Homogeneity of melt-rocked Ge-Se glasses and the effect of impurities
Pierre Lucas, Shuo Cui, Dmitriy P. Bayko, Ozgur Gulbiten, Garrett J. Coleman, Johann Troles

To cite this version:

HAL Id: hal-03163704
https://hal.archives-ouvertes.fr/hal-03163704
Submitted on 29 Mar 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Homogeneity of melt-rocked Ge-Se glasses and the effect of impurities

Pierre Lucas¹, Shuo Cui¹,†, Dmitriy P. Bayko¹, Ozgur Gulbiten¹,², Garrett J. Coleman¹,⁎, Johann Troles³

¹ Department of Materials Science and Engineering, University of Arizona, Tucson, Arizona 85721, USA
² Science and Technology Division, Corning Incorporated, Corning, New York 14831, USA
³ Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR 6226, F-35000 Rennes, France

Abstract

The impact of glass synthesis methods on the properties of Ge-Se glasses is investigated. The homogeneity of a GeSe₄ glass produced by mechanical convection in a rocking oven for 12 h at 950°C is characterized by Raman spectroscopy and Electron Microprobe analysis. It is found that the melt-rocked glass is chemically and structurally homogeneous at all length scales investigated. In order to compare the effect of synthesis methods, another glass is produced following a static synthesis for 192 h. Their physical, structural and dynamic properties are then characterized for comparative analysis. The molar volume and structure of both glasses is found to be identical when
subJECTED TO THE SAME THERMAL HISTORY. THE STRUCTURAL DYNAMICS OF GeSe₄ INVESTIGATED BY HEAT CAPACITY SPECTROSCOPY IS IDENTICAL FOR THE STATIC AND ROCKED GLASS AND ALSO COMPARED WITH THAT OF GeSe₉ AND GeSe₃. OVERALL, THE TWO SYNTHESIS METHODS DO NOT LEAD TO ANY DIFFERENCE IN MEASURED PROPERTIES. FINALLY, THE EFFECT OF IMPURITIES IS INVESTIGATED IN THREE GLASSES. THE PRESENCE OF WATER AND OXYGEN IMPURITIES UP TO 30 ppm LEVELS IS SHOWN TO HAVE NO SIGNIFICANT EFFECT ON PHYSICAL AND STRUCTURAL PROPERTIES. HENCE THE PRESENCE OF WATER IMPURITIES CANNOT BE ATTRIBUTED TO MISMATCH IN PHYSICAL PROPERTIES.

1 INTRODUCTION

IN ADDITION TO THEIR BROAD APPLICATIONS IN INFRARED OPTICS¹, CHALCOGENIDE GLASSES HAVE RAISED MUCH INTEREST AS TESTBED MATERIALS FOR STRUCTURAL MODELS SUCH AS TOPOLOGICAL CONSTRAINT THEORIES.²⁻⁴ SUCH MODELS AIM AT PROVIDING CORRELATIONS BETWEEN COMPOSITION AND GLASS PROPERTIES WITHOUT THE NEED FOR PROHIBITIVELY COMPLEX AB-INITIO MOLECULAR DYNAMIC SIMULATIONS⁵. THESE THEORIES ARE BASED ON CONSTRAINT COUNTING PRINCIPLES DERIVED FROM THE VALENCE AND LOCAL GEOMETRY OF EACH CONSTITUENT ELEMENT.³ HIGHER VALENCE ELEMENTS INCREASE THE NUMBER OF TOPOLOGICAL CONSTRAINTS WHICH INCREASES THE STRUCTURAL NETWORK RIGIDITY THAT IS BELIEVED TO CONTROL SOME OF THE GLASS PHYSICAL PROPERTIES. IN THAT RESPECT THE Ge-Se SYSTEM HAS BEEN THE FIRST AND ONE OF THE MOST COMMONLY INVESTIGATED CHALCOGENIDE SYSTEMS TO CORRELATE STRUCTURAL RIGIDITY TO PHYSICAL PROPERTIES.²⁻⁴ HOWEVER, IT WAS RECENTLY SUGGESTED THAT CHALCOGENIDE GLASS PROPERTIES WERE GREATLY DEPENDENT ON THE SYNTHESIS METHOD AND, IN PARTICULAR, THE MELT HOMOGENIZATION STEP.⁶, ⁷ MORE SPECIFICALLY, IT WAS ARGUED THAT MELTS MUST BE HOMOGENIZED STATICALLY FOR EXTENDED PERIODS OF TIME UP TO 17 DAYS, AND THAT MECHANICAL CONVECTION THROUGH MELT-ROCKING IS NOT EFFECTIVE TO OBTAIN HOMOGENOUS MELTS AND GLASSES.⁶⁻⁸ AS A RESULT, IT WAS IMPLIED THAT GLASSES PRODUCED BY MELT-ROCKING EXHIBITED A DEVIATION IN PHYSICAL PROPERTIES FROM THOSE PRODUCED BY STATIC HOMOGENIZATION, AS ILLUSTRATED FOR MOLAR VOLUME IN FIGURE 1 ⁸⁻¹³. FURTHERMORE, IT WAS ALSO IMPLIED THAT THE PRESENCE OF WATER IMPURITIES IN THE GLASS COULD ALSO AFFECT PHYSICAL PROPERTIES AND ACCOUNT FOR DEVIATIONS IN MEASURED QUANTITIES SUCH AS THE MOLAR VOLUME.⁸
The structure of Ge-Se glasses has been extensively studied and it is now well established that Se-rich glasses satisfy chemical order while compositions near GeSe$_2$ contain homopolar bonds.\textsuperscript{14} Importantly it is also found that Se-rich glasses do not follow the chain crossing model but instead exhibit a non-uniform distribution of Ge-centered tetrahedra including corner- and edge-sharing pairs.\textsuperscript{14, 15}

Rocking furnaces have been used by the research community to homogenize chalcogenide melts for more than five decades.\textsuperscript{16, 17} In addition, chalcogenide glasses are currently produce industrially using the melt-rocking method.\textsuperscript{18} Clarifying whether melt-rocking is an effective homogenization technique therefore has a deep applied and fundamental relevance as it puts into question many decades of chalcogenide glass research that have relied on this method. In this study, we therefore characterize a Ge-Se glass rod produced by melt-rocking using Electron Microprobe analysis (EMP) and Raman spectroscopy over a length of ~ 6 cm. We show that the glass is structurally and chemically homogeneous at all length scales investigated. Furthermore, we compare the physical properties of two Ge-Se glasses, one produced statically and one produced by melt-rocking from the same elements. It is found that the structure, the molar volume, and the structural dynamics measured by heat-capacity spectroscopy are all identical, in agreement with previous studies.\textsuperscript{19} Finally, we show that the presence of water impurities in the glass at the level of tens of ppms has no significant effects on physical properties such as the molar volume.

2 EXPERIMENTAL

2.1 Glass synthesis

A glass of composition GeSe$_4$ was selected for this study due to its low fragility and high viscosity as recently shown in the extensive study of Zeidler et al.\textsuperscript{20}. synthesized using the melt-rocking method. Ge and Se elements (All Chemie Ltd) with 6N purity were introduced in a low-OH silica (Advalue Technology) tube 8 mm in inner-diameter previously cleaned with HF, rinsed with ultrapure water, and baked at 800°C to remove any water molecules adsorbed on the tube surface. The tube containing
18 g of the as-received elements was then put under a vacuum of $10^{-6}$ Torr and sealed with a hydrogen/oxygen blow torch. The resulting ampoule was introduced in a rocking oven and heated to 950 °C at a rate of 5 °C /min and held there for 12 h with a rocking frequency of 6 oscillations per minute and a rocking angle of 45°. The glass was then cooled to 650 °C, quenched in water and annealed 10 °C below $T_g$ for 12h. Another glass was produced from 2 g of the same batch of elements using the method described in Ref [6] and heated statically at 950 °C for 192 h (8 days). This glass was also quenched in water and annealed 10 °C below $T_g$. A high purity GeSe$_4$ glass was also produced using the method of Troles$^{21}$ by sequential distillations.

### 2.2 EMP

EMP, also known as wavelength dispersive spectroscopy (WDS) was performed with a Cameca SX100 on a freshly polished surface of the glass rod along ten equally spaced points through the length of the rod as depicted in Figure 2. Compositional maps were also acquired at three length scales ranging from 5 µm to 500 µm and line scans were obtained from these images.

### 2.3 Raman spectroscopy

Raman spectroscopy was performed with a Renishaw InVia spectrometer equipped with a 1200 lines/grating and a diode laser at a wavelength of 785 nm focused with a 50X objective. Spectra were collected on samples polished with 0.05 microns alumina powder suspensions. A low power of 3 mW and short acquisition times of 10 seconds were used to avoid any photostructural changes. Each spectrum was averaged over four acquisitions.

### 2.4 Heat Capacity Spectroscopy

Heat capacity spectroscopy was performed using a Modulated Differential Scanning Calorimeter model Q1000 from TAInstrument. Approximately 13 mg of Ge-Se glass were ground and inserted in a sealed aluminum pan. An empty aluminum pan was used as a reference. The sample was first heated above $T_g$ to erase its thermal history. Then it was cooled and immediately reheated at 3°C/min while applying a sinusoidal temperature oscillation of period 180 seconds and amplitude 2°C. The complex heat capacity was then obtained by dividing the amplitude of the modulated heat flow by the modulated heating rate, and the imaginary heat capacity $\text{Cp}''$ was obtained from the phase lag as
described in ref [22]. Lissajous curves were plotted to ensure that the response of the heat flow was linear.

2.5 Fourier Transformed Infrared Spectroscopy

Fourier Transformed Infrared Spectroscopy (FTIR) was performed with a Brucker Tensor 27 spectrometer in transmission mode. Transmission spectra were collected on 13mm long glass rods to detect the presence of impurities in the glass. The glass rods were polished on each parallel face using 0.05 microns alumina powder suspensions. The spectra were collected with a resolution of 4 cm^{-1} from 2-18 microns.

3 RESULTS

3.1 Homogeneity of melt-rocked Ge-Se glasses

3.1.1 Electron Microprobe Analysis

The homogeneity of the melt-rocked GeSe_{4} sample was characterized over the length of a ~ 6 cm rod and down to the micron scale. The sample was found to be chemically homogeneous from the macroscale down to the microscale. The macroscale homogeneity was characterized by measuring the composition along 10 fixed points throughout the rod length, as depicted in Figure 2(c). The local stoichiometries reported in Table I indicate that the composition is fixed along the length of the glass rod within the error of the measurement. In order to characterize the homogeneity on the microscale, compositional maps were acquired at scales ranging from millimeters down to microns. The compositional maps for Ge and Se shown in Figure 2(a) demonstrate that the glass is chemically homogeneous down to the micron scale. A compositional line scan along a 2 mm region shown in Figure 2(b) confirms that the composition is homogeneous up to the millimeter scale.
The EMP results therefore clearly indicate that mechanical convection effectively induces the homogeneous dispersal of Ge and Se atoms throughout the entire volume of the glass and down to the microscopic scale.

3.1.2 Raman Spectroscopy

In order to confirm that the glass is not only compositionally homogeneous but also structurally homogeneous, Raman spectra were acquired along the same 10 points shown in Figure 2(c). The 10 spectra superimposed in Figure 3 are identical within the noise of the measurements. This result indicates that the melt-rocked GeSe$_4$ glass is also structurally homogeneous throughout the entire volume of the sample.

The Raman data therefore also confirm that mechanical convection is an effective method for homogenizing chalcogenide melts on the macroscale in only a few hours.

3.2 Comparison of glasses produced by static synthesis and active convection

In order to compare the effect of synthesis methods on physical properties, two glasses were synthesized from the same batch of elements following the melt-rocked method and the static method of Bhosle et al. \textsuperscript{6}. Their physical, structural and dynamic properties were then characterized for comparative analysis.

3.2.1 Molar Volume

The molar volume was selected as a relevant physical property due to the broad literature data available for comparison. The molar volumes of the rocked and static glasses were also compared with that of a purified glass produced by distillation\textsuperscript{21}. The molar volumes of the rocked and static glasses were identical within experimental error with values of 17.92(2) and 17.93(2) cm$^3$·mol$^{-1}$,
respectively. These values are in line with literature data and well within the range of reported values, as shown in Figure 4. The purified glass had a molar volume of 17.88(2), which is slightly lower but still within the error bar and consistent with the fact that it was synthesized in different conditions and may have been subjected to a slightly different thermal history. In comparison, the molar volume reported by Bhosle et al. is far in excess and well outside of the range of literature values. The systematic deviation observed for the data of Bhosle et al. in Figure 4 confirm the systematic deviation previously discussed in Figure 1. Overall, the results of Figure 4 demonstrate that glasses produced by static synthesis or active convection (rocking) have identical molar volumes when they are subjected to the same thermal history. Hence, rapid convective melt homogenization in a rocking furnace leads to the same molar volume as relying solely on diffusion for melt homogenization. It is not clear why the results of Bhosle et al. are systematically different from the rest of the literature.

3.2.2 Raman Spectroscopy
A potential structural difference between the rocked, static and purified glass was also investigated by Raman spectroscopy. The three Raman spectra shown in Figure 5 are identical except for a minute decrease in intensity (~2.5%) of the edge-sharing peak at 213 cm\(^{-1}\) for the purified glass. This minute structural difference is consistent with the lower molar volume observed in Figure 4. These results confirm that static diffusion and mechanical convection lead to glasses with identical structures.

3.2.3 Heat Capacity Spectroscopy
Heat capacity spectroscopy was used to investigate the dynamic properties of the two GeSe\(_4\) glasses. Heat capacity spectroscopy consists in applying a sinusoidal temperature oscillation superimposed on a linear temperature ramp\(^{22,24}\). This permits to collect the imaginary component of the heat capacity \(C_p''\) to characterize the distribution of relaxation times in the glass\(^{24}\). The \(C_p''\) constitutes a very fine probe of dynamic heterogeneities in the system and it was previously used to characterize the distribution of density fluctuations in amorphous Se \(^{22}\), as well as the dynamics of molecular
inclusions in As-Se glasses. Glasses of different compositions have very distinct responses, as shown in Figure 6 for GeSe$_9$ and GeSe$_3$. Compositional heterogeneity in the glass would therefore generate multiple distinct $C_p^*$ peaks as previously shown for As-Se glasses. Instead, the GeSe$_4$ glasses synthesized statically and through convection show a single identical peak within the noise of the measurement. This result demonstrates that the melt-rocked glass is dynamically homogeneous and that static diffusion and mechanical convection lead to glasses with identical dynamic properties.

### 3.3 Effect of impurities

Previous studies have suggested that the difference in physical properties observed in Figure 1 may be due to the presence of impurities such as water and oxygen. However, no attempt at characterizing the impurity content was made to support that conjecture. In order to investigate the possible effect of impurities on the glass properties, the level of impurity was characterized by measuring infrared transmission throughout long rods of glass (13 mm). Infrared spectroscopy is a very sensitive technique for detecting the vibrational modes of impurities in chalcogenide glasses, as shown in Figure 7. The presence of impurities is revealed by the mode of molecular H$_2$O at 6.31 µm as well as O-H (2.9 µm), Se-H (4.57 µm), and Ge-O (7.9 and 12.6 µm) modes.

The glass produced following the method of Bhosle et al. (192h) was found to contain molecular H$_2$O while the two other glasses do not. This is consistent with the difference in conditioning of the synthesis tubes. The tubes used following the method of Bhosle et al. were dried at 90°C while the tubes used for the rocked glass were baked at 800°C to remove water molecules adsorbed on the glass surface. Contamination by water is also revealed by the strong O-H and Se-H absorptions in the 192h glass. On the other hand, the presence of oxygen contamination is found in both static and rocked glasses as revealed by the Ge-O modes at 7.9 and 12.6 µm. Based on the intensity of the Ge-O band, the two non-purified glasses contain roughly ~30 ppm of oxygen. This is consistent with the fact that constituent elements were not purified prior to the synthesis and that surface oxidation is known to cause contamination. In contrast, the purified glass was treated with Mg to capture oxygen prior to
sequential distillation.\textsuperscript{21} Oxygen impurities were therefore removed from this glass, as shown by the absence of Ge-O mode at 7.9 µm. For the purified glass, the shoulder near 13 µm corresponds to an overtone of the fundamental network vibration\textsuperscript{1} and is an intrinsic feature of the GeSe\textsubscript{4} glassy backbone.

The FTIR spectra of Figure 7 therefore indicate that the three glasses contain distinct amounts and type of contaminants. In view of the identical physical, structural and dynamic properties reported in Figure 4-6, it can be concluded that the presence of impurities, water in particular, has no significant effect on the measured glass properties for the impurity level investigated.

4 DISCUSSION

The EMP and Raman data of Figure 2&3 conclusively demonstrate that glasses synthesized by mechanical convection in a rocking oven can reach full homogeneity on a macroscopic scale after only 12h of agitation. This result is consistent with the very low viscosity of the melt at the synthesis temperature (950°C). At the beginning of synthesis, atomic diffusion would occur mostly through molten Se due to its much lower melting point, while at the end of synthesis, it would occur throughout the GeSe\textsubscript{4} melt. The viscosity of pure Se is η = 1.3 × 10^{-3} Pa·s and that of GeSe\textsubscript{4} is η = 2.2 × 10^{-3} Pa·s at the synthesis temperature\textsuperscript{27, 28}. Using the Stokes-Einstein equation \( D = k_B T / 6 \pi \eta r \), these viscosities yield a diffusion coefficient \( D = 5.7 \times 10^{-5} \) cm\(^2\)/s for Se and \( D = 3.4 \times 10^{-5} \) cm\(^2\)/s for GeSe\textsubscript{4} assuming an atomic radius of 1.2 Å. The corresponding mean square displacement is \( l = \sqrt{6Dt} \) assuming isotropic diffusion. This yields a diffusion length \( l \sim 180 \) µm for Se and \( l \sim 140 \) µm for GeSe\textsubscript{4} melts over only 1 s. This implies that atomic diffusion can occur over hundreds of microns within seconds of homogenization. This is consistent with the compositional mapping shown in Figure 2(a). This also confirms that the glass is homogeneous at the microscopic scale, as implied by the heat capacity spectroscopy data. In effect, the glass is homogeneous at all length scales down to the level of molecular fragments such as edge and corner sharing tetrahedra which are determined by chemical effect rather than homogenization time.
The present results are in good agreement with a previous study on Ge$_{22}$Se$_{78}$ glasses by Li et al.\textsuperscript{19}. It was found that glasses subjected to homogenization for 34 h and 192 h had identical structures by X-ray diffraction and Raman spectroscopy. The two glasses did not show significant differences in calorimetric properties either. These results are consistent with the Raman spectra and heat capacity spectroscopy data shown in Figure 6&7 and support the idea that homogenization can be achieved in short times.

Finally, it is important to note that the presence of impurities at the level of tens of ppms does not have a significant effect on physical properties such as molar volume and structure. It was previously implied by Bohles et al.\textsuperscript{8} that the presence of water in Ge-Se glasses could account for the difference in molar volume between their glass and the rest of the literature as shown in Figure 1.\textsuperscript{8} However, no spectroscopic or chemical analyses were performed on the glass samples to assess the impurity level and support that assertion. Instead, the FTIR data of Figure 7 provides unambiguous evidence that glasses containing tens of ppms of impurities do not exhibit significant changes in physical properties. The mismatch in molar volume found in Figure 1 for Bhosle et al. therefore cannot be attributed to water impurities as they suggested.

Overall, this study establishes that melt rocking is an effective method for obtaining glasses with homogeneous structures and it therefore support the validity of the large number of studies that uses this method to investigate the structure-property of these glasses as recently reviewed by Zeidler et al.\textsuperscript{20}. These results are also consistent with the broad use of melt-rocking in the manufacture of advanced infrared optics, which require high level of control on the homogeneity of the refractive index\textsuperscript{13}.

5 CONCLUSION

The static homogenization procedure is shown to yield identical glasses as the rock-melting method. Both glasses show identical physical, structural and dynamic properties reported in Figure 4-6, and the melt-rocked glass is found to be fully homogeneous at all length scales down to the microscale. This is consistent with the large diffusion length of hundreds of microns found at the synthesis temperature of 950°C. It can therefore be concluded that static diffusion and mechanical convection lead to glasses with identical structures and properties. In addition these results establish that rock-melting is an efficient method to achieve homogenization at all length scales down to molecular
features at the nanoscale that are determined by chemical effects, not homogenization time. Hence, it is not necessary to wait for self-diffusion to operate over days, as fully homogeneous glasses can be obtained in only 12 h. In addition, it is found that the presence of water and oxygen impurities at the level of tens of ppms does not measurably affect the structure, dynamics and molar volume of the glass.

Acknowledgement

PL acknowledges financial support from NSF-DMR under grant#: 1832817. We also acknowledge TRIF funding through the Kuiper Imaging Center.

† Now at Saint Gobain Research, Northborough, MA 01532
# Now at Advalue Photonics, 2700 E Bilby Rd, Tucson, AZ 85706

REFERENCES

Table I. Elemental analysis by WDS on 10 points along the length of a GeSe₄ rod produced by melt-rocking. The compositional fluctuation between points is well within the standard deviation for each element.

<table>
<thead>
<tr>
<th>Points</th>
<th>Ge</th>
<th>StdDev%</th>
<th>Se</th>
<th>StdDev%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.95</td>
<td>0.39</td>
<td>79.04</td>
<td>1.25</td>
</tr>
</tbody>
</table>
FIGURE 1 Molar volume as a function composition for Ge-Se glasses produced by melt-rocking (Ota et al., Yang et al., Feltz et al., Mahadevan et al.) compared to those produced by static homogenization (Bhosle et al.). Adapted from Ref [13].

FIGURE 2 (a) Compositional maps of a melt-rocked GeSe$_4$ sample acquired by EMP at length scales ranging from millimeters to microns. (b) Compositional line-scan along a 2 mm region. (c) Glass rod used from compositional analysis along 10 equidistant points.

FIGURE 3 Raman spectra collected along a 6 mm long melt-rocked GeSe$_4$ rod at 10 equidistant points (Figure 2c). The structure is identical along the entire length of the glass rod.

FIGURE 4 Molar volume of GeSe$_4$ glasses synthesized statically, melt-rocked, and purified by distillation in comparison to the results of Bhosle et al. and a literature average detailed in Ref.[13]
FIGURE 5 Raman spectra of GeSe₄ glasses produced by mechanical convection for 12h, by static homogenization for 192h and purified through distillation. The structure is identical regardless of the synthesis method.

FIGURE 6 Imaginary component of the heat capacity $C_p''$ of static and melt-rocked GeSe₄ glasses compared to that of GeSe₉ and GeSe₃. The two GeSe₄ glasses have identical dynamic behavior.

FIGURE 7 FTIR spectra of GeSe₄ glasses produced by mechanical convection for 12h, by static homogenization for 192h, and purified through distillation. The samples were 13 mm thick. The presence of impurities is revealed by sharp absorption lines.