Structure and physical properties of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses with the same mean coordination number of 2.5

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We have prepared and analyzed five different compositions of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses that have the same mean coordination number (MCN) of 2.5 in order to understand whether MCN or chemical composition has the dominant effect on the physical properties of the glass. Density measurements showed a maximum for the chemically stoichiometric $\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}$ sample and suggested that some rearrangement of the atoms was occurring as one atom substituted for another. The measurements of T_g , however, showed that the glasses had almost same glass transition temperature and suggested that the glass network connectivity did not change much with composition. Although Raman scattering and x-ray photoelectron spectra of the glasses indicate that the percentage of the different structural units changes with the composition, there was no evidence of the existence of structural units that could change the overall connectivity of the glass network. Therefore, we concluded that glasses with same MCN but different composition have similar glass network connectivity, and that chemical composition has only a secondary effect on the physical properties of the glasses. © 2011 American Institute of Physics. [doi:10.1063/1.3544309]

I. INTRODUCTION

In glass science it remains challenging to identify the structure of disordered solids since almost all the experimental methods available can only be used to measure crystals whose structure is periodic. A practical approach is, therefore, to investigate the dependence of physical properties on composition.¹ Our particular interest is in chalcogenide glasses which contain the chalcogen elements such as S or Se covalently bonded to network formers such as Ge, As, Sn. Mean field theory using a constraint counting algorithm has been proposed to explain the observation of a threshold behavior where the physical parameters change abruptly as a function of the chemical composition in these glasses.^{2,3} According to this theory, glasses having the number of Lagrangian constraints per atom (N_c) less than the space dimensionality form underconstrained while those with larger N_c form an overconstrained glass networks. Phillips and Thorpe first identified a floppy-to-rigid transition at a mean coordination number (MCN, defined as the sum of the respective elemental concentrations times their covalent coordination number) of 2.4. Tanaka suggested that a second phase transition existed at $\text{MCN}=2.67$ which represents a topological change from a two-dimensional to three-dimensional “stressed rigid” phase.¹ Increasingly experimental evidence has indicated that many physical properties of chalcogenide glasses change abruptly at these MCN values. For example, in the Ge—As—Se glass system which has an exceptionally large glass forming range, such transitions have been found in the material density; the elastic moduli; the index of refraction; the band-gap, etc., as shown in several of our recent publications.^{4–6}

Recently on the basis of data obtained from Raman scattering and temperature-modulated differential scanning calorimetry (DSC), Boolchand identified a rigid but stress-free intermediate phase containing a thermally reversing compositional window with glasses within this window being generally nonaging.^{7–9} This behavior makes chalcogenide glasses very interesting for photonics applications since structural relaxation observed in most amorphous materials is detrimental to the stability of all photonic devices.¹⁰ The Boolchand intermediate phase, for example, in $\text{As}_x\text{Se}_{1-x}$ has been identified at MCN from 2.29 to 2.37, and in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses containing the same concentrations of Ge and As identified at MCN from 2.27 to 2.46.¹¹ For the case of binary glasses or specific ternary glasses which have the same concentration of two of its elements as were used in these studies, MCN has a one to one correspondence with chemical composition. However this is not generally true for all ternary compositions. For example, in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ ternary glasses, the Ge, As, and Se atoms in the $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses are 4, 3, and 2 coordinated, respectively. Therefore the MCN for such a glass can be written as $\text{MCN}=4x+3y+2(1-x-y)=2+2x+y$. The stoichiometric ratio for the Se concentration is given by $(4x+3y)/2$ when Se is shared with two different structural units. Therefore, one can make several glasses with the same MCN value spanning from Se-rich through the stoichiometric composition into the Se-poor range. From the structural viewpoint, glasses with the same MCN but different compositions will certainly contain different local bond coordination and this would be expected to affect their physical properties. Therefore, the degree to which MCN can be used as the metric for the physical properties in a ternary glass system remains the subject of debate

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and a deeper understanding must be sought between structure and material properties (physical and chemical) for these ternary chalcogenide systems.

To elucidate this issue we prepared five samples of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses with the same MCN of 2.5. The chemical compositions of these five samples were $\text{Ge}_{7.5}\text{As}_{35}\text{Se}_{57.5}$, $\text{Ge}_{10}\text{As}_{30}\text{Se}_{60}$, $\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}$, $\text{Ge}_{15}\text{As}_{20}\text{Se}_{65}$, and $\text{Ge}_{20}\text{As}_{10}\text{Se}_{70}$ which cover the range from being as much as 10% Se-poor, through stoichiometric to 10% Se-rich. We measured their density, glass transition temperature T_g , elastic moduli, and Raman and x-ray photoelectron spectra (XPS) to determine whether the physical properties are predominantly controlled by MCN or by the chemical compositions.

II. EXPERIMENTS

Chalcogenide glasses were prepared from 50 g batches of high purity (5N) Germanium, Arsenic and Selenium metals. The required amounts of these raw materials were weighed inside a dry nitrogen glove box and loaded into a precleaned quartz ampoule. The loaded ampoule was dried under vacuum (10^{-6} Torr) at 110 °C for 4 h to ensure removal of surface moisture from the raw materials. The ampoule was then sealed under vacuum using an oxygen hydrogen torch, and introduced into a rocking furnace for melting of the contents at 900 °C. The melt was homogenized for a period not less than 30 h, then the ampoule was removed from the rocking furnace at a predetermined temperature and air quenched. The resulting glass boule was subsequently annealed at a temperature 30 °C below its glass transition temperature T_g , then slowly cooled to room temperature. Following the annealing process, the glass boules were sectioned to form disks of 25 mm diameter and approximately 2 mm thick. The disks had opposite surfaces ground plane parallel and then polished to optical quality.

The bulk glass was ground into powders with a size of ~ 100 μm before the glass transition temperature T_g was measured using a DSC (Shimadzu DSC-50) with 10 K/min scanning rate in a nitrogen gas flow of 30 ml/min, and no devitrification or crystallization was observed for the samples in this study. In all cases, the position of the dip in the DSC scans was defined as T_g . The density, ρ , of the samples was measured using a Mettler H₂O balance (Mettler-Toledo Ltd., Switzerland) with a MgO crystal used as a reference. Samples from each glass composition were weighed five times in air and ethanol, respectively, and the average density was recorded. The error for each measurement was less than 0.005 g/cm³. Ultrasonic pulse interferometry was employed to measure both shear and compressional wave velocities at room temperature within the transducer response envelope centered at a resonant frequency of 20 MHz. The ultrasonic travel times were systematically corrected to reduce the effect of the bonding layer between the sample and the transducer. The shear C_s and compressional C_c elastic moduli were calculated using the formula $C_s = \rho V_s^2$ and $C_c = \rho V_c^2$, where V_s and V_c are, respectively, the shear and compressional wave velocities. The er-

FIG. 1. Density (squares, left axis) and the average atomic weight of each glass (cross-circles, right axis).

rors in the measurements of both shear and compressional elastic moduli were estimated to be less than 0.5%.

XPS spectra of these bulk glasses were collected using an EscaLab 220-IXL system under a vacuum of 10^{-10} Torr, using monochromatic Al K_{α} x-rays ($h\nu=1486.6$ eV) at a power of 250 W as the excitation source. All high-resolution spectra were recorded using a pass-band of 20 eV and a step of 0.05 or 0.1 eV. The adsorbed hydrocarbon was used as the internal reference and the binding energies of C 1s line was referenced at 285.0 eV.

All Raman spectra were recorded in backscattering geometry using a custom micro-Raman system. The emission from an 808 nm single mode diode laser was filtered using a pair of 808 nm notch filters (Semrock LL01-808) to eliminate amplified spontaneous emission noise from the laser before being focused onto the sample using an $\times 40$ objective. The scattered light collected was passed through a long pass edge filter (Semrock LP02-808RU), into a QE65000 scientific-grade spectrometer with a spectral resolution of ≈ 3 cm^{-1} (Ocean Optics) and a Hamamatsu full-frame transfer charged-coupled devices detector. The laser power at the sample was < 800 μW and intensity did not exceed 2 kW/cm^2 leading to a typical integration time of 5 s for all spectra. We measured the spectra of both fresh and samples after 20 min of laser radiation using different laser powers. If no difference between these two spectra was apparent, we considered any photo-induced effects were totally suppressed.

III. RESULTS AND DISCUSSION

The densities of the five samples of glass are shown in Fig. 1. The average atomic weight of each glass was also calculated on the basis of their respective chemical composition and is also presented. Clearly the chemically stoichiometric composition of Ge12.5 has the highest density. With changing chemical compositions, if we supposed that the replacement of one element by another does not change the arrangement of the atoms, then the density should be proportional to the average atomic weight of the glass. The measurements follow this trend for the Se-poor samples up to the stoichiometric composition but not for Se rich samples. The experimental results, therefore, suggest that the arrangement of the atoms significantly changes with changing chemical composition most likely in the Se-rich samples due to the appearance of Se chains.

We note that, Savage *et al.*^{12–14} reported the density of four samples with the same MCN of 2.5, i.e., $\text{Ge}_5\text{As}_{40}\text{Se}_{55}$, $\text{Ge}_{10}\text{As}_{30}\text{Se}_{60}$, $\text{Ge}_{15}\text{As}_{20}\text{Se}_{65}$, and $\text{Ge}_{20}\text{As}_{10}\text{Se}_{70}$. The densities they reported were 4.53 g/cm^3 , 4.49 g/cm^3 , 4.47 g/cm^3 , and 4.41 g/cm^3 , respectively, and did not show a maximum as a function of the chemical composition. The reasons for the difference from the results presented here could be twofold. First, based on the phase diagram,⁸ the low Ge-content glass $\text{Ge}_5\text{As}_{40}\text{Se}_{55}$ is located in a region where phase separation occurs on the nanoscale. Although Savage *et al.*¹² claimed there was no phase separation in their sample as evidenced by scanning electron microscopy (SEM), it is not really possible to identify phase separation on a scale less than 100 nm using SEM. Second, although Savage *et al.* did not examine every sample they prepared, in all of the glasses they did examine by SEM crystals up to $1 \text{ }\mu\text{m}$ in size were apparent, sometimes in clusters of the order of $10 \text{ }\mu\text{m}$ in size. This indicates that some devitrification was present in their samples which could cause density values to deviate from those of an amorphous solid. By comparison, crystallites in our samples were totally absent.

The glass transition temperature T_g is a metric for network connectivity, and consequently the rigidity of the vitreous network.¹⁵ The values of T_g for the glasses were $239.5 \text{ }^\circ\text{C}$, $243.0 \text{ }^\circ\text{C}$, $247.9 \text{ }^\circ\text{C}$, $251.8 \text{ }^\circ\text{C}$, and $245.0 \text{ }^\circ\text{C}$, for $\text{Ge}_{7.5}\text{As}_{35}\text{Se}_{57.5}$, $\text{Ge}_{10}\text{As}_{30}\text{Se}_{60}$, $\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}$, $\text{Ge}_{15}\text{As}_{20}\text{Se}_{65}$, and $\text{Ge}_{20}\text{As}_{10}\text{Se}_{70}$, respectively. The T_g values is about $30 \text{ }^\circ\text{C}$ higher than those glasses with the same compositions in Refs. 12–14. Several factors could induce the difference of the glass transition temperature, the scanning rate, the particle size of the measured glass, and the method to determine T_g . Generally an increasing scanning rate and the decreasing particle size will lead to a higher T_g .^{16,17} On the other hand, if T_g is defined as an onset temperature for the glass transition is significantly lower than that is defined as a dip in the DSC curves used in these measurements as demonstrated in Ref. 18. For example, $\text{Ge}_{10}\text{As}_{30}\text{Se}_{60}$ glass has an onset temperature for the glass transition at $216 \text{ }^\circ\text{C}$ using a scanning rate of 10 K/min , which is in good agreement with the value of $210 \text{ }^\circ\text{C}$ in Ref. 12 using a scanning rate of 5 K/min . Here we emphasize that, although the method to define T_g is different in Ref. 12 from that in our paper, T_g values in the glasses samples with the same MCN of 2.5 are quite similar from 209 to $212 \text{ }^\circ\text{C}$, except that in $\text{Ge}_5\text{As}_{40}\text{Se}_{55}$ glass which has a lower T_g of $196 \text{ }^\circ\text{C}$. As mentioned above, $\text{Ge}_5\text{As}_{40}\text{Se}_{55}$ glass is located in the nanoscale phase separation region in the phase diagram. This could be the reason to have a reduced T_g .⁷ Therefore, the fact that these values are almost the same in spite of the large change (by almost a factor of 3) in Ge content suggests that the chemical composition has very little effect on the network connectivity.

Figure 2 shows the shear and compressional wave elastic constants for the glasses. With changing chemical compositions, the difference of the elastic constants is $<5\%$ for the shear wave, and $<10\%$ for the compressional wave, respectively. Between MCN of 2.4 and 2.65, several experimental results have confirmed that chalcogenide glasses have a layer-type structure which contains flexible segments.^{19–21}

FIG. 2. The shear and compressional elastic moduli for each glass.

Thus, when compressing the samples, the van der Waals forces between the segments are mainly responsible for the moduli, while the covalent bonds within an individual segment are almost unperturbed by pressure. Therefore all the glasses have moduli of similar magnitude, irrespective of their detailed chemical compositions.

Raman spectra of the glasses are shown in Fig. 3. Basically the whole spectra consist of a peak around 200 cm^{-1} and another broad band from 210 to 300 cm^{-1} . Let us start from the individual vibrational modes of Ge—Se and As—Se glasses since Ge—Se and As—Se units are the basic blocks from which the Ge—As—Se glass network is built. For $\text{Ge}_x\text{Se}_{1-x}$, Tronc *et al.* assigned two peaks at 195 cm^{-1} and 213 cm^{-1} to the vibrational modes in the corner-sharing and the edge-sharing $\text{GeSe}_{4/2}$ tetrahedra, respectively.^{22,23} One peak at 175 cm^{-1} and another peak at 300 cm^{-1} for $\text{Ge}_{40}\text{Se}_{60}$ sample were also reported from the ethanellike modes.^{22,24,25} Regarding $\text{As}_x\text{Se}_{1-x}$, Boolchand reported two principal modes of $\text{AsSe}_{3/2}$ pyramidal units at 225 and 243 cm^{-1} for As_2Se_3 and As_4Se_4 monomers could appear in $\text{As}_x\text{Se}_{1-x}$ when $x > 0.50$.²⁶

Clearly, the sharp peak at 200 cm^{-1} comes from the vibrations in the corner-sharing $\text{GeSe}_{4/2}$ tetrahedra. The vibration of the edge-sharing $\text{GeSe}_{4/2}$ tetrahedra could be buried under the low wavenumber side of the broad band from 210 to 300 cm^{-1} in the glasses containing low concentration of Ge. A slight trace of the edge-sharing $\text{GeSe}_{4/2}$ tetrahedra as shown by an arrow can be found in $\text{Ge}_{15}\text{As}_{20}\text{Se}_{65}$ and

FIG. 3. Raman spectra of the glasses. The inset is the ratio of the scattering intensity at 200 cm^{-1} to that at 227 cm^{-1} as a function of the ratio of Ge/As concentration in the glasses, the dotline is a linear fitting of the scattering experimental data.

FIG. 4. Raman scattering spectrum of As_4Se_4 monomer. The spectrum is calculated using GAUSSIAN 03 package with restricted Hartree–Fock approximation and 3–21G basic set.

$\text{Ge}_{20}\text{As}_{10}\text{Se}_{70}$ glasses, indicating that the vibrational intensity of the edge-sharing $\text{GeSe}_{4/2}$ tetrahedra increases with increasing Ge concentration. On the other hand, the assignment of the broad band from 210 to 300 cm^{-1} in the glasses is significantly complicated due to the presence of several possible contributions. As shown in the insert of Fig. 3, the ratio of the scattering intensity at 200 cm^{-1} (due to corner-sharing $\text{GeSe}_{4/2}$ tetrahedra) to that at 227 cm^{-1} is proportional to the ratio of Ge/As concentration in the glasses, supporting the assignment of the 227 cm^{-1} to the vibration of $\text{AsSe}_{3/2}$ structural unit. The asymmetric lineshape of the broad band is assigned to the contribution from the As—As=Se structure. Since As is lighter than Se, the replacement of Se by As will shift the vibrational band of As—As=Se to higher wavenumber. One band at 260 cm^{-1} appears in $\text{Ge}_{20}\text{As}_{10}\text{Se}_{70}$ glass. This could be due to the vibration of Se-clusters since the glass is Se-rich.²²

From these data we have concluded that separated clusters, for example, As_4Se_4 monomers, cannot be found in the glasses. Raman spectrum of As_4Se_4 monomer as shown in Fig. 4 consists of number of strong and sharp peaks. In particular there is a strong peak at 330 cm^{-1} which clearly cannot be observed in any of the spectra of these Ge—As—Se glasses. This indicates that the change in the chemical compositions does not produce any separated structural units and therefore has no effect on the connectivity of the glass network.

We also measured and analyzed XPS spectra of the glasses in order to understand the evolution of the different structural units. Typical As 3d spectra of the glasses are shown in Fig. 5. It is evident that $\text{AsSe}_{3/2}$ structural units

FIG. 5. Typical As 3d spectra of the glasses, the square dots are experimental data and the dotted lines are simulation results.

dominate all the spectra. In the glasses containing a high concentration of As, the Se=As—As structure, where one As atom links with two Se and one As atoms, appears but the number is small. We did not observe evidence of the presence of the Se—As=As structure or the As_4Se_4 monomer in the glasses—the latter being in agreement with our conclusions from the Raman spectra. Table I shows the binding energy, linewidth, and the percentage of the different structural units obtained by decomposing the Ge, As, and Se 3d XPS spectra. Due to the difference in the electronegativity, Ge rather than As first reacts with Se, and, therefore, all the Ge atoms are bonded with Se.²⁷ In Se-poor samples like Ge7.5 and Ge10, homopolar As—As bonds will form to compensate the deficiency of Se content. However, Se—As=As (one As atom linking with one Se and two As atoms) and Ge—Ge containing units are not observed in any of the compositions since Se-deficiency is below 10%. On the other hand, a small number of Se-trimmers appear in the Se-rich glasses such as Ge15 and Ge25. We expect Se-poor glasses to be more rigid; therefore, the freedom for the network to rearrange as one atom is substituted for another is small. Hence replacing Ge by As would be expected to cause the density to increase in proportion to the average atomic weight as was observed. On the other hand, when chain-like Se-trimers appear in the Se-rich glasses, the number of cross-

TABLE I. The decomposed parameters for XPS Ge, As, and Se 3d spectra. BE/W/R represent the binding energy (eV), full width of half maximum (eV), and the ratio of the integrated area for different structural units, respectively.

	Se—Se—Se	Ge(As)—Se—Se	Ge(As)—Se—Ge(As)	$\text{AsSe}_{3/2}$	Se=As—As	$\text{Ge}_{4/2}$
	BE/W/R (%)	BE/W/R (%)	BE/W/R (%)	BE/W/R (%)	BE/W/R (%)	BE/W/R (%)
$\text{Ge}_{7.5}\text{As}_{35}\text{Se}_{57.5}$		55.6/0.86/29	55.1/0.87/71	43.2/1.01/69	42.8/0.98/31	31.6/0.95/100
$\text{Ge}_{10}\text{As}_{30}\text{Se}_{60}$		55.5/0.89/32	55.0/0.78/68	43.2/0.88/78	42.8/0.89/22	31.6/0.86/100
$\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}$		55.5/0.77/48	55.0/0.79/52	43.3/0.74/82	43.0/0.85/18	31.6/0.91/100
$\text{Ge}_{15}\text{As}_{20}\text{Se}_{65}$	56.0/0.83/10	55.5/0.87/39	55/0.86/51	43.2/0.88/100		31.5/0.91/100
$\text{Ge}_{20}\text{As}_{10}\text{Se}_{70}$	56.0/0.76/14	55.5/0.76/40	55/0.78/46	43.2/0.75/100		31.5/0.81/100

linking Ge—Se or As—Se bonds has to decrease and hence covalent bonding is substituted by van der Waals bonding and this likely leads to an expansion of the network and hence a drop in density as occurred for the Ge15 and Ge20 samples.

IV. CONCLUSION

We have prepared five pieces of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses with the same MCN of 2.5. The density measurements exhibit a maximum for the chemically stoichiometric $\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}$ sample, suggesting a re-arrangement of the atoms occurs when one element is replaced by another. However, T_g measurements show that the glasses have almost same glass transition temperature, indicating that the glass network connectivity changes very little with chemical composition. Although the Raman and XPS spectra of the glasses indicate that the percentage of the different structural units does change with the changing chemical compositions, there is no evidence of the existence of separated structural units that can cut the glass network connectivity. Therefore, the glasses with same MCN but different compositions have similar glass network connectivity, and the chemical compositions only slightly modify the physical properties of the glasses.

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