1.2). Small portions of the fiber were crushed into a fine powder to perform the analysis, where all test conditions (heating rate, glass mass) were kept consistent. Glass transition temperature of fibers specimens was compared to that of the parent bulk glass.

2.2.4 Physical properties: Density

Various techniques were investigated to measure the density of our fiber. The common Archimede’s method did not yield proper results [17]. Gas pycnometer measurements were performed but the mass of our sample was too small to obtain reliable data. Values of density were determined by calculating the volume of approximately 50 cm of fiber samples. Knowing the diameter of the fiber, the volume was determined via the following equation:

\[ V = \pi (d/4)^2 \times L \]  

(20)

where \( d \) is the diameter of the fiber and \( L \) is the total length of the fiber.
The sample was then weighed and the density was simply obtained by dividing the dried mass by the volume occupied by the fiber as shown in the following equation:

\[ \rho = \frac{m}{v} \quad (21) \]

Errors in the calculated density come from errors on both the volume and the mass measurements. The measurements were performed on sample as large as possible to lower the resulting error. Typically, the tests were performed on 70 cm of fiber corresponding to a mass higher than 0.1 g. The error in the volume values are due to errors in the measurement of length of the fiber (less than 1 mm) and error in the measurement of the fiber diameter (less than 5 microns). The error on the mass measurement was estimated to be only due to the instrumental error (1 mg). However additional error in the measurement has to be taken into account from the surface quality and porosity of the fiber.

3.0 Summary

As discussed in this chapter, experiments and methods to characterized properties of glass fibers in both bulk and fiber forms have been developed. Thermal properties are characterized by Differential Scanning Calorimetry and Thermo-Mechanical Analysis; physical properties by the density measured with the Archimede’s method; the mechanical properties explained by the hardness measured by Vickers method, the fiber bending and tensile strength were determined by using bending and tensile testers; the optical properties by Fourier Transform Infrared and UV-Visible Spectroscopies and the structural properties by Raman spectroscopy, X-Ray Diffraction and by Elemental Dispersive Spectroscopy/Scanning
Electron Microscopy. Protocols to synthesize glass and purify them to produce low oxide and hydride content glass were presented.

These tools and the methods described will be used to evaluate any qualitative and quantitative changes in the bulk glass or glass fiber that results from the defined purification protocol used.

4.0 References

[34] A. Abdallah Belal, "Infrared and Raman studies on Sn_xSb_2Se_95-x chalcogenide glasses," Journal of King Saud University - Science, 21, 93-97 (2009)


[38] http://www.emeraldinsight.com/content_images/fig/1280470502003.png


[40] http://www.gordonengland.co.uk/hardness/vickers_2.gif


CHAPTER IV: RESULT AND DISCUSSION

In this chapter, results of the glass characterization are shown. Following an assessment of the resulting property homogeneity within the prepared glass preforms, a comparison of the reference bulk glass properties to that of purified bulk glass properties are described. Then, the evolution of the properties between that of the bulk material to that of glass fiber is presented. Trends on the correlation of the physical property with glass purity and with mechanical properties are reported.

1.0 Evolution of properties from bulk to preform (5 slices)

This experiment was carried out on sliced preform to determine the uniformity of the glass preform in density. Five slices were selected from bottom to top to obtain information on homogeneity and deviation of the properties throughout the sample. The homogeneity of density, mechanical properties, optical properties and structural properties, as measured on slices of glass as a function of position within the preform, were evaluated.

1.1 Density analysis

The density measurements were made using the Archimede's method. Both dry and wet measures were average from 3 values. Figure IV-1 shows the evolution of the density throughout the bulk from bottom to top. (Slice #1 being at the bottom part of the preform rod).
A density variation with position in the rod was observed. A slightly higher density value has been found for the bottom part of the preform. Moreover, the top part of the preform exhibited a smaller density than the reference (unpurified material, point on the rightmost of the curve) and the bottom part a higher one. The overall variation in the density value from bottom to top was 0.01 g/cm$^3$. The density variation could be induced by slight change in composition within the melt as it remains in the vertical position during the stabilization step for 4-6 hours (right before the quench). Selenium ($M = 78.96$ g.mol$^{-1}$) is a heavier element than the arsenic ($M = 74.92$ g.mol$^{-1}$). Therefore the stabilization step could result in a higher concentration of selenium in the bottom part of the tube due to gravity effect. Selenium (density = 5.727 g.cm$^{-3}$) also exhibits a higher density than arsenic (density = 4.28 g.cm$^{-3}$). Hence, a slightly higher concentration of selenium in the bottom part of the tube would induce an increase of the resulting density. And, the selenium concentration being lower on the top part of the preform, the density would then be lowered. The EDX experiment performed on the samples (see Table IV-1), did not show this change in composition but the error of the measurement was too high. A smaller time of stabilization could
reduce this phenomenon, but the concentration of bubble remaining in the preform could increase.

1.2 Structural homogeneity in preform.

1.2.1 Raman spectroscopy

Raman spectroscopy has been used to analyze and understand the evolution of the bonding in the glass network. Difference in bonding structure can be determined when difference in intensity or apparition of additional peaks are observed.

Figure IV-2 shows the comparison of Raman spectra obtained from two sets of five slices of two preforms and the ten grams batch reference. A total of 11 spectra are presented in this figure.

![Figure IV-2 Comparison Raman spectroscopy between two unpurified 40 g preform of As$_2$Se$_3$ and the reference](image)

No change in peak intensity and no additional peak are observed in all spectra. We can conclude that the increase in batch size does not induce change in the
bonding and in the glass matrix conformation. In the case of a change in stoichiometry in the sample throughout the sample, the generation of homopolar As-As bonds would be detected by the appearance of an additional peak (or shoulder), around 300 cm\(^{-1}\) [52], along with changes in the normalized intensity of the peaks.

1.2.2 Energy dispersive X-ray (EDX) spectroscopy.

EDX was performed on two different areas, within each slice to obtain an average composition throughout the sample. Five slices were analysed and carbon traces were removed from the calculation since its presence was due to pollution of the SEM/EDX sample chamber. Figure IV-3 shows a typical EDX spectra of one of the sample studied with the assignements for every peaks.

![EDX spectra of a slice of a As\(_2\)Se\(_3\) preform](image)

The atomic composition of the samples can be extrapolated from this experiment. Table IV-1 illustrates the EDX results obtained for an unpurified As\(_2\)Se\(_3\) preform. This preform was sliced in 20 pieces. Slice #1 was the bottom part of the rod and #20
corresponds to the top part of the glass rod. The reading from the instrument was given to the first decimal.

<table>
<thead>
<tr>
<th></th>
<th>Atomic% As</th>
<th>Atomic% Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>#19</td>
<td>39.6</td>
<td>60.4</td>
</tr>
<tr>
<td>#13</td>
<td>39.6</td>
<td>60.4</td>
</tr>
<tr>
<td>#10</td>
<td>39.6</td>
<td>60.4</td>
</tr>
<tr>
<td>#4</td>
<td>39.6</td>
<td>60.4</td>
</tr>
<tr>
<td>#2</td>
<td>39.5</td>
<td>60.5</td>
</tr>
<tr>
<td>Average</td>
<td>39.58</td>
<td>60.42</td>
</tr>
</tbody>
</table>

The calibration being performed on copper, the elements present in our glasses are much less sensitive to the signal. Therefore, the actual accuracy of these measurements on chalcogenide glasses is around 1%. The targeted atomic composition of the glass was \( \text{As}_{40}\text{Se}_{60} \). The atomic composition results are very homogeneous throughout the rod. This trend shows that the arsenic content is higher in the top part of the rod, which was expected since selenium (\( M = 78.96 \text{ g.mol}^{-1} \)) is heavier than arsenic (\( M = 74.92 \text{ g.mol}^{-1} \)). However, this observation is minimal and most likely outside of the range detectable since the composition variation is within the measurement error of the instrument (± 1%).

1.3 Vickers microhardness

Shown below on Figure IV-4 is a figure showing the microhardness homogeneity of different slices of the same preform.
The values of the unpurified preform slices are homogeneous and within the standard deviation (error bars shown) of the unpurified reference measurement. The average value for the hardness is 1.42 GPa. The values obtained for the different slices were slightly higher than the one found in literature (1.40 GPa) but all the microhardness observed for the preform slices are within the standard deviation of the reference value found for the reference prepared in our lab. Therefore the homogeneity of the mechanical properties of the preform has been demonstrated.

1.4 Fourier Transform Infrared spectroscopy

The ultimate goal of this study is to obtain lower optical loss in fiber through a purification protocol applied to the bulk glass that forms the fiber preform. All fibers were directly drawn from the 35 – 40 g preform; therefore homogeneity of the transmission in the different slices cut from the preform is important. The transmission of four slices from the same preform was examined and compared and shown in Figure IV-5. A comparison between the preform and a reference batch is
also shown in this figure. The preform spectra are drawn in plain-line; the reference is the dotted line.

The difference in baseline on these samples was due to slight differences in the quality of the polishing. From these spectra, one can infer that there is a high homogeneity in the impurity content throughout the sample. Indeed, looking at the relative height of all impurity bands present in the spectra, especially the hydroxide (2.9 µm) and water (6.3 µm) bands, one can assess that the same impurity content was present throughout the preform. Moreover, the increase of the batch from 10 to 40 grams induced changes in the impurity distribution. As seen on Figure IV-5, the hydroxide and water level were both decreased in the preform. However, the oxides content (14-16 µm) was increased in the preform slices as compared to the reference. This observation could be explained by a transfer of hydroxides and molecular water into oxides during the melting of the glass.
2.0 Characterization of bulk glass properties

In this section, the optical, mechanical, thermal, structural and physical properties of As$_2$Se$_3$ bulk glass are characterized. Unpurified and purified glasses of the same composition melt history and batch sizes are compared. The effect of the purification treatments used on each property is quantified.

2.1 Thermal properties

A typical DSC curve of an unpurified As$_2$Se$_3$ glass (our reference unpurified sample) is shown on the following Figure IV-6.

![Figure IV-6 Typical DSC curve of an As$_2$Se$_3$ glass](image)

The first endothermic event around 190 °C corresponds to the glass transition of the glass. The following exothermic event is due to crystallization of the sample at that temperature around 360 °C. The last sharp endothermic event corresponds to the melting of the glass. The small endothermic event occurring around 100 °C is due to the presence of an artifact in the instrument, this artifact was present in all the
run made using this instrument and could be due to presence of water in the sample chamber.

The thermal properties: glass transition, crystallization temperature, melting temperature and $\Delta T$ of the glasses prepared at different purification steps are listed in Table IV-2. The composition of the glass is the same: $\text{As}_2\text{Se}_3$.

Table IV-2 Effect of the purification method used, on thermal properties of $\text{As}_2\text{Se}_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (± 2°C)</th>
<th>$T_x$ (± 2°C)</th>
<th>$T_m$ (± 2°C)</th>
<th>$\Delta T = T_x - T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature [1] [14]</td>
<td>193</td>
<td>363</td>
<td>380</td>
<td>170</td>
</tr>
<tr>
<td>Unpurified</td>
<td>191</td>
<td>357</td>
<td>380</td>
<td>166</td>
</tr>
<tr>
<td>Oxide volatilization</td>
<td>192</td>
<td>357</td>
<td>381</td>
<td>165</td>
</tr>
<tr>
<td>$\text{As}_2\text{Se}_3 + \text{AlCl}_3$ in the melt</td>
<td>196</td>
<td>370</td>
<td>383</td>
<td>174</td>
</tr>
<tr>
<td>After Vacuum distillation</td>
<td>194</td>
<td>370</td>
<td>383</td>
<td>176</td>
</tr>
<tr>
<td>After glass distillation</td>
<td>188</td>
<td>366</td>
<td>383</td>
<td>178</td>
</tr>
</tbody>
</table>

The $T_g$ of the glass were measured at the onset of the peak, the crystallization ($T_x$) and melting temperature ($T_m$) were obtained from the maximum of the peak. Similar melting temperature were observed, a slight increase of the temperature was present with the getter and distillation process. The oxide volatilization did not change the thermal properties of the glass synthesized. However, significant changes were observed for both the glass transition temperature and the crystallization temperature with the addition of the impurity getter. The addition of $\text{AlCl}_3$ in the glass matrix yielded a glass system exhibiting higher $T_g$ and $T_x$. The addition of getters generated changes in the impurity content and especially with water. The removal of the water from the glass matrix and the presence of $\text{Al-(OH)}_3$
clusters generated distortion of the glass matrix that increased free volume of the glass. Hence, the \( T_g \) of the glass was higher (see Figure I-1). After the glass distillation, we can assume that all the large particles will be removed from the glass network, and hence the free volume would decrease and the resulting \( T_g \) would be lower. The addition of getter in the glass matrix increased \( T_x \) event because of the different thermal properties of the new species generated (due to the getter).

These results shows that difference thermal properties were induced by the various purification methods used.

2.2 Microhardness analysis

2.2.1 Load independent microhardness

The load independent hardness is a region where the range of load does not affect the resulting hardness of the sample [42]. As discussed above, the applied load for hardness tests must be selected to be at a level that does not result in the formation of additional cracking at the corners of the indent. A linear relationship between hardness and the applied load can be observed at lower load value. After the load free region, cracks usually occur, measurements cannot be made on indentations with such flaws since part of the loading energy is dispersed in the cracks and hence the out coming hardness is not relevant.

The study of crack-free load-independent indentation (\( H_v^0 \)) has been made for As\(_2\)Se\(_3\) using a load range from 50 to 350 mN. The following results were averaged from 10 measurements. Results can be seen on the following Figure IV-7:
Figure IV-7 shows that a maximum hardness was reached for a 100 mN load. It has been determined that the load applied affects the resulting hardness, which is called to indentation size effect (ISE) [50], [51]. Different models have been examined to explain the different behavior observed for all materials [50]. However, all materials exhibit a range of load (or indentation size) where the load applied does not induce change in the resulting microhardness measured, this range of loads being called the load-independent region. In our glass system the load-independent region appeared to be from 150 to 300 mN. Cracks started to be observed for a load higher than 330 mN as shown on Figure IV-8. The hazy, faint lines seen in the image behind the indentation are faint micro-scratches that are left after polishing. These micro-scratches are expected to impact the hardness measured. Indeed, such flaws ease the deformation of the surface under an applied load and hence are expected to slightly reduce the resulting microhardness value.
All microhardness tests reported in subsequent sections were made at a 200 mN load, in the “load-independent” region.

2.2.2 Effect of purification on hardness

Hardness measurements were performed on all samples. The resulting load-independent hardness measurements were obtained averaging ten measures in different area of the sample. The tests were performed on two glasses made from the same purification method to see the reliability of the measurements from melt to melt. The effect of impurity content on hardness can be seen on Figure IV-4. The error bars show the standard deviation on the same sample. The difference between two points of the same sample illustrates the deviation from melt to melt.

All measurement were measured in flawless region of the sample, if a flaw was detected close to where the indentation (less than 50 µm) was located, the measurement was removed from the statistical analysis. The data presented in Figure IV-9 a) shows two sets of points each corresponding to a different glass
synthesized. The differences of hardness values from points to point correspond to a melt-to-melt variation, whereas the thin error bars represent the standard deviation within a single point. Figure IV-9 b shows the variation of the OH and water content with purification methods.

As can be seen, purification method used and the resulting glass matrix chemistry has a definite impact on the hardness of the sample. The oxygen-containing species concentration is different between all samples, as can be seen in Table IV-4 and Figure IV-9 b). The lower the oxides content in the glass, the higher the microhardness is for a same load. The removal of a Se-O or As-O bond is replaced by either As-Se heteropolar bond or As-As Se-Se homopolar bond in the glass matrix, which strengthens the glass network and hence induces a higher microhardness. However, the microhardness of the material has also to be correlated with the hydrogen-containing impurities concentration. Indeed the sample with AlCl₃ in the melt has a lower oxides concentration but a significantly higher Se-H band and
its microhardness is lower than the thermally threatened sample, which has a lower hydrides concentration.

We could assume that the maximum microhardness could be achieved by reaching low oxides and hydrides content, regarding in Table IV-4 and Figures IV-8, 9.

2.3 Optical properties

2.3.1 Fourier Transform Infrared spectroscopy

The ultimate goal of this study is to reach the lower optical loss in fiber. The material was melted from high purity raw materials, but additional purification processes were investigated to remove both extrinsic and intrinsic impurities from the melt. The presence of such contaminants affects the transparency of the glass and hence the optical loss of the resulting fiber. The study of the effect of the purification techniques was first made on bulk materials to quantify their effect and relative interest towards the material studied. All glasses transmission will be compared to the reference made from a 10 g batch. Figure IV-10 shows the effect of the oxide volatilization via thermal treatment process on the glass purity.
The individual thermal treatment of arsenic and selenium significantly reduce the oxides and hydroxides concentration in the material. A reduction of 61% of the 15.5 \( \mu \text{m} \) band corresponding to the oxides was observed. A similar reduction of approximately 55% the hydroxides band at 2.84 \( \mu \text{m} \), 2.92 \( \mu \text{m} \) and water band at 6.3 \( \mu \text{m} \) has been determined.

Figure IV-11 shows the effect of a distillation process using the getter AlCl\(_3\) on the purity of the material. A series of measurement have been made at different steps of the process to quantify the effect of each technique on the transparency of the same glass sample: a measurement with AlCl\(_3\) included in the glass matrix, another after vacuum-assisted distillation, and finally one after a chemical distillation of the glass.
As shown on Figure IV-11, oxygen-containing species contents as defined by the absorption bands at 2.93 \( \mu \)m, 6.3 \( \mu \)m and 15.5 \( \mu \)m, were strongly reduced after the addition of AlCl\(_3\) in the melt. The use of such getter appeared to have significantly reduced the water content in the resulting glass. By looking at the relative heights of the absorption band corresponding to hydroxides (2.84 \( \mu \)m, 2.93 \( \mu \)m), a decrease of 90\% of the OH band had been determined.

A closer view on the critical region of the FTIR spectra allows a better analysis and understanding of what is happening in the glass system. Figure IV-12 shows the zoom in of the most important transmission region of the spectra.
Figure IV-12 illustrates the two main hydroxide bands present (2.84 & 2.93 \( \mu \text{m} \)) in the 2.5 - 4 \( \mu \text{m} \) window. A drastic decrease in hydroxide concentration is observed between the unpurified material and the material after the glass distillation process. The distilled material seemed to have no remaining hydroxide traces when looking at the relative peak height. However, traces of hydroxide were still found in the two intermediate steps of the purification.
The water absorption band (6.3 µm) along with the Se-H band (4.57 µm) are presented in the 4 – 6.5 µm window. A relatively high signature of water was found in the unpurified material (~0.3 cm⁻¹). The purification technique was very efficient on the water content reduction. Traces of water were still obvious in the sample containing the getter (AlCl₃) but after the glass distillation process all traces of water appeared to be removed. However, the purification method used showed an increased in the Se-H band. The further in the purification process, the higher the concentration of the Se-H was reported to be.

The 12 - 18 µm absorption window shows the decrease in the oxide concentration induced by the purification method. A maximum reduction of 73% for the peak at 15.50 µm was observed, but this signal increases again after the glass distillation process.

A correlation between the Se-H band (4.57 µm) and the water (6.30 µm) and hydroxide (2.84 µm and 2.93 µm) band could exist. A proposed mechanism on a reaction showing this correlation will be explained in a following section (section 4.1.1).

Table IV-3 summarizes the effect of the purification technique on the absorption coefficient of the main impurity bands present in the FTIR of As₂Se₃.
Table IV-3 Effect of the purification method on the absorption coefficient of impurity bands of As$_2$Se$_3$ glass.

<table>
<thead>
<tr>
<th>Main absorption bands (µm)</th>
<th>OH</th>
<th>OH</th>
<th>Se-H</th>
<th>H$_2$O</th>
<th>Se-O</th>
<th>As-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpurified</td>
<td>2.84</td>
<td>2.93</td>
<td>4.57</td>
<td>6.30</td>
<td>12.50</td>
<td>16.00</td>
</tr>
<tr>
<td>Thermal treatment</td>
<td>0.23</td>
<td>0.05</td>
<td>0.05</td>
<td>0.37</td>
<td>0.1</td>
<td>1.23</td>
</tr>
<tr>
<td>AlCl$_3$ in the melt</td>
<td>0.10</td>
<td>0.02</td>
<td>0.02</td>
<td>0.13</td>
<td>0.02</td>
<td>0.474</td>
</tr>
<tr>
<td>Vacuum distillation</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.465</td>
</tr>
<tr>
<td>After glass distillation</td>
<td>0.05</td>
<td>0.06</td>
<td>0.06</td>
<td>0.01</td>
<td>“0”</td>
<td>0.346</td>
</tr>
<tr>
<td>Relative height of the absorption band (cm$^{-1}$)</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.19</td>
<td>0</td>
<td>0.441</td>
</tr>
</tbody>
</table>

Table IV-3 shows that the use of getters reduces significantly the concentration of oxides and hydroxides in the glass, but unfortunately increases the concentration of Se-H containing species in the glass matrix.

2.3.2 Ultraviolet-Visible spectroscopy, bandgap calculation

Figure IV-13 shows a typical UV-Vis spectrum of an unpurified 10 g batch of As$_2$Se$_3$.
The little change in absorption coefficient observed in the curve at ~800 nm is due to a change of detector. It is possible to extrapolate the bandgap energy ($E_{\text{gap}}$) using the cutoff wavelength determined from the UV-Vis spectrum. In this case, the UV cutoff was estimated to be 841 nm.

Knowing:

\[ E_{\text{gap}} = \frac{hc}{\lambda_{\text{cutoff}}} \]  \hspace{1cm} (22)

With:

- $h$: Planck’s constant = $6.626 \times 10^{-34}$ m$^2$.kg/s
- $c$: speed of light = $3 \times 10^8$ m/s
- $\lambda_{\text{cutoff}}$: Cutoff wavelength

In this case:

\[ E_{\text{gap}} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{841 \times 10^{-9}} = 2.314 \times 10^{-19} \text{ J} \]  \hspace{1cm} (23)

And since $1eV = 1.602 \times 10^{-19} \text{ J}$:
\[ E_{\text{gap}} = \frac{2.314}{1.602} = 1.48 \text{ eV} \quad (24) \]

(This result is close to the literature value: 1.51 eV [1])

Measurements were performed on all samples with different purification treatments. Table IV-4 below shows the bandgap values as a function of the sample purity.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Bandgap Energy (eV)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpurified</td>
<td>1.48</td>
<td>± 2%</td>
</tr>
<tr>
<td>Oxide volatilization</td>
<td>1.495</td>
<td>± 2%</td>
</tr>
<tr>
<td>( \text{AlCl}_3 ) in the melt</td>
<td>1.511</td>
<td>± 2%</td>
</tr>
<tr>
<td>Dynamic vacuum</td>
<td>1.510</td>
<td>± 2%</td>
</tr>
<tr>
<td>Glass distillation</td>
<td>1.513</td>
<td>± 2%</td>
</tr>
</tbody>
</table>

A noticeable change in the bandgap energy of our materials was induced by the purity. The bandgap energy of the glass increased with purity. The highest bandgap energy recorded was the one of the sample purified via glass distillation. The bandgap energy could hence be related to the water and oxides-containing impurity content. This change in band gap energy could be explained by local polarization occurring due to the presence of these impurities (oxides, water and hydroxides). The polarization due to presence of impurities could easily produce local internal electric fields. These electric fields may then induce modification in the energy level of the band structure and hence generate modifications in the bandgap energy [45].
2.3.3 Raman spectroscopy

Raman spectroscopy was performed to determine the effect on purification methods on the final structure of the glass. The evolution of the bonding of the glass is also observed through Raman spectroscopy. All Raman spectra have been normalized to the entire intensity with the standard deviation. Figure IV-14 shows Raman spectra of glasses prepared using different purification techniques.

Two broad peaks are present at 245 cm$^{-1}$ and 454 cm$^{-1}$. The first peak contains As-Se-As and As-Se bonds in the network. The second one is a harmonic of the main band [35].

As seen on the figure all spectra are perfect matches, very slight differences in intensity can be identified when a zoom in of the main peak is done but no definite
trend can be determined from this measurements. The difference between the different spectra is within the line width of the curve.

2.4 Physical properties: density

The glass densities of the As₂Se₃ glass were examined using the Archimede’s method. Results from the density measurements are shown in Table IV-5.

Table IV-5 Effect of purification on density of As₂Se₃ glass

<table>
<thead>
<tr>
<th>Purification Method</th>
<th>Density</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpurified</td>
<td>4.6179 ± 2%</td>
<td>0.005</td>
</tr>
<tr>
<td>Oxide volatilization</td>
<td>4.6147 ± 2%</td>
<td>0.004</td>
</tr>
<tr>
<td>AlCl₃ in the melt</td>
<td>4.6183 ± 2%</td>
<td>0.001</td>
</tr>
<tr>
<td>After dynamic vacuum</td>
<td>4.6175 ± 2%</td>
<td>0.006</td>
</tr>
<tr>
<td>After glass distillation</td>
<td>4.6196 ± 2%</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The density in all glasses prepared was in the range of the literature value [7]. A decrease of the density is observed after the oxide volatilization process. One could expect the free volume of the glass network to increase after the removal of a part of the molecular water from the glass network and hence the density to increase but the opposite phenomenon was observed. Although the error and the standard deviation have to be taken into account, this observation was following the trend from the decrease in Tᵥ for the same purification method used. The addition of the impurity getter in the glass sample increased the resulting density of the system. In the
sample with the AlCl$_3$ in the melt and the sample after the vacuum the water, hydroxides and oxides contents are very low but AlO$_3$ and Al(OH)$_3$ are remaining in the glass (even though they don’t absorb in the FTIR spectra). The presence of these heavy compounds had the effect of increasing the density of the material. The highest density obtained was for the sample after the glass distillation. It can be explained by the removal of the oxides, hydrides and hydroxides, which are partially replaced by smaller hydrides impurities, as seen in Table IV-3. Therefore the distilled sample exhibits a more compact structure and has the highest density.

3.0 Characterization of unclad fibers

In this section, the mechanical, thermal, physical and optical properties of the fibers are presented. Effect of both the fiber diameter (from 150 to 250 µm) and the purification method used to prepare the fiber are investigated.

3.1 Physical properties, density analysis

The density of all fibers prepared was evaluated using the Archimede’s method (see section 2.1.1). The influence of the fiber diameter on the resulting density of the fiber as well as the effect of purity is shown on Table IV-6.

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Purification method</th>
<th>Unpurified</th>
<th>Oxide</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µm</td>
<td></td>
<td>N/A</td>
<td>5.786</td>
<td>N/A</td>
</tr>
<tr>
<td>150 µm</td>
<td></td>
<td>4.663</td>
<td>4.816</td>
<td>N/A</td>
</tr>
<tr>
<td>200 µm</td>
<td></td>
<td>4.542</td>
<td>4.714</td>
<td>N/A</td>
</tr>
<tr>
<td>250 µm</td>
<td></td>
<td>4.360</td>
<td>4.587</td>
<td>N/A</td>
</tr>
</tbody>
</table>
The fiber drawing parameters generates changes in the density of the material. As seen in Table IV-6, variations of the fiber density are induced by the diameter of the fiber drawn. It can be explained by the difference of thermal history and cooling rate of the fiber after the draw. A smaller diameter fiber core would cool faster than the core of a bigger diameter; therefore its structure would be closer to the one of the corresponding crystal. Hence, the density of smaller diameter fibers is higher than the bigger diameter one.

The density of the fiber shows an increase with purity, as observed previously with the bulk glass. This effect is due to the removal of impurities that strengthen the glass network connectivity and yield a more compact structure, therefore, an increase in density.

3.2 Thermal properties

The thermal properties of the fibers were investigated using DSC. The presented resulted are an average of 2 measurements. The effects of the diameter size of the fiber as well as the effect of the purity of the material on the thermal properties are shown in Table IV-7. $T_g$ is the glass transition temperature of the glass, $T_x$ is the crystallization temperature and $T_m$ is the melting temperature. The error bar on all the temperatures shown is ±2 °C.
Table IV-7 Effect of diameter and purification of the glass on the thermal properties of As$_2$Se$_3$ fibers

<table>
<thead>
<tr>
<th>Purification method</th>
<th>Unpurified</th>
<th>Oxide volatilization</th>
<th>Glass distillation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$</td>
<td>$T_x$</td>
<td>$T_m$</td>
</tr>
<tr>
<td><strong>Fiber diameter</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120 µm</td>
<td>186</td>
<td>326</td>
<td>379</td>
</tr>
<tr>
<td>170 µm</td>
<td>189</td>
<td>348</td>
<td>380</td>
</tr>
<tr>
<td>220 µm</td>
<td>190</td>
<td>357</td>
<td>380</td>
</tr>
<tr>
<td>Bulk</td>
<td>191</td>
<td>357</td>
<td>380</td>
</tr>
</tbody>
</table>

As seen on this table, a modification of the thermal properties was induced by the drawing of the fiber. Although no change in the melting temperatures were observed, the fiber drawing modified both the glass transition temperature and the onset of the crystallization event. Moreover, it was found that the purity of the fiber induced changes in the thermal properties of the fibers. The biggest change of temperature was observed for $T_x$. Additionally, the fiber diameter had also an impact of the resulting characteristic temperature of the fiber drawn. $T_x$ and $T_g$ increased with increasing fiber diameter. This observation was not expected since fiber of smaller diameter would have a higher cooling rate and hence according to Figure I-1 a higher $T_g$. It was found that As-As bound were formed during the fiber drawing process in As$_2$Se$_3$, the formation of such bonds induces changes in the glass network and therefore change in the glass properties such as density (see Table IV-6) and $T_g$. The smaller the diameter is, the higher the As-As concentration. A difference as high as 30 °C was also observed for the onset of the crystallization temperature between the smaller and the bigger diameter. Overall a slight increase of the thermal properties was observed with purity.
Table IV-7 shown that a 220 μm fiber exhibits similar thermal properties (within the error of the measurements) than bulk material.

3.3 Structural properties

3.3.1 X-ray Diffraction

No sharp peaks were observed, and a typical broad signal located around 2θ = 33°, signature of the amorphous character of the material was present. The materials could be described as X-Ray diffraction amorphous.

3.3.2 Raman spectroscopy

Raman spectroscopy acquisitions were only performed on the fiber surface, getting flat surface on the cross-section of such small fibers being too challenging.

As compare to the Raman data obtained on the bulk glass, it was observed that traces of the laser beam were remaining after the radiation using the same power settings. This phenomenon was due to the change of the magnification to obtain a good focus of the top of round shape of the fiber as compared to the flat surface of our disk samples. The energy of the laser was hence focused on a smaller area of the glass sample. The energy was higher than the bond energy of the glass bond, generating hole at the surface.

Figure IV-15 shows the diameter effects on the Raman spectra of fibers made from the same perform, which was thermally purified to remove the surface oxide of the raw elements.
As seen on Figure IV-15, slight changes were induced by the change in diameter. The bigger the fiber has its maximum around 222 cm$^{-1}$ and the smallest at 225 cm$^{-1}$.

To determine the effect of the drawing process on the bonding energy, comparison between Raman spectra of the fiber and bulk glass synthesizing via the same process (oxide volatilization via thermal treatment) is shown in Figure IV-16.
As seen on the previous figure (IV-16), a slight change in peak position is observed between the glass in the bulk form and a fiber. A shift of 3 cm\(^{-1}\) from 226 to 223 cm\(^{-1}\) in the maximum intensity of the main peak. Therefore, the drawing has the effect of modifying (lowering) the average bond energy in the As\(_2\)Se\(_3\) system. The slight change observed could be explained by the fact that the fiber drawing induces only small modifications of the bond angle or bond lengths, and change in orientation of the As\(_2\)Se\(_3\) planes of the glass network. This change could also be due to the slight increase of the As-As bond content.

Due to the small size of the fiber drawn, it was impossible to perform a Raman experiment on the core of the fiber. Difference in structure between the core and the surface of the fiber could have been determined from this quick experiment.

3.4 Mechanical properties

3.4.1 Vickers microhardness

The Vickers microhardness measurements were done on top of the surface of the fiber and compare to the 10 g batch reference. Resulting hardness were obtained from 10 individual measurements with a load of 200 mN and a hold time of 20 seconds. The resulting microhardness are reported in the next Table IV-8, and the effect of the fiber drawing on the hardness is reported.

Table IV-8 Effect of the fiber drawing on the hardness of As\(_2\)Se\(_3\) glass system

<table>
<thead>
<tr>
<th></th>
<th>Vickers Hardness (GPa)</th>
<th>Standard deviation (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 g batch</td>
<td>1.470</td>
<td>0.016</td>
</tr>
<tr>
<td>Preform (5 slices average)</td>
<td>1.465</td>
<td>0.015</td>
</tr>
<tr>
<td>Fiber (250 µm)</td>
<td>1.359</td>
<td>0.019</td>
</tr>
</tbody>
</table>
As seen on this table above, the drawing affects the hardness of the material. The resulting hardness of the fibers is lower than the one of the preform and bulk. An important decrease of \( \sim 0.12 \) GPa is observed between the bulk glass and the biggest diameter fiber. This effect could be due to a change in density in the material after the fiber drawing. The rearrangement of the layers can induce change in the free volume of the material. A material with more free volume would be less resistant to crack initiation.

Fibers of four different diameters were drawn from the same preform. This preform was purified using oxide volatilization via thermal treatment. The effect of the diameter size on the resulting hardness is shown Figure IV-17. Measurements were made on flawless region of the surface of the fiber.

![Figure IV-17 Effect of the diameter size on the Vickers microhardness of As\(_2\)Se\(_3\) fibers](image)

The fiber diameter appeared to have a notable effect on the resulting hardness of the fiber. A significant drop in the fiber hardness of approximately 7% is observed when the fiber diameter is increased from 1.465 GPa to 1.364 GPa. The value of the hardness of the 100 \( \mu \)m diameter fiber is found to be very close to the bulk value. The variation of density with diameter tracks well with the change in the density of the
material induced by the drawing condition, as seen in Table IV-6. However, looking at the cooling kinetics, this observation is unexpected since the highest density fiber is the one of smaller diameter. The cooling rate of a small diameter fiber is higher than the one of higher diameter. Therefore the free volume of the 100 µm fiber is the highest, hence, its density should be the lowest. Indeed, the core of a smaller fiber in diameter is cooling faster than the core a bigger diameter fiber. The experimental observation has also been recorded previously. It has been demonstrated that the fiber drawing was generating As-As bond in the resulting fiber structure [17]. Moreover, the higher the As-As bond concentration the higher the density obtained. It was also shown that the drawing rate has an effect on the generation of such bonds: the highest the As-As bonds content the highest the density. [17]

To complete this study, the effect of the purity on the Vickers microhardness of the fiber was investigated. A trend similar to that of the bulk is expected for the fiber as well. Comparison on fiber of 150 µm is shown Figure IV-18. The hardness values of the as-drawn fibers were all taken 18 days after the draw. The fibers were stored in air at ambient temperature in our laboratory. It was shown that strong variations of the hardness values exist up to 8 days (200 hours) after the drawing. An important increase of 15% [17] can occur when the fibers are stored in air.
As expected, the purity or impurity content of the fiber also impacts the hardness of the arsenic selenide fibers. An increase of 6%, similar to the one quantified for the bulk, was observed.

3.4.2 Tensile testing

The tensile tests were used to determine the maximum tensile stress the fiber could sustain before breaking. Moreover the Young’s modulus required to determine the maximum bending stress at failure was obtained from the tensile experiments.

The Young’s modulus corresponds to the slope of the strain-stress curve as seen on Figure IV-19. The slope of the curve was obtained from the trend line analysis of the straight region of the curve.
From this analysis, Young’s Modulus were reported to be 24800 MPa and 23641 MPa for respectively unpurified and the thermally (oxide volatilization) purified 200 µm diameter As$_2$Se$_3$ fiber. The Young’s modulus is a measure of the stiffness of the material under a uniaxial stress. The Young’s modulus is also a measure of the elasticity of the fiber. The unpurified fiber exhibits a higher Young’s modulus than the one purified via oxide volatilization. It could be explained by a difference in the orientation of the plane in the fibers. A fiber with its plane oriented along the length of the fiber would exhibit a higher elasticity, hence, a higher Young’s modulus.

The maximum tensile stress at failure was 208 MPa and 380 MPa for the unpurified and for the thermally (oxide volatilization) purified diameter As$_2$Se$_3$ fiber respectively.

3.4.3 Flexural, bending testing

Weibull distribution was used to describe the bending data. It was named after Waloodi Weibull, who developed it in detail in 1951. Weibull analysis is a method used for modeling data sets of values higher than zero. Weibull analysis can make
predictions about a product's lifetime. Weibull distribution was used in this study to give a more accurate representation of the maximum stress of bending at failure.

The Weibull equation used to yield the distribution is described as following:

\[ F(x) = 1 - e^{-\left(\frac{x}{\lambda}\right)^m} \]  \hspace{1cm} (25)

Where \( F(x) \) is the probability density function of the variable \( x \), \( x \) is the maximum bending stress at failure, \( \lambda \) is the scale parameter and \( m \) is the shape parameter or Weibull modulus. The \( m \) parameter is an indication of the evolution of the distribution failure rate. A \( m \) value lower than one indicates that the failure rate decreases (typical for a product failing during its "burn-in" period”). A \( m \) value equal to one indicates that the failure is constant. A \( m \) value greater than one indicates that the failure rate increases, which means an aging process occurs (typical of products that are wearing out). A high value for the Weibull modulus also corresponds to a homogeneous flaw distribution along the fiber [29]. The scale parameters gives information on the survivability of the distribution, it corresponds to the \( x \) value when 63.2\% of the population has already failed.

Derivation of the Weibull equation results in:

\[
F(x) = 1 - e^{-\left(\frac{x}{\lambda}\right)^m} \\
1-F(x) = e^{-\left(\frac{x}{\lambda}\right)^m} \\
\ln(1-F(x)) = -\left(\frac{x}{\lambda}\right)^m \\
\ln(1/(1-F(x))) = \left(\frac{x}{\lambda}\right)^m \\
\ln(\ln(1/(1-F(x)))) = m\ln(x/\lambda) \\
\ln(\ln(1/(1-F(x)))) = m\ln(x) - m\ln(\lambda)  \hspace{1cm} (26)
\]
Hence, plotting \( \ln(\ln(1/(1-F(x)))) \) vs \( \ln(x) \) will allow the extrapolation of both the scale and the shape parameter of the Weibull distribution.

All the data were measured on 16 days old, non-annealed as drawn fibers. After 16 days, it has been demonstrated that the aging does not affect the bending properties anymore \([49]\).

Overall 30 measurements for each fiber were performed to produce a Weibull distribution of the bending measurement. All measurements with an unusual breaking behavior were removed from the calculation.

The maximum bending stress at failure was respectively 334 MPa and 415 MPa for and for the unpurified and the thermally (oxide volatilization) purified diameter \( \text{As}_2\text{Se}_3 \) fibers respectively. The difference of impurity content in the two fibers induced difference in the glass network connectivity. The purified fiber had lower oxides and hydroxides concentration. Therefore, As-Se bonds replaced As-OH or

---

**Figure IV-20** a) Evolution of the Weibull distribution for bending stress at failure of \( \text{As}_2\text{Se}_3 \) fibers as a function of the purity. b) Weibull distribution analysis.
Se-OH bonds. Moreover bending failure starts at the surface of the fiber. Hardness is a measure of the resistance of a material to crack initiation. It was shown in this study, that the purification induced higher hardness in our material. Therefore the purified glass exhibits higher bending stress at failure.

Bending distribution of the material can be considered as a representation of the flaw population in our material. The failure of the fiber under a bending stress starts at its surface. The presence of a flaw right at the point of compression (or extension) contributes largely to the failure of the material.

Fibers of higher diameter seemed to exhibit a higher bending stress at failure than smaller fibers, even though the diameter of the fiber is included in the stress calculation.

Figure IV-20 b shows a representation of $\ln(\ln(1/(1-F(x))))$ vs $\ln(x)$. A trend line analysis gives a $y = ax + b$ type of equation where $a$ corresponds to the shape parameter $m$, and $b$ corresponds to $m\ln(\lambda)$. The scale parameter $\lambda$ can be extracted using $\lambda = e^{b/m}$.

### Table IV-9 Weibull parameters of the unclad, as-drawn fibers.

<table>
<thead>
<tr>
<th>Weibull parameters</th>
<th>Unpurified</th>
<th>Oxide volatilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$</td>
<td>5.2</td>
<td>6.1</td>
</tr>
<tr>
<td>$\lambda$ (MPa)</td>
<td>230</td>
<td>317</td>
</tr>
</tbody>
</table>

Both $m$ values of the Weibull distributions are greater than one, which demonstrates that the rate of failure increases with $x$. Moreover, an increase of 38% of the $\lambda$ parameter is observed with purification. The survivability of the material is therefore increased by 38% by the oxide volatilization purification process.
3.5 Optical loss measurement.

Unfortunately, only one measurement could have been done on a 200 µm As₂Se₃ purified via thermal treatment to promote oxides volatilization.

The input and output powers were recorded using a detector. Two different laser powers were available for near-IR application. One was powered at 1.31 µm, the second at 1.532 µm.

Following is a calculation example for the 1.31 µm laser, since the output and input powers recorded were in Watts, a conversion is required to obtain the power in dB, see next equation:

\[
Power \ (dBW) = 10 \times \log_{10}(Power \ (W)) \quad (27)
\]

The power recorded with the full-length fiber connected to the system was 119.4 µW. The power recorded with the reduced length fiber (after the cutback) was 588 µW.

\[Power_{full \ length \ fiber} \ (dBW) = 10 \times \log_{10}(0.0001194) = -39.23 \ dB\]

\[Power_{cutback \ fiber} \ (dBW) = 10 \times \log_{10}(0.000588) = -32.31 \ dB\]

Using equation III-7, length of the fiber being 0.194 m:

\[Attenuation \ coefficient \ (dB/m) = \frac{(-39.23 + 32.31)/0.60}{0.194} = 59.48 \ dB/m\]

The two values are divided by the transmission at this wavelength to take into account the Fresnel losses at both end of the fiber. Using the same calculation
process the optical loss recorded with a laser power delivery of 1.532 mW was 54.05 dB/m.

4.0 Discussion of the results

In this section, the results of all characterization technique will be discussed and the mechanism and trends will be explained. Key findings of this study are presented. The mechanism of the appearance of the Se-H band at 4.57 µm is proposed. The effect of the removal of specific impurities in the structure as well as the effect of the fiber drawing on the structure is shown. The evolutions of all properties with purity are also identified.

4.1 Trends observed in As$_2$Se$_3$ glass

4.1.1 Effect of the purity on the Vickers microhardness of the material

Figure IV-21 shows the correlation between the evolutions of the Vickers microhardness of our glass with the absorption coefficient of the main impurities present in the glass network. The absorption coefficient relates directly to the concentration of impurities.
As seen on Figure IV-21 a, the different purification methods induce changes in the resulting hardness of our material. The different purification methods increased the hardness of our glass from 1.425 GPa up to 1.473 GPa.

This observation can be correlated with the absorption coefficient of the main impurities present in the glass network. We can see that the reduction of the OH and water bands increase the hardness of our samples. The only difference between the unpurified sample and the sample purified via thermal treatment is the important reduction (approximately 50%) of the OH and molecular water concentration in the
glass system. This decrease in impurity content induces a 0.05 GPa increase in the microhardness of the system.

Similar observations can be made for the mechanical properties (hardness and bending) observed for the fibers, as seen on Figures IV-17, 19. The purified fiber via oxide volatilization has average bending stress at failure of approximately 80 MPa higher than the unpurified fiber. The same trend in hardness variation than the bulk one is observed for the fiber. An increase of the hardness (approximately 0.05 GPa) was observed when the hydroxides, oxides and hydrides concentrations were reduced.

These results can be correlated with the effect of the glass network structure induced by the reduction of the impurity concentration. Figure IV-22 shows a molecular representation of the As$_2$Se$_3$ glass network with M being the continuity of the glass matrix.

Figure IV-22 Molecular representation of As$_2$Se$_3$ glass network. a) Effect of the removal of molecular water on the glass network. b) Effect of the removal of OH on the glass network connectivity.

The removal of molecular water does not change the network connectivity of the glass but increases its density as shown Table IV-6. The reduction of the OH content generates higher network connectivity in the system, since an As-OH or Se-OH bond is replaced by an As-Se-M bond. A higher density and a higher network connectivity
induce a higher hardness in the material, therefore the observation made is relevant. Moreover, all properties are influenced by the glass network connectivity. Thermal properties of the glass are also modified when the purity of the glass is increased as seen in Table IV-3. This study showed that an increase in the $T_g$ was induced by the removal of impurities. A modification of the $T_x$ was observed but the origin of this change is due to another phenomenon described in section 2.1 of chapter IV. A modification of the bandgap energy was also induced by the change in structure; the bandgap energy tends to increase when the OH concentration decreases.

However, even though the OH and molecular water content keep decreasing in the 3 steps of the glass distillation experiment, the hardness of the material is unexpectedly decreasing. This phenomenon can be correlated with the apparition of the Se-H bond in the glass network. The effect of the creation of a Se-H bond in the glass network is shown in Figure IV-23, with M being the continuity of the glass matrix.
The creation of a Se-H bond replacing an As-Se bond in the glass has the effect of decreasing the glass network connectivity.

The combination of both effects can explain the value of hardness found for the sample prepared using glass distillation. The OH and water are in very low concentration in the material but the generation of new Se-H bonds counterbalances this effect; therefore the hardness value is between the unpurified material and the sample prepared by surface oxide volatilization.

4.1.2 Proposed Mechanism of formation of Se-H bond in the glass network.

As seen previously the use of the getter did not yield the expected level of purity. Indeed, after the glass distillation, an increased concentration of Se-H bond was reported.

This phenomenon can be explained by the fact that aluminum and chlorine ions do not dissociate in the melt to react as two distinct species but the reaction was occurring between the impurities and aluminum chloride. It is well known that aluminum chloride is present in the Al₂Cl₆ dimeric configuration at room temperature. When the temperature overcomes 500 °C, the stable conformation is then AlCl₃, as shown in Figure IV-24.
Taking this consideration in account a plausible mechanism can then be determined showing the reaction between AlCl$_3$ and the main impurities present in the As$_2$Se$_3$ glass matrix as seen in Figure IV-25. This figure is a representation of the short-range order of the glass matrix with $M$ standing for the glass matrix.

Knowing the high reactivity of aluminum chloride with water, we can assume that the very first reaction happening in the melt will happen with the molecular water traces present in the melt. The electron rich atoms of oxygen will react with the electron poor aluminum atoms (due to the high electronegativity of the chlorine...
atom). The ejected chlorine anion can then recombine with an arsenic atom of the glass matrix. The creation of such chlorine-arsenic bonds will result in the breaking of an arsenic-selenide bond and furthermore it will generate a negatively charged selenium atom. The negatively charged selenium will then recombine with the extra hydrogen attached to the oxygen. This mechanism results in the generation of AlCl$_2$OH, Se-H bond and As-Cl bonds. The following table summarizes the bond energy of the species prior to the suggested reaction and after the reaction between aluminum chloride and the glass matrix [20].

Table IV-10 Change in bond energy (at room temperature) induced by the proposed mechanism

<table>
<thead>
<tr>
<th>Bond</th>
<th>Before the reaction Bond energy (kJ.mol$^{-1}$)</th>
<th>After the reaction Bond energy (kJ.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Cl</td>
<td>511</td>
<td>511</td>
</tr>
<tr>
<td>As-Se</td>
<td>96</td>
<td>448</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>427.6</td>
<td>314.47</td>
</tr>
<tr>
<td>Total energy</td>
<td>971.6</td>
<td>Total energy 1273.47</td>
</tr>
</tbody>
</table>

Table IV-9 demonstrates that the proposed reaction mechanism for the generation of the undesired Se-H bonds yields a more stable system in terms of bond energies. This observation reinforces the validity of our hypothesis. Although the bond energy presented were found at room temperature while the reaction is occurring at 750 °C (during the melting of the material), it gives an approximate representation on the possible bond creation favored in the melt.
4.1.3 HCl post-synthesis treatment: Se-H band removal

This post synthesis purification method was experimented on the distillated glass since they exhibited the highest Se-H band and the highest overall purity. Different time and temperature were tried. The effect of the treatment on the Se-H band is shown on Figure IV-26. A drop in the overall transmission (around 25% of maximum transmission) of the glass was observed. However the shape and the other impurity bands remained the same.

![Graph showing the effect of the reaction between the glass and HCl on the Se-H band.](image)

**Figure IV-26** Effect of the reaction between the glass and HCl on the Se-H band.

After 30 minutes of treatment at moderate temperature (<100 °C), no real differences were observed from the previous sample. The temperature of the reaction was then elevated and maintained for 1h30. A change in the sample aspect was observed; the edges of the polished disk were rounded. This observation proved the temperature range was higher than the glass transition (> 200 °C) of our glass sample. At such temperatures, bond mobility is increased and the chlorine ions
diffusion is promoted. Repeatability in the experiment was obtained on all sample tested.

It has been demonstrated that ions can diffuse in chalcogenide glasses, especially silver [46]. Yet no work has been done on chlorine diffusion despite Cl\(^-\) and Ag\(^+\) have close ionic radii, 167 pm and 129 pm respectively [47]. When the temperature is high enough and hence the mobility of the glass matrix bonds enhanced, it is then possible for the highly reactive chlorine anions to enter the glass matrix and react with the hydrogen attached to the selenium. Furthermore, the bond energy of HCl is higher than the Se-H bond energy, as seen in Table IV-9.

4.2 Effect of drawing on properties

Fiber drawing has an effect on the glass structure: the bond angles and the free space of the fiber is different than the one of bulk glass. The largest modification in the structure are coming from the Van der Waals interactions between the As\(_2\)Se\(_3\) pyramidal layers since these energy interactions are weaker.
As seen in Figure IV-27, the drawing would have an effect on the chemical bonding and bond angles of As-Se bond. One would expect a fiber of a larger diameter to have a structure closer to the one of the bulk glass. Hence a fiber of bigger diameter would exhibit a microhardness closer to the one of the bulk.

However, a different observation was made, the fiber of smallest diameter exhibit the bigger microhardness. The density of the fiber has to be taken into account. Density measurements give us more insight on this observation.

5.0 Summary of material properties and the influence of purification

5.1 Bulk glass properties

The purification processes had an impact on the thermal properties of the glass. The stability to crystallization (ΔT) was increased since $T_g$ decreased and $T_x$
increased. A decrease of this stability was expected in the glass distillation process since alumina and chlorine-containing species were introduced in the glass network. Such species could have acted as nucleation sites and therefore generate glasses less stable to crystallization. The increase in the onset of the crystallization peak was explained by the fact that alumina possess a higher crystallization temperature than the glass studied. Therefore the new glass generated possessed a slightly higher $T_x$.

It was shown previously in section 1.1 that the purity (hence optical properties) of the material affects significantly the mechanical properties. The water, oxides and hydrides contents had to be reduced to a minimum to obtain the highest microhardness. The highest hardness was obtained for the sample purified via thermal treatment to induce surface oxides volatilization.

A noticeable change in the bandgap energy of our material was induced by the purity. The bandgap energy of the glass increased with purity. The highest bandgap energy recorded was the one of the sample purified via glass distillation. The bandgap energy could hence be related to the water and oxides-containing impurities. This change in bandgap energy could be explained by local polarization occurring due to the presence of these impurities (oxides, water and hydroxides). The polarization due to presence of impurities could easily produces local internal electric fields. These electric fields may then induce modification in the energy level of the band structure and hence generate modifications in the bandgap energy [45].

No changes in the bond energies were observed via Raman spectroscopy. The glass bond energies and bond angles remaining the same regardless of the purity of the glass. No trend can be assessed on the physical properties of the glass, the density. All samples showed a density within the error of the measurement.
5.2 Fiber properties

As stated previously, it was demonstrated that fiber drawing induces the generation of As-As bond in the fiber glass-network even for the stoichiometric As$_2$Se$_3$. Higher concentration of such bonds was found for smaller diameter fibers [17]. This high concentration of As-As resulted in higher density fibers. As shown in Table IV-6, the same phenomenon was observed in our study, the smaller diameter fibers (100 µm) exhibit a higher density than the larger fibers (250 µm). All changes in properties with diameter result from this appearance (and increase with diameter) of As-As bonds.

Structural analysis via Raman spectroscopy demonstrated that no assessment could be made in the variation of the bond energy with either purity or diameter of the fibers. But, as expected changes in the bond energies were observed when comparing bulk spectra to fiber. Both intensity and bond energy of the main band were slightly modified. The nature of the bond being the same and the structure still remaining an interconnection of planes by Van der Waals energies, only small changes in the average bond energy were expected. Appearance of As-As bonds could also be the explanation for the variations observed.

Drawing parameters affect the thermal history of the glass as shown in Table IV-7. Fibers of smaller diameter exhibit lower glass transition temperatures and higher crystallization temperatures than fibers of higher diameter. This observation was not expected since fiber of smaller diameter would have a higher cooling rate and hence according to Figure I-1 a higher $T_g$. Therefore fibers of smaller diameter possess a smaller $\Delta T$; hence a smaller stability to crystallization. Fibers with larger diameter have a structure closer to the one of the bulk glass, which correlates with their thermal properties (same temperature than the bulk material).
It was shown that 100 microns diameter fibers yield the highest Vickers microhardness and that the hardness was decreasing with increasing diameter. Values close to the one of the bulk were obtained for the 100 microns fibers, even though the structure of the bigger fiber was expected to be closer to the one of the bulk. A decrease in the hardness of 8% was observed from 100 to 250 µm. It was found that the density tended to track well with the microhardness. Moreover, it was demonstrated that aging affects both hardness and density of the glass in the same way [17]. Therefore the density is the key factor in the change of microhardness observed.

Both tensile and bending stress measurements showed that the purity had a direct effect on the resulting fiber mechanical properties. The mechanical properties were increased by the purity of the glass, the low OH and water content increasing the interlayer connectivity and the overall network connectivity. Fibers observed the same trend as bulk As$_2$Se$_3$. An approximate change of 38% of the $\lambda$ factor corresponding to the survivability of the distribution of the bending stress failure was determined from the Weibull distribution (Figure IV-20). A wider range was observed for the tensile measurements.

Fiber measurements of the properties showed significant impact of the diameter of the fiber on its properties. In the goal of creating an optimal As$_2$Se$_3$ fiber system, 200 µm diameter would be the best choice since the bending and tensile failure strength were higher in this region. The 100 µm showed hardness value similar to the one of the bulk. But a commercial product would be a core-clad fiber and therefore the surface resistance to crack initiation is not the most important parameter in that case. The cladding would protect the fiber surface and enhance both the bending and tensile properties [48].
6.0 References


CHAPTER V: CONCLUSION AND KEY FINDINGS

This study was focused only on the As$_2$Se$_3$ system. This system was a perfect candidate for fiber drawing due to its large stability to crystallization ($\Delta T > 100$ K). The main goal was to evaluate the effect of both increasing the batch size and fiber drawing on the properties of the physical, thermal and optical and mechanical glass. Moreover the effect of the purity of the glass on properties was also quantified. The impurity content was monitored by the optical properties of the material using the FTIR spectroscopy.

To obtain high purity, homogeneous glass; special techniques were used, such as surface oxide volatilization by thermal treatment, impurity getters and glass distillation.

The uniformity (within melt) of various properties in the preform has been studied. It was demonstrated that the impurity content remained similar in all preform slices. Uniformity in the chemical composition has been demonstrated; the variation observed from bottom to top was only 0.1 % (the error on the measurement being $\sim$1%). The hardness variation between the different slices was found to be within the standard deviation of the measurements (maximum variation of 0.007 GPa). However, noticeable changes in the density of the preforms were determined. An overall decrease of 0.012 g/cm$^3$ of the density was quantified from bottom to top. A slightly higher concentration of selenium in the bottom part of the tube would induce an increase of the resulting density since the density of raw selenium is higher than the one of arsenic. A shorter stabilization time (when the tube is held in a vertical position) should decrease this variation.
This study was focused on the comparison of the unpurified bulk glass properties to the properties of the glass purified with various treatments. As expected the effect of the purity on the thermal, and physical properties was minimal. However a direct correlation between the purity and the mechanical properties of the glass and fiber (microhardness, tensile and bending) was determined. The impurity content connectivity was found to modify on the glass network. The removal of impurities had the effect of strengthening the glass network and hence increasing the strength (maximum increase of 4% in the Vickers microhardness) of the glass. However, the best purification technique yielding a non-oxide containing glass appeared to increase the selenium hydride content in the system, which affects significantly the mechanical properties of the glass.

The highest bandgap energy was obtained for the distilled glass as shown in Table IV-5, the lowest bandgap energy was obtained for the unpurified glass. It seems that a direct correlation between the bandgap energy and the impurity concentration exists. The lowest oxides, hydroxides and molecular content were yielded from the distilled glass. No traces of these impurities could be detected from the FTIR spectra. However, the sample obtained after glass distillation showed a strong increase in the hydrides content, especially for the Se-H band present at 4.57 µm. The lower hydrides content were obtained in the sample purified with oxide volatilization. A mechanism was proposed to explain that the removal of oxides, hydroxides and molecular water lead to an increase of the hydride-containing impurities with the use of AlCl₃ as a getter. Other mechanisms corresponding to the effect of the removal of impurities on the glass structure were showed, and correlation between the impurity removal effect on the structure and the glass properties were examined.
The fiber properties were modified by both the drawing condition and the purity of the fiber. Smaller diameter fiber exhibited higher microhardness value but higher diameter fiber shown higher bending and tensile stress, as shown in Figures IV-16, 19. Both hardness and bending stress were increased with removal of molecular water, oxides and hydroxides, as shown in Figures IV-17, 19. The overall goal is to reach a fiber combining high strength and low optical loss. The application would be to use the fiber in a close system in a bundle in the shape of a spring. In such application, the key mechanical property is the bending strength of the fiber. The targeted bending stress at failure value for this application is 450 MPa. Although this target was not reached, a strong increase of 38% was observed with purification. Moreover the values obtained were measured from as-drawn unclad fibers. A commercial product would be coated, therefore, the flaw population at the surface of the fiber would be reduced and hence, the bending strength of the fiber will be increased since the failure starts from the surface of the fiber. Moreover, a cladding could be added to further increase the strength of the material.

Overall the effect of the removal of impurities induces changes in the properties of the material studied in this thesis. The impact of the impurity content in the structure of the glass dictates some of its properties. It was demonstrated that a direct correlation between the hardness and the relative content of the different species present in the glass was present.
CHAPTER VI: FUTURE WORK

The drawing of the next fiber will be done shortly. A preform already has been realized but its homogeneity was clearly not high enough. Another unpurified preform is ready to be drawn. It will be interesting to compare from melt to melt the evolution of the properties of the resulting fibers.

The next step would be to determine the validity of the proposed reaction mechanism between AlCl$_3$ and impurities in As$_2$Se$_3$ glass.

A study of the effect of a polymer cladding on the mechanical properties, especially the hardness and bending strength, is under development. It will be interesting to see if the same trends are observed for such a system or if the polymer layer is predominating in the mechanical properties of the resulting fibers.

A deeper study of the post-synthesis purification using a HCl solution can be done to examine the exact mechanism of the reaction and determine if the reaction is dependent of the time of penetration of the glass material by the solution.

A study of the effect of the annealing and ageing of the fibers on their bending strength, Young’s modulus, and tensile strength can be investigated.

The next step in this project will be to extend the work into a ternary glass system. The goal will be to successfully draw Ge-As-Se fibers and see if the same trends are observed in this system.