Structure and Physical Properties of Glasses in the System

Ag₂Se-Ga₂Se₃-GeSe₂

M. A. T. Marple^a, D. C. Kaseman^a, I. Hung^b, Z. Gan^b, S. Sen^a

^aDept. of Materials Science & Engineering, University of California at Davis,
Davis, CA 95616, USA

^bCenter for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory,
1800 East Paul Dirac Drive, Tallahassee, FL 32310, USA

Abstract

Homogeneous glasses in the ternary system $\text{Ag}_2\text{Se}-\text{Ga}_2\text{Se}_3-\text{GeSe}_2$ are synthesized and their structure is characterized using Raman and one- and two-dimensional ^{77}Se , ^{71}Ga and ^{69}Ga nuclear magnetic resonance (NMR) spectroscopy. The structure of these glasses consists predominantly of a charge-compensated network of corner-sharing $(\text{Ga/Ge})\text{Se}_{4/2}$ tetrahedra where the negatively charged $\text{GaSe}_{4/2}$ tetrahedra are charge balanced by the Ag cations. The deficiency in Se required to satisfy the tetrahedral coordination of Ga in glasses with $\text{Ag}_2\text{Se}:\text{Ga}_2\text{Se}_3 < 1$ is accommodated by the formation of homopolar Ge-Ge bonds. Progressive addition of Ag_2Se to these glasses efficiently removes Ge-Ge bonding such that their concentration essentially goes to zero at the chemical threshold $\text{Ag}_2\text{Se}:\text{Ga}_2\text{Se}_3 = 1$. Further addition of Ag_2Se beyond this threshold (i.e., $\text{Ag}_2\text{Se}:\text{Ga}_2\text{Se}_3 > 1$) results in the modification of the Ga,Ge-Se tetrahedral network via depolymerization and formation of non-bridging Se atoms. Moreover, all glasses irrespective of their $\text{Ag}_2\text{Se}:\text{Ga}_2\text{Se}_3$ ratio contain a small fraction of Se-Se bonds, implying violation of chemical order. Therefore, the compositional evolution of the structure of these glasses displays the characteristics of both the isoelectronic alkali/alkaline-earth aluminosilicate glasses and the purely covalent, continuously alloyed chalcogenide networks. Such composition-dependent structural evolution is shown to be consistent with the corresponding variation in glass transition temperature and molar volume.

1. Introduction

Multicomponent chalcogenide glasses constitute an important class of materials with technological applications in areas ranging from infrared photonics and telecommunication to non-volatile phase change memory as well as in electrochemical devices as solid electrolytes and chemical sensors [1-4]. An extensive understanding of the structure-property relationship is required in order to optimize the performance of these glasses for their various applications. The majority of structure-property relationship studies in the literature to date have focused on Ge-As-P-X (X=S, Se, Te) glasses that are characterized primarily by fully connected covalent networks where constituent atoms follow the 8-N bonding rule [5-10]. In contrast to these network chalcogenide glasses, relatively little is known regarding the structural characteristics and structure-property systematics of chalcogenide glasses with modified networks. From a practical point of view, however, simply modified chalcogenide networks are not good glass-formers due to their thermal instability against devitrification and low solubility of alkali and/or alkaline-earth sulfides and selenides in Ge-As-P-X networks [11-15]. One way to improve the thermal stability and to incorporate significant amounts of alkali or alkaline-earth modifiers and rare earths in these glasses is to create a compensated network via addition of refractory trivalent cations that are glass-forming intermediates such as Ga^{3+} [16-18]. In this case the modifier cations are expected to charge balance the $[\text{Ga}(\text{S/Se})_{4/2}]^-$ tetrahedra and depending on the modifier:intermediate ratio R one can create a partially or fully compensated network, much like the alkali/alkaline-earth aluminosilicate glasses. These glass compositions are isoelectronic with oxide glasses in the system $\text{M}_2\text{O}(\text{M}'\text{O})\text{-Al}_2\text{O}_3\text{-SiO}_2$ (M= alkali, M' = alkaline-earth) that have been extensively studied in the literature. Since the interatomic bonding is largely covalent in nature in chalcogenides and ionic in oxides, a comparison between the glasses in these systems

may provide important information on how the structure is controlled by the ionic vs. covalent nature of the constituent bonds. This idea prompted us to recently explore the structure-property relationships in ternary stoichiometric chalcogenide glasses in the systems $\text{Na}_2\text{Se-Ga}_2\text{Se}_3\text{-GeSe}_2$ (NGGS) and $\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ (BGGs) [19-21]. These studies have demonstrated that similar to their oxide counterparts, the modifier:intermediate ratio R plays an important role in the compositional evolution of the network structure in NGGS and BGGs glasses. In the case of $R < 1$, these glasses can be considered to be Se-deficient for satisfying the tetrahedral coordination of heteropolar bonded Ga and Ge atoms. This Se deficiency is accommodated via the formation of Ge-Ge homopolar bonds in the structure. On the other hand, for $R > 1$ there are strong indications for the formation of non-bridging Se (NBSe) atoms, although a direct and unequivocal experimental observation of such species remains elusive. Recently we have extended such studies to the system $\text{Ag}_2\text{Se-Ga}_2\text{Se}_3\text{-GeSe}_2$ (AGGS) where we have reported the formation of homogeneous glasses and Ag was shown to behave as a modifier cation with significant mobility leading to superionic conduction even at ambient temperature [22]. In the present study, we report the results of a detailed investigation of the homogeneous glass-forming region and structural characteristics of glasses in the AGGS system using Raman and ^{77}Se , ^{69}Ga , and ^{71}Ga nuclear magnetic resonance (NMR) spectroscopic techniques. The compositional evolution of the structure of these glasses is linked to the corresponding variation in molar volume and glass transition temperature T_g .

2. Experimental Methods

2.1 Synthesis

All AGGS glasses were synthesized by conventional melt quenching method. The glasses were prepared in 2 g batches from mixtures of constituent elements with 99.9999% purity level. The mixtures were sealed in evacuated ($\sim 10^{-4}$ Torr) fused silica ampoules and melted in a rocking furnace. The mixtures were heated to 1050 °C at a rate of 100 °C/h, held at temperature for 6 h and were subsequently cooled to 950 °C and held at temperature for 24 hours followed by quenching in ice water. The amorphous nature of the samples was verified using powder X-ray diffraction measurements.

2.2 Raman Spectroscopy

The Raman spectra of the AGGS 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 64 to 128 scans collected in backscattering geometry using a resolution of 2 cm^{-1} and a laser power of 30 mW.

2.3 NMR Spectroscopy

2.3.1 Experiments at high magnetic field (19.6 T)

All experiments at the field of 19.6 T were performed at the National High Magnetic Field Laboratory using an ultra-narrow bore magnet equipped with a Bruker DRX console operating at resonance frequencies of 158.8, 253.6 and 199.7 MHz for ^{77}Se , ^{71}Ga and ^{69}Ga , respectively. High-resolution two-dimensional (2D) ^{71}Ga quadrupolar magic-angle-turning (QMAT) and ^{77}Se magic-angle-turning phase-adjusted sideband separation (MATPASS)

experiments were performed with Car-Purcell-Meiboom-Gill (CPMG) echo-train acquisition [23, 24]. Crushed samples were packed in 4 mm ZrO₂ rotors and spun at 10 kHz. For each ⁷¹Ga and ⁶⁹Ga 2D QMAT/CPMG experiment 64 hypercomplex t_1 points were acquired with 2000 (6000 for ⁶⁹Ga) transients per point, 33 CPMG echoes per transient and a 0.5 s recycle delay. The details of the QMAT/CPMG pulse sequence can be found elsewhere [22,23]. Each transient was obtained using the MAT sequence of nine π -pulses. The MAT sequence is followed by CPMG pulses for multiple-echo acquisition. The $\pi/2$ - and π -pulse lengths were 2.0 and 4.0 μ s, respectively. The ⁷⁷Se 2D MATPASS/CPMG experiment used a series of five MAT π -pulses (4.0 μ s) followed by CPMG pulses for data acquisition. Each of the 16 hypercomplex t_1 points were acquired with 36 transients per point, 64 CPMG echoes per transient, and a 60 s recycle delay. The inter π -pulse delays for both QMAT and MATPASS experiments were incremented according to the timings detailed by Hung et al. [24]. Hypercomplex data acquisition was employed for both QMAT and MATPASS experiments, using the method of States et al. [25] to the phases of the CPMG pulses and the receiver. Referencing for ⁷¹Ga/⁶⁹Ga and ⁷⁷Se was done externally by recording the ¹⁷O signal of neat, natural abundance H₂O and then using the frequency ratios reported in the IUPAC recommendations [26].

2.3.2 Experiments at low magnetic field (11.7 T)

All NMR measurements at 11.7 T were performed using a Bruker AQS spectrometer operating at 95.4 MHz for ⁷⁷Se. The ⁷⁷Se magic angle spinning (MAS) experiments were performed using a 5 mm Doty XC probe with crushed glass samples spinning in a Si₃N₄ rotor at ~15 kHz. A Hahn echo pulse sequence was employed 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 200 s. Approximately 900 FIDs were

averaged and Fourier transformed to obtain each spectrum. The ^{77}Se chemical shifts were referenced to the ^{77}Se isotropic shift of crystalline $(\text{NH}_4)_2\text{SeO}_4$ ($\delta_{\text{iso}} = 1040.2$ ppm). All simulations of the NMR spectra were performed using the Dmfit software package [27]. The reported chemical shift anisotropy (CSA) tensors follow the Haeberlen convention defined as:

$$\delta_{zz} - \delta_{\text{iso}} \geq \delta_{xx} - \delta_{yy} \geq \delta_{yy} - \delta_{\text{iso}},$$

$$\delta_{\text{iso}} = \frac{1}{3}(\delta_{zz} + \delta_{xx} + \delta_{yy}),$$

$$\Delta = \delta_{zz} - \delta_{\text{iso}},$$

$$\eta = \frac{\delta_{xx} - \delta_{yy}}{\Delta},$$

where δ_{xx} , δ_{yy} , and δ_{zz} are the principal components of the CSA tensor. The magnitude of the CSA is Δ , while the asymmetry of the CSA is denoted by η .

2.4 Differential Scanning Calorimetry (DSC)

Conventional DSC scans were taken using a Mettler-Toledo DSC1 calorimeter. Scans were performed in a flowing nitrogen environment on 10–20 mg of sample loaded into 40 μL aluminum crucibles. The glass transition temperature T_g is determined to within $\pm 2^\circ\text{C}$ as the onset of the glass transition region, when heating at a rate of $20^\circ\text{C}/\text{min}$.

2.5 Density measurements

Density measurements were carried out using a Micromeritics AccuPyc II gas expansion pycnometer under a helium environment of 6N purity. Approximately 1 to 2 g of each sample was loaded into a 1 cm^3 cup. Reported densities are averages of 10 consecutive measurements at 20°C and are determined to within $\pm 0.005\text{ g/cm}^3$.

3. Results

3.1 Glass Formation Range

The homogeneous glass formation range is shown in Fig. 1. Previous studies reported the formation of homogeneous binary glasses along the Ga_2Se_3 - GeSe_2 join with 0 to 30 mol% Ga_2Se_3 [28]. At least 10 mol% Ga_2Se_3 is required to form a homogeneous ternary glass with Ag_2Se as a component with up to 40 mol% Ag_2Se . On the other hand, glass formation for compositions with 1:1 ratio of $\text{Ag}_2\text{Se}:\text{Ga}_2\text{Se}_3$ extends down to 50 mol% GeSe_2 . The homogeneous glass formation range is surrounded by a narrow composition region where crystallization can still be avoided at typical cooling rates but the resulting glasses are heterogeneous, i.e., phase separated (Fig. 1). These phase separated glasses are characterized by two distinct glass transitions in the DSC scans (Fig. 2). For example, the ternary phase separated glass of composition $(\text{Ag}_2\text{Se})_{10}(\text{Ga}_2\text{Se}_3)_{40}(\text{GeSe}_2)_{50}$ displays two glass transitions that are situated above and below the single glass transition observed for the $(\text{Ag}_2\text{Se})_{25}(\text{Ga}_2\text{Se}_3)_{25}(\text{GeSe}_2)_{50}$ glass (Fig. 2). The heterogeneous glass is therefore, likely separating into a low- T_g Ag rich glass in the matrix of a high- T_g glass composed primarily of Ga-Ge-Se, given the similarity between the higher T_g value in comparison with those characteristic of the binary Ga_2Se_3 - GeSe_2 glasses [28]. This type of phase separation has been observed before in the binary Ag_2Se - GeSe_2 glass system [29] and a representative case is shown in Fig. 2 for comparison. As the extent of phase separation in these glasses is difficult to determine, here we use the criterion that glasses that lack a detectable second glass transition are homogeneous and the structure-property relations in these glasses are the focus of the present study. Liquids in the composition region surrounding the homogeneous and heterogeneous glass formation devitrify readily upon cooling (Fig. 1). All of the bulk glasses are a lustrous dark grey in color, however,

increasing the Ag:Ga ratio changes the color of the crushed glass from a dark reddish orange to black for the $R > 1$ glasses indicating a redshift of the optical absorption edge. The compositions of the homogeneous AGGS glasses prepared in this study and their T_g and density are listed in Table 1.

3.2 Raman Spectroscopy

The Raman spectra of all AGGS glasses are shown in Fig. 3. All spectra display three distinct regions: (i) a broad band from ~ 60 to 160 cm^{-1} , (ii) a sharp peak at 200 cm^{-1} with shoulders near ~ 175 and $\sim 215\text{ cm}^{-1}$, and (iii) a broad band centered at ~ 250 to 263 cm^{-1} with a shoulder at $\sim 305\text{ cm}^{-1}$. The broad band in region (i) contains various bending modes of the $\text{GeSe}_{4/2}$ tetrahedra. Previous studies have assigned the primary band at 200 cm^{-1} in region (ii) to the A_1 symmetric stretching of the corner sharing $\text{GeSe}_{4/2}$ tetrahedra [30]. The shoulders at 175 and 215 cm^{-1} are assigned to the stretching of homopolar Ge-Ge bonds in an ethane like unit $(\text{Se}_3)\text{Ge-Ge}(\text{Se}_3)$ and of Ge-Se bonds in edge-shared $\text{GeSe}_{4/2}$ tetrahedra, respectively. The main band in region (iii) near ~ 250 to 260 cm^{-1} corresponds to the stretching mode of homopolar Se-Se bonds and a coupled bending and asymmetric stretching mode of the $\text{GeSe}_{4/2}$ tetrahedra while the shoulder near 305 cm^{-1} corresponds to the asymmetric stretching of the $\text{GeSe}_{4/2}$ tetrahedra [19]. A sharp but weak peak at 80 cm^{-1} from the sample holder can be discerned in some spectra.

Changes in the Raman spectra for the $R > 1$ glasses are shown in Fig. 3 (a) where the concentration of Ag_2Se is increased relative to GeSe_2 along a fixed concentration of 10 mol% Ga_2Se_3 . The most prominent change with increasing Ag_2Se is the decreasing intensity of the shoulder near 215 cm^{-1} indicating the disappearance of the edge-sharing $\text{GeSe}_{4/2}$ tetrahedra in the glass structure and a consequent shift to a predominantly corner-sharing network. Additionally

the peak position of the high-frequency band shifts progressively with increasing Ag_2Se from $\sim 261 \text{ cm}^{-1}$ to $\sim 252 \text{ cm}^{-1}$. This shift has been attributed in the literature to the increased involvement of non-bridging Se on the $\text{GeSe}_{4/2}$ tetrahedra forming Ge-Se-Ag linkages [31].

The Raman spectra for the $R = 1$ glasses are shown in Fig. 3 (b) as a function of the total GeSe_2 content. The compositional evolution shows significant asymmetric broadening of the main mode at $\sim 200 \text{ cm}^{-1}$ and increasing intensity near 175 cm^{-1} as GeSe_2 content decreases. At the same time the definition of the 215 cm^{-1} band disappears and the band at $\sim 260 \text{ cm}^{-1}$ broadens and shifts slightly to lower wavenumbers with decreasing GeSe_2 content.

Fig. 3 (c) shows the Raman spectra for the $R < 1$ glasses with a narrow range of 7.5 to 10 mol% Ag_2Se , where the Ga_2Se_3 content is increased relative to GeSe_2 . In contrast to the other series of glasses, increasing the Ga content has no effect on region (iii). In region (ii) there is a pronounced increase in the intensity of the 175 cm^{-1} band indicating the formation of homopolar Ge-Ge bonds. As discussed in section 3.4, the ^{71}Ga NMR spectroscopic results indicate that Ga atoms do not participate significantly in homopolar bonding in these glasses. The increased number of homopolar Ge-Ge bonds results from Se deficiency as Ga is added in the stoichiometric form of $\text{GaSe}_{3/2}$, thus lacking enough Se atoms to satisfy a fourfold coordination for Ga atoms in the glass structure [32].

3.3 ^{77}Se NMR

The ^{77}Se MAS NMR spectra of AGGS glasses with 10 mol% Ga_2Se_3 and with Ag_2Se content varying between 16 and 40 mol% are shown in Fig. 4. These spectra consist of a main peak centered at $\sim 390 \text{ ppm}$, characteristic of two-coordinated Se sites corner-shared by $(\text{Ge,Ga})\text{Se}_4$ tetrahedra [32]. However, these spectral line shapes cannot be simulated well with a single

Gaussian peak at this position. Excess intensity is apparent in the form of a high-frequency shoulder near 700 ppm and a low-frequency shoulder near 0 ppm. Although the intensity of the high-frequency shoulder appears to be independent of the Ag concentration, intensity on the low-frequency side increases with increasing Ag content (Fig. 4). A 2D ^{77}Se MATPASS/CPMG NMR spectrum was collected on the sample with 40 mol% Ag_2Se (Fig. 5a) in order to gain further insight on the constituent NMR line shapes under the MAS spectra in Fig. 4. The isotropic projection of a MATPASS/CPMG NMR spectrum is free of CSA broadening effects. This projection for the ^{77}Se MATPASS/CPMG NMR spectrum in Fig. 5a is shown in Fig. 5b. It can be simulated well with three Gaussian peaks with δ_{iso} centered near 550, 375 and 130 ppm with relative fractions of 5, 50 and 45%, respectively. The corresponding CSA tensors are obtained from simulating the spinning sidebands in the corresponding projections on the anisotropic dimension (Fig. 5c). The simulation for the site with $\delta_{\text{iso}} = 550$ ppm (375 ppm) yields a CSA tensor with $\Delta = 290$ ppm ($\Delta = 250$ ppm) and $\eta = 0.85$ ($\eta = 0.9$). These δ_{iso} and CSA values are consistent with the assignment of these two peaks to Ge-**Se**-Se and corner-sharing Ge-**Se**-Ge environments in the glass structure, respectively [33]. In contrast, the peak with $\delta_{\text{iso}} \sim 130$ ppm is characterized by a significantly larger Δ of ~ -450 ppm and $\eta = 0.7$. This peak can be assigned on the basis of its δ_{iso} value to non-bridging Se (NBSe) atoms in Ge-**Se**-Ag environments of the glass structure [22]. The relatively large Δ associated with this Se environment is also consistent with the structural and chemical symmetry of this environment. The δ_{iso} and CSA parameters obtained from the ^{77}Se MATPASS NMR spectrum allows for a fairly accurate simulation of the MAS spectral line shapes of the AGGS glasses, even when the peak positions and their full widths at half maximum are kept constrained. These simulations are shown in Fig. 4 and the corresponding parameters are listed in Table 2. The results of these

simulations directly show the progressively increasing concentration of NBSe environments in AGGS glasses with increasing Ag concentration. The total fraction of NBSe environments as obtained from these simulations is compared in Fig. 6 to the values calculated from the chemical composition of these glasses, under the assumption that the excess Se incorporated via the addition of Ag_2Se minus that required to satisfy the tetrahedral coordination of Ga goes to form these Se environments. The agreement in the compositional trend between the measured and calculated values indicates that the structural network of the AGGS glasses behaves much like that in charge-compensated aluminosilicate glasses where the modifier cations in excess of those required to charge balance the $[\text{AlO}_{4/2}]^{-1}$ tetrahedra generate non-bridging oxygen atoms. However, the origin of the large offset between the two sets of values remains unclear at this stage. It is likely that the MAS NMR line shape simulations overestimate the fraction of NBSe environments as the corresponding signal may contain overlapping contributions from other types of bridging Se sites. This hypothesis is corroborated by the fact that for the sample with 40 mol% Ag_2Se , the NBSe fraction obtained from the ^{77}Se MATPASS/CPMG NMR spectrum (45%) is $\sim 5\%$ lower than that obtained from the simulation of the corresponding MAS spectrum (see Table 2).

3.4 $^{71/69}\text{Ga}$ QMAT/CPMG NMR

The ^{71}Ga central transition QMAT/CPMG NMR spectra for three representative glasses with $R < 1$, $R = 1$, and $R > 1$ are shown in Fig. 7. The $R < 1$ and $R = 1$ (32.5% and 20% Ga_2Se_3 respectively) glasses in Fig. 7a display a single asymmetric peak 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 . Simulation of these lineshapes using the Czjzek model of distribution of C_Q in the software DMfit [34] yields an isotropic chemical shift $\delta_{\text{iso}} \sim 175 \pm 4$ ppm and a quadrupolar coupling constant $C_Q \approx 10.5$ to 11.0 MHz. These NMR parameters are in good agreement with those reported for the ^{71}Ga MAS NMR spectra corresponding to the tetrahedral GaSe_4 environment found in stoichiometric $\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ glasses [21]. The ^{71}Ga δ_{iso} for these AGGS glasses is also consistent with that reported (130 ppm) for the Ga_2Se_3 crystal where Ga atoms are tetrahedrally coordinated to Se. Hence, it is safe to conclude that the Ga atoms in AGGS glasses with $R \leq 1$ are predominantly tetrahedrally coordinated to Se in corner-sharing $\text{GaSe}_{4/2}$ environment. It should be noted here that the tetrahedral coordination of Ga is known to be preserved even in glasses with $R = 0$, i.e., those along the $\text{Ga}_2\text{Se}_3\text{-GeSe}_2$ join [27]. In contrast, the AGGS glasses with $R > 1$ show significantly complicated Ga NMR line shapes (Fig. 7b). Comparison between ^{69}Ga and ^{71}Ga NMR line shapes at 19.6 T for the glass with $R = 4$ suggest the presence of multiple Ga resonances. In fact these spectra can only be simulated in a self-consistent manner with contributions from three Ga resonances. The components for the ^{71}Ga NMR spectrum are characterized by sites with $\delta_{\text{iso}} \sim 80, 180$ and 250 ppm and $C_Q \sim 8, 11$ and 9 MHz, respectively. Although the resonance with $\delta_{\text{iso}} = 180$ ppm and $C_Q = 11$ MHz, that constitute $\sim 65\%$ of the total area under the line shape, can be readily assigned to tetrahedral $\text{GaSe}_{4/2}$ environments, the other two resonances cannot be assigned to specific Ga environments *a priori*. Previous report of ^{71}Ga NMR results on $\text{GeS}_2\text{-P}_2\text{S}_5\text{-Ga}_2\text{S}_3$ glasses indicated that the δ_{iso} for the resonance for octahedrally coordinated Ga shifts to lower frequency (lower ppm) by ~ 350 ppm compared to that for tetrahedrally coordinated Ga atoms [35]. Therefore, it may seem reasonable to assign the resonance at $\delta_{\text{iso}} \sim 80$ ppm to five-coordinated Ga atoms in AGGS

glasses with $R > 1$. However, typically network intermediates such as Ga and Al are expected to be pushed to higher than fourfold coordination either in glasses deficient in chalcogen atoms or in those with high field strength cations such as phosphorus. Therefore, the formation of higher than fourfold coordinated Ga atoms in $R > 1$ glasses seems unlikely. On the other hand, formation of NBSe in glasses with $R > 1$ and their association with Ga in the glass structure may give rise to these additional ^{71}Ga resonances near ~ 80 and 250 ppm, although the exact nature of such structural units remains unclear at this stage.

3.5 Differential Scanning Calorimetry

The compositional variation of T_g for all AGGS glasses span a relatively narrow range between 214 and 295 °C (Table 1). The variation in T_g with R for AGGS glasses is shown in Fig. 8a. These glasses show a monotonic decrease in T_g with increasing R . The variation of T_g with GeSe_2 content for the $R = 1$ and $R < 1$ glasses is shown in Fig. 8b. A monotonic decrease in T_g is observed in all glasses with increasing GeSe_2 content.

3.6 Molar Volume

The influence of composition on structural packing is best revealed in the molar volume data as the density is dominated by the presence of heavy elements such as Ag. Fig. 9 shows a nearly linear increase in molar volume for all AGGS glasses with increasing GeSe_2 content. On the other hand, for comparable GeSe_2 contents, molar volume shows small but systematic decrease with increasing R (Fig. 9).

4. Discussion

When taken together, the Raman and NMR spectroscopic results indicate that the structure of the AGGS glasses is primarily based on a corner sharing network of $(\text{Ge/Ga})\text{Se}_{4/2}$ tetrahedra. Some edge-sharing between these tetrahedra is observed, particularly in glasses with high GeSe_2 content. All glasses including those that are Se-deficient (i.e., $R < 1$) display the presence of a small concentration of Se-Se linkages, implying violation of chemical order. In glasses with $R > 1$, the $(\text{Ge/Ga})\text{Se}_{4/2}$ tetrahedral network is modified via formation of NBSe atoms as Ag plays the role of a typical modifier cation. On the other hand, Se-deficient glasses with $R < 1$ display the formation of Ge-Ge homopolar bonds.

A comparison of the modes of structural modification between glasses in the AGGS system studied here and their isoelectronic analogues in alkali or alkaline-earth aluminosilicate system reveals interesting similarities and differences. In both systems, for $R > 1$ the presence of excess modifier results in the depolymerization of the tetrahedral network via formation of non-bridging Se or O species. However, the chalcogenide and oxide networks behave differently when $R < 1$. In the oxide system, the network accommodates the oxygen deficiency either by formation of threefold coordinated oxygen atoms while keeping the Al tetrahedrally coordinated or by forcing Al into a network-modifier like environment in five- and/or six-fold coordination with oxygen [36]. In contrast, in the AGGS system, the Ga remains tetrahedrally coordinated but the Se deficiency is accommodated in the network via formation of Ge-Ge homopolar bonds. Similar observation was also made recently in chalcogenide glasses with modified and compensated networks in $\text{BaSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ and $\text{Na}_2\text{Se-Ga}_2\text{Se}_3\text{-GeSe}_2$ systems [20, 21].

This compositional evolution of the atomic structure of AGGS glasses is consistent with the concomitant variation in T_g as shown in Fig. 8 that display two major trends. One of these is

the monotonic drop in T_g with increasing R at a fixed Ga_2Se_3 concentration (Fig. 7a). This trend in glasses with $R \geq 1$ can be associated with the progressive depolymerization of the tetrahedral network via the formation of NBSe environments. On the other hand, for $R < 1$ such a trend can be explained by considering the Raman and ^{77}Se NMR spectroscopic results, both of which indicate formation of weak Se-Se linkages and violation of chemical order as Ag_2Se is added to binary Ga_2Se_3 - GeSe_2 glasses. The other trend is that at constant R , T_g decreases with increasing concentration of GeSe_2 . This trend is consistent with the fact that for comparable degrees of network connectivity, i.e., similar R values, the replacement of Ge-Se bonds with Ga-Se bonds would be expected to give rise to a stronger network as the dissociation energy of the Ga-Se bond is significantly higher than that of the Ge-Se bonds [37, 38]. Similar compositional trends were also reported for analogous Na_2Se - Ga_2Se_3 - GeSe_2 glasses in a previous study [20].

Similar to T_g , the molar volume also appears to be controlled in a systematic fashion as a function of GeSe_2 content and R . The decrease in molar volume with increasing R is consistent with the progressive depolymerization of the open tetrahedral network via formation of NBSe which allows for efficient structural packing via collapse of the network. Similar effect of non-bridging oxygen on the packing of aluminosilicate networks is well documented in the literature [39]. On the other hand, the relatively rapid increase in molar volume with increasing GeSe_2 content clearly suggests that the tetrahedral GeSe_2 network is significantly more open compared to the charge compensated network formed by the $\text{Ag}^+[\text{GaSe}_{4/2}]^-$ units. This trend is quite the opposite of that observed in alkali aluminosilicate liquids where the molar volume at constant R increases with decreasing SiO_2 content [37].

5. Conclusions

The structure-property relationship in homogeneous AGGS glasses in the ternary system Ag_2Se - Ga_2Se_3 - GeSe_2 is investigated. The results of Raman and multinuclear NMR spectroscopy indicate that the structure of these glasses is based on a $(\text{Ga}/\text{Ge})\text{Se}_{4/2}$ tetrahedral network where Ag plays the role of a conventional network modifier in glasses with $R > 1$. This role of Ag is manifested in the progressively increasing concentration of NBSe species and a monotonic decrease in T_g upon increasing R beyond its threshold value of 1. In contrast, glasses with $R < 1$ display the formation of Ge-Ge homopolar bonds resulting from the deficiency in Se required to satisfy the tetrahedral coordination requirements for both Ga and Ge atoms. At the same time a small fraction of Se-Se homopolar bonds is observed in all glasses investigated in this study, irrespective of their R value. The formation of these weak homopolar bonds upon addition of Ag is responsible for a drop in T_g in AGGS glasses with $R < 1$. For comparable R values, T_g decreases with increasing GeSe_2 content which appears to be related to the replacement of stronger Ga-Se bonds with weaker Ge-Se bonds in the tetrahedral network. The effect of R on molar volume appears to be rather subtle as the latter is primarily controlled by the partial molar volume of the open tetrahedral network of the GeSe_2 component.

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Table 1: Composition (mol%), T_g , T_x (crystallization temperature), and density for all homogeneous AGGS glasses synthesized in this study.

Ag₂Se	Ga₂Se₃	GeSe₂	T_g (°C)	T_x (°C)	Density (g cm⁻³)
8	10	82	264	379	4.588
16	10	74	231	344	4.934
22	10	68	240	337	5.076
26	10	64	234	325	5.214
30	10	60	219	328	5.345
40	10	50	214	312	5.502
40	15	45	226	336	5.633
5	5	90	245	375	4.397
20	20	60	269	328	5.067
25	25	50	285	349	5.224
10	20	70	285	366	4.726
7.5	32.5	60	295	395	4.669

Table 2: Line shape simulation parameters for ^{77}Se MAS NMR spectra of the AGGS glass series with 10 mol% Ga_2Se_3 .

% Ag_2Se	δ_{iso} (± 15 ppm)	Width (ppm)	Δ (ppm)	η	relative fraction ($\pm 10\%$)
16 %					
Ge- Se -Ge	390	240	250	0.9	51.64
Ge- Se -Ag	130	240	-450	0.7	27.80
Se- Se -Ge	570	240	290	0.85	20.56
26 %					
Ge- Se -Ge	388	240	250	0.9	44.87
Ge- Se -Ag	130	240	-450	0.7	37.80
Se- Se -Ge	570	240	290	0.85	17.33
40 %					
Ge- Se -Ge	390	240	250	0.9	39.16
Ge- Se -Ag	130	240	-450	0.7	50.50
Se- Se -Ge	570	240	290	0.85	10.35

Figure Captions

Figure 1

Glass formation region in the AGGS system. Blue area denotes homogenous glass formation and squares indicate homogenous glasses synthesized for this study. The surrounding green area corresponds to glass formation where glasses are phase separated (circles). Red crosses mark the compositions that devitrify upon cooling with ice water.

Figure 2

Representative DSC traces for a homogeneous AGGS glass with $R = 1$ (red) and a heterogeneous AGGS glass with $R = 0.25$ (green), both containing 50 mol% GeSe_2 . The onset of the glass transition is taken as T_g and its locations are denoted with the intersection of lines. The blue line corresponds to the DSC trace for a Ga-free phase separated glass of composition $\text{Ag}_{1.5}\text{Ge}_3\text{Se}_9$ composition, showing two glass transitions.

Figure 3

Unpolarized Raman spectra of AGGS glasses for (a) the compositional series with 10 mol% Ga_2Se_3 and variable Ag_2Se concentration. The composition series with $R = 1$ as a function of the GeSe_2 content (b) and the composition series with nearly constant (7.5 to 10 mol%) Ag_2Se content but variable Ga_2Se_3 : GeSe_2 ratio (c). The dashed line aids in showing the shift in the band intensity with increasing Ag_2Se content in (a) and (c).

Figure 4

Experimental (black) and simulated (red) 11.7 T ^{77}Se MAS line shapes for AGGS glasses with 10 mol% Ga_2Se_3 and variable Ag_2Se concentration. Simulation components corresponding to Se-**Se**-Ge, Ge-**Se**-Ge and Ge-**Se**-Ag sites are shown in green, blue and pink, respectively. The simulation parameters are listed in Table 2.

Figure 5

(a) Contour plot of the 2D ^{77}Se MATPASS/CPMG spectrum for the AGGS glass of composition $(\text{Ag}_2\text{Se})_{40}(\text{Ga}_2\text{Se}_3)_{10}(\text{GeSe}_2)_{60}$ with the total isotropic projection (top) and the two anisotropic projections (right) along the dotted lines A and B. (b) The experimental (black line) and simulated (red line) isotropic projection of the MATPASS/CPMG spectrum. Simulation components corresponding to Se-**Se**-Ge, Ge-**Se**-Ge and Ge-**Se**-Ag (NBSe) sites are shown in green, blue 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 Ge-**Se**-Ge and Ge-**Se**-Ag environments .

Figure 6

Comparison between composition dependence of the fraction of NBSe sites obtained from simulated MAS line shapes in Fig. 4 (black squares) and the corresponding values (red circles) calculated from stoichiometry (see text for details). Data point denoted by the blue diamond is obtained from simulation of the MATPASS/CPMG isotropic spectrum in Fig. 5b.

Figure 7

(a) Experimental (black and purple) and simulated (green) ^{71}Ga QMAT NMR spectra for two AGGS glasses with 60% GeSe_2 and $R \leq 1$. The glass compositions are shown alongside the spectra.

b) Experimental (black) and simulated (green) ^{71}Ga (top) and ^{69}Ga (bottom) QMAT NMR spectra for AGGS glass with 60% GeSe_2 and $R = 4$. Both spectra are simulated with three components, each with a Czjzek model of distribution of C_Q . See text for details.

Figure 8

Compositional variation of T_g in AGGS glasses (a) as a function R for different Ga_2Se_3 contents and (b) as a function of GeSe_2 content for glasses with $R < 1$ (circles) and $R=1$ (triangles). The error bars are within the size of the symbols.

Figure 9

Compositional variation of molar volume of AGGS glasses as a function of GeSe_2 content for $R < 1$ (triangles); $R = 1$ (squares); $R > 1$ (circles). The molar volume for glassy GeSe_2 (inverted triangle) from [5] is also shown for comparison.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 5

Fig. 6

a)

Fig. 7

Fig. 7

Fig. 8

Fig. 9