

Homogeneity of melt-rocked Ge-Se glasses and the effect of impurities

Pierre Lucas¹, Shuo Cui^{1,†}, Dmitriy P. Bayko¹, Ozgur Gulbitten^{1,2}, Garrett J. Coleman^{1,#}, 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. 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 dynamic 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 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 1⁸⁻¹³. 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.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.^{14, 15} These local atomic organizations are not dependent on homogenization methods as diffusion on that scale would occur within seconds.

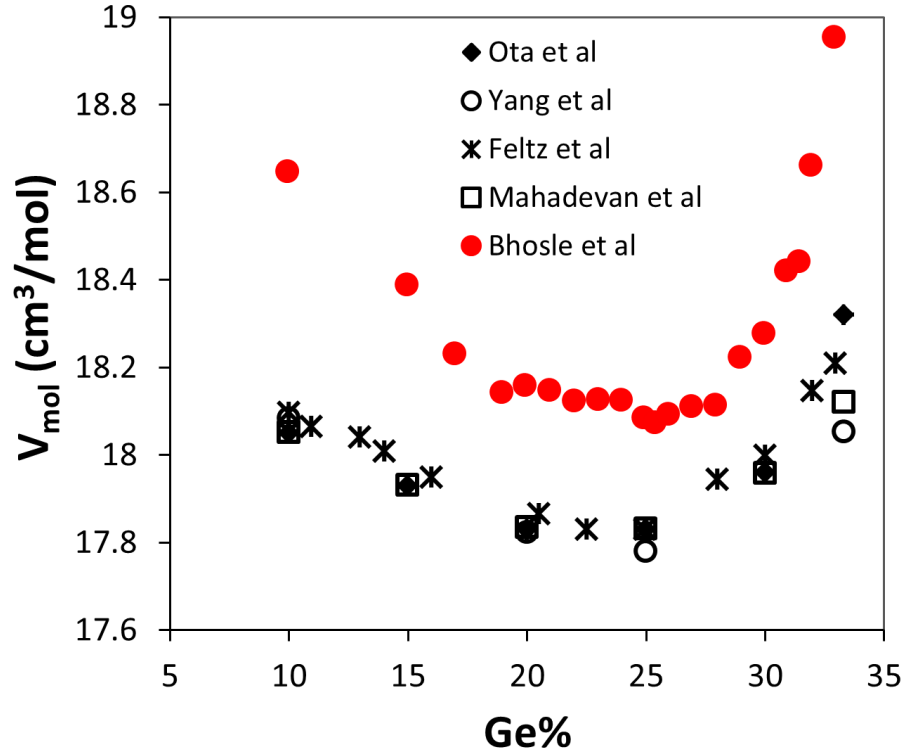


FIGURE 1 Molar volume as a function composition for Ge-Se glasses produced by melt-rocking (Ota *et al.*⁹, Yang *et al.*¹⁰, Feltz *et al.*¹¹, Mahadevan *et al.*¹²) compared to those produced by static homogenization (Bhosle *et al.*⁸). Adapted from Ref [13].

Rocking furnaces have been used by the research community to homogenize chalcogenide melts for more than five decades.^{16, 17} In addition, chalcogenide glasses are currently produced industrially using the melt-rocking method.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 (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 dynamic measured by heat-capacity spectroscopy are all identical, in agreement with

previous studies.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 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 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 Troles²⁰ 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 C_p'' was obtained from the phase lag as described in ref [21]. Lissajous curves were plotted to ensure that the response of the heat flow was linear²¹.

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

The homogeneity of the melt-rocked GeSe₄ 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 GeSe₄ 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.

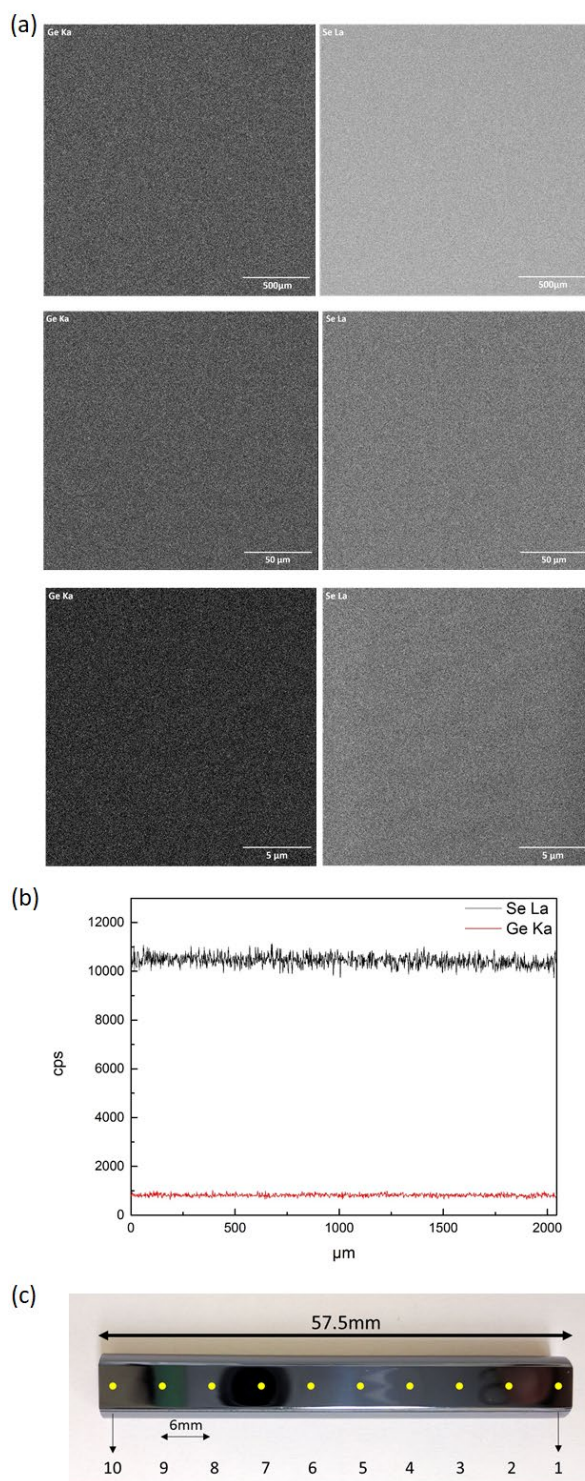


FIGURE 2 (a) Compositional maps of a melt-rocked GeSe_4 sample acquired by EMP at length scales ranging from millimeters to microns. (b) Compositional line-scan along a 2 mm region. (c) Glass rod used from compositional analysis along 10 equidistant points.

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.

Points	Ge		Se	
	Atom%	StdDev%	Atom%	StdDev%
1	20.95	0.39	79.04	1.25
2	20.97	0.39	79.02	1.25
3	20.85	0.39	79.14	1.25
4	20.76	0.39	79.23	1.25
5	20.66	0.38	79.33	1.26
6	20.73	0.38	79.26	1.25
7	20.82	0.39	79.17	1.25
8	20.73	0.38	79.26	1.25
9	20.73	0.38	79.26	1.25
10	20.70	0.38	79.29	1.26

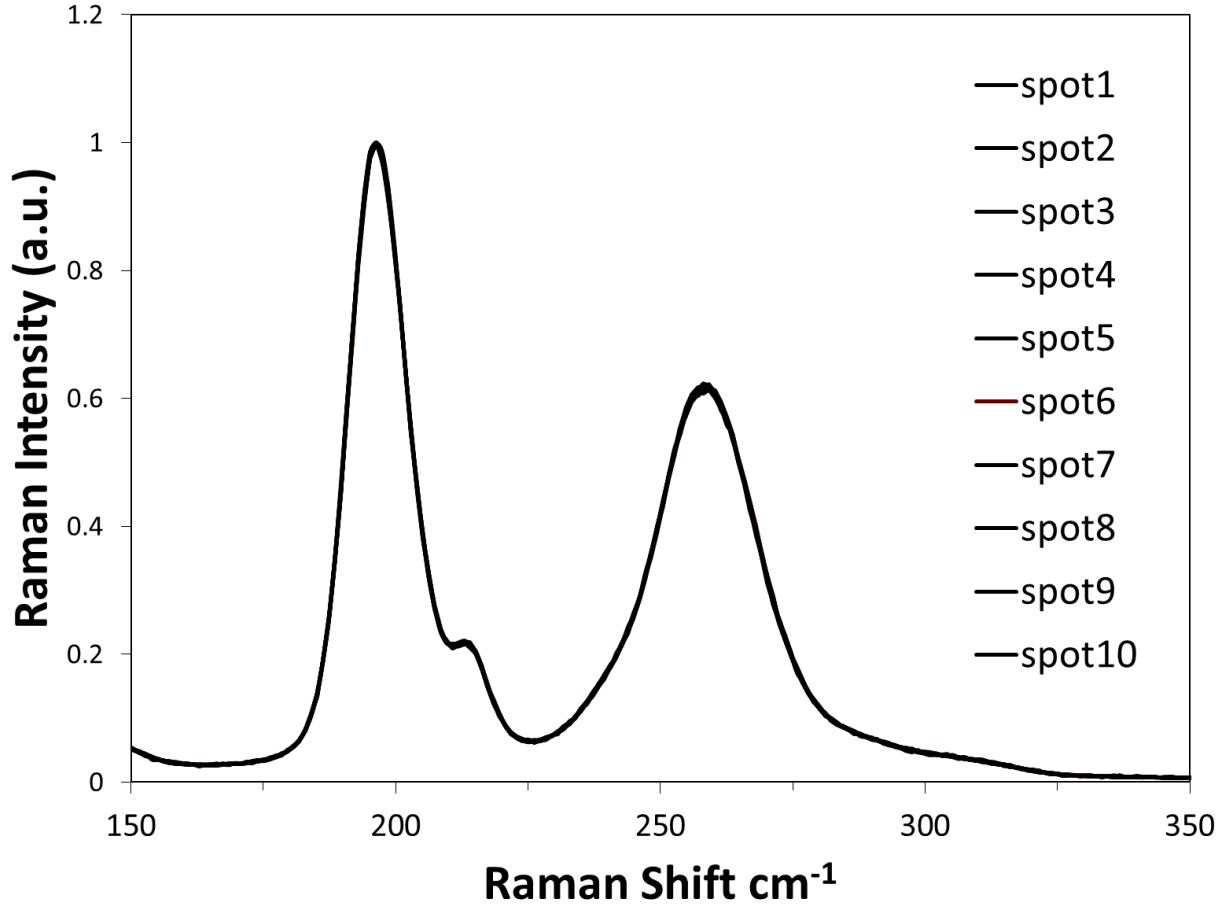


FIGURE 3 Raman spectra collected along a 6 mm long melt-rocked GeSe₄ rod at 10 equidistant points (Figure 2c). The structure is identical along the entire length of the glass rod.

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.*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 distillation²⁰. The molar volumes of the rocked and static glasses were identical within experimental error with values of 17.92(2) and 17.93(2) cm³·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.

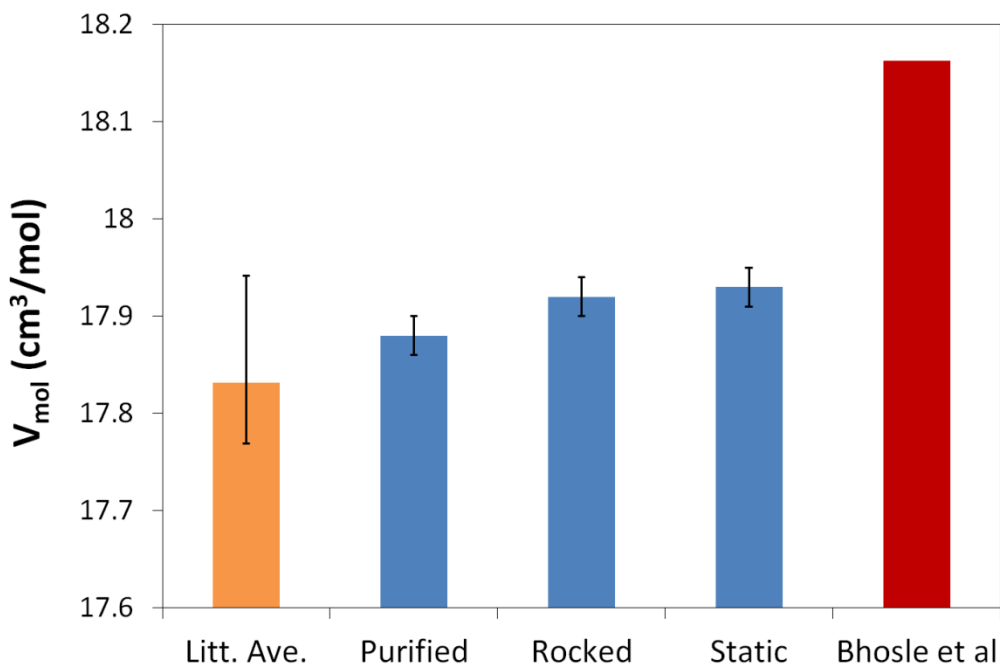


FIGURE 4 Molar volume of GeSe₄ glasses synthesized statically, melt-rocked, and purified by distillation in comparison to the results of Bhosle *et al.*⁶ and a literature average detailed in Ref. [13]

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 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 4²². These results confirm that static diffusion and mechanical convection lead to glasses with identical structures.

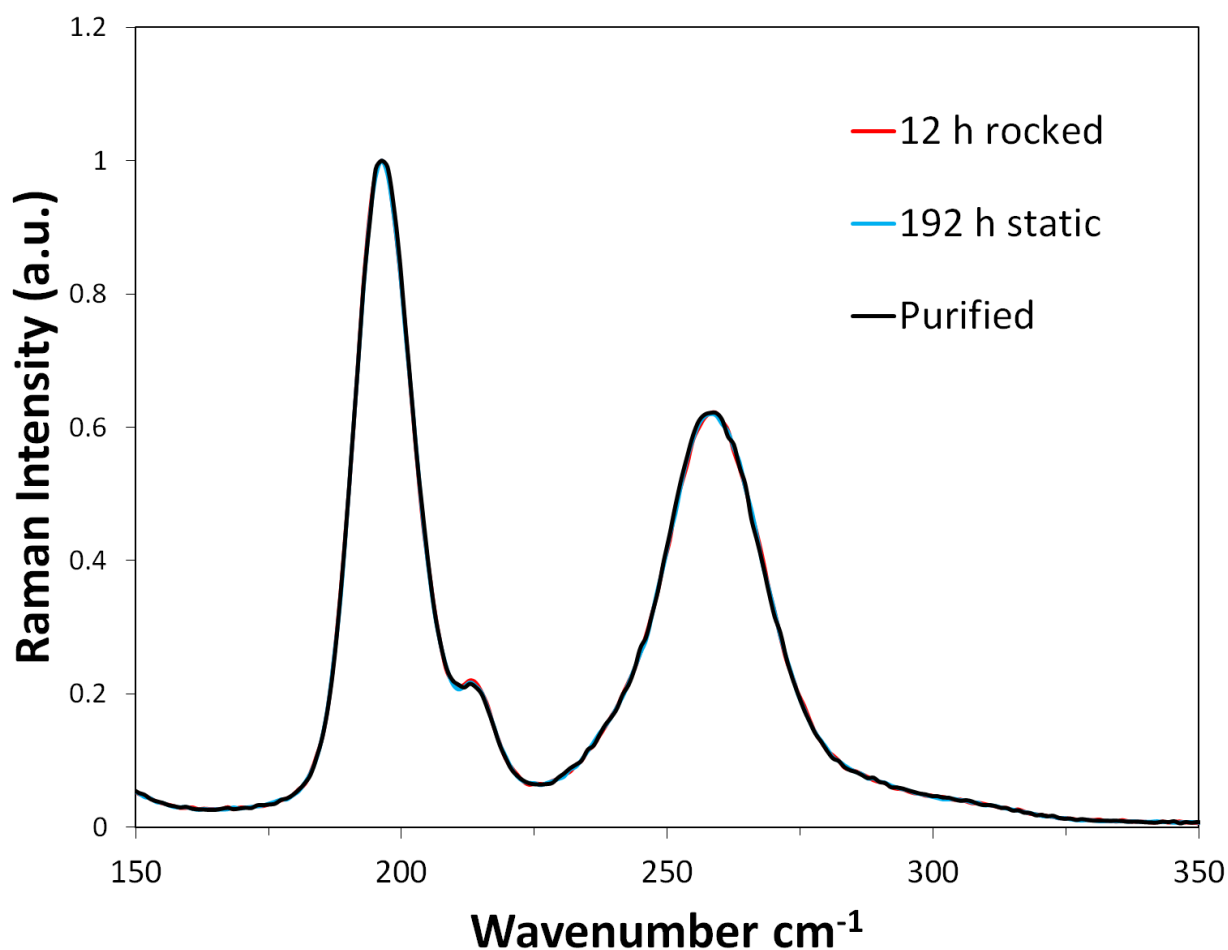


FIGURE 5 Raman spectra of GeSe_4 glasses produced by mechanical convection for 12h, by static homogenization for 192h and purified through distillation. The structure is identical regardless of the synthesis method.

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^{21, 23}. This permits to collect the imaginary component of the heat capacity C_p'' to characterize the distribution of relaxation times in the glass²³. 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 Se²¹, as well as the dynamic of molecular inclusions in As-Se glasses²⁴. 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 glasses²⁴. 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.

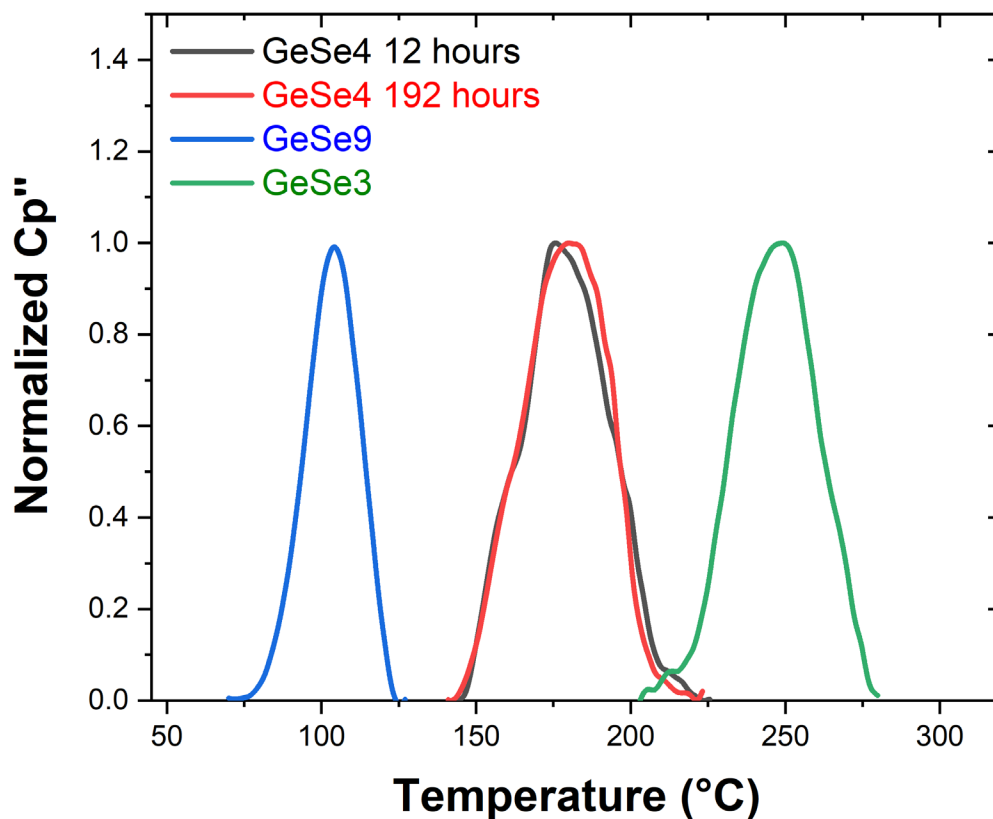


FIGURE 6 Imaginary component of the heat capacity C_p'' of static and melt-rocked GeSe_4 glasses compared to that of GeSe_9 and GeSe_3 . The two GeSe_4 glasses have identical dynamic behavior.

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 oxygen⁸. 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 H₂O 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) modes²⁰.

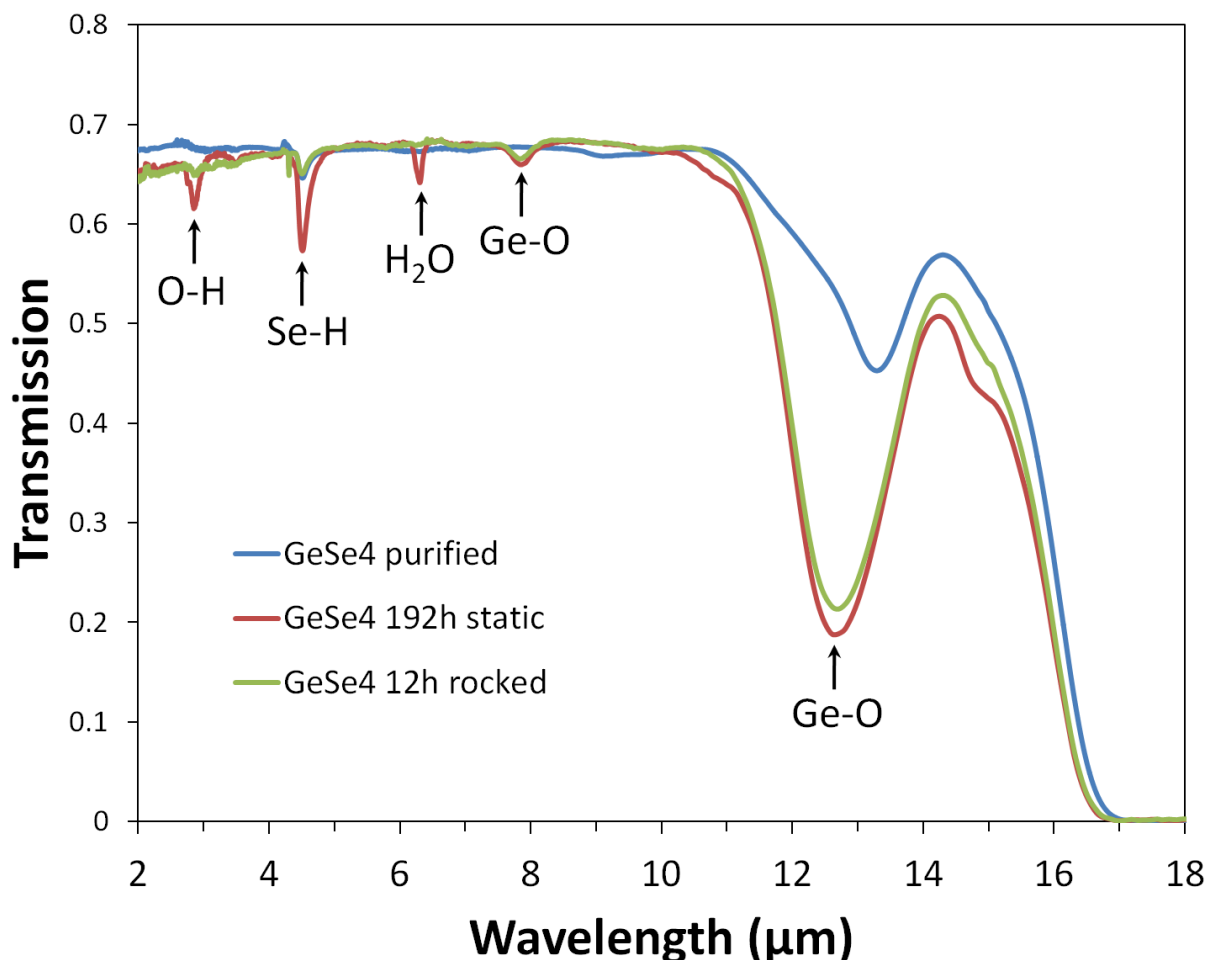


FIGURE 7 FTIR spectra of GeSe₄ glasses produced by mechanical convection for 12h, by static homogenization for 192h, and purified through distillation. The samples were 13 mm thick. The presence of impurities is revealed by sharp absorption lines.

The glass produced following the method of Bhosle *et al.*⁶ (192h) was found to contain molecular H₂O 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°C⁶ 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.²⁵ 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.²⁰ 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 vibration¹ and is an intrinsic feature of the GeSe_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, while at the end of synthesis, it would occur throughout the GeSe_4 melt. The viscosity of pure Se is $\eta = 1.3 \times 10^{-3} \text{ Pa}\cdot\text{s}$ and that of GeSe_4 is $\eta = 2.2 \times 10^{-3} \text{ Pa}\cdot\text{s}$ at the synthesis temperature^{26, 27}. Using the Stokes-Einstein equation $D = k_B T / 6\pi\eta r$, these viscosities yield a diffusion coefficient $D = 5.7 \times 10^{-5} \text{ cm}^2/\text{s}$ for Se and $D = 3.4 \times 10^{-5} \text{ cm}^2/\text{s}$ for GeSe_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 $l \sim 180 \mu\text{m}$ for Se and $l \sim 140 \mu\text{m}$ for GeSe_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 $\text{Ge}_{22}\text{Se}_{78}$ glasses by Li *et al.*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.*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 1.⁸ 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.

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, 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 homogeneization 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, dynamic 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

1. Lucas P, Coleman GJ, Jiang S, Luo T, Yang Z. Chalcogenide glass fibers: Optical window tailoring and suitability for bio-chemical sensing. *Opt Mater (Amsterdam, Neth)*. 2015; 47:530-536.
2. Phillips JC. Topology of covalent non-crystalline solids. I. Short-range order in chalcogenide alloys. *J Non-Cryst Solids*. 1979; 34:153-81.
3. Thorpe MF. Continuous deformations in random networks. *J Non-Cryst Solids*. 1983; 57:355-70.
4. Gupta PK, Mauro JC. Composition dependence of glass transition temperature and fragility. I. A topological model incorporating temperature-dependent constraints. *J Chem Phys*. 2009; 130:094503/1-094503/8.
5. Mauro JC. Topological constraint theory of glass. *Am Cer Soc Bull*. 2011; 90:31-37.
6. Bhosle S, Gunasekera K, Boolchand P, Micoulaut M. Melt homogenization and self-organization in chalcogenides-part I. *Int J Appl Glass Sci*. 2012; 3:189-204.
7. Gunasekera K, Bhosle S, Boolchand P, Micoulaut M. Superstrong nature of covalently bonded glass-forming liquids at select compositions. *J Chem Phys*. 2013; 139:164511/1-164511/9.
8. Bhosle S, Gunasekera K, Boolchand P, Micoulaut M. Melt homogenization and self-organization in chalcogenides-part II. *Int J Appl Glass Sci*. 2012; 3:205-220.
9. Ota R, Yamate T, Soga N, Kunugi M. Elastic properties of Ge-Se glass under pressure. *Journal of Non-Crystalline Solids*. 1978; 29:67-76.

10. Yang G, Gueguen Y, Sangleboeuf J-C, Rouxel T, Boussard-Pledel C, Troles J, et al. Physical properties of the $\text{Ge}_x\text{Se}_{1-x}$ glasses in the $0 < x < 0.42$ range in correlation with their structure. *J Non-Cryst Solids*. 2013; 377:54-59.
11. Feltz A, Aust H, Blayer A. Glass formation and properties of chalcogenide systems XXVI: Permittivity and the structure of glasses $\text{As}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{Se}_{1-x}$. *Journal of Non-Crystalline Solids*. 1983; 55:179-190.
12. Mahadevan S, Giridhar A, Singh AK. Elastic properties of Ge-Sb-Se glasses. *Journal of Non-Crystalline Solids*. 1983; 57:423-430.
13. Lucas P, Coleman GJ, Sen S, Cui S, Guimond Y, Calvez L, et al. Structural and chemical homogeneity of chalcogenide glass prepared by melt-rocking. *J Chem Phys*. 2019; 150:014505/1-014505/9.
14. Rowlands RF, Zeidler A, Fischer HE, Salmon PS. Structure of the Intermediate Phase Glasses GeSe_3 and GeSe_4 : The Deployment of Neutron Diffraction With Isotope Substitution. *Frontiers in Materials*. 2019; 6.
15. Gjersing EL, Sen S, Aitken BG. Structure, Connectivity, and Configurational Entropy of $\text{Ge}_x\text{Se}_{100-x}$ Glasses: Results from ^{77}Se MAS NMR Spectroscopy. *J Phys Chem C*. 2010; 114:8601-8608.
16. Nemilov SV, Petrovskii GT. Viscosity of oxygen-free vitrified systems. II. Study of the viscosity of glasses in the selenium-arsenic system. *Zh Prikl Khim (S-Peterburg, Russ Fed)*. 1963; 36:977-81.
17. Golovchak R, Jain H, Shpotyuk O, Kozdras A, Saiter A, Saiter JM. Experimental verification of the reversibility window concept in binary As-Se glasses subjected to a long-term physical aging. *Phys Rev B: Condens Matter* 2008; 78:014202/1-014202/6.
18. Guimond Y, Bellec Y, Rogers K. A new moldable infrared glass for thermal imaging and low cost sensing. *Proc SPIE-Int Soc Opt Eng*. 2007; 6542:654225/1-654225/6.
19. Li P, Zhang Y, Chen Z, Gao P, Wu T, Wang L-M. Relaxation dynamics in the strong chalcogenide glass-former of $\text{Ge}_{22}\text{Se}_{78}$. *Scientific Reports*. 2017; 7:40547.
20. Troles J, Shiryayev V, Churbanov M, Houizot P, Brilland L, Desevedavy F, et al. GeSe_4 glass fibres with low optical losses in the mid-IR. *Opt Mater (Amsterdam, Neth)*. 2009; 32:212-215.
21. Gulbitten O, Mauro JC, Lucas P. Relaxation of enthalpy fluctuations during sub- T_g annealing of glassy selenium. *J Chem Phys*. 2013; 138:244504/1-244504/7.
22. Edwards TG, Sen S. Structure and Relaxation in Germanium Selenide Glasses and Supercooled Liquids: A Raman Spectroscopic Study. *J Phys Chem B*. 2011; 115:4307-4314.
23. Birge NO, Nagel SR. Specific-heat spectroscopy of the glass transition. *Phys Rev Lett*. 1985; 54:2674-7.
24. Yang G, Gulbitten O, Gueguen Y, Bureau B, Sangleboeuf J-C, Roiland C, et al. Fragile-strong behavior in the $\text{As}_x\text{Se}_{1-x}$ glass forming system in relation to structural dimensionality. *Phys Rev B: Condens Matter* 2012; 85:144107/1-144107/8.
25. Nishii J, Yamashita T, Yamagishi T. Oxide impurity absorptions in Ge-Se-Te glass fibres. *Journal of Materials Science*. 1989; 24:4293-4297.
26. Ruska J, Thurn H. Change of short-range order with temperature and composition in liquid germanium selenide ($\text{Ge}_x\text{Se}_{1-x}$) as shown by density measurements. *J Non-Cryst Solids*. 1976; 22:277-90.
27. Glazov VM, Situlina OV. Physicochemical analysis of Group IV element-selenium binary liquid systems. *Doklady Akad Nauk SSSR*. 1969; 187:799-802.