Synthesis and Structural Characterization of Stoichiometric Li-Ga-Ge Sulfo-Selenide Glasses

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Abstract

Homogeneous glasses in the mixed-chalcogen pseudo-ternary system $\text{Li}_2\text{S}-\text{Ga}_2\text{Se}_3-\text{GeSe}_2$ are synthesized and their structure is characterized using Raman and one- and two-dimensional ^6Li , ^{77}Se , and ^{71}Ga nuclear magnetic resonance (NMR) spectroscopy. The structure of these glasses can be described as a charge-compensated network predominantly consisting of corner sharing $(\text{Ga/Ge}) (\text{Se,S})_{4/2}$ tetrahedra. The compositional evolution of the atomic structure is heavily influenced by the $\text{Li}_2\text{S}:\text{Ga}_2\text{Se}_3$ ratio R where charge compensation is accommodated by the formation of different structural units and preferential chemical ordering for S atoms. Glasses with $R < 1$ are deficient in chalcogens required to satisfy the tetrahedral coordination of Ga and consequently form ethane-like $\text{X}_3\text{Ge}-\text{GeX}_3$ ($\text{X}=\text{S}, \text{Se}$) units and S atoms preferentially participate in these structural units. On the other hand, the structure of chalcogen-excess glasses with $R > 1$ are characterized by the formation of non-bridging Se (NBSe) and S (NBS) sites. The Se atoms show a preference over S for these non-bridging sites and form Ge-NBSe linkages, while the S atoms preferentially bond to Ga, resulting in the formation of $\text{GaS}_{4/2}$ tetrahedra. This structural scenario is shown to be consistent with the corresponding changes in the glass transition temperature.

1. Introduction

Chalcogenide glasses, owing to their unique optical and semiconducting properties, have found wide ranging applications in the areas of telecommunication, remote sensing, energy and memory storage [1-3]. Compared to oxide glasses, the compositional flexibility of chalcogenides allows for excellent tuning of their electronic and optical properties. However, the majority of studies in the literature have focused on the structure-property relationships in Ge-As-P-X (X=S, Se, Te) glasses that are characterized by fully connected covalent networks that follow the 8-N bonding rule [4-8]. In comparison, relatively little is known about chalcogenide glasses with modified networks [9-11].

Chalcogenide networks modified with alkali and/or alkaline-earth sulfides or selenides are prone to devitrification and phase separation. Addition of glass forming intermediates such as Ga can often alleviate these shortcomings [12, 13] via creation of a compensated network that allows for homogeneous incorporation of high concentration of modifiers. The modifier cations charge balance the $[\text{Ga}(\text{S/Se})_{4/2}]^-$ tetrahedra in the structure. In fact, it is possible to synthesize pseudo-ternary glasses in the stoichiometric system $\text{M}_2\text{X}/\text{M}'\text{X}-\text{Ga}_2\text{X}_3-\text{GeX}_2$ [M=alkali; M'=alkaline-earth] that are isoelectronic analogues of alkali/alkaline-earth aluminosilicate glasses with partially or fully compensated network. Recent works on $\text{Ag}_2\text{Se}/\text{Na}_2\text{Se}/\text{BaSe}-\text{Ga}_2\text{Se}_3-\text{GeSe}_2$ glasses have shown that the ratio of modifier to intermediate content $R = \text{M}_2\text{X}/\text{M}'\text{X}:\text{Ga}_2\text{X}_3$ is of critical importance in controlling the structural evolution of the network in these compensated chalcogenide glasses [14-16]. In the case of $R < 1$, these glasses are considered to be chalcogen deficient for satisfying the tetrahedral coordination of heteropolar bonded Ga and Ge atoms and this deficiency is accommodated in the structure primarily via the formation of Ge-Ge homopolar bonds. On the other hand, for $R > 1$ the glasses contain an excess of

chalcogen which results in the formation of non-bridging S/Se (NBS/NBSe), similar to the formation of non-bridging oxygen (NBO) in modifier-excess oxide glasses. As continuation of our efforts to understand the structure-property relationships of chalcogenide glasses with compensated networks, we have investigated glasses in the system $\text{Li}_2\text{S-Ga}_2\text{Se}_3\text{-GeSe}_2$ (LGGS/Se). Sulfur is incorporated in these glasses, in addition to selenium, in order to probe how the structure of these compensated networks, containing mixed chalcogen atoms with different electronegativities and therefore, with different degrees of ionicity of the constituent heteropolar bonds is influenced by the variation in R. In the present study, we report the results of an investigation into glass formation and structural characteristics of glasses in the LGGS/Se system, using Raman and multi-nuclear (^6Li , ^{77}Se , and ^{71}Ga) magnetic resonance (NMR) spectroscopy. The compositional evolution of the atomic structure of these glasses is then linked to corresponding variation in the glass transition temperature T_g .

2. Experimental Methods

2.1. Glass Synthesis

All glasses were prepared by a melt-quench method. The compositions were batched within a nitrogen atmosphere glovebox with the H_2O and O_2 levels less than 0.1 ppm. A two-step melting procedure was used in order to minimize possible reaction of Li with the walls of the fused quartz ampoules. Approximately 25g batches of precursor Ga-Ge-Se alloys were prepared for each composition by melting mixtures containing appropriate amounts of constituent elements Se, Ga and Ge (99.9999% purity) in sealed fused quartz ampoules evacuated to 8×10^{-5} torr. The mixtures were melted in a rocking furnace for three days at 950°C

and subsequently quenched in water. The material was extracted from the ampoule and crushed into powder. Approximately 10g batches of glass were made by mixing appropriate amounts of Li_2S (99.99% purity) and precursor Ga-Ge-Se alloy powder and melting the mixtures in silicon coated fused quartz ampoules. The ampoules were sealed under vacuum at 8×10^{-5} torr and loaded into a vertical furnace at 950°C . After 15 minutes of melting, the ampoules were removed and tilted to homogenize the liquid and then loaded back into the furnace to melt for another 15 minutes. The ampoules were subsequently quenched in water and annealed in a furnace at 200°C for 30 minutes. The glasses were extracted from the ampoules within an Ar glovebox as the Li rich compositions are extremely hygroscopic and react within less than 30 minutes of exposure to ambient air. The Ga rich compositions display better stability to ambient air and showed no signs of degradation while being stored in a desiccator for more than a week. The possible devitrification of the samples was checked with powder x-ray diffraction. The T_g of the x-ray amorphous samples was determined using 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 20 K/min.

2.2. Raman Spectroscopy

Raman spectra of the glasses were collected on a Bruker RFS 100/S Fourier-transform (FT) Raman spectrometer equipped with a Nd:YAG laser operating at an excitation wavelength of 1064 nm. Glass powder was packed into a sample holder and covered with clear tape to prevent contamination with moisture. Each spectrum is the average of 128 scans collected in backscattering geometry at room temperature using a power level of 30 mW and a resolution of 2

cm⁻¹ resolution. Additionally, Raman spectra were collected as a function of time after removing the tape to monitor spectral changes resulting from the interaction of the sample with ambient moisture.

2.3. NMR Spectroscopy

2.3.1. Measurements at low magnetic field (11.7 T)

The NMR spectra at 11.7 T were collected using a Bruker Avance500 spectrometer operating at resonance frequencies of 73.6, 95.4, and 152.5 MHz for ⁶Li, ⁷⁷Se and ⁷¹Ga, respectively. The glass samples were crushed into powder and packed into 4mm or 5mm ZrO₂ or Si₃N₄ rotors. Due to the hygroscopic nature of the samples, all packing was carried out in an Ar-filled glovebox to avoid any exposure to moisture. The one-pulse ⁶Li NMR spectra were collected using a Bruker triple-resonance magic-angle-spinning (MAS) probe, a $\pi/4$ pulse (2.25 μ s) and a recycle delay of 10s. Samples were spun at 12 kHz and 16 free induction decays (FID) were averaged and Fourier transformed to obtain each spectrum. The ⁷⁷Se MAS NMR spectra were collected using a Doty MAS probe. Samples were taken in a 5 mm Si₃N₄ rotor and spun at ~14 kHz. A Hahn echo pulse sequence was used with a rotor synchronized delay between the $\pi/2$ (2.2 μ s) and π (4.4 μ s) pulses and a recycle delay of 120 s. At least 512 FIDs were averaged and the entire echo was Fourier transformed to obtain each spectrum. The ⁷¹Ga NMR spectra were obtained using the two-dimensional (2D) quadrupolar magic angle turning (QMAT) experiment as reported in the literature [17]. The QMAT pulse sequence uses nine central transition selective pulses with linearly varied delays to produce a MAS spectrum free of sidebands. Crushed glass was packed in a 4 mm ZrO₂ rotor and was spun at 10 kHz. For each QMAT experiment 16 t_1 increments were employed over the rotor period with 10000 transients

per t_1 increment and a recycle delay of 0.2 s between each transient. The central transition selective $\pi/2$ and π pulse lengths were 1.2 and 2.4 μs , respectively. After data collection, the 16 t_1 increments are sheared and summed together, then Fourier transformed in the direct and indirect dimensions to produce an “infinite” spinning speed ^{71}Ga MAS spectrum. The ^6Li , ^{77}Se , and ^{71}Ga chemical shifts were externally referenced to the isotropic chemical shift δ_{iso} of solid LiCl ($\delta_{\text{iso}}=0$ ppm), crystalline $(\text{NH}_4)_2\text{SeO}_4$ ($\delta_{\text{iso}}= 1040.2$ ppm), and 1M aqueous solution of $\text{Ga}(\text{NO}_3)_3$ ($\delta_{\text{iso}}=0$ ppm), respectively.

2.3.2. *Measurements at high magnetic field (19.6 T)*

Two-dimensional (2D) ^{77}Se magic angle turning phase adjusted sideband separation (MATPASS) spectra were collected at the field of 19.6 T at the National High Magnetic Field Laboratory using an ultra-narrow bore magnet equipped with a Bruker DRX console operating at a resonance frequency of 158.8 MHz for ^{77}Se . The crushed glass sample was packed into a 3.2 mm ZrO_2 rotor and spun at 10 kHz. High-resolution 2D ^{77}Se MATPASS data were collected with Carr-Purcell-Meiboom-Gill (CPMG) echo-train acquisition to enhance sensitivity. The MATPASS experiment separates the isotropic chemical shift from chemical shift anisotropy (CSA) into two dimensions. The MATPASS/CPMG pulse sequence uses a series of five MAT π -pulses (4.4 μs) with incremented inter-pulse delays according to the timings detailed by Hung et al. [18]. The experiment acquired 16 hypercomplex t_1 points with 36 transients per point and 32 CPMG echoes per transient with a recycle delay of 60 s. Hypercomplex data acquisition was employed using the method of States et al. to the phases of the CPMG pulses and the receiver [19].

Following the Haeberlen convention the principle components of the chemical shift tensor (δ_{xx} , δ_{yy} , and δ_{zz}) are expressed in terms of the isotropic chemical shift δ_{iso} , the magnitude of anisotropy Δ , and the asymmetry parameter η . These terms are defined as:

$$\delta_{iso} = \frac{1}{3}(\delta_{zz} + \delta_{yy} + \delta_{xx}); \Delta = \delta_{zz} - \delta_{iso}; \eta = \frac{\delta_{xx} - \delta_{yy}}{\Delta}$$

where, $\delta_{zz} - \delta_{iso} \geq \delta_{xx} - \delta_{iso} \geq \delta_{yy} - \delta_{iso}$ [20]. All simulations of the NMR spectra were performed using the Dmfit software package [21].

3. Results

3.1. Glass Formation Range

The composition range for glass formation for the pseudo-ternary system LGGS/Se is shown in Fig. 1. The circles mark compositions that are x-ray amorphous and have a clear signature of glass transition in their DSC trace. It is immediately obvious that the glass formation region in this system is quite limited with only compositions rich in Li_2S ($R > 1$) or rich in Ga_2Se_3 ($R < 1$) forming homogeneous glasses. The compositions near $R = 1$ show various degrees of crystallinity in the x-ray powder patterns forming a region of devitrification along the center of the pseudo-ternary diagram. Glasses in this composition region are prone to devitrification upon cooling, forming the stable crystalline phase $\text{LiGaGe}_2\text{Se}_6$. Similar glass formation regions have also been reported for other alkali and alkaline-earth containing Ga_2X_3 - GeX_2 ($\text{X} = \text{S}, \text{Se}$) glasses [14, 22-24] with analogous crystalline compounds forming upon devitrification for compositions nearing $R = 1$. It is interesting to note the glass formation region along the $\text{Li}_2\text{S} + \text{GeSe}_2$ join resembles that of the $\text{Li}_2\text{Se} + \text{GeSe}_2$ join where glass formation is observed only for 40% Li_2Se

using conventional water quenching [9]. The analogous sulfide system, on the other hand, can form glasses for compositions extending from 0 to 50% Li_2S [10]. The color of the LGGS/Se glasses synthesized in the present study varies from deep red for Ga_2Se_3 rich compositions to a lighter red for the Li_2S rich compositions reflecting a narrowing of the optical band gap with increasing amount of Se relative to S.

3.2. Glass Transition Temperature

The glass transition temperatures for all homogeneous LGGS/Se glasses synthesized in this study are listed in Table 1. Overall there is relatively little change in the glass transition temperature within each of the regions with $R>1$ or, with $R<1$. The glasses with $R>1$ are characterized by T_g in the range $\sim 290^\circ\text{C}$ - 304°C with a monotonic decrease in T_g as GeSe_2 is replaced with Li_2S . Comparison between glasses with 40 mol% Li_2S , with or without Ga indicates an increase in T_g by $\sim 10^\circ\text{C}$ with the substitution of 10 mol % Ga_2Se_3 for GeSe_2 . The $R<1$ glasses are characterized by T_g ranging between $\sim 360^\circ\text{C}$ - 376°C and there is a monotonic increase in T_g with decreasing GeSe_2 content. The relatively large difference between the T_g values of glasses with $R>1$ and those with $R<1$, suggests a correspondingly significant difference between them in their network structure and bonding characteristics.

3.3. Raman Spectroscopy

The Raman spectra of all LGGS/Se glasses synthesized in this study are shown in Fig. 2. Spectral features for these glasses extend from $\sim 50\text{ cm}^{-1}$ to $\sim 450\text{ cm}^{-1}$. The spectral region between 50 and 150 cm^{-1} is characterized by relatively broad bands associated with the various symmetric and asymmetric bending modes of corner-shared $\text{GeS}_n\text{Se}_{4-n}$ tetrahedra. This spectral region remains relatively invariant with composition for glasses with $R<1$ (Fig. 2a). With

increasing Li content, the glasses with $R > 1$ (Fig. 2b) show an increase in intensity of the ν_2 and ν_4 modes of the $\text{GeS}_n\text{Se}_{4-n}$ tetrahedra near 110 and 150 cm^{-1} , respectively [25]. A relatively sharp peak at 86 cm^{-1} is distinguishable in all Raman spectra, which originates from the Al-alloy sample holder used in these experiments.

The spectral region between 150 and 270 cm^{-1} in all glasses is dominated by a compositionally invariant band at $\sim 200 \text{ cm}^{-1}$ corresponding to the symmetric breathing mode of the corner sharing $(\text{Ge/Ga})\text{Se}_{4/2}$ tetrahedra. Within this spectral region, the Ga_2Se_3 rich glasses with $R < 1$ (Fig. 2a) display bands at 175 and 215 cm^{-1} that can be readily assigned to the stretching of homopolar Ge-Ge bonds in ethane-like $(\text{Se}_3)\text{Ge-Ge}(\text{Se}_3)$ units and to the breathing mode of edge sharing $\text{GeSe}_{4/2}$ tetrahedra, respectively. These features are most prominent in the Raman spectrum of the glass with the lowest modifier (Li_2S) content and strongly resemble the Raman spectra of binary Ga_2Se_3 - GeSe_2 glasses previously reported in the literature. Moreover, the Raman spectra of glasses with $R < 1$ also display a broadening of the 175 cm^{-1} mode and the disappearance of the 215 cm^{-1} mode with increasing Li_2S content, along with a concomitant appearance of two new bands at 190 and 230 cm^{-1} (Fig. 2a). These additional modes must correspond to tetrahedral environments containing sulfur as these features are absent in the Raman spectra of binary Ga_2Se_3 - GeSe_2 glasses and their intensities increase with increasing S:Se ratio as the GeSe_2 content decreases (Fig. 2a). This hypothesis is corroborated by the results of a previous study by Griffiths et al. on the effects of substitution of S for Se on the Raman spectrum of glassy GeSe_2 [25]. Substitution of S for Se does not affect the tetrahedral character of the structural network and thus, similar spectral features are present and are progressively shifted to higher energy as the heavier Se atoms connecting the GeX_4 tetrahedra are replaced with lighter S atoms. This substitution has a minor influence on the Raman shift of the $(\text{X}_3)\text{Ge-Ge}(\text{X}_3)$

stretching mode as the main vibrational displacement is between the Ge atoms [26]. A mode at 190 cm^{-1} is expected for a homopolar $(\text{Se}_2\text{S})\text{Ge-Ge}(\text{Se}_2\text{S})$ dimer stretch. The rise in the mode at 226 cm^{-1} is also expected for the symmetric breathing mode of Ge/Ga tetrahedra containing one S and 3 Se atoms. This spectral region for the Li_2S rich compositions with $R>1$, only displays two prominent modes at ~ 200 and 225 cm^{-1} with the former mode being the dominant one, indicating that the tetrahedral network in the glasses is primarily composed of $\text{Ge/GaSe}_{4/2}$ tetrahedra (Fig. 2b). Increasing addition of Li_2S or Ga_2Se_3 to the binary $\text{Li}_2\text{S-GeSe}_2$ glass does not result in the appearance of any new modes, rather a broadening of the two modes at ~ 200 and 225 cm^{-1} along with a rise in the relative intensity of the 225 cm^{-1} mode are observed, which is consistent with the increasing replacement of Se with S in the tetrahedral units.

The broadened line shape between 225 cm^{-1} and 270 cm^{-1} is expected to contain the various ν_1 modes of $\text{GeSe}_n\text{S}_{4-n}$ tetrahedra where $n= 3, 2$, or 1 as well as the mode corresponding to the out-of-phase stretching of the edge-sharing $\text{GeSe}_n\text{S}_{4-n}$ tetrahedra [15].

The spectral region between 270 and 450 cm^{-1} mostly consists of bands corresponding to the ν_3 modes of $\text{GeS}_n\text{Se}_{4-n}$ tetrahedra with the highest intensity at $\sim 310\text{ cm}^{-1}$ indicating that the GeSe_4 tetrahedra dominate the network. The frequencies of these modes continuously increase to up to 430 cm^{-1} to form a broad envelope in this spectral region in the Raman spectra of $R>1$ glasses with high S:Se ratio (Fig. 2b). Additional intensity in this spectral region for the $R>1$ compositions may arise from asymmetric stretching modes of Ge tetrahedra associated with non-bridging anions. The characteristic frequency of these modes for NBS is at $\sim 325\text{ cm}^{-1}$ [14] and that for NBS is at $\sim 420\text{ cm}^{-1}$ [27, 28]. Finally, the lack of intensity at $\sim 490\text{ cm}^{-1}$ in these Raman spectra indicates the absence of homopolar S-S bonds in these glasses [29].

The effect of introducing S to an alkali-modified GeSe₂ glass can best be seen by comparing the Raman spectrum of the 40% Li₂S – 60% GeSe₂ glass to that of an analogous Na₂Se- GeSe₂ composition reported in a previous study [14]. It is clear from a close inspection of these two spectra in Fig. 2b that, in spite of their general similarity the addition of S is manifested in significant broadening of the main breathing mode of (Ga/Ge)Se_{4/2} tetrahedra at ~200 cm⁻¹ and in a shift of the peak maximum to higher frequency. This change is likely due to the introduction of the additional breathing modes of mixed-chalcogen GeS_nSe_{4-n} tetrahedra at correspondingly higher wavenumbers. Concomitant broadening of the bands between 270 and 350 cm⁻¹ as well as the appearance of new bands in the region between ~ 400-450 cm⁻¹ are also observed in the spectrum of the 40% Li₂S – 60% GeSe₂ glass (Fig. 2b). These changes can be related to the introduction of the asymmetric stretching modes of the mixed-chalcogen GeS_nSe_{4-n} tetrahedra with and without NBS.

All the LGGS/Se glasses appear to have some degree of hygroscopicity as monitored using Raman spectroscopy. The R>1 compositions reacted upon immediate exposure to ambient atmosphere showing a rapid change of the original spectra. The R<1 compositions did not show any change in their Raman spectral characteristics within the first 24 hours of exposure.

3.4.NMR Spectroscopy

3.4.1. ⁶Li NMR

Despite the high natural abundance (92.58%) of the ⁷Li nuclide, the line width of the ⁷Li NMR signal is observed to be on the order of ~500 Hz, resulting in insufficient resolution for identification of resonances with subtle chemical shift differences. In comparison, the ⁶Li NMR

line shapes, on the other hand, are significantly narrower (45-60 Hz) due to weaker homonuclear dipolar interactions and quadrupolar broadening effects. Figure 3 shows the ^6Li MAS NMR spectra of select glass compositions. All ^6Li MAS NMR spectra have a Lorentzian character to their line shapes and are characterized by two partially overlapping resonances for compositions with $R>1$ (Fig. 3). Simulations of these line shapes yield the chemical shift ranges for the two resonances to be 1.75-1.90 ppm and 1.42-1.60 ppm (Table 2). Structural assignment of these two resonances is somewhat difficult due to the lack of a ^6Li chemical shift scale for chalcogenide compounds. However, systematic trends in chemical shifts from ^7Li NMR should apply well to the ^6Li NMR spectra. The ^7Li isotropic chemical shift of crystalline Li_2S is found to be higher by ~ 0.37 ppm compared to that for crystalline Li_2Se [30-32]. This difference agrees well with the separation between the two resonances observed in the ^6Li MAS NMR spectra of the glasses with $R>1$ in Fig. 3, thus, allowing for the tentative assignment of the resonance at higher ppm values (Li-II) to Li in a S rich environment and of that at lower ppm values (Li-I) to Li in a Se rich environment. The Lorentzian character of the line shape and narrowed line width possibly suggests some degree of motional averaging from the mobility of Li ions in these glasses. The ^6Li MAS NMR spectrum of the glass with $R<1$ is characterized by a single resonance centered at 0.93 ppm whose chemical shift is consistent with Li coordinated to primarily to Se atoms [33].

3.4.2. ^{77}Se NMR

The isotropic projection of the ^{77}Se MATPASS NMR spectrum is effectively an “infinite spinning speed” MAS spectrum with enhanced resolution while projection along the anisotropic dimension results in a spinning sideband pattern that allows for the extraction of the principle axes of the CSA tensor for a specific isotropic shift. The ^{77}Se MATPASS NMR spectrum of the

glass of composition 40 Li₂S - 10 Ga₂Se₃ - 50 GeSe₂ glass is shown in Fig. 4a. The ⁷⁷Se isotropic projection spectrum can be simulated with two peaks centered at 316 and 100 ppm (Fig. 4b) that can be assigned, respectively, to bridging selenium (BSe) sites in Ga/Ge-**Se**-Ge/Ga linkages between corner sharing Ge(Ga)S_nSe_{n-4} tetrahedra and to NBSe sites in Ge-**Se**-Li environments [16, 34, 35]. The magnitude of the CSA Δ for these two sites can be gleaned from the 2D contour plot where it is clear that Δ for the NBSe site is larger than that of the BSe site, consistent with previous reports of such sites in selenide glasses with compensated networks [16, 35]. Simulation of the spinning sideband patterns for these two peaks in the anisotropic dimension (Fig. 4c) yields a CSA tensor with $\Delta=210$ ppm ($\Delta=-405$ ppm) and $\eta= 0.9$ ($\eta= 0.6$) for the isotropic peak at 316 ppm (100 ppm). These CSA values are consistent with previous reports [16, 35]. These isotropic shifts and CSA parameters are used to constrain the simulation of the ⁷⁷Se MAS NMR spectra of compositionally closely related glasses with R>1 (Fig. 5). These MAS spectra are significantly broadened by the CSA and the chemical shift distribution. However, using the δ_{iso} and CSA parameters obtained from the ⁷⁷Se MATPASS/CPMG spectrum the MAS spectrum of the same glass can be accurately simulated to obtain site fractions that are consistent between the two experiments. The remaining ⁷⁷Se MAS NMR spectra of the R>1 glasses can be simulated well with the same δ_{iso} and CSA parameters for the BSe and NBSe environments. These simulation parameters are listed in Table 2.

The results of these simulations show a steady increase in the fraction NBSe environments relative to the BSe fraction with increasing Li₂S content. In addition there is an increase in the NBSe environment when Ga₂Se₃ is added to replace GeSe₂ in the pseudo-binary Li₂S-GeSe₂ glass system. It is interesting to note that the isotropic chemical shift of the BSe environment (316 ppm) in these R>1 glasses is significantly lower than the value typically

observed in Ge-Se glasses (380-400 ppm). This difference is likely related to the substitution of S in the nearest-neighbor environment of Ge atoms, as Ge-S bonds are shorter (~ 2.22 Å) and more ionic compared to the Ge-Se bonds (~ 2.35 Å) and the electronic and steric effects associated with their coexistence in the GeX_4 tetrahedra may easily influence the ^{77}Se chemical shift [36].

The ^{77}Se MAS NMR spectra for the $R < 1$ glasses can also be simulated with two resonances centered near ~ 400 ppm and ~ 180 ppm (Fig. 5, Table 2). These peak positions are consistent with those reported in the literature for binary $\text{Ga}_2\text{Se}_3\text{-GeSe}_2$ glasses with $R=0$. The resonance at ~ 400 ppm was previously ascribed to Ge/Ga-**Se**-Ge type BSe environments and that at ~ 180 ppm was assigned to (Ga/Ge)-**Se**-Ge-Ge sites where the Se atom is in an ethane like unit where one of the nearest neighbor Ge atoms is homopolar bonded to another Ge atom [37, 38]. A gradual increase in the relative fraction of the (Ga/Ge)-**Se**-Ge-Ge sites relative to the BSe sites is observed in these $R < 1$ glasses, with decreasing GeSe_2 content (Fig. 5, Table 2). The inset of Fig. 5 highlights the effect of S substitution on the ^{77}Se isotropic chemical shift of the BSe sites in the LGGS/Se glasses. A similar effect was reported in the literature for various S substituted Se compounds [39-41].

3.4.3. ^{71}Ga QMAT NMR

The ^{71}Ga QMAT central transition spectra for the representative glasses with $R > 1$ and $R < 1$ are shown in Fig. 6. These ^{71}Ga QMAT spectra display a single peak with a low frequency tail characteristic of a distribution of electric field gradients at the Ga site, typical of disordered materials. Simulation of these central transition line shapes using the Czjzek model for the distribution of C_q yields an isotropic shift of ~ 160 ppm and a C_q of ~ 10 MHz for both

compositions with $R < 1$. These NMR parameters are in good agreement with previously published reports of the ^{71}Ga NMR spectra in binary $\text{Ga}_2\text{Se}_3\text{-GeSe}_2$ glasses corresponding to tetrahedral $\text{GaSe}_{4/2}$ environments [15, 16, 38]. On the other hand, the ^{71}Ga QMAT spectrum for the $R > 1$ glass is characterized by a δ_{iso} of ~ 320 ppm and a C_q of 11 MHz. This spectrum is rather similar to that reported for the $\text{GaS}_{4/2}$ environment in Ge-Ga-P-S glasses, which suggests that Ga is fourfold coordinated and is predominantly bonded to the S atoms in this glass with $R=4$ [42].

4. Discussion

When taken together the Raman and multinuclear NMR spectroscopic results indicate that the structure of the LGGS/Se glasses consists of a network of primarily corner sharing $\text{GeSe}_{4/2}$ and $\text{GaSe}_{4/2}$ tetrahedra. As sulfur is introduced into the glass as a second chalcogen, the appearance of additional vibrational modes in the Raman spectra suggests the formation of mixed chalcogen $\text{GeS}_n\text{Se}_{4-n}$ tetrahedra. Otherwise, the general structural evolution in the LGGS/Se glasses with composition is in agreement with the results of previous studies on isoelectronic selenide analogues in the stoichiometric $\text{Ag}_2\text{Se}/\text{Na}_2\text{Se}/\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ systems [14-16, 22] where the coordination numbers of Ge, Ga, and Se are 4, 4, and 2, respectively, irrespective of glass composition. For $R > 1$, these selenide glasses contain NBSe that are charge compensated by the modifier cations. On the other hand, the $R < 1$ glasses are too deficient in chalcogen content to satisfy the tetrahedral coordination of Ga atoms and this deficiency is accommodated by the formation of homopolar Ge-Ge bonds. Furthermore, the $[\text{GaSe}_{4/2}]^-$ tetrahedra in glasses with either $R < 1$ or $R > 1$ are charge balanced by the modifier cation similar to the scenario in alkali/alkaline-earth aluminosilicate glasses.

In spite of these general similarities, the compositional evolution of the network structure of mixed-chalcogen LGGS/Se glasses has additional complexities associated with the chemical ordering of the S vs. Se atoms, which is found to be quite different between glasses with $R > 1$ and those with $R < 1$. The Raman spectra of the $R > 1$ glasses (Fig. 2b) display additional bands at wavenumbers higher than 200 cm^{-1} , corresponding to $\text{GeS}_n\text{Se}_{4-n}$ units with $n > 1$ and from contributions of NBSe at $\sim 325\text{ cm}^{-1}$ and of NBS at 420 cm^{-1} . These results indicate that a majority of the Ge/Ga tetrahedra have at least one S and both Se and S can form non-bridging environments. The mixed chalcogen tetrahedral network is thus, modified by the addition of Li to form NBSe and NBS species, of which the concentration of the former can be directly identified and its concentration can be estimated using ^{77}Se NMR (Fig. 5). As shown in Fig. 5 and Table 2, the simulation of the ^{77}Se MAS NMR spectrum of the pseudo-binary 40% Li_2S -60% GeSe_2 glass indicates that $\sim 40\%$ of the Se atoms are NBSe, which, within experimental error, compares well with the expected value of 50% for equal probability of formation of NBS and NBSe. However, the pseudo-ternary composition 40% Li_2S -10% Ga_2Se_3 -50% GeSe_2 with the same Li_2S content shows the opposite: simulation of the ^{77}Se MAS NMR spectrum yields 67% NBSe while the predicted amount from a random probability model is only 42% NBSe. In fact, the experimentally observed fraction of NBSe in both glasses with $R > 1$ is significantly larger than that expected from the random model (Table 2), which suggests a strong bonding preference between Ga and S in $R > 1$ glasses. This interpretation is corroborated by the ^{71}Ga NMR results as the ^{71}Ga δ_{iso} shows an abrupt shift from $\sim 160\text{ ppm}$ in $R < 1$ glasses to $\sim 320\text{ ppm}$ in $R > 1$ glasses, with the latter shift being characteristic of Ga atoms in tetrahedral coordination with S atoms. The preference to form Ga-S over Ge-S bonds in $R > 1$ glasses is likely due to the greater electronegativity difference between Ga and S than that between Ge and S, thus creating a

stronger heteropolar bond. It is important to note here that the ^6Li NMR spectra of the pseudo-ternary LGGS/Se glasses with $R>1$ show the existence of two different Li environments, one of which is characterized by a preference for bonding with S atoms. This result is consistent with the scenario that a large fraction of Li^+ charge balances the $[\text{GaS}_{4/2}]^-$ tetrahedra in the structure of these glasses. The second Li environment has a higher Se:S ratio in the nearest neighbor coordination shell, which would suggest that, besides S, these Li are bonded to NBSe atoms that are in the nearest neighbor shell of Ge atoms- thus forming Ge-NBSe-Li linkages. However, and more interestingly, two ^6Li resonances with similar δ_{iso} are also observed in the ^6Li MAS spectrum of the pseudo-binary 40% Li_2S -60% GeSe_2 glass. The stoichiometry of this glass implies the formation of 1.33 NBS/Se per Ge tetrahedron in the structure, i.e. the network must consist primarily of a mixture of Ge tetrahedra with 1 and 2 NBS/Se in an approximate ratio of 67:33. Therefore, considering a S:Se ratio of 1:3, the presence of two different Li environments in this glass in sub-equal concentration may suggest a spatial segregation of these two types of tetrahedra, instead of a segregation of S and Se, in the structural network. This structural scenario would imply the presence of GeX_4 tetrahedra in configurations with either one NBSe or with 1 NBS + 1 NBSe.

In contrast, the $R<1$ glasses are deficient in chalcogen and form homopolar Ge-Ge bonds to accommodate this deficiency as the Raman spectra (Fig. 2a) of these glasses show a rise in intensity for the 190 cm^{-1} mode corresponding to homopolar $(\text{Se}_2\text{S})\text{Ge-Ge}(\text{Se}_2\text{S})$ dimer stretching. The ^6Li and ^{71}Ga NMR spectra (Figs. 3,6) are consistent with this scenario, showing only resonances corresponding to Li and Ga coordinated exclusively to Se atoms with Ga being in tetrahedral coordination. These results suggest that the primary role of Li^+ is to charge

balance the $[\text{GaSe}_{4/2}]^-$ tetrahedra in the structure of $R < 1$ glasses, as neither the Raman nor ^{77}Se NMR spectra show any evidence for the presence of NBS/Se.

This structural scenario for the LGGS/Se glasses is consistent with the observed compositional variation of T_g (Table 1). Overall the same compositional trends were also observed in analogous selenide glasses in the stoichiometric $\text{Ag}_2\text{Se}/\text{Na}_2\text{Se}/\text{BaSe}-\text{Ga}_2\text{Se}_3-\text{GeSe}_2$ systems [14, 16, 22]. The T_g of the LGGS/Se glasses with $R > 1$ is significantly lower than that of glasses with $R < 1$. This difference can be readily ascribed to the loss of network connectivity and lowering of average coordination number via formation of NBS and NBSe in modifier rich glasses with $R > 1$. For $R < 1$ glasses, T_g increases only slightly as Ga_2Se_3 replaces GeSe_2 , which is consistent with an increase in the average bond energy of the network as Ga-Se bonds are stronger than Ge-Se bonds [43, 44]. Overall, the narrow range of T_g values for these glasses ($\sim 360 - 380^\circ\text{C}$) attests to the fact that the structural network is dominated by the corner-shared $(\text{Ga,Ge})\text{X}_{4/2}$ tetrahedra, such that the influence of the modifier is minimal. Within the $R > 1$ glasses T_g decreases with increasing Li_2S content as it leads to increasing concentration of NBS and NBSe atoms that act to depolymerize the network. The influence of S on the network is best illustrated by comparing T_g values of the pseudo-binary $\text{Li}_2\text{S}-\text{GeS}_2$, $\text{Li}_2\text{S}-\text{GeSe}_2$, and $\text{Li}_2\text{Se}-\text{GeSe}_2$ systems. For an equal modifier content of 40 mol%, the pure sulfide system has a T_g of 324°C , and the pure selenide system has a T_g of 248°C [9] while the mixed-chalcogen $\text{Li}_2\text{S}-\text{GeSe}_2$ glass studied here has a T_g of 293°C . It is clear from this comparison that for similar degrees of network connectivity, T_g is a function of the average bond strength of the network which is the highest in the pure sulfide system. The T_g increases upon addition of Ga_2Se_3 to the $\text{Li}_2\text{S}-\text{GeSe}_2$ glass as the network is re-polymerized via removal of non-bridging chalcogen and

possibly due to a shift in the type of non-bridging chalcogen from a mix of NBS and NBSe to almost exclusively NBSe.

5. Conclusions

The structure of the LGGS/Se glasses is characterized by a network of predominantly corner-sharing (Ga/Ge) (Se,S)_{4/2} tetrahedra. The negatively charged Ga(Se,S)_{4/2} tetrahedra are charge balanced by the Li cations. Glasses with R>1 contain NBS and NBSe species that result in a lowering of the network connectivity consistent with a lowering in T_g. On the other hand, glasses with R<1 are deficient in chalcogen required to satisfy the tetrahedral coordination of both Ge and Ga atoms. This deficiency is accommodated via formation of Ge-Ge homopolar bonds. S atoms show a strong preference for bonding to these Ge atoms in glasses with R<1. In contrast, for glasses with R>1, S preferentially bonds to Ga, which substantially increases the NBSe:NBS ratio compared to its expected value for a random distribution of chalcogen atoms in the structure. This preferential chemical ordering of S is likely related to the higher ionicity of the Ge/Ga-S bonds compared to their Se analogues.

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Table 1: Nominal composition (mol %), T_g , and T_x (crystallization temperature) for all homogeneous LGGS/Se glasses synthesized in this study.

Li_2S	Ga_2Se_3	GeSe_2	$\text{S}/(\text{S}+\text{Se})$	T_g ($^{\circ}\text{C}$)	T_x ($^{\circ}\text{C}$)
40	0	60	0.250	293	353
40	10	50	0.235	304	370
45	10	45	0.273	290	366
50	10	40	0.313	287	366
5	20	75	0.023	363	443
7.5	32.5	60	0.033	366	423
15	25	60	0.071	369	421
20	30	50	0.095	376	419

Table 2: Line shape simulation parameters for the ^{77}Se and ^6Li MAS NMR spectra of the LGGS/Se glasses (see Figs. 3 & 5).

^{77}Se NMR Parameters					
$\text{Li}_2\text{S}:\text{Ga}_2\text{Se}_3:\text{GeSe}_2$	$\delta_{\text{iso}} (\pm 10 \text{ ppm})$	Width (ppm)	Δ (ppm)	η	Relative fraction ($\pm 10\%$)
5:20:75					
Ge- Se -Ge	400	320	250*	0.9*	56
Ge- Se -Ge-Ge	170	320	250*	0.9*	44
15:25:60					
Ge- Se -Ge	400	320	250*	0.9*	40
Ge- Se -Ge-Ge	130	320	250*	0.9*	60
20:30:50					
Ge- Se -Ge	400	320	250*	0.9*	32
Ge- Se -Ge-Ge	110	320	250*	0.9*	68
40:00:60					
Ge- Se -Ge	330	250	210	0.9	62
Ge- Se -Li	100	240	-405	0.6	38
40:10:50					
Ge- Se -Ge	320	250	210	0.9	33
Ge- Se -Li	100	240	-405	0.6	67
50:10:40					
Ge- Se -Ge	320	250	210	0.9	11
Ge- Se -Li	100	240	-405	0.6	89
40:10:50 MATPASS					
Ge- Se -Ge	316	180	210	0.9	33
Ge- Se -Li	100	190	-405	0.6	67
^6Li NMR Parameters					
$\text{Li}_2\text{S}:\text{Ga}_2\text{Se}_3:\text{GeSe}_2$	$\delta_{\text{iso}} (\pm 10 \text{ ppm})$	Width (ppm)	$xG(1-x)L^{**}$	Relative fraction ($\pm 5\%$)	
20:30:50					
Li -Se	0.93	0.61	0.59	100	
40:10:50					
Li -I	1.42	0.36	0.27	37	
Li -II	1.75	0.36	0.27	63	
50:10:40					
Li -I	1.50	0.35	0.27	37	
Li -II	1.84	0.35	0.27	63	
40:00:60					
Li -I	1.60	0.38	0.22	40	
Li -II	1.90	0.38	0.22	60	

*denotes Δ and η values from Mao et al.[37]. Other Δ and η values are from the simulation of the MATPASS anisotropic spectra (see text for details)

** denotes fractional Gaussian character of the mixed Gaussian-Lorentzian line shape

Figure Captions

Figure 1. Glass formation region of the LGGS/Se system. Green circles denote homogeneous glass forming compositions. The blue circles are homogeneous glass compositions of the Ga_2Se_3 - GeSe_2 join from Mao et al. [36]. The green area surrounding the circles marks the continuous glass formation regions. Compositions shown with black squares devitrified upon quenching.

Figure 2 . Raman spectra of homogeneous LGGS/Se glasses with $R < 1$ (a) and with $R > 1$ (b). The inset in (a) is an expanded view of the spectra in the region marked by the dashed box. Asterisks mark the peak corresponding to the Al alloy sample holder. Glass composition is denoted alongside each spectrum in the form of three numbers separated by short dashes that from left to right correspond to the mol% Li_2S , Ga_2Se_3 and GeSe_2 , respectively. Dashed spectra of 40 % Na_2Se – 60 % GeSe_2 from Mao et al. [14].

Figure 3. ^6Li MAS NMR spectra of representative LGGS/Se glasses with $R < 1$ and $R > 1$. Glass composition is denoted alongside each spectrum using the same convention as in Fig. 2. Experimental and simulated spectra are shown with solid black lines and dashed red lines, respectively. Two components Li-I (orange) and Li-II (green) are used to simulate the line shapes for the $R > 1$ glasses. All line shapes have a mixed Gaussian-Lorentzian character (see Table 2).

Figure 4. (a) Contour plot of the 2D ^{77}Se MATPASS/CPMG spectrum for the LGGS/Se glass of composition 40 Li_2S – 10 Ga_2Se_3 – 50 GeSe_2 with the total isotropic projection (top) and the two anisotropic projections (right) along the dashed lines corresponding to BSe and NBSe environments. (b) The experimental (black line) and simulated (dashed red line) isotropic projection of the MATPASS/CPMG spectrum. Simulation components corresponding to Ge–**Se**–Ge (BSe) and Ge–**Se**–Li (NBSe) sites are shown in green and pink, respectively. (c) The experimental (black solid lines) and simulated (red dotted lines) CSA sideband patterns taken at the isotropic chemical shifts of the BSe and NBSe environments.

Figure 5. ^{77}Se MAS NMR spectra for representative LGGS/Se glasses with $R > 1$ (left) and $R < 1$ (right). Experimental and simulated line shapes are shown with solid black and dashed red lines, respectively. Individual Gaussian simulation components for Ge–**Se**–Ge and Ge–**Se**–Li

environments in $R > 1$ glasses are shown in green and pink, respectively. Those for Ge-**Se**-Ge and Ge-**Se**-Ge-Ge environments in $R < 1$ glasses are shown in green and blue, respectively. Inset shows the chemical shift dependence of the Ge-**Se**-Ge environment with sulfur content. Glass composition is denoted alongside each spectrum using the same convention as in Fig. 2.

Figure 6. The experimental (solid line) and simulated (dashed line) ^{71}Ga QMAT NMR spectra of representative LGGS/Se glasses with $R < 1$ and $R > 1$. Glass composition is denoted alongside each spectrum using the same convention as in Fig. 2. Each spectrum is simulated with a single component using a Czjzek model of distribution for C_q .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig.6