Structure and dynamics of a silver-doped chalcogenide glass: An ab initio study

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ABSTRACT

A ternary glassy chalcogenide material, Ag$_{2+y}$Ge$_{25}$Se$_{75-y}$, is analyzed for structural, electronic, vibrational, and ion dynamical properties. The structural analysis has revealed some interesting substructures, which are typically found only in Se-rich or Ge-rich materials. The radial distribution function of the Ag$_{2+y}$Ge$_{25}$Se$_{75-y}$ model illustrates reasonably good agreement with experiment. The vibrational density of states (VDS) is characterized, and the nature of the modes is revealed as a function of energy. Finally, the dynamics of Ag are explored by investigating diffusion and hopping characteristics of Ag, and the character of trapping centers.

1. Introduction

In the mid-1960s [1] it was realized that silver could be incorporated into chalcogenide glasses via photo-dissolution resulting in new materials with unique technological properties. When Ag is used to dope Ge$_{1-x}$Se$_x$ glasses, solid electrolytes, Ag$_x$(Ge$_{1-x}$Se$_x$)$_{1+y}$, are created, having very high ionic conductivities [2]. Many current and potential applications in the areas of optics, optoelectronics, chemistry, and biology exist [3].

The host network, Ge$_{1-x}$Se$_x$, has been broadly investigated for many years experimentally [4–8] and theoretically [9–16]. These studies have revealed that, in general, the Ge(Se$_1$)$_2$(Se$_2$)$_2$ tetrahedra dominate for x ≤ 0.34, Ge(Se$_1$)$_2$(Se$_3$)$_2$ units for x ≥ 0.36 and x ≤ 0.41, and orthorhombic (distorted rocksalt) GeSe units for x ≥ 0.42 [17].

The Ag$_x$(Ge$_{1-x}$Se$_x$)$_{1+y}$ system has been studied extensively over the years both for academic and technological reasons. Several experimental studies [17–20] have been performed which showed that for Se-rich glasses (i.e. GeSe$_x$) phase separation produced an Ag$_x$Se glass phase and a Se-deficient matrix, whereas stoichiometric glasses (i.e. GeSe$_2$) contained a GeSe$_2$ glass phase and Ge$_2$Se$_3$ glass phase for y > 0.2. Ge-rich glasses (i.e. Ge$_2$Se$_3$) had a mixture of Ge$_2$Se$_3$ and GeSe phases. Computer simulations [21–24] have been performed in order to better understand the structural, electronic and silver ion dynamics of these systems, in particular, Ag$_x$(Ge$_{1-x}$Se$_x$)$_{1+y}$ glasses. In a recent publication [25] it was shown that Ag$_x$(Ge$_{1-x}$Se$_x$)$_{1+y}$ glasses (for y = 0.15 and 0.25) possess insulating and metallic phases with nearly the same energies.

In this paper, we will present not only the structural, electronic, and Ag ion dynamics, but also, to the best of our knowledge, a first treatment of the vibrational attributes of such systems. Amorphous Ag$_{2+y}$Ge$_{25}$Se$_{75-y}$ structure was modeled because of its interest as a CBRAM material [20,26]. Better understanding of the static and dynamical properties of the particular material is of great interest to researchers; for example, those involved in the development of CBRAM devices. Besides being also fundamentally interesting, this composition has not been previously examined.

This paper is arranged in the following manner. Section II describes the computational methodology used. In section III, the model and preparation methods are explained, followed by a presentation and discussion of the structural, electronic, silver ion dynamics, and vibrational properties of the model in section IV. Section V presents the conclusion of the results.

2. Methodology

Several methods [27–29] exist for computational modeling of complex materials. These methods are: empirical potentials, empirical tight-binding methods, and density functional theory (DFT). Obtaining accurate results for chemically complex systems requires the utilization of an ab initio molecular dynamics approach, which incorporates DFT. ab initio molecular dynamics (AIMD) allows realistic simulations to be performed without adjustable parameters [30], and is suitable for relatively small systems.

The amorphous Ag$_{2+y}$Ge$_{25}$Se$_{75-y}$ structure was fabricated using a melt and quench (MQ) approach which utilizes ab initio molecular dynamics (AIMD) based on density functional theory (DFT) [31] incorporated in VASP [32–34]. Projected-augmented wave (PAW) [35]...
pseudo-potentials were used for the description of the core electron-ion interactions and an exchange-correlation functional [36] within the local density approximation (LDA) [37] was considered. The \( \Gamma(k = 0) \) point was utilized for these calculations along with periodic boundary conditions. The kinetic energy cutoff of the plane-wave varied between 300 and 450 eV with the energy difference criteria being \( 10^{-4} - 10^{-5} \) eV. A time step of 2 fs was used for the integration of Newton’s equations of motion and a constant temperature was achieved by employing the Nose–Hoover thermostat [38].

3. Model

The initial configuration of the Ag\(_{20}\) (Ge\(_{52}\)Se\(_{50}\))\(_{1.8}\) system consisted of a random-generated structure of 20 Ag atoms, 28 Ge atoms, and 52 Se atoms for a total of 100 atoms. Due to the lack of an experimental atomic density value, an initial guess of 5.0 g/cm\(^3\) was considered for the initial cubic simulation cell. The initial guess was obtained from an experimental investigation of a similar MQ structure. A minimum acceptable distance of 2 Å was used to prevent unrealistic interatomic distances.

The MQ model was constructed by forming an equilibrated liquid at 2500 K for 12 ps, followed by quenching from 2500 K to 1500 K over 10 ps, then equilibration at 1500 K for 6 ps, and quenching from 1500 K to 300 K within 12 ps and equilibration at 300 K for 20 ps. Relaxation at zero pressure was performed which resulted in a triclinic cell having lengths of 13.907 Å, 13.334 Å and 13.936 Å, and a corresponding atomic density of 5.348 g/cm\(^3\). The B/A and C/A ratios for this cell are 0.9568 and 0.9979, respectively. We relaxed the MQ model so the forces were smaller than 0.01 eV/Å. The final structure was then analyzed for the structural, electronic, vibrational, and Ag ion dynamics properties. For the Ag dynamics calculations a temperature of 1000 K for 40 ps was used.

4. Results and discussion

4.1. Structural properties

The total and partial pair correlation functions are illustrated in Fig. 1. The first and second peaks of the total \( g(r) \) correspond to the contributions of AgSe and GeSe, and AgGe, GeGe, and SeSe correlations, respectively. The first peak of \( g_{\text{GeSe}} \) for 2.52 Å \( \leq r \leq 2.67 \) Å is associated with the three Ge–Ge homopolar bonds and the Ge\(_2\)Se\(_2\) compounds. The second peak at \( r = 4.0 \) Å is quite broad and represents the second-nearest neighbors. The distance between Ge atoms of the Ge\(_2\)Se\(_2\) tetrahedra was found to be at \( r = 4.65 \) Å. The \( g_{\text{GeSe}} \) correlations within the range of 2.33 Å \( \leq r \leq 2.64 \) Å are linked to the Ge\(_2\)Se\(_2\) compounds, corner-sharing Ge(Se\(_3\))\(_2\) tetrahedra and GeSe\(_2\) compounds. Three Se–Se homopolar bonds are represented by the \( g_{\text{SeSe}} \) correlations for 2.50 Å \( \leq r \leq 2.80 \) Å whereas the second-nearest neighbors are located in the range of 3.25 Å \( \leq r \leq 4.63 \) Å. There exist \( g_{\text{AgAg}} \) correlations within the range of 2.62 Å \( \leq r \leq 3.48 \) Å. Also, the AgSe compounds have \( g_{\text{AgSe}} \) correlations in the range of 2.42 Å \( \leq r \leq 2.63 \) Å.

Fig. 2 depicts the static structure factors (total and partials) and reveals that the first sharp diffraction peak (FSDP), a signature of medium range order, is due to the correlations of AgSe and GeSe, which is in contrast to previous studies for other materials that indicate Ge–Ge correlations, located between tetrahedra, are responsible for FSDP [9,15,39,40]. We have produced a rather realistic model for this composition that will now be the “simulation benchmark” for future studies of this material. The total structure factor \( S(q) \) of our model as compared to the experimental data of Piarristeguy and co-workers [41] is of similar profile and magnitude, but for our model there is a slight shift to the right for most of the peaks. The experimental value of FSDP is approximately 1.08 Å\(^{-1}\), reasonably close to our value of 1.29 Å\(^{-1}\). This variation is not surprising in part because the experimental results were for a Ag\(_{20,2}\) (Ge\(_{52}\)Se\(_{50}\))\(_{1.8}\) system. The first primary peak is basically a result of AgAg, AgGe, GeGe, and SeSe correlations. Both the first and second primary peaks correspond to short-range order (SRO).

A comparison of the radial distribution function (RDF) between the experiment of Fischer-Colbrie et al. [42] and our model was performed. The experimental data, shown in Table 1, was obtained from a photodiffused 1500 Å film of Ag\(_{25}\)Ge\(_{25}\)Se\(_{50}\) structure with an atomic density of 5.5 g/cm\(^3\), where our model had 5.35 g/cm\(^3\). As reported in [42], the experimental Ag\(_{25}\)Ge\(_{25}\)Se\(_{50}\) structure was prepared in a three-step process: 1) thermal evaporation of 1500 Å a-GeSe\(_2\) onto a single crystal Si substrate; 2) thermal evaporation of Ag onto a- GeSe\(_2\); and 3) exposure to UV light for causing the Ag photo-diffusion. The a-GeSe\(_2\) film was created from a source of 99.999%-pure Ge and Se materials, and were degassed, melted together, and homogenized at 800 °C for 2 days.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak positions (Å)</th>
<th>Additional peaks (Å)</th>
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</thead>
<tbody>
<tr>
<td>Experiment (ref. [42])</td>
<td>2.62</td>
<td>3.97</td>
</tr>
<tr>
<td>Model</td>
<td>2.59</td>
<td>3.99</td>
</tr>
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</table>

The peak positions correspond to the three primary peaks and the additional peaks associated with the model are probably due to the small structure size.
The rates of deposition were 10 Å/s for a-GeSe2 and 1 Å/s for Ag. Operating pressure was < 10^-9 Torr. For the UV exposure, an unfiltered 200 W Hg lamp was used as well as a one-hour exposure time for complete Ag diffusion.

For comparison, this composition Ag₂Ge₂Ge₅Se₂₀ is closest to our composition of Ag₂Ge₂Ge₅Se₂₀. The peak positions for both the model and experimental sample are shown in Table 1. As seen from Table 1, three peaks exist experimentally and five for our model. The locations of the first and third peaks of our model are in agreement with the first and second peaks of the experimental results. Our model has an additional two peaks at 3.55 Å and 5.87 Å, which may be due to small model size.

The total and partial coordination numbers and first peak positions for the glassy phases of Ge₅Se₇₋ₓ are provided in Table 2 for this work, a simulation study [14], and an experimental investigation [43]. According to Table 2, Ge is somewhat under-coordinated and Se two-fold coordinated as compared to experiment. The partial coordination numbers indicate, in general, reasonable agreement with experiment, except for Se pairs which is significantly reduced due to bonding with Ag, resulting in other substructures.

The host network (Ge₅Se₇₋ₓ) according to Phillips and Thorpe constraint theory [44-46], has an average coordination number < n > of 2.58 as compared to the “rigidity percolation threshold” value < nₚ > of 2.4 implying that the host network is ‘rigid’ or ‘over-constrained’.

The 100-atom Ag₂Ge₂Ge₅Se₂₀ model includes corner-shared Ge(Se₁₋₃)₄ tetrahedra as exemplified by Fig. 3. Because the bond angles of these tetrahedra vary significantly (~90° to 130°) the tetrahedra are quite distorted. As mentioned earlier, this Ag₂Ge₂Ge₅Se₂₀ model has revealed some interesting substructures, in particular Ag₅Se and Ge₅Se₃, only found in Se-rich and Ge-rich materials, respectively. These substructures are depicted in Fig. 4 along with some bond angles.

To obtain further insight into the Ag₂Ge₂Ge₅Se₂₀ structure and its connectivity, ring statistics for each type of atom were computed as illustrated in Fig. 5. The 3- and 6-member rings are dominating for Ag and Se, whereas 3-, 4- and 8-member rings dominated for Ge. All three atom types consisted of 10-member rings whereas Se also has 12-member rings. The ring statistics results were obtained by utilizing King’s method [47] from the ISAACS software [48].

**4.2. Electronic properties**

The electronic density of states (EDOS) is a key physical quantity which may be indirectly probed from photo-emission and optical absorption experiments. Fig. 6 reveals the EDOS results for the Ag₂Ge₂Ge₅Se₂₀ structure. We considered the localization of electronic states by calculating the inverse participation ratio (IPR) given by

\[
I_r(p) = \frac{1}{\left( \sum_{i=1}^{N} |\psi_i|^4 \right)^2} \sum_{i=1}^{N} |\psi_i|^4
\]

where i represents atom i, \( \psi_i \) the kth eigenfunction, N the total number of atoms, and \( a_i \) the atomic orbital projection of atom i.

As seen in Fig. 6, there are extended states near the Fermi level for both the valence and conduction bands in agreement with previous work of Talen et al. [21]. The LDA energy gap for the Γ-point is approximately 0.40 eV, which is about half of the actual value since it is well known that LDA underestimates the gap energy.

**4.3. Vibrational properties**

Generally speaking, a dynamic model, one that considers the motion of atoms, provides valuable information on the thermodynamics of a material (e.g., thermal properties, thermal expansion, existence of phase transitions, etc.) where a static model cannot. Considering the dynamics of a material reveals a much fuller picture of that material as a function of temperature.

The Ag₂Ge₂Ge₅Se₂₀ structure can be thought of as two subnetworks (Ag and GeSe host), where the Ag and GeSe subnetworks are weakly and strongly bonded, respectively. It is interesting and novel to understand the dynamics of each subnetwork as well as collectively. One would expect “soft phonons” for the Ag system, in particular. Conceptually, there is something akin to an Ag melting transition in which the Ag can hop, but the host is rigid.

A comprehensive understanding of the eigenvectors and eigenvalues of the dynamical matrix enables a detailed analysis of this new composition. The mode analysis consists of the following investigations: i) the degree of mode localization, ii) the amount of bond stretching and bending, iii) mode character (acoustic-like or optical-like), iv) amount of atomic vibrational participation, v) substructure unit vibrations, and vi) tetrahedral breathing A₁ vibration modes of the host network tetrahedra.

VIPR, similar to the electronic IPR, quantifies which normal modes are extended or localized. Following the notation of Zotov et al. [49], VIPR is defined as

\[
I_r(p) = \frac{1}{\left( \sum_{i=1}^{N} |\psi_i|^4 \right)^2} \sum_{i=1}^{N} |\psi_i|^4
\]
where $u^p_i$ represents the eigenvector or displacement of atom $i$ for a given mode $p$ of frequency $\omega_p$, which is summed over all atoms. A complete localization of the eigenvectors is characterized by $I_v = 1$, whereas an extended or de-localization when $I_v$ is close to 0.

The VDOS and VIPR results, which are presented in Fig. 7, indicate extended vibrational states at the low frequencies (0–150 cm$^{-1}$) and more localized states from approximately 200–310 cm$^{-1}$. When compared to the work done by Cobb and co-workers [9] our VDOS results show the influence of the Ag atoms with additional peaks across the vibration spectrum, while our VIPR results having a similar trend with de-localized states at low frequencies and localized ones at higher.

For the total and partial VDOS calculations, Gaussian broadening with a standard deviation sigma value of 3.0 cm$^{-1}$ was employed. As illustrated in Fig. 8, the partial VDOS for Se is mostly responsible for the profile and magnitude of the total VDOS which is in reasonable agreement with [9]. Silver makes no contribution beyond approximately 270 cm$^{-1}$, whereas Ge and Se do.

Another important property is the stretching character [49,50] which quantifies bond stretching or bending as determined by Eq. (3)
where $\hat{b}_i$ represents a unit vector along the bond for atoms $i$ and $j$. The summations are over all nearest-neighbor atom pairs $(i,j)$ in the model. Its value will be close to $+1$ if the mode has predominantly bond-bending (compressing) characteristics and fairly close to 0 if the mode has mostly bond-stretching characteristics as elucidated in Fig. 9. There are basically three regions of interests: 0–50, 80–160, and 160–310 cm$^{-1}$. The long-frequency region is mostly of bond-bending character (S $\leq 0.2$) with a small amount of stretching, mid-frequency range has a mixture of bending and stretching characteristics (0.2 $\leq S \leq 0.55$) with the stretching contribution increasing with frequency, and the high-frequency range having approximately an equal mixture of bending and stretching characters ($S \approx 0.55$). An interesting feature is the abrupt change of S that occurs at 160 cm$^{-1}$, which may be a result of the Ge and Se atoms beginning to increase and decrease their vibrational contribution, respectively, as revealed in Fig. 12. The plateau in the high-frequency range is due to the Ge atoms increasing their participation at a higher rate than Se atoms decreasing theirs, and the fact that there are almost twice as many Se atoms as Ge atoms.

The character of the correlations between individual atomic displacements is obtained by considering the phase quotient $q$ [51], as well as its parallel and perpendicular components, of the modes. This amounts to determining if the relative motion of neighboring atoms is in-phase (acoustic-like) or out-of-phase (optical-like) over the whole Ag$_{20}$Ge$_{28}$Se$_{52}$ structure. For example, $q_1(p)$ represents the projected motion that is parallel to the bonds and $q_1(p)$ the projected motion perpendicular to the bonds. These quantities are conveniently defined as

$$q(p) = \frac{\sum_{ij} |u_{ij}^p \cdot \hat{b}_i|}{\sum_{ij} |u_{ij}^p|}$$

(4)

$$q_1(p) = \frac{\sum_{ij} |u_{ij}^p (\hat{R}_j - \hat{R}_i) \cdot \hat{b}_i|}{\sum_{ij} |u_{ij}^p|}$$

(5)

$$q_1(p) = \frac{\sum_{ij} |u_{ij}^p (\hat{R}_j - \hat{R}_i) \cdot \hat{b}_i|}{\sum_{ij} |u_{ij}^p|}$$

(6)

Sums are again over all nearest-neighbor atom pairs $(i,j)$ in the model. $\hat{b}_i$ represents the unit vector in the direction of bond $(i,j)$ and $\hat{R}_j - \hat{R}_i$ a dyadic quantity. We calculate the phase quotient $q$ along with its parallel $q_1$ and perpendicular $q_1$ components as illustrated in Fig. 10. All three phase quotients can vary from +1 (acoustic-like modes) to −1 (optical-like modes).

The overall phase quotient $q$ is varying almost linearly from the acoustic-like modes to optical-like modes. The parallel phase quotient $q_1$ exhibits an abrupt change in the range of 100–150 cm$^{-1}$, whereas the perpendicular phase quotient $q_1$ is, in general, changing linearly in the acoustic-like range until reaching a frequency of 100 cm$^{-1}$ where its remains relatively constant to 150 cm$^{-1}$; thus, exhibiting weak optical-like characteristics. Beyond 150 cm$^{-1}$ there are progressively increasing oscillations of $q_1$ until reaching a frequency of 300 cm$^{-1}$. After careful observation of the vibrational behavior of the structure, it appears that this abnormality is due to severe rocking vibrations of a Ge–Ge bond where one of the Ge atoms is bonded to three Se atoms and the other Ge atom to two Ag and Se atoms. This compound is illustrated in Fig. 11.

Atomic participation ratios [49], as defined by (7), were calculated to determine the amount of contribution that each atomic type provided over the vibrational frequency spectrum.

$$P_i(p) = \frac{\sum_{a=1}^{N_a} |u_a^p|}{\sum_{a=1}^{N_a} |u_a^p|}$$

(7)

where the numerator is summed over all atoms of atomic type $a$, the denominator is summed over all atoms in the model, and $\sum_{a} P_a = 1$, $\forall a$. As depicted in Fig. 12, the Se atoms contribute the most with a peak around 160 cm$^{-1}$, which is also where the Ge and Ag atoms begin to diverge.

Three different types of atomic motion [52] are illustrated in Figs. 13 and 14. Fig. 13 represents the three types of atomic motion associated with Ge atoms that are bonded to two Se atoms; whereas, the motions described in Fig. 14 are linked to the Se atoms which are bonded to two Ge atoms. These motions are quantified by

$$B_a(p) = \frac{\sum_{i=1}^{N_a} |u_i^p \cdot \hat{b}_i|}{\sum_{i=1}^{N_a} |u_i^p|}$$

(8)
Fig. 10. Phase quotients of the vibrational modes. The parallel quotient represents the longitudinal modes and perpendicular the traverse modes.

Fig. 11. Compound responsible for large variations of the perpendicular phase quotient. The colour scheme is the same as Fig. 4.

Fig. 12. Atomic participation ratios for the three atomic species.

\[ S_a(p) = \frac{\sum_{i=1}^{N_a} |\mathbf{u}_i p \cdot \mathbf{e}_i|}{\sum_{i=1}^{N_a} |\mathbf{u}_i|} \]  

\[ R_a(p) = \frac{\sum_{i=1}^{N_a} |\mathbf{u}_i p \cdot \mathbf{e}_i|}{\sum_{i=1}^{N_a} |\mathbf{u}_i|} \]  

(9)

(10)

Fig. 13. Projections of bending, stretching and rocking motions for Ge atoms bonded to two Se atoms.

Fig. 14. Projections of bending, stretching and rocking motions for Se atoms bonded to two Ge atoms.
where $\alpha \in \{\text{Ge, Se}\}$, $\hat{n}_i$ represents a unit vector parallel to the bisector of the \text{SeGeSe} or \text{GeSeGe} angle, $\hat{r}_i$ an in-plane unit vector perpendicular to the bisector, and $\hat{r}$ a unit vector perpendicular to both. Summations are over all atoms of atomic type $\alpha$. The quantities $B_i(p)$, $S_i(p)$, and $R_i(p)$ can all vary from +1 for complete bending, stretching, or rocking motion to zero and $B_i(p) + S_i(p) + R_i(p) = 1$ for each $p$. Figs. 14 and 15 reveal that the rocking motion dominates for both Ge and Se atoms, but more for the Se atoms.

The host network of the Ag$_{20}$Ge$_{28}$Se$_{62}$ model consists of corner-sharing tetrahedra, which exhibits $A_1$ vibration modes \cite{53,54}. The $A_1$ modes (arrows) are illustrated in Fig. 15. The quantification of $A_1$ breathing modes was performed by considering the equation

$$BM(p) = \frac{\sum_{i=1}^{N_\alpha} \hat{n}_i \cdot \hat{r}_i | \alpha = \text{Ge, Se} | \sum_{i=1}^{N_\alpha} \hat{n}_i | \alpha = \text{Ag} |}{N_\alpha}$$

(11)

where $i$, $N_\alpha$, $\hat{n}_i$, and $\hat{r}_i$ represent neighboring atoms, total number of neighboring atoms, unit displacement and unit distance vector of central atom and neighboring atoms, respectively. The results from Eq. (11) are shown in Fig. 16.

An interesting feature is that the tetrahedrons have $A_1$ modes that are non-local and include mixing with modes of different symmetry as depicted in Fig. 16, where there exist two bands of $A_1$ breathing modes. These bands have a range of 140 cm$^{-1}$ to 200 cm$^{-1}$ (top panel) and 165 cm$^{-1}$ to 205 cm$^{-1}$ (bottom panel) of Fig. 16. This feature may be due to having different types and number of atomic species bonded to the Se atoms of the corner-sharing tetrahedra, resulting in significant chemical disorder. The modes with the largest $A_1$ breathing mode values are located at 191.2 cm$^{-1}$ with 0.864 and 189.14 cm$^{-1}$ with 0.901.

4.4. Silver ion dynamics

A key property for applications of these materials is the high mobility of silver \cite{55} in a Ge$_{28}$Se$_{62}$ host network. We computed the mean square displacement (MSD) functions for the three atomic species as depicted in Fig. 17. The MSD functions were determined by using

$$\langle |r(t) - r(0)|^2 \rangle = 6Dt + C$$

(13)

where $\langle |r(t) - r(0)|^2 \rangle$ was performed for the three atomic species $\alpha$. As shown, the MSD of the Ag ions are increasing rapidly with time in contrast to Ge and Se, which implies that Ag ions are more mobile than Ge and Se. The diffusion calculations were performed at a temperature of 1000 K. From Fig. 17, the self-diffusion coefficient $D$ is calculated using the Einstein relation \cite{56}

$$D = \frac{\langle |r(t) - r(0)|^2 \rangle}{6Dt}$$

(14)

where $\sigma$ represents an integration constant. The conductivity of Ag atoms is calculated using the equation

$$\sigma = \frac{ne^2D}{k_BT}$$

(15)

where $n$ is the number density of the Ag atoms. Table 3 provides a comparison of the diffusion coefficient and conductivity for the Ag$_{20}$Ge$_{28}$Se$_{62}$ model, Ag$_{0.2}$ (GeSe)$_{0.8}$ model \cite{23}, and Ag$_{0.2}$ (GeSe)$_{0.8}$ experimental data \cite{57}. As shown in Table 3, the $D_{\text{Ag}}$ and $\sigma$ values are less for the Ag$_{0.2}$ (GeSe)$_{0.8}$ model as compared to Ag$_{0.2}$ (GeSe)$_{0.8}$ (model) and Ag$_{0.2}$ (GeSe)$_{0.8}$ (experimental). This discrepancy may be because of the host network of the Ag$_{0.2}$ (GeSe)$_{0.8}$ model is more

Table 3

<table>
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<th>Source</th>
<th>$D_{\text{Ag}}$ (cm$^2$/s)</th>
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<td>This work</td>
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<td>Ref. \cite{23}</td>
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Fig. 15. $A_1$ modes of a corner-sharing tetrahedron.

Fig. 16. Normalized $A_1$ breathing modes for two corner-sharing Ge(Se)$_{28}$ tetrahedrons utilizing Eq. (11). Two bands of $A_1$ breathing modes exist having a range of 140 cm$^{-1}$ to 200 cm$^{-1}$ (top panel) and 165 cm$^{-1}$ to 205 cm$^{-1}$ (bottom panel).

Fig. 17. Mean square displacement for the three atomic species for the Ag$_{20}$Ge$_{28}$Se$_{62}$ structure at $T = 1000$ K.
processes. To accurately determine when a particle is trapped or not is very difficult; thus, a new algorithm is being developed with the possibility of predicting more precisely the release and capture of a particle. At high temperatures the thermal fluctuations would decrease the chances of Ag atoms being trapped resulting in larger diffusion distances. The Ag diffusion appears similar to the “Fluctuating Bond Center Detachment” (FBCD)-assisted diffusion as described by Abetew and coworkers [58].

5. Conclusion

Several properties, such as structural, electronic, vibrational, and Ag dynamics were considered for evaluation. Interesting substructures (Ag$_2$Se, Ge$_2$Se$_3$) were revealed, which are commonly associated with Se-rich or Ge-rich systems. Our model showed a FSDP for a high Ag concentration in agreement with other published results, but was due to correlations of AgSe and GeSe, not from GeGe correlations as is typically reported. We revealed that the radial distribution function of our model yielded fairly good agreement with experiment. We believe that this is a first attempt to provide a detailed analysis of the vibrational modes for a AgGeSe system. Both the vibrational density of states and atomic participation ratios calculations revealed that Se atoms are a major contributor across the vibrational spectrum. The abrupt change and plateau of the stretching character may be due to vibrational contribution changes and a difference in the rate of change for the Ge and Se atoms, respectively. We learned that the divergence of the perpendicular phase quotient is due to the rocking motion of a Ge–Ge compound. We investigated $A_1$ breathing modes of the corner-sharing tetrahedra which revealed that these breathing modes are non-local and involve the mixing of modes of different symmetry resulting in two bands of $A_1$ breathing modes. Despite the existence of some interesting substructures the self-diffusion coefficient and conductivity values were reasonably close to published results. Trapping and release processes associated with the most diffusing Ag ion were briefly discussed.

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