Structure and Properties of Off-Stoichiometric Ba-Ga-Ge Selenide Glasses

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Abstract

Off-stoichiometric glasses in the Ba-Ga-Ge-Se system with Se excess or deficiency ($\text{BGGSe}_{\pm\text{Se}}$) are synthesized and their structure is characterized using Raman and multinuclear (^{77}Se , ^{71}Ga) magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The results reveal that the structure of these off-stoichiometric $\text{BGGSe}_{\pm\text{Se}}$ glasses consists of a charge-compensated, partially covalent network of corner-sharing (Ga/Ge) Se_4 tetrahedra where $[\text{GaSe}_4]^-$ tetrahedra charge balance the Ba^{2+} cations. Addition of excess Se to a stoichiometric $\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ glass with $\text{BaSe}:\text{Ga}_2\text{Se}_3 > 1$ results in the formation of Se-Se linkages, while Se deficiency is accommodated via the formation of homopolar Ge-Ge bonds, in agreement with the continuously-alloyed structural scenario of purely covalent chalcogenide glasses. Such composition-dependent structural evolution is shown to be consistent with the corresponding variation in density and glass transition temperature.

1. Introduction

Chalcogenide glasses are important candidate materials for wide ranging technological applications in the areas of phase change memory, infra-red photonics, sensors and solid-state batteries [1-6]. Although many studies can be found in the literature that have focused on establishing structure-property relationships for network chalcogenide glasses in the system Ge-As-P-X (X=S, Se, Te) [7-13], relatively little is known about such glasses that contain network modifying alkali and/or alkaline-earth elements [14-21]. In this regard, the ternary stoichiometric chalcogenide glasses in the system $M_2Se(M'Se)-Ga_2Se_3-GeSe_2$ (M = alkali, M' = alkaline earth) are particularly interesting as they are isoelectronic with oxide glasses in the system $M_2O(M'O)-Al_2O_3-SiO_2$ that have been extensively studied in the literature.

The composition dependent changes in the structures of modified and charge-compensated $M_2Se(M'Se)-Ga_2Se_3-GeSe_2$ glasses can be potentially described using two different models. The first is the continuous-alloying model which is typically associated with network chalcogenide glasses [12, 13]. In this structural model the constituent Group IV, V and VI atoms in the covalently bonded network are characterized by nearest-neighbor coordination numbers that are given by the 8-N rule where N is the number of valence electrons. As a result, the structure of glasses at stoichiometric compositions such as GeX_2 and As_2X_3 consist primarily of corner-sharing, heteropolar-bonded GeX_4 and AsX_3 coordination polyhedra. Off-stoichiometry in the form of excess X (chalcogen-excess) therefore results in the formation of homopolar X-X bonds within the structural network, while a deficiency of X atoms results in the formation of metal-metal bonds to satisfy the 8-N rule. Such continuous alloying allows chalcogenide glasses to be formed over relatively wide ranges of compositions.

The second structural model is the charge-compensated network scenario of oxide glasses such as those in the systems $M_2O(M'O)-Al_2O_3-SiO_2$ with more ionic character of bonding compared to chalcogenides. The compositional evolution of the structure of charge-compensated $M_2O(M'O)-Al_2O_3-SiO_2$ glasses is better described in terms of the ratio $R = M_2O(M'O):Al_2O_3$. For $R = 1$, every atom of oxygen introduced through $M_2O(M'O)$ completes one formula unit of Al_2O_4 , or two $AlO_{4/2}$ tetrahedra, which effectively replaces two $SiO_{4/2}$ units in the tetrahedral network. $R > 1$ thus implies that there is an excess of oxygen atoms, which break the corner-shared tetrahedral network to form non-bridging oxygen. Similarly, $R < 1$ implies a deficiency of oxygen atoms, which causes the formation of five-fold and six-fold coordinated Al [22].

Recent studies by us [23-27] have addressed the structure-property relationships in stoichiometric glasses in the systems $Na_2Se-Ga_2Se_3-GeSe_2$ (NGGS) [26] and $BaSe-Ga_2Se_3-GeSe_2$ (BGGS) [23, 25] to elucidate the structural effects of modifier addition and to determine which of the two aforementioned scenarios provides a better description of the structure of modified chalcogenide glasses. These studies have demonstrated that the stoichiometric $Ga_2Se_3-GeSe_2$ (GGS) glasses generally behave according to the continuous-alloying structural scenario while the BGGS and NGGS glasses exhibit aspects of both structural models. In particular, glasses in the latter two systems tend to form Ge-Ge homopolar bonds for compositions with $R < 1$ where $R = Na_2Se(BaSe):Ga_2Se_3$, while non-bridging Se are thought to form in glasses with $R > 1$. It should be noted that since addition of Na_2Se or $BaSe$ introduces Se atoms into the structure, $R > 1$ ($R < 1$) implies an excess (deficiency) of Se with respect to the amount required to satisfy heteropolar tetrahedral bonding for Ga and Ge atoms in the network. In this study, we investigate the structural characteristics of off-stoichiometric $BGGS_{\pm Se}$ glasses with fixed R using Raman and nuclear magnetic resonance (NMR) spectroscopy. Given the lack

of studies in the literature concerning non-stoichiometric chalcogenide glasses containing M(M')-type modifiers, the objective of this investigation is two-fold, namely: 1) to determine the extent of glass formation and, 2) to elucidate the structural role of Se-excess or deficiency, in modified selenide networks with off-stoichiometry. The composition-dependent structural evolution of these glasses is then linked to the corresponding variation in density and glass transition temperature T_g .

2. Experimental

2.1 Sample preparation

Glasses in the system $(\text{BaSe})_x-(\text{Ga}_2\text{Se}_3)_{100-x-y}-(\text{GeSe}_2)_y \pm (\text{Se})_z$ were synthesized using the melt-quench method where special care was taken to minimize the uptake of oxygen by elemental Ba. As a first step, the Ba-free Ga-Ge-Se precursor alloy was prepared by batching the constituent elements in a dry nitrogen atmosphere. The batches were loaded into fused silica ampules evacuated to $\sim 10^{-5}$ torr. Loaded ampules were flame sealed and placed into a rocking furnace, and the temperature was slowly ramped to 950 °C over several hours. The melts were rocked for ~ 1.5 days and water-quenched. In the second step, these GaGeSe precursor alloys were mixed in a dry nitrogen atmosphere with the appropriate amount of Ba to create 10 g final batches that were loaded into fused-silica ampules whose inner walls were pre-coated with a thin layer of Si by vapor deposition. These ampules were then evacuated and flame-sealed. The temperature was then slowly ramped to 900 °C in order to minimize corrosion of the Si film. The melts were rocked for ~ 3 hours, followed by quenching in water.

For purposes of comparison, the compositions of off-stoichiometric BGGS $\pm$ Se glasses are based on previously studied stoichiometric BGGS glasses, where $y = 60$ and 75 [23, 25]. In

this way, four series of off-stoichiometric glasses were synthesized with $y = 60$, where $x = 7.5$, 15, 25, and 32.5. Similarly, three series were synthesized with $y = 75$, where $x = 5$, 12.5, and 20. The deviation of Se from stoichiometry expressed as z (in mol%) ranged between -40 and $+20$ and was calculated relative to the Se content in the corresponding stoichiometric glass. For example, a BGGS $\pm$ Se glass of composition $(\text{BaSe})_{20}-(\text{Ga}_2\text{Se}_3)_5-(\text{GeSe}_2)_{75}+(\text{Se})_{10}$ contains 10% more total moles of Se compared to the stoichiometric glass $(\text{BaSe})_{20}-(\text{Ga}_2\text{Se}_3)_5-(\text{GeSe}_2)_{75}$. The glass compositions synthesized in this study are reported in Table 1 and in graphical form in Figure 1. These glass compositions will hereafter be referred to using the notation $(y)\text{Ba}(x)+(z)\text{Se}$, where x is the BaSe content, y is the GeSe_2 content, and z is the off-stoichiometric content of Se, all in mole percent.

2.2 Raman spectroscopy

The Raman spectra of all glasses were collected using a Bruker RFS 100/S Fourier-transform (FT) Raman spectrometer equipped with a Nd:YAG laser operating at a wavelength of 1064 nm. Each Raman spectrum is the average of 32–256 scans collected in backscattering geometry using a resolution of 4 cm^{-1} and laser power ranging between 32 and 75 mW.

2.3 NMR spectroscopy

All ^{77}Se and ^{71}Ga NMR spectroscopic measurements were carried out at an external magnetic field of 11.7 T using a Bruker Avance spectrometer operating at the Larmor frequencies of 152.5 and 95.3 MHz for ^{71}Ga and ^{77}Se , respectively. The ^{77}Se magic-angle-spinning (MAS) NMR spectra were collected using a rotor synchronized Hahn-echo pulse sequence with a $\pi/2$ pulse length of 2.5 μs . Crushed glass samples were taken in a 4 mm ZrO_2 rotor and were spun at 12.5 kHz. A recycle delay of 120 s was employed for all glasses and no differential relaxation was observed when the delay was increased to 300 s. 300–500 scans were

averaged and Fourier transformed to obtain each ^{77}Se MAS NMR spectrum. All ^{77}Se chemical shifts were referenced to the isotropic ^{77}Se chemical shift δ_{iso} of crystalline $(\text{NH}_4)_2\text{SeO}_4$ ($\delta_{\text{iso}} = 1040.2\text{ppm}$) [28].

High-resolution ^{71}Ga NMR spectra were obtained using the quadrupolar magic-angle-turning (QMAT) pulse sequence as reported in the literature [29]. Crushed samples were taken in a 7 mm ZrO_2 rotor and spun at 7 kHz. QMAT NMR is a two-dimensional technique that uses linearly varying delays between ten central transition selective pulses to yield an “infinite” spinning speed MAS spectrum. The central transition selective $\pi/2$ and π pulse lengths were 1.3 and 2.6 μs respectively, corresponding to a radio frequency field of 112 kHz. A total of 32 t_1 increments were employed over a single rotor period. 10k transients were collected for each t_1 slice using a 0.2 s relaxation delay between each transient, allowing a full 2D spectrum to be acquired in under 18 hrs. The “infinite” spinning speed ^{71}Ga MAS NMR spectra were obtained through summation of the 32 t_1 increments after shearing and Fourier transforming both direct and indirect dimensions. All ^{71}Ga chemical shifts were referenced to the isotropic chemical shift of 1 M $\text{Ga}(\text{NO}_3)_3$ ($\delta_{\text{iso}} = 0\text{ ppm}$).

2.4 Density measurements

Density measurements were carried out using a Micromeritics AccuPyc II gas expansion pycnometer under a helium environment of 6N purity. Approximately 0.5–2.0 g of each sample was loaded into a 1 cm^3 cup. Reported densities are averages of 10 consecutive measurements at 20 $^\circ\text{C}$ and are determined to within $\pm 0.005\text{ g/cm}^3$.

2.5 Differential scanning calorimetry (DSC)

Conventional DSC scans were taken using a Mettler-Toledo DSC1 calorimeter. Scans were performed in a flowing nitrogen environment on 15–20 mg of sample loaded into 40 μL

aluminum crucibles. The glass transition temperature T_g is determined as the onset of the glass transition region, when heating at a rate of 10 K/min.

3. Results

3.1 Mapping the glass-forming region in the BGGS±Se system with off-stoichiometry

Figure 1 shows the tentative glass-forming region, as determined by the lack of any detectable evidence of crystallization in the powder x-ray diffraction patterns of BGGS and BGGS±Se glasses. It was shown in previous studies of stoichiometric BGGS glasses [23, 25] that glass formation is favored toward the edges of the ternary composition space—that is, toward pure GeSe₂ and the binary tie lines between Ga₂Se₃-GeSe₂ and BaSe-GeSe₂, but away from the region near R = 1, i.e. BaSe:Ga₂Se₃ = 1:1. A lack of glass formation near R = 1 was also observed in the analogous sulfide system BaS-Ga₂S₃-GeS₂ [17] and it suggests that in both the sulfide and selenide systems, devitrification near the center of the ternary diagram might be attributed to the existence of crystalline phases such as Ba_{2.7}Ga_{5.4}Ge_{3.6}S₁₈ [16] and BaGa₂GeX₆ (X = S, Se) [30, 31], where the ratio of BaX:Ga₂X₃ is 1:1.

Addition of BaSe to binary Ga₂Se₃-GeSe₂ slightly increases the maximum allowable content of Ga₂Se₃ for glass formation from 30 mol% to at least 32.5 mol%, which is consistent with the similar effect of the addition of Na₂Se as reported in a recent study on glasses in the stoichiometric Na₂Se-Ga₂Se₃-GeSe₂ system [26]. Along the BaSe-GeSe₂ binary, there have been reports of crystalline compounds such as Ba₂GeSe₄ [32] and Ba₂Ge₂Se₅ [33]; however, information about glass formation remains lacking. The same is true for the BaSe-Ga₂Se₃ binary, which contains crystalline compounds such as BaGa₂Se₄ [34], BaGa₄Se₇ [35, 36], Ba₅Ga₂Se₈ [37], and Ba₅Ga₄Se₁₀ [38].

For the off-stoichiometric Se-excess or Se-deficient $\text{BGGS}_{\pm}\text{Se}$ compositions that are above or below the plane of the ternary $\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ composition space, the trend in glass-forming ability changes only slightly. In general, the glass formation tends to be favored for compositions that contain an excess of Se over stoichiometry or contain a high ratio of $\text{BaSe:Ga}_2\text{Se}_3$. The largest glass-forming ranges with respect to Se content were observed for the two series based on the stoichiometric glasses $75\text{Ba}20+0\text{Se}$ and $60\text{Ba}32.5+0\text{Se}$, where glasses could be made for z values between -30 and $+20$ for the former and between -20 and $+20$ for the latter. Therefore, in the subsequent discussion we specifically focus on the structure-property relationships in glasses that belong to these two series.

3.2 Raman spectroscopy

The Raman spectra of the two series with the greatest number of glassy samples, i.e. $75\text{Ba}20+(z)\text{Se}$ and $60\text{Ba}32.5+(z)\text{Se}$, are shown in Figures 2 and 3 and are normalized to the intensity of the peak near 200 cm^{-1} . Regardless of composition, all Raman spectra exhibit three general regions that are characteristic of vitreous Ga-Ge-Se networks [39-41]: i) a broad, relatively featureless band extending from $\sim 50\text{ cm}^{-1}$ to 160 cm^{-1} ; ii) a group of three peaks located at $\sim 175\text{ cm}^{-1}$, $\sim 200\text{ cm}^{-1}$, and $\sim 215\text{ cm}^{-1}$; and iii) a high wavenumber band extending from about 225 cm^{-1} to 340 cm^{-1} . The peak at 200 cm^{-1} in region (ii) is generally the major feature in the Raman spectra of binary $\text{Ga}_2\text{Se}_3\text{-GeSe}_2$ glasses and corresponds to the symmetric A_1 vibrations of corner-sharing (CS) $(\text{Ga/Ge})\text{Se}_4$ tetrahedra that make up the backbone of the structural network. The neighboring peaks at 175 cm^{-1} and 215 cm^{-1} can be attributed to the vibrations of Ge-Ge bonds in ethane-like $(\text{Se}_3)\text{Ge-Ge}(\text{Se}_3)$ units and Ge-Se bonds in edge-sharing (ES) $(\text{Ga/Ge})\text{Se}_4$ tetrahedra, respectively. In region (i), the low wavenumber band contains various bond-bending modes, while the high wavenumber band in region (iii) consists of many

overlapping bands that may include the symmetric stretching of Se chains near 270 cm^{-1} and the asymmetric vibration of GeSe_4 tetrahedra near 310 cm^{-1} . It should be noted at this point that the relatively sharp feature exhibited by all of the Raman spectra near 85 cm^{-1} is a background signal from the sample holder.

As excess Se is added to the stoichiometric glass $75\text{Ba}20+0\text{Se}$ (Fig. 2), the intensities of both peaks near 175 cm^{-1} and 215 cm^{-1} (henceforth denoted as I_{175} and I_{215}) decrease. I_{175} decreases abruptly to zero as z increases from 0 to $\geq +10$, while the decrease in I_{215} is more gradual such that residual intensity remains even at $z = +20$. Additionally, increasing z results in the appearance and progressive growth of a new band near 265 cm^{-1} . On the other hand, for Se-deficient glasses with negative z , I_{215} again decreases to zero for $z < -10$ while I_{175} shows a sharp increase with decreasing values of z and even exceeds the intensity of the primary peak (I_{200}) for $z < -20$. Increasing Se deficiency (decreasing z) also results in a continuous increase of the intensities of regions (i) and (iii). Since all spectra are normalized to I_{200} , and the ratio of the intensities in regions (i) and (iii) remains approximately constant, this observation may alternatively be interpreted as a continuous decrease in I_{200} . The Raman spectra of glasses in the $60\text{Ba}32.5+(z)\text{Se}$ series (Fig. 3) largely exhibit the same trends seen in the $75\text{Ba}20+(z)\text{Se}$ series, with the most notable differences being the lack of intensity near 175 cm^{-1} at $z = 0$ as well as less definition in the peak shoulders near $\sim 215\text{ cm}^{-1}$ and 240 cm^{-1} .

3.3 NMR spectroscopy

The ^{77}Se MAS NMR spectra of three representative glasses in the $75\text{Ba}20+(z)\text{Se}$ series with $z = +20$, 0, and -30 are compared in Figure 4. These spectra exhibit a broad lineshape extending from about 750 ppm to 50 ppm that resembles Se in glassy Ge-Se and Ga-Ge-Se networks. In general, these spectra can be modeled using a set of three peaks centered near 600,

400, and 250 ppm that respectively correspond to the following Se environments: 1) Ge-**Se**-Ge in ES (Ga/Ge)Se₄ tetrahedra or Ge-**Se**-Se linkages between chains and tetrahedra, 2) Ge-**Se**-Ge in CS (Ga/Ge)Se₄ tetrahedra, and 3) Ge-**Se**-Ge in (Se₃)Ge-Ge(Se₃) ethane-like units that contain Ge-Ge homopolar bonds [9, 24, 27, 42]. In the ⁷⁷Se MAS NMR spectrum of the 75Ba20+0Se glass, the lineshape is essentially symmetric and centered near 400 ppm with possible small contributions from the resonances near 600 ppm and 250 ppm. As z is increased from 0 to +20, the ⁷⁷Se MAS NMR spectrum remains largely the same except for a small increase in intensity near ~ 650 ppm, which makes the line shape slightly wider and more asymmetric. In contrast, when z is decreased from 0 to -30, the center of gravity of the ⁷⁷Se MAS NMR line shape shifts significantly to ~250 ppm and broadens, due to a drastic increase in the contribution from resonances at lower frequencies. The ⁷⁷Se MAS NMR spectra of the 60Ba32.5+(z)Se glasses with z = +20, 0, and -20 show similar behavior as a function of z (Fig. 5).

Figure 6 shows the ⁷¹Ga central transition QMAT NMR spectra of the 75Ba20+(z)Se glasses with z = +20 and -30. These spectra, unlike their MAS counterparts, are free of spinning sidebands and are characterized by a single resonance that exhibits a maximum near 130 ppm and a low frequency tail that is typical of MAS NMR spectra of quadrupolar nuclides in disordered materials where it is associated with a distribution of quadrupolar coupling constants C_Q [43, 44]. Simulation of the lineshape using the Czjzek model of distribution of C_Q in the software DMfit [45] yields an isotropic chemical shift $\delta_{\text{iso}} \approx 180$ ppm and a quadrupolar coupling constant C_Q ≈ 10 MHz, which is in good agreement with the parameters reported for the ⁷¹Ga MAS NMR spectra corresponding to the tetrahedral GaSe₄ environment found in stoichiometric BGGS glasses [25]. As a result, it seems reasonable to conclude that the nearest-neighbor coordination environment of Ga atoms remains unaffected by the departure from stoichiometry.

3.4 Glass transition temperature T_g

The T_g of glasses in the $75\text{Ba}20+(z)\text{Se}$ series are shown in Figure 7, as the most complete and representative set for the off-stoichiometric $\text{BGGs}\pm\text{Se}$ glasses. The T_g values range between $\sim 280^\circ\text{C}$ and 400°C . As $|z|$ increases, i.e. as the Se content deviates from stoichiometry, the T_g decreases from the maximum value of about 395°C for $z = 0$. In glasses with Se excess ($z > 0$) the T_g drops precipitously by over 100°C as z increases from 0 to +20. In the Se-deficient regime ($z < 0$), T_g decreases less rapidly from $z = 0$ to $z = -20$ and subsequently levels off slightly around $z = -30$.

3.5 Glass density

Density and molar volume data for glasses in the $75\text{Ba}20+(z)\text{Se}$ series are shown in Figure 8. The densities of all glasses range between $\sim 4.4\text{ g/cm}^3$ and 4.9 g/cm^3 and exhibit a monotonic drop with increasing z , although the rate of change is lower in the Se-excess regime compared to that in the Se-deficient regime. Molar volume shows an exactly opposite trend compared to density.

4. Discussion

When taken together, both the Raman and NMR spectra indicate that the structure of off-stoichiometric $\text{BGGs}\pm\text{Se}$ glasses with an excess or deficiency of Se is characterized by the same network of primarily corner-sharing and some edge-sharing $(\text{Ga/Ge})\text{Se}_{4/2}$ tetrahedra found in the stoichiometric BGGs and GGS glasses. In this network, Ga and Ge both adopt four-fold coordination, regardless of composition, while Se primarily adopts two-fold coordination [41, 46]. The concentration of homopolar Ge-Ge bonds in Se-deficient $\text{BGGs}\pm\text{Se}$ glasses with $z < 0$ decreases upon addition of Se and becomes negligible in the stoichiometric composition with

$z = 0$, as indicated by the intensities of the Raman band near 175 cm^{-1} and of the low-frequency component in the ^{77}Se MAS NMR spectra near 250 ppm (Figs. 2-5). Se-excess BGGS $\pm$ Se glasses with $z > 0$ contain Se-Se linkages, as evidenced by an increase in the intensity of the Raman band near 265 cm^{-1} in these glasses with increasing Se concentration. This conclusion is consistent with the observation of an increase in the intensity near $\sim 650\text{ ppm}$ in the ^{77}Se MAS NMR spectra of Se-excess BGGS $\pm$ Se glasses that corresponds to Se-**Se**-Ge/Ga environments. However, the lack of any significant intensity in these ^{77}Se MAS NMR spectra in the region 750-850 ppm suggests the absence of significant concentration of Se-**Se**-Se environments, i.e. longer Se chains in these Se-excess glasses. Finally, the content of ES tetrahedra decreases with any deviation from the $z = 0$ composition in either direction. This fact is most apparent in the Raman spectra, which show a decrease in I_{215} with increasing $|z|$. All in all, these trends suggest that the structure of BGGS $\pm$ Se glasses behaves in accordance with the continuously-alloyed structural scenario of chalcogenide glasses.

Although the chalcogenide structural scenario effectively describes the structural evolution of off-stoichiometric BGGS $\pm$ Se glasses as a function of increasing excess or deficiency of Se, it may be noted that the stoichiometric BGGS glasses are electronically analogous to the alkaline-earth aluminosilicate glasses. Therefore, as mentioned earlier, it is informative to also consider the charge-compensated structural scenario of oxide glasses within the context of the structural evolution of stoichiometric and off-stoichiometric BGGS($\pm$ Se) glasses in terms of the ratio $R = \text{BaSe}:\text{Ga}_2\text{Se}_3$. Raman and NMR spectroscopic results have shown that Ge-Ge homopolar bonds exist in both stoichiometric and off-stoichiometric BGGS($\pm$ Se) glasses with $R < 1$ and that their concentration tends to increase in the former with decreasing R , and in the latter with increasing Se deficiency at a constant R [25, 26]. On the

other hand, similar to their alkaline-earth aluminosilicate counterparts, non-bridging Se (NBSe) have been suggested to form in stoichiometric BGGS glasses with $R > 1$ [25]. In particular, as the molar concentration of BaSe exceeds that of Ga_2Se_3 in stoichiometric BGGS glasses, the glass structure contains more Se atoms than are needed to satisfy the fourfold coordination of Ga atoms, which results in the formation of NBSe. In contrast to the stoichiometric glasses, the accommodation of excess Se in off-stoichiometric $\text{BGGS}_{\pm}\text{Se}$ glasses with $R > 1$ is accomplished via the formation of Se-Se homopolar bonds rather than that of NBSe atoms. While the trend in off-stoichiometric $\text{BGGS}_{\pm}\text{Se}$ glasses with $R < 1$ is less clear due to the limited glass-forming region, preliminary evidence from Raman spectroscopy indicates that Se-excess in these glasses also results in the formation of Se-Se bonds instead of NBSe atoms (Fig. 9). Therefore, it is clear that stoichiometry plays an important role in the Se accommodation mechanism in $\text{BGGS}(\pm\text{Se})$ glasses.

It is reasonable to argue that the observed difference in Se accommodation mechanism between the stoichiometric and off-stoichiometric $\text{BGGS}(\pm\text{Se})$ glasses with $R > 1$ stems from the ionic vs. covalent nature of bonding in these glass-forming systems. Given the difference in electronegativity between Ba (0.9) and Se (2.4), it is likely that Ba^{2+} ions in compensated $\text{BGGS}(\pm\text{Se})$ networks with $R \geq 1$ are charge balanced by $[\text{GaSe}_4]^-$ tetrahedra as in the case of crystalline BaGa_2Se_4 [34]. A similar charge balancing role has also been suggested in the literature for $\text{MS-Ga}_2\text{S}_3$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) glasses where the positive charge on the M^{2+} cation is balanced by the negative charge on the $[\text{GaS}_4]^-$ tetrahedra [47]. The partially ionic nature of the Ga-Se bonds was also suggested in crystalline GaSe [48]. Furthermore, a study on rare-earth and Ga doped Ge-As-S and Ge-Sb-Se glasses indicated that the positively charged rare-earth ions tend to be preferentially located near $[\text{Ga}(\text{S}/\text{Se})_4]^-$ tetrahedra [49, 50]. On the other hand, the

formation of the charge-neutral, covalent network in bulk Ga-containing chalcogenide glasses (e.g. in the $\text{Ga}_2\text{Se}_3\text{-GeSe}_2$ system) is often explained on the basis of dative-covalent bonds between Ga and the chalcogen element [51, 52]. In this case, Ga forms three covalent bonds with Se using its three valence electrons, while the fourth dative-covalent bond is formed between Ga and Se by exploiting a lone electron pair that originated on Se. This bonding configuration allows the Ga-Se bonds to retain a more covalent character, and is related to the formation of three-coordinated Se species [24, 27]. It is interesting to observe that the ionic-covalent character of the Ga-Se bonds may also be related to the higher affinity for the formation of heteropolar Ga-Se bonds compared to Ge-Se bonds, because the energy of the Ga-Se bond (65 kcal/mol) is larger than the covalent Ge-Se bonds (55.4 kcal/mol) [53]. A direct consequence of this affinity is the preferential formation of Ge-Ge bonds over Ga-Ga or Ga-Ge bonds in stoichiometric BGGs glasses with $R < 1$ or in Se-deficient off-stoichiometric $\text{BGGs}_{\pm}\text{Se}$ glasses with $R > 1$ [25]. On a related note, this preference for the formation of Ge-Ge bonds over other less stable metal-metal bonds involving Ga or Ba may explain the wide range of Se-deficiency that can be accommodated by $\text{BGGs}_{\pm}\text{Se}$ glasses with $R > 1$ (Table 1).

The chalcogenide-like structural behavior of the off-stoichiometric $\text{BGGs}_{\pm}\text{Se}$ glasses with the formation of homopolar Se-Se (Ge-Ge) bonds in Se-excess (Se-deficient) regime is nicely consistent with the composition dependence of T_g . The sharper decrease in T_g with increasing z in the region where $z > 0$ (Se-excess) is consistent with the formation of Se-Se linkages, while the shallower decrease in T_g with decreasing z in the region where $z < 0$ (Se-deficient) can be attributed to the formation of homopolar Ge-Ge bonds (Fig. 7). This observation is in excellent agreement with the behavior shown by off-stoichiometric Ge-Se glasses [13]. The trends in the density and molar volume of these off-stoichiometric $\text{BGGs}_{\pm}\text{Se}$

glasses are also consistent with this structural scenario in the sense that the linear trends in the variation of density and molar volume with z changes slope near $z = 0$ (Fig. 8) which coincides with the shift in the nature of the homopolar bonds in the structure from Ge-Ge to Se-Se. In slight contrast to the off-stoichiometric $\text{BGGSe}_{\pm}\text{Se}$ glasses, the Ge-Se glasses show a minimum (maximum) in density (molar volume) near the stoichiometric composition as a function of the degree of Se deficiency or excess since the formation of both Ge-Ge and Se-Se homopolar bonds tends to decrease molar volume or increase density [13, 54]. The lack of such an extremum in the case of the off-stoichiometric $\text{BGGSe}_{\pm}\text{Se}$ glasses might be due to the fact that the effect of Se-Se linkages on density or molar volume of glasses with $z > 0$ is offset, at least partially, by the presence of larger and heavier Ba atoms. This conjecture is borne out by the observation that the increase in density in these glasses is effectively linear with the concentration of Ba (Fig. 10), and hence, it is likely that the heavier Ba atoms exercise important control on the observed density trends.

5. Conclusions

Glasses are synthesized in the system $\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2\pm\text{Se}$ with off-stoichiometric amounts of Se. As in their stoichiometric $\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ counterparts, the structure of the off-stoichiometric glasses consist of a network of $(\text{Ga/Ge})\text{Se}_4$ tetrahedra where Ga and Ge are four-fold coordinated and Se is two-fold coordinated. Raman and NMR spectroscopic results indicate that in glasses with $\text{BaSe:Ga}_2\text{Se}_3 > 1$, the Se-excess induces the formation of homopolar Se-Se bonds while Se-deficiency results in the appearance of homopolar Ge-Ge bonds. Moreover, the concentration of edge-sharing tetrahedral configurations is maximized at stoichiometric compositions. These observations are consistent with the continuously-alloyed

scenario of chalcogenide glasses and can explain the compositional variation of density and glass transition temperature. Finally, the stoichiometry and the ionic vs. covalent nature of the structural network are shown to play key roles in controlling the composition-dependent mode of Se incorporation in the structure of these glasses.

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Figures:

Table 1: Summary of the nominal compositions of all samples synthesized (see also Figure 1). The state of each sample after quenching is denoted G for glassy and GC for partially devitrified glass.

Nominal composition (mole %)				Atom % of constituent elements				State
BaSe (x)	Ga ₂ Se ₃	GeSe ₂ (y)	z (mol%)	Ba	Ga	Ge	Se	
5	20	75	20	1.32	10.58	19.84	68.25	G
5	20	75	-10	1.59	12.76	23.92	61.72	GC
5	20	75	-20	1.71	13.70	25.68	58.90	GC
12.5	12.5	75	20	3.55	7.09	21.28	68.09	G
12.5	12.5	75	-20	4.59	9.17	27.52	58.72	GC
20	5	75	20	6.12	3.06	22.94	67.89	G
20	5	75	10	6.48	3.24	24.31	65.96	G
20	5	75	-10	7.37	3.68	27.62	61.33	G
20	5	75	-20	7.91	3.95	29.64	58.50	G
20	5	75	-30	8.53	4.26	31.98	55.22	G
20	5	75	-40	9.26	4.63	34.72	51.39	GC
7.5	32.5	60	20	1.86	16.15	14.91	67.08	GC
7.5	32.5	60	-10	2.24	19.40	17.91	60.45	GC
32.5	7.5	60	20	10.24	4.72	18.90	66.14	G
32.5	7.5	60	10	10.83	5.00	20.00	64.17	G
32.5	7.5	60	-10	12.26	5.66	22.64	59.43	G
32.5	7.5	60	-20	13.13	6.06	24.24	56.57	G
32.5	7.5	60	-30	14.13	6.52	26.09	53.26	GC
32.5	7.5	60	-40	15.29	7.06	28.24	49.41	GC
15	25	60	20	3.98	13.26	15.92	66.84	GC
15	25	60	-20	5.12	17.06	20.48	57.34	GC
25	15	60	20	7.29	8.75	17.49	66.47	GC
25	15	60	-20	9.36	11.24	22.47	56.93	GC

Figure 1: 2D representation of the tentative glass-forming region for stoichiometric BGGs (black symbols) and off-stoichiometric BGGs $\pm$ Se (red symbols) glasses. The compositions for black symbols can be read from the outer ternary diagram [23, 25]. Red squares represent off-stoichiometric series based on the two horizontal stoichiometric composition lines with 75 and 60 mol% GeSe_2 . The off-stoichiometric compositions are above or below the ternary plane and are denoted by the z value alongside the horizontal lines. Filled and open symbols correspond to glassy and partially devitrified samples, respectively.

Figure 2: Raman spectra of BGGS $\pm$ Se glasses in the 75Ba20+(z)Se series. Values of z are denoted alongside the spectra.

Figure 3: Raman spectra of BGS±Se glasses in the 60Ba32.5+(z)Se series. Values of z are denoted alongside the spectra.

Figure 4: ^{77}Se MAS NMR spectra of select BGGS $\pm$ Se glasses in the $^{75}\text{Ba}_{20}+(\text{z})\text{Se}$ series. Values of z are denoted alongside the spectra.

Figure 5: ^{77}Se MAS NMR spectra of select BGGS $\pm$ Se glasses in the $60\text{Ba}32.5+(z)\text{Se}$ series. Values of z are denoted alongside the spectra.

Figure 6: ^{71}Ga central transition QMAT NMR spectra of select BGGS $\pm$ Se glasses in the 75Ba20+(z)Se series. A representative simulation of the line shape using the Cjzek model is also shown (dashed red line). Values of z are denoted alongside the spectra.

Figure 7: Glass transition temperature of glasses in the 75Ba20+(z)Se series as a function of z . The dashed line serves as a guide for the eye.

Figure 8: Density (black ■) and molar volume (blue ▲) of glasses in the $75\text{Ba}_{20}+(z)\text{Se}$ series as a function of z . The dashed lines serve as a guide for the eye.

Figure 9: Raman spectra of BGGS $\pm$ Se glasses (1) 75Ba5+0Se (solid line) and (2) 75Ba5+20Se (dashed line). Note the decrease (increase) in the intensity of the band near 175 cm^{-1} (265 cm^{-1}) upon addition of excess Se.

Figure 10: Density of glasses in the 75Ba20+(z)Se series as a function of the Ba atomic percent. The dashed line serves as a guide for the eye.