

A Comparative Study of Purification Routes for As₂Se₃ Chalcogenide Glass

Sylvain Danto,[†] Daniel Thompson, Peter Wachtel, Jonathan D. Musgraves, and Kathleen Richardson*

School of Materials Science and Engineering / COMSET, Clemson University, 91 Technology Drive, Anderson, South California 29625

Baptiste Giroire

School of Materials Science and Engineering / COMSET, Clemson University, 91 Technology Drive, Anderson, South California 29625

Chemistry Departments, Bat A11, University of Bordeaux I, 351 Cours de la Libération, 33405 TALENCE cedex, France

Chalcogenide glasses have been widely studied due to their extraordinary transparency in the mid-infrared region. Their transparency, combined with tailorable thermo-mechanical properties, makes them ideal candidates for various optic applications. Extrinsic impurities within the glass matrix can impede their integration in components where low optical loss is a requirement. Additionally, chalcogenide materials typically exhibit low mechanical strength due to the comparatively weaker average bond strength of constituents. Here, we report findings of efforts to explore various purification methods on As₂Se₃ glasses to improve their optical and mechanical properties. These methods involve oxides removal by thermal treatment of the reagents, and addition of AlCl₃ impurity-getters in the melt followed by distillation. We show that these techniques yield very effective results on the removal of hydroxyls, water, and oxide impurities. We also observe a recurrent increase in the Se-H vibrational band, with the concentration of the Se-H species escalating to several tens-of-ppm, depending on the purification method. These increases are associated with the preferential dissociation of hydrogen-containing species. Investigations of the structural, thermal, and mechanical properties of the glass were compared as a function of purification method, and the influence of impurity content on these material attributes is presented.

Introduction

Chalcogenide glasses (ChGs) contain either sulfur (S), selenium (Se), and/or tellurium (Te), with these elements combined in a continuous fashion with glass-

[†]sdanto@clemson.edu

*Prof K. Richardson is member of the ACerS

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modifiers such as As, Sb, Ge, or Ga to tune their thermo-mechanical and optical properties. ChGs are an extensively studied class of materials due to their high mid-infrared (mid-IR) transparency, optical nonlinearity, photo-sensitivity, and phase-change ability.^{1–4} Their good resistance to devitrification makes them suitable for hot-forming (extrusion, molding, fiber drawing) and other forms of shaping. Bulk ChG materials can be deposited as thin films in a range of devices for memory,⁴ or photonic applications.⁵ ChG-based IR fibers operating at longer mid-IR wavelengths than silica fiber ($>3\text{--}4\ \mu\text{m}$) are used in IR light-wave propagation and modulation,^{6–8} remote temperature monitoring,⁹ or chemical detection.¹⁰

Despite their attractive attributes, the full potential of ChGs has not yet been realized, largely due to technological barriers that prevent their synthesis with requisite ultra-high levels of purity for low optical loss applications, and the associated times required to process them. Primary impurity contaminants in ChGs can include oxygen, hydrogen, carbon, or combinations of these species, as well as stable dissolved compounds and heterogeneous inclusions. These optically degrading embedded impurities can be largely attributed to trace-level constituents in starting raw materials, and persist despite often high levels (i.e., 5N or 99.999%) of purity in the elemental starting materials. Additionally, as these glasses are melted in oxygen-free glass ampoules, the corrosion of the reaction silica tube walls by the glass-melt can be a source of SiO_2 hetero-phase inclusions in ChGs.¹¹ Together these unwanted defects subsequently behave as possible crystallite nucleating sites and scattering centers. Hence, as they can also serve as the origin of density and refractive index inhomogeneities, and/or constituents that reduce thermo-mechanical stability,¹¹ they often serve as the cause of specific absorption bands, which can interfere with light propagation through the material in the spectral region of interest. As an illustration, while low-loss fabrication efforts have been extensively studied^{11–24} over the past decades, the lowest attenuation published to date in As_2Se_3 optical fibers remains ~ 1000 times higher than calculated intrinsic losses for the same material (0.08 dB/km at $6.1\ \mu\text{m}$ ²⁵) and ~ 400 times higher than the attenuation of commercially available silica fibers (0.2 dB/km at $1.55\ \mu\text{m}$ ²⁶).

The present effort has focused on developing and evaluating the effectiveness of combining purification strategies on the preparation of high-purity bulk ChGs. Specifically, we describe the design and construction of

an innovative dynamic-vacuum glass processing system. This system relies on the difference of vapor pressure between a metal oxide and its parent metal, to carry out the preferential volatilization of the oxides when heated up to appropriate temperatures. In addition, we have synthesized glasses over getter materials, followed by distillation. In this approach, we modify the chemical form of the impurity through reaction with a getter added to the glass batch in small quantity (0.1% in weight). The impurity-containing species and residues are removed from the melt by vacuum distillation. Metallic oxygen getters (Al, Mg, Zr...) are the most commonly used scavenging materials during the glass purification process to reduce optical losses.^{23, 24, 27} For the current effort, we have selected aluminum tri-chloride compound as a candidate getter material. Churbanov *et al.*²⁸ have shown that when using aluminum-based getters (i.e., Al, AlCl_3 , and $\text{Al}+\text{TeCl}_4$), oxygen impurities react with aluminum to form nonvolatile aluminum oxide Al_2O_3 , removed from the melt by distillation. During this process, hydrogen impurities react with chlorine to form hydrogen chloride, which is removed from the melt by vaporization.²⁹ To keep compositional variation limited, we have selected for this study stoichiometric As_2Se_3 glass within the As-Se binary system, due to its good thermo-mechanical stability. We have thoroughly characterized the thermo-mechanical and optical properties of the fabricated bulk materials, carried out the side-by-side comparison of the evolution of their properties with purification method, and compared these results with unpurified reference materials.

Experimental

Standard Glass Processing

ChGs are produced by the co-fusion of the adequate raw elements, in the appropriate amounts, under vacuum in quartz reaction tubes. The melt is rocked at T_m to ensure melt homogeneity and then is rapidly quenched, usually in air or water, in order to freeze the material into an amorphous bulk structure. For comparison with the different purification protocols described in next section, we first prepared bulk As_2Se_3 glasses by the standard melt-quenching technique.³⁰ The starting high-purity elemental materials (As: Alfa Aesar 5N, Se: Alfa Aesar 5N), which made up the “reference” material, were weighed and batched inside a nitrogen-purged glove box and sealed using a gas–oxygen torch under vacuum into

quartz ampoules. Prior to sealing and melting, the batch was preheated at 100°C for 4 h under vacuum to remove surface moisture from the quartz ampoule and the raw materials. This latter low-temperature moisture removal treatment is the only purification step applied to the “reference” material. The ampoule was then sealed and heated up for 24 h at 800°C while kept under constant rocking to increase the homogeneity of the melt. The melt-containing ampoule was finally air-quenched to room temperature. In order to relax quench-induced stress in the glass ingot and to avoid its fracture during fabrication, the ampoule was subsequently returned to the furnace for annealing for 15 h at 155°C, that is to say 40°C below the glass transition temperature of the glass.

Dynamic-Vacuum Glass Purification System

Although the glasses produced in a standard melt protocol are melted from high-purity 5N reagents, measurement of their absorption spectra confirms the presence of impurities and the need for further batch purification steps to yield glasses with lower absorption loss. As discussed previously, extrinsic impurities in ChGs are largely attributable to starting materials. Indeed, as-received, commercially available “high-purity” chemicals (even those listed as 99.999% pure or 5N) are typically analyzed only on a cation basis; thus, their purity rating does not reflect the presence of anionic impurities, such as carbon or hydrogen. Therefore, the removal of these species is needed to reduce mid-IR active absorption associated with their bonding to glass matrix constituents.

To achieve lower loss levels in ChGs by removing these impurities, we have designed and constructed a new dynamic-vacuum purification system (Fig. 1 panel (a) picture and (b–d) illustrated layout). The experimental design consists of a three-tube manifold quartz system in which the different glass-former elements (i.e., elements A, B, and C in the figure) are introduced into separate tubes where they are subjected to element-specific presynthesis purification under dynamic vacuum. (In this specific work, we introduced only two elements in the setup: arsenic in tube A and selenium in tube B). Elements are individually heated while under vacuum at the appropriate thermal processing temperature, whereby the metal–impurity bond can be broken, and the impurity removed by vacuum (Fig. 1b). Subsequent to this treatment, the now purified elemental materials (As and Se) are collected in the final reaction tube (tube 1) and

sealed under vacuum (Fig. 1c). The mixture is then heated up to the melting (liquidus) temperature, rocked, and quenched in the standard manner as described previously for the sealed, unpurified ampoule (Fig. 1d). In all processes, strict temperature control is employed, and the process takes place within a fume hood to ensure safe venting of all volatilized species. This system allows for the separate prepurification in subreaction tubes of the different raw elements with different levels of impurity. Subsequently, the prepurified metals, now void of surface oxide and/or moisture, can be brought together into a final reaction tube under vacuum, while maintaining their treated state. This capability ensures the batch avoids any possible reoxidation or rehydration. The closed system process capability also leads to the elimination of residual water or hydroxyl which may be present in the silica tube or on the element’s surface, as long as the reaction tube is open to the vacuum allowing residue to be vented out.

Using this system, we have conducted multiple initial tests with arsenic and selenium (As: Alfa Aesar 5N, Se: Alfa Aesar 5N) starting materials in the preparation of a binary arsenic triselenide glass. Commercial raw materials were weighed in 40/60 As/Se atomic ratio and introduced into two dry and clean tubes of the setup. The system was then evacuated under vacuum (10^{-3} mmHg). The selenium and arsenic starting materials were heated up at 250°C and 290°C, respectively, and held at temperature under vacuum, for 2 h. As the vapor pressures of the commonly formed oxides SeO_2 and As_2O_3 are several orders-of-magnitude higher than those of the pure metals, this process yields dissociation and preferential volatilization of the surface oxide contamination. In addition, the procedure favors the elimination of moisture from the batch. The purified Se and As elements contained in the individual tubes are then combined in the final tube, which was then sealed under vacuum. The mixture is then heated up at 800°C overnight and quickly quenched in air. The results from the surface oxide removal samples as compared to reference glass are discussed in section “Results and Discussion.”

Additional Purification Protocols: Getters and Distillation

In addition to the building of a dedicated purification setup, we have conducted tests involving melting of the glass components over a getter material. This process of combining metal with a halide-containing species allows the preferential formation of thermody-

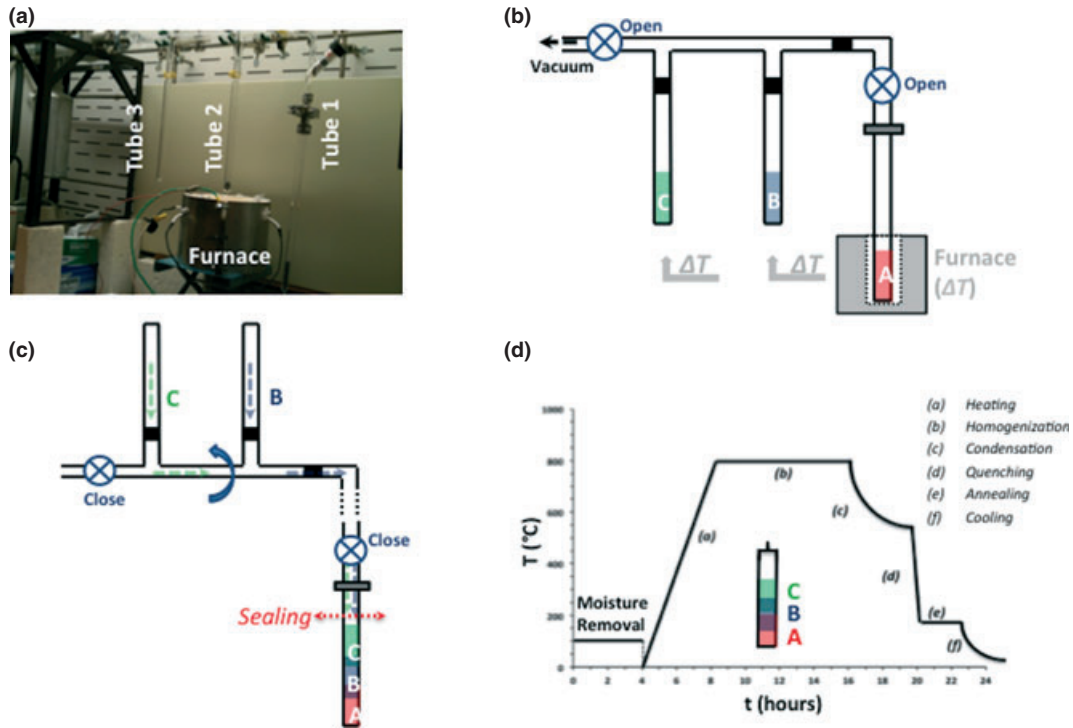
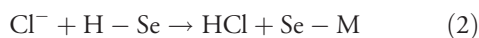
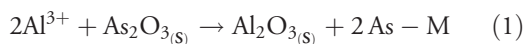


Fig. 1. Dynamic-vacuum CbG purification system (a) Experimental setup (b) Schematic diagram of the separate purification of the elements (A, B, C: glass-modifiers elements) (c) Postpurification, the elements are brought together in the final reaction tube (d) Thermal profile of the reaction tube.

namically stable compounds with residual hydrogen and/or oxygen atoms left in the precursor materials. These products are then subsequently removed from the melt by distillation to reduce further the impurity concentrations. For this effort, we have selected aluminum tri-chloride, AlCl_3 , as the getter material (Sigma Aldrich 5N; St. Louis, MO trace metals <20 ppm). Here, both the anion and the cation play a role in binding to impurity species initially associated with the metals associated with the glass matrix. The expected chemical reactions between the getter compound and the target impurities are described in Eqs. (1) and (2) (with M being the other constituents in the glass matrix).



These chemical reactions present the advantage of generating two new species that can be individually

removed from the glass. HCl is known to be volatile above room temperature; hence, it can be removed via a dynamic-vacuum extraction. The alumina (Al_2O_3) formed from the reaction between Al^{3+} and any oxides present, exhibits a high melting point of 2015°C. Therefore, a distillation process carried out under this melting point can remove the alumina from the glass network.

We have conducted a panel of purification routes combining synthesis over AlCl_3 getter followed by distillation on a series of 10-gram batches of As_2Se_3 . For each one of the following procedures, the exact same amount of getter, 0.1% in weight, was used:

AlCl₃ getter

The starting materials (As, Se and getter), in the appropriate amounts, are loaded inside a nitrogen-purged glove box into a clean quartz reaction tube, which is then evacuated. The batch is preheated at 100°C for

4 h to remove surface moisture from the quartz ampoule and the raw materials. The ampoule is then sealed and heated up at 800°C for 12 h while kept under constant rocking to ensure the homogeneity of the melt. The ampoule is finally air-quenched to room temperature, and subsequently annealed at 155°C for 15 h.

AlCl₃ getter + dynamic-vacuum distillation

The starting materials (As, Se and getter) are loaded inside a nitrogen-purged glove box into a reaction tube, which is then evacuated. The batch is then heated up until 400°C following an increment of 25°C every 15 min under dynamic vacuum. The ampoule is then sealed and heated to 800°C for 12 h before being air-quenched to room temperature and annealed at 155°C for 15 h.

AlCl₃ getter + static-vacuum distillation

The starting materials (As, Se and getter) are loaded inside a nitrogen-purged glove box into a reaction tube, which is then evacuated. The batch is pre-heated at 100°C for 4 h to remove surface moisture. The ampoule is then sealed and heated up at 800°C and held for 12 h before being air-quenched to room temperature. The melted glass sample is transferred into a new silica ampoule designed with two distinct physical sections. The multi-chamber tube is then evacuated and inserted in a four-zone furnace to be distilled to separate the As_2Se_3 material from impurity-containing residue. The chalcogenide will vaporize, transfer, and condense in the “cooler” section of the tube, whereas the higher temperature residue remains behind in the initial zone of the tube.

Characterization of the Materials

We have thoroughly characterized the thermal, mechanical, and optical properties of the fabricated bulk glasses with the goal of assessing purification protocol and the subsequent role of impurity content on these physical properties. In all cases, purified material resulting from one of the specific purification protocols were compared with the properties of a reference sample made from high-purity 5N reagents. The characteristic temperatures of the glass As_2Se_3 were determined by differential scanning calorimetry (DSC) at a heating

rate of 10°C/min using a commercial apparatus (DSC 2920 from TA Instrument Inc.). Sections of the glasses were cut and ground down to powder for analysis. Approximately 20 mg of powdered glass was inserted into a sealed Al pan and placed in the DSC instrument along with an empty reference pan. The characteristic temperatures of the glass As_2Se_3 were measured at a heating rate of 10°C/min, with a precision of $\pm 2^\circ\text{C}$ on the measurement. The glass transition temperature T_g is taken at the inflection point of the endotherm (obtained by taking the first derivative of the curve) and the crystallization temperature T_x at the maximum of the exothermic peak.

The density of bulk glass materials was determined by the Archimedes' method using a diethyl phthalate solution of known density as a function of temperature. These density measurements were performed on polished samples inside a glove box to improve the accuracy and repeatability of the result. The accuracy of the measurement was 0.05 g/cm³. To evaluate the role of glass impurities on glass hardness, Vickers micro-hardness has been measured with a Shimadzu DUH-211S micro-hardness tester. The apparatus uses a diamond tip with a square base and an angle of 136° between opposite triangular faces. Loads of 200 mN were used with a loading rate of 1.0 mN/s, and the force was held 20 s to determine the load-independent indentation region. Once this level was determined and no cracking was confirmed on the resulting indent, the diagonal length of the indentation was measured, and the micro-hardness value was subsequently calculated. To minimize the error on the study, 15 measurements were performed all over the surface of optically polished disks, in regions of the sample that were free of scratches, pits, or other damage. Errors for micro-hardness measurements were $\pm 2\%$. To assess melt-to-melt measurement variation, the reported measurements were collected for samples prepared from two different batches of the same glass synthesized using the exact same purification method.

Energy-dispersive X-ray spectroscopy (EDS) measurements have been conducted to establish the chemical constituents present in the glasses. The experiments were carried out using a SEM/EDS SU 6600 on polished samples. The accuracy of the measurement is estimated to be ± 1 atomic percent. A magnification of a $\times 1000$ was used, and the energy of the incident electron beam was 20 keV. Prepared materials were also analyzed with Raman and Fourier Transform Infra-Red

(FTIR) spectroscopy. For both techniques, a glass rod was cut into slice nominally 1.50 mm in thickness, which were subsequently ground and polished to achieve mirror-like, inspection polished, parallel faces. The transmission spectra of the investigated glasses have been measured using a Nicolet Magna-IR 560 FTIR spectrometer with a spectral resolution of 4 per cm and a dual beam Vis-NIR Perkin Elmer Lambda 900 spectrophotometer. Prior to transmission measurement, the samples were placed in the spectrometer chamber and purged with nitrogen for 30 min. Raman spectra were recorded on a Bruker Senterra micro-Raman spectrometer using a 785 nm excitation line with 10 mW of incident power. The backscattered Raman spectrum was collected by a spectrograph equipped with a cooled CCD camera. Raman spectra in the range of 70 to 800 per cm were recorded with a resolution of 3–5 per cm.

Results and Discussion

Efforts have been made to tackle the challenge of developing a manufacturing-compatible solution for the purification of As_2Se_3 glasses, with the goal of producing low optical loss materials. The purification methods investigated here to remove extrinsic impurities from the melt consist of surface oxide removal by thermal treatment of the raw material and the addition of AlCl_3 impurity-getters in the melt followed by distillation. Using these different purification strategies, we have prepared a series of As_2Se_3 glasses. We plot in Fig. 2 the absorption coefficient as a function of wavenumber of these samples, all compared with a reference material shown in red ([a] oxide volatilization; [b] AlCl_3 getter; [c] AlCl_3 getter and dynamic-vacuum distillation; [d] AlCl_3 getter and static-vacuum distillation).

We observe that the reference material prepared in a standard fashion exhibits large peaks centered at 3400–3600 per cm, 1550–1600 per cm, and at 600–800 per cm, which correspond to extrinsic absorption due to hydroxyl groups, molecular water, and oxide impurities, respectively. This result emphasizes the limitation of relying solely on high-purity reagents and on low-temperature moisture removal treatment (100°C/4 h) to fabricate high-purity glasses.

In addition, we note that all four investigated purification procedures (panels [a] to [d]) are, as compared with the reference material, extremely effective in

reducing the intensity and hence concentration of the hydroxyl species, molecular water, and oxide constituents as quantified by the shown absorption peaks. To quantify the evolution of the impurity content, we have extracted the concentration of impurity species contained in glasses from their IR transmission spectra using the following relation (Eq. 3):

$$[\text{impurity}] = \frac{\alpha_{dB/m}}{\varepsilon_{dB/m\text{-ppm}}} \quad (3)$$

with α the absorption coefficient (dB/m), and ε the extinction coefficient (dB/m/ppm) of a particular species of interest at a specific wavelength. From the literature, we find for the extinction coefficient of O-H and Se-H: $\varepsilon_{OH} = 5.0$ dB/m/ppm at 3424 per cm (2.92 μm),¹¹ $\varepsilon_{SeH} = 1.0$ dB/m/ppm at 2174 per cm (4.6 μm),¹¹ and $\varepsilon_{\text{H}_2\text{O}} = 34$ dB/m/ppm at 1587 per cm (6.3 μm),³¹ and for the oxides $\varepsilon_{\text{Se-O}} = 0.38$ dB/m/ppm at 943 per cm (10.60 μm).¹¹ When using these values, we calculate from Eq. (3) the following impurity concentrations for H_2O , O-H, Se-H, and Se-O as summarized in Table I. Arsenic oxide compounds exhibit a multiplicity of forms (As_4O_6 , As_2O_3 , As-O, As-O-As, As-O-H), which span in an intricate manner the 625–1250 per cm (8–16 μm) spectral range.²³ The extinction coefficient for most of these impurities species is not available. To provide an estimation of the evolution of the arsenic oxides impurities with the purification methods, we include the value of the absorption coefficient peak α obtained from the Fig. 2 in the range 600–800 per cm.

As shown in Table I, irrespective of the purification method employed ([a] to [d]), the concentration of O-H and H_2O groups impurities is drastically lowered, from 43 to \sim 4.0 ppm or less for O-H, and from 5.68 to 0 ppm (i.e., below detection limit) for H_2O . In a similar manner, the Se-O impurity band is minimized below the detection limit. Finally, the absorption coefficient α for the arsenic oxides species (centered in the range 600–800 per cm) drops 80%, for all the purified glasses, that is to say from 2.6 per cm (sample [a]) to 0.50 per cm. This latter value is in the range of the intrinsic minimum of the multi-phonon absorption of the glass As_2Se_3 .

As a drawback however, we observe an increase in the Se-H vibrational band centered on 2175 per cm, with the concentration of the Se-H species escalating to several tens-of-ppm, depending on the purification method. This suggests that the treatment processes used

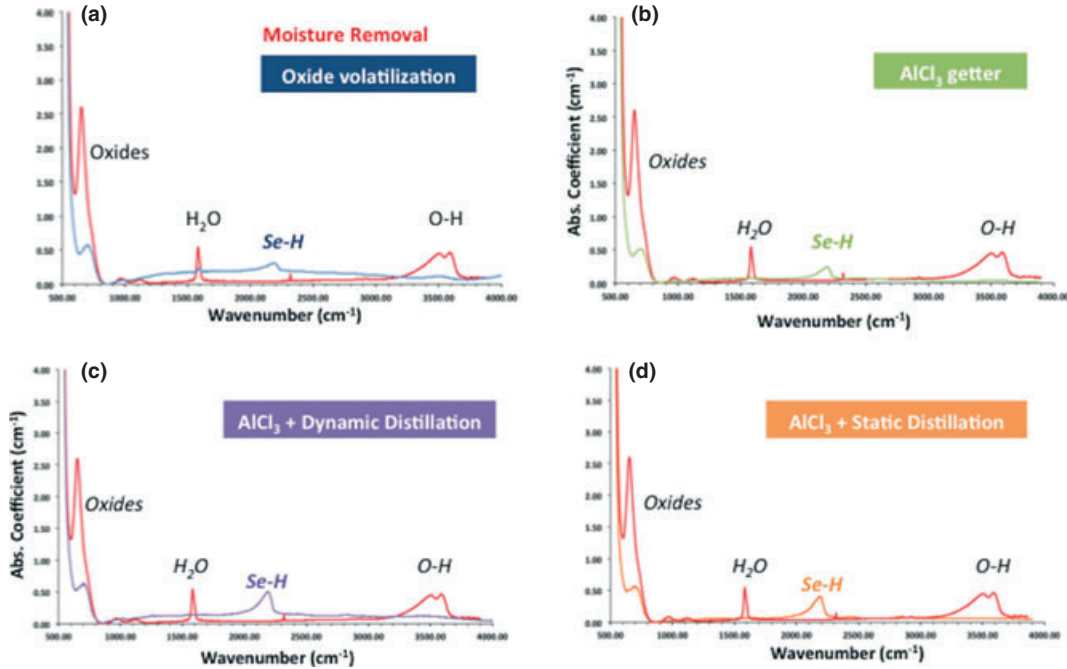


Fig. 2. Side-by-side comparison of the absorption spectrum of a reference glass As_2Se_3 made via the standard melt-quenching technique (in red) with glasses prepared via (a) oxide volatilization; (b) $AlCl_3$ getter; (c) $AlCl_3$ getter and dynamic-vacuum distillation; (d) $AlCl_3$ getter and static-vacuum distillation.

Table I. Concentration as a Function of Purification Methods for Hydroxyls, Molecular Water, and Oxides Impurities in As_2Se_3 Glasses

Processing	Hydride content			Oxide content	
	[O-H] ppm	[Se-H] ppm	[H ₂ O] ppm	[Se-O] ppm	$\alpha_{\text{Arsenic Oxide}}$ (/cm)
Moisture Removal	43.00	0	5.68	250	2.60
(a) Oxides volatilization	1.1	24.70	0	0	0.50
(b) $AlCl_3$ getter	1.3	72.50	0	0	0.50
(c) $AlCl_3$ + Dynamic Distillation	4.1	150.5	0	0	0.50
(d) $AlCl_3$ + Static Distillation	0	152.44	0	0	0.50

leads to the elemental hydrogen transferring from the oxygen to the selenium as the oxygen is progressively removed from the system by purification.

The glass compositions were examined by Elemental Dispersive Spectroscopy (EDS) and were found to be identical to the initial elemental concentration within the measurement accuracy (± 1 atomic percent). The characteristic temperatures (glass transition T_g , crystallization T_x , melting T_m , and $\Delta T = T_x - T_g$) of the investigated glasses are listed in Table II. The

melting temperature increases only slightly with the purification. The oxide volatilization (sample [a]) does not change the thermal properties of the glass. However, the addition of the $AlCl_3$ impurity getter in the matrix significantly modifies both the glass transition and crystallization temperatures of the glasses. It yields an increase of the T_g for the samples (b) and (c) and an increase of the T_x for all the samples. In addition, it induces an increase of the difference $\Delta T = T_x - T_g$ from 8°C (b) to 12°C (d) indicating an improvement

Table II. Effect of the Purification Method Used on Thermal Properties and Density of the Glass As_2Se_3

Processing	Characteristic temperatures				Density ρ ($g/cm^3 \pm 0.05$)
	$T_g (\pm 2^\circ C)$	$T_x (\pm 2^\circ C)$	$T_m (\pm 2^\circ C)$	$\Delta T = T_x - T_g$	
Moisture Removal	191	357	380	166	4.6179
(a) Oxides volatilization	192	357	381	165	4.6147
(b) $AlCl_3$ getter	196	370	383	174	4.6183
(c) $AlCl_3$ + Dynamic Distillation	194	370	383	176	4.6175
(d) $AlCl_3$ + Static Distillation	188	366	383	178	4.6200

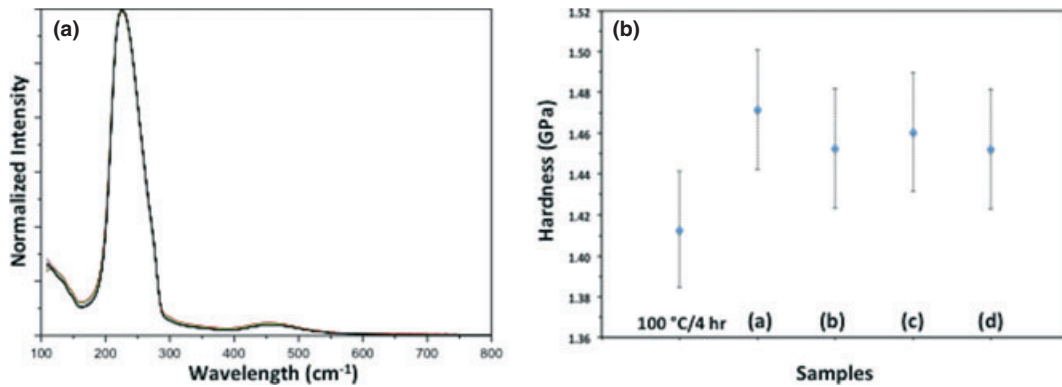


Fig. 3. Evolution as a function of the purification protocols of the (a) Raman spectra and (b) Vickers micro-hardness of the As_2Se_3 glasses (Moisture removal sample and (a) oxide volatilization; (b) $AlCl_3$ getter; (c) $AlCl_3$ getter and dynamic-vacuum distillation; (d) $AlCl_3$ getter and static-vacuum distillation).

in the resistant to devitrification of these glasses. The thermal properties of glasses have to be correlated with the network connectivity, and hence the purity of the glass. The addition of the $AlCl_3$ getter removes impurities and particulates from the glass matrix, which favors chemical cross-linking of the network, and thus a decrease of the free volume of the glass. Such internal densification of the network raises the T_g of the glass and improves its resistance to crystallization.

We observe in Table II that, in the limit of the error of measurement, the density of the purified glasses stays constant or increases slightly in comparison with the reference material. While not appreciably changing the network density, one could expect the removal of molecular water contributes to a change in network volume and mass by allowing a contraction of the free volume, and a minor reduction of mass with oxide loss within the glass. Furthermore, the reduction of the dangling O–H bonds can generate higher network

connectivity in the system, because As–OH or Se–OH bonds are replaced by As–Se– M bonds (M is standing for glass matrix). Evidence of any micro-level change in the density and network connectivity will further be corroborated by hardness measurements in the materials.

Raman spectroscopy was performed to determine the effect on purification methods on the final chemical bonding of the glass. Fig. 3a shows Raman spectra of all five glasses. Raman spectra have been normalized to the maximal intensity. All spectra are perfect matches, the difference between them being within the line width of the curve. The broad peak at 245 per cm is typical of the As–Se–As and As–Se bonds in the network. The second peak at 454 per cm is a harmonic of the main band.

Hardness gives a measure of the surface resistance of a material to crack initiation. The effect of purification protocol on Vickers micro-hardness is shown on Fig. 3b. The tests were performed on two glasses prepared from the same purification method to see

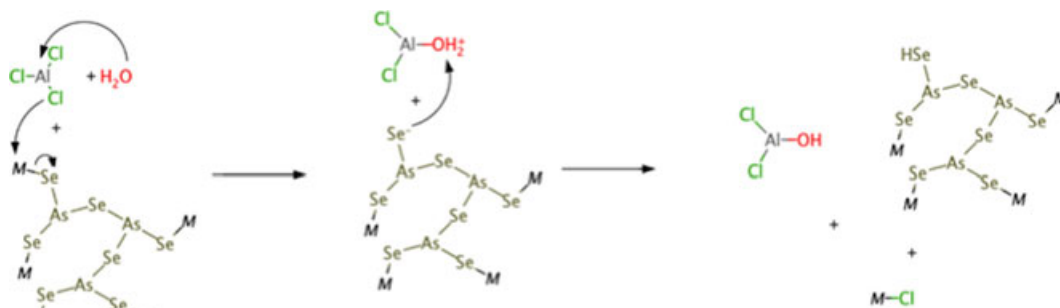


Fig. 4. Proposed reaction mechanism between aluminum chloride and water impurity present in the glass matrix (M is indicative of the remaining for glass matrix).

the reliability of the measurements from melt to melt. As can be seen, irrespective of the method, the glass purification has a definite impact on the hardness of the sample. It rises from 1.412 GPa (reference sample) to 1.471, 1.453, 1.46, and 1.452 GPa for samples (a) to (d), respectively (errors of measurements: $\pm 2\%$). As confirmed in the earlier chemical and spectroscopic analysis, the presence of hydrogen- and oxygen-containing species in the glass system has an impact on the glass network connectivity. Although bridging impurities may eventually lead to the generation of stronger bonds, the one can envision that the presence of these metal-hydride and/or metal-oxide bonds in the glass matrix can cause the depolymerization of the later one. Indeed as dangling O-H bonds, and Se-O or As-O bonds are replaced by either As-Se hetero-polar or As-As / Se-Se homo-polar bonds, it can be seen that the glass network is strengthened as noted by the slight increase in material micro-hardness. On the contrary, while hydroxyls, water, and oxides removal may lead to network strengthening, the creation of Se-H dangling bonds decreases the glass' network connectivity, reducing the micro-hardness of the material as a function of Se-H impurity concentration. The combination of both of these proposed mechanisms can explain the value of hardness found for the samples (b), (c), and (d). The hydroxyl groups and molecular water are in very low concentration in these materials, but the generation of new Se-H bonds counterbalances and apparently outweighs this effect; the outcome of the oxide and moisture removal combined with Se-H increase results in a lowering of the hardness value.

Although encouraging, the results presented here do not yield the expected level of purity in all spectral

regions of interest for mid-IR transparency, defined as the 3–5 μm wavelength range. Indeed, we observe that, regardless of the purification method used, the concentration of Se-H bonds persists, and even significantly escalates after synthesis over getter and glass distillation. Such a similar increase in the Se-H absorption band while producing ChGs with Al-based oxygen getters has already been observed.³² In hydride-containing ChGs, the hydrogen preferentially bonds either with the oxygen or with the chalcogen. As the oxygen is removed from the system, the product of the dissociation of the hydroxide to hydride results in hydride being recaptured by the selenium. An additional explanation lies in the mode of dissociation of the aluminum chloride getter. While at room temperature, the getter is in the Al_2Cl_6 dimeric configuration; upon heating the stable conformation becomes $AlCl_3$ when the temperature reaches 500°C. This means that aluminum and chlorine ions do not dissociate in the melt to react as two distinct species but instead remain partially bonded. Taking this consideration into account, we formalize a plausible mechanism of interaction between $AlCl_3$ and the main impurities present in the glass matrix, as seen in Fig. 4. 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 occurring in the melt is with the residual H_2O . 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. It generates a negatively charged

selenium atom, which can then recombine with the extra hydrogen attached to the oxygen, as described in Fig. 4. This mechanism results in the generation of AlCl_2OH , Se-H , and As-Cl bonds. Thermo-dynamic considerations reinforce the validity of our hypothesis. The bond energy at room temperature of the species prior to reaction is $E_{\text{Al-Cl}} = 511$ kJ/mol, $E_{\text{As-Se}} = 96$ kJ/mol, $E_{\text{H}_2\text{O}} = 427.6$ kJ/mol, for a total $E_{\text{Initial}} = 971.6$ kJ/mol. Postreaction, we have $E_{\text{Al-O}} = 511$ kJ/mol, $E_{\text{As-Cl}} = 448$ kJ/mol, $E_{\text{Se-H}} = 314.47$ kJ/mol, for a total $E_{\text{Final}} = 1273.47$ kJ/mol.³³ This quantitative explanation suggests that the proposed reaction mechanism for the generation of the undesired Se-H bonds yields a more stable system in terms of bond energies. Although the bond energy presented here is found at room temperature (while the reaction is occurring at 800°C during the melting of the material), the proposed mechanism gives an approximate representation on the possible bond creation that is favored in the melt.

In conclusion, the purification tests involving surface oxide removal by thermal treatment of the raw material and the addition of AlCl_3 impurity-getters in the melt followed by distillation show very effective results on the removal of hydroxyl groups, molecular water, and oxides impurities. The removal of these impurities modifies the glass network connectivity, and thus influences the glass properties. We observe that the enhancement of the transparency of the glasses purified using the getter is accompanied by an improvement of their thermal stability, as defined by the increase of their difference $\Delta T = T_x - T_g$, up to 12°C . Furthermore, the higher connectivity of the purified materials yields an increase in the Vickers micro-hardness, which indicates better mechanical characteristics of the glasses following purification. We can assume that the micro-hardness could be enhanced even further by lowering both oxide and hydride contents. Further improvements at the experimental set-up design and at the synthesis procedures are in progress to refine the low-loss optimization procedures presented here, with corresponding evaluation of improved mechanical robustness. Special attention will be paid to the removal of residual hydrides impurities from the glass batch. The first solution to achieve this goal will consist in using more aggressive getters, such as aluminum metal combined with tellurium tetra-chloride,²⁸ in conjunction with multiple static-distillations. Alternatively, we have demonstrated recently that microwave-assisted processing permits the fabrication in minutes of ChGs with a high level of pur-

ity.³⁴ We believe that this innovative process, combined with the purification methods proposed above, can be applicable to a wide variety of elemental starting materials used to make ChGs, and therefore will help reducing the potential for absorption loss in the resulting glasses.

Conclusion

The objective of the present work has been to establish new ChGs material purification capabilities and demonstrating improvements to trace impurity levels in the raw materials and resulting glasses. In this framework, we have designed a new dynamic-vacuum glass synthesis system for surface oxide treatment and developed synthesis protocols involving the use of extrinsic impurities getters and subsequent glass distillation. The initial tests conducted on As_2Se_3 samples show very encouraging results, especially for removal of hydroxyl groups, molecular water, and metal-oxides impurities. Among potential application, the scaling up of these glass purification techniques is under development to form higher-quality bulk glass of size suitable for fabricating preforms dedicated to fiber drawing. It will yield IR-transmitting fibers that are stronger, more transparent and less susceptible to high power damage than the currently available chalcogenide fibers, because all three of these fiber parameters are a direct function of the purity of the base materials. By improving the purity of the base materials and resulting glasses, we expect a drastic improvement of the fiber transparency, strength, and resistance to laser-induced damage.

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