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JOURNAL OF NON-CRYSTALLINE SOLIDS

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

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



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ARTICLE INFO	ABSTRACT
Keywords: Ab initio Electronic structure Density of states Phonons Ion dynamics Trap centers	A ternary glassy chalcogenide material, Ag ₂₀ Ge ₂₈ Se ₅₂ , 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 ₂₀ Ge ₂₈ Se ₅₂ model illustrates reasonably good agreement with experiment. The vibrational density of states (VDOS) 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 $Ge_x Se_{1-x}$ glasses, solid electrolytes, $Ag_y (Ge_x Se_{1-x})_{1-y}$, 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_xSe_{1-x} , has been broadly investigated for many years experimentally [4-8] and theoretically [9-16]. These studies have revealed that, in general, the $\text{Ge}(\text{Se}_{1/2})_4)_4$ tetrahedra dominate for $x \le 0.34$, Ge(Se_{1/2})₆ units for $x \ge 0.36$ and $x \le 0.41$, and orthorhombic (distorted rocksalt) GeSe units for $x \ge 0.42$ [17].

The $Ag_y(Ge_xSe_{1-x})_{1-y}$ 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 Serich glasses (i.e. GeSe₄) phase separation produced an Ag₂Se glass phase and a Se-deficient matrix, whereas stoichiometric glasses (i.e. GeSe₂) contained a GeSe₂ glass phase and Ge₂Se₃ glass phase for y > 0.2. Gerich glasses (i.e. Ge₂Se₃) had a mixture of Ge₂Se₃ 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, $Ag_{\gamma}(GeSe_3)_{1-\gamma}$ glasses. In a recent publication [25] it was shown that $Ag_y(GeSe_3)_{1-y}$ 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_{0.2} (Ge₃₅Se₆₅)_{0.8} structure was modeled because of its interest as a CBRAM material [20,26]. Better understanding of the static and dynamic 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_{0.2} (Ge₃₅Se₆₅)_{0.8} 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]

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https://doi.org/10.1016/j.jnoncrysol.2019.03.012

Received 8 January 2019; Received in revised form 7 March 2019; Accepted 11 March 2019 Available online 27 March 2019

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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 $\Gamma(\vec{k} = 0)$ 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_{0.2} (Ge₃₅Se₆₅)_{0.8} 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 with an associated lattice constant of 14.0199 Å 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/cm³. 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_{GeGe} for $2.52 \text{ Å} \le r \le 2.67 \text{ Å}$ is associated with the three Ge–Ge homopolar bonds and the Ge₂Se₃ 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



Fig. 1. Total (top) and partial (center and bottom) pair correlation functions for the $Ag_{20}Ge_{28}Se_{52}$ model.



Fig. 2. Total and partial static structure factors for the Ag₂₀Ge₂₈Se₅₂ model.

 $(\text{Se}_{1/2})_4$ tetrahedra was found to be at r = 4.65Å. The g_{GeSe} correlations within the range of 2.33 Å $\leq r \leq 2.64$ Å are linked to the Ge₂Se₃ compounds, corner-sharing Ge(Se_{1/2})₄ tetrahedra and GeSe₂ compounds. Three Se–Se homopolar bonds are represented by the g_{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_{AgAg} correlations within the range of 2.62 Å $\leq r \leq 3.48$ Å. Also, the Ag₂Se compounds have g_{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_{0.2} (GeSe₃)_{0.8} 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/cm³, where our model had 5.35 g/cm³. 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- GeSe₂ onto a single crystal Si substrate; 2) thermal evaporation of Ag onto a- GeSe₂; and 3) exposure to UV light for causing the Ag photo-diffusion. The a- GeSe₂ 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	
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Peak positions for experimental sample (Ag_{25}Ge_{25}Se_{50}) and model (Ag_{20}Ge_{28}Se_{52}).

Sample	Peak positions (Å)		Additional peaks (Å)		
Experiment (ref. 42) Model	2.62 2.59	3.97 3.99	6.15 6.25	3.55	5.87

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.

Table 2

Total and partial coordination numbers and first peak positions for the glassy phases of $\text{Ge}_x\text{Se}_{1-x}$. Ref. 14 is a simulation and ref. 43 an experimental study.

Structure	$Ge_{35}Se_{65}$ (this work)	GeSe ₂ (ref. 14)	$GeSe_2$ (ref. 43)
$n_{GeGe} + n_{GeSe}$ $n_{SeGe} + n_{SeSe}$ n_{GeGe} n_{GeSe} n_{SeSe} r_{GeGe}	3.75 1.94 0.21 3.54 0.04 2.60	3.80 2.08 0.25 3.55 0.30 2.44 2.27	4.00 2.05 0.25 3.70 0.20 2.42
r _{GeSe} r _{SeSe}	1.85 2.00	2.36 2.37	2.36 2.32

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 Ag25Ge25Se50 is closest to our composition of Ag₂₀Ge₂₈Se₅₂. The peak positions for both the model and experimental sample are shown in Table 1. As seen from Table 1, three peaks exists 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 Ge_xSe_{1-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 (Ge₃₆Se₆₅), 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 $< n_p >$ of 2.4 implying that the host network is 'rigid' or 'overconstrained'.

The 100-atom $Ag_{20}Ge_{28}Se_{52}$ model includes corner-shared $Ge(Se_{1/2})$ ₂)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 Ag₂₀Ge₂₈Se₅₂ model has revealed some interesting substructures, in particular Ag₂Se and Ge₂Se₃, 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 $Ag_{20}Ge_{28}Se_{52}$ 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 12member 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 Ag₂₀Ge₂₈Se₅₂ structure. We considered the localization of electronic states by calculating the inverse participation ratio (IPR) given by

$$I_{e}(\psi_{k}) = \frac{\sum_{i=1}^{N} |a_{i}^{k}|^{4}}{\left(\sum_{i=1}^{N} |a_{i}^{k}|^{2}\right)^{2}}$$
(1)



Fig. 3. An illustration of the two Ge(Se_{1/2})₄ units of the Ag₂₀Ge₂₈Se₅₂ structure. The Ag, Ge and Se atoms are represented by the colour white, blue and red, respectively. The tetrahedra are depicted by the blue shaded regions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where *i* represents atom *i*, ψ_k the *k*th eigenfunction, *N* the total number of atoms, and a_i^k 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 Tafen 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 Ag₂₀Ge₂₈Se₅₂ 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 A_1 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

$$=\frac{\sum_{i=1}^{N}|a_{i}^{k}|^{4}}{\left(\sum_{i=1}^{N}|a_{i}^{k}|^{2}\right)^{2}}$$
(1)

$$f_{\nu}(p) = \frac{\sum_{i=1}^{N} |u_i^p|^4}{\left(\sum_{i=1}^{N} |u_i^p|^2\right)^2}$$

N

(2)

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Fig. 4. Some substructures that exists in the Ag₂₀Ge₂₈Se₅₂ model, (a) a corner-sharing tetrahedra, (b) two Ge₂Se₃, and (c) three Ag₂Se. The green, gold and silver balls represent the Ge, Se and Ag atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)







Fig. 6. Electronic density of states (black line) and Inverse participation ratio (red drop lines) for the $Ag_{20}Ge_{28}Se_{52}$ structure. The Fermi energy is represented by the green line at 0 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where u_i^p represents the eigenvector or displacement of atom *i* for a given mode *p* of frequency ω_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 $(0-150 \text{ cm}^{-1})$ and more localized states from approximately $200-310 \text{ cm}^{-1}$. 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)



Fig. 7. Vibrational density of states (red line) and Inverse participation ratio (green drop lines) for the $Ag_{20}Ge_{28}Se_{52}$ structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. Total and partial vibrational density of states for Ag₂₀Ge₂₈Se₅₂ structure.

$$S(p) = \frac{\sum_{i,j} |(\boldsymbol{u}_i^p - \boldsymbol{u}_j^p) \cdot \hat{\boldsymbol{\imath}}_{ij}|}{\sum_{i,j} |(\boldsymbol{u}_i^p - \boldsymbol{u}_j^p)|}$$
(3)

where \hat{r}_{ij} 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 prodominantly bondstretching (compressing) characteristics and fairly close to 0 if the mode has mostly bond-bending characteristics as elucidated in Fig. 9. There are basically three regions of interests: 0-50, 80-160, and 160-310 cm⁻¹. The low-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 $(0.2 \le S \le 0.55)$ with the stretching contribution increasing with frequency, and the high-frequency range having approximately an equal mixture of bending and stretching characters (S \ge 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



Fig. 9. Stretching character of the vibrational modes. Note the abrupt change at 160 cm^{-1} .

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 Ag₂₀Ge₂₈Se₅₂ structure. For example, $q_{\parallel}(p)$ represents the projected motion that is parallel to the bonds and $q_{\perp}(p)$ the projected motion perpendicular to the bonds. These quantities are conveniently defined as

$$q(p) = \frac{\sum_{ij} \boldsymbol{u}_i^{p} \cdot \boldsymbol{u}_j^{p}}{\sum_{ij} |\boldsymbol{u}_i^{p} \cdot \boldsymbol{u}_j^{p}|},$$
(4)

$$q_{\parallel}(p) = \frac{\sum_{i,j} \boldsymbol{u}_{i}^{P} \cdot (R_{ij}R_{ij}) \cdot \boldsymbol{u}_{j}^{P}}{\sum_{i,j} |\boldsymbol{u}_{i}^{P} \cdot (\widehat{R}_{ij}\widehat{R}_{ij}) \cdot \boldsymbol{u}_{j}^{P}|},$$
(5)

$$q_{\perp}(p) = \frac{\sum_{i,j} \boldsymbol{u}_i^{p} \cdot (1 - \widehat{R}_{ij} \widehat{R}_{ij}) \cdot \boldsymbol{u}_j^{p}}{\sum_{i,j} |\boldsymbol{u}_i^{p} \cdot (1 - \widehat{R}_{ij} \widehat{R}_{ij}) \cdot \boldsymbol{u}_j^{p}|}.$$
(6)

Sums are again over all nearest-neighbor atom pairs (i,j) in the model. \hat{R}_{ij} represents the unit vector in the direction of bond (i,j) and $\hat{R}_{ij}\hat{R}_{ij}$ a dyadic quantity. We calculate the phase quotient *q* along with its parallel q_{\parallel} and perpendicular q_{\perp} 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_{\parallel} exhibits an abrupt change in the range of 100–150 cm⁻¹, whereas the perpendicular phase quotient q_{\perp} , in general, is 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_{\perp} 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.

$$\boldsymbol{P}_{\alpha}(\boldsymbol{p}) = \frac{\sum_{i=1}^{N_{\alpha}} |\boldsymbol{u}_{i}^{\boldsymbol{p}}|}{\sum_{i=1}^{N} |\boldsymbol{u}_{i}^{\boldsymbol{p}}|}$$
(7)

where the numerator is summed over all atoms of atomic type α , the denominator is summed over all atoms in the model, and $\Sigma_{\alpha}P_{\alpha} = 1$, $\forall \alpha$. 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

$$B_{\alpha}(p) = \frac{\sum_{i=1}^{N_{\alpha}} \boldsymbol{u}_{i}^{p} \cdot \hat{\boldsymbol{r}}_{b}}{\sum_{i=1}^{N_{\alpha}} |\boldsymbol{u}_{i}^{p}|}$$
(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.

$$S_{\alpha}(p) = \frac{\sum_{i=1}^{N_{\alpha}} \boldsymbol{u}_{i}^{p} \cdot \hat{r}_{s}}{\sum_{i=1}^{N_{\alpha}} |\boldsymbol{u}_{i}^{p}|}$$
(9)

$$R_{\alpha}(p) = \frac{\sum_{i=1}^{N_{\alpha}} \boldsymbol{u}_{i}^{p} \cdot \hat{r}_{r}}{\sum_{i=1}^{N_{\alpha}} |\boldsymbol{u}_{i}^{p}|}$$
(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.

6



Fig. 15. A1 modes of a corner-sharing tetrahedron.

where $\alpha \in [Ge, Se]$, \hat{r}_b represents a unit vector parallel to the bisector of the SeGeSe or GeSeGe angle, \hat{r}_s an in-plane unit vector perpendicular to the bisector, and \hat{r}_r a unit vector perpendicular to both. Summations are over all atoms of atomic type α . The quantities $B_\alpha(p)$, $S_\alpha(p)$, and $R_\alpha(p)$ can all vary from +1 for complete bending, stretching, or rocking motion to zero and $B_\alpha(p) + S_\alpha(p) + R_\alpha(p) = 1$ 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 $Ag_{20}Ge_{28}Se_{52}$ model consists of cornersharing tetrahedra, which exhibits A_1 vibration modes [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

$$BM(p) = \left| \frac{\sum\limits_{i=1}^{N_b} \hat{u}_i^{p} \cdot \hat{r}_i}{N_b} \right|$$
(11)

where *i*, N_b , \hat{u}_i^p , 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



Fig. 16. Normalized A_1 breathing modes for two corner-sharing Ge(Se_{1/2})₄ 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 $Ag_{20}Ge_{28}Se_{52}$ structure at T = 1000 K.

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 [55] in a $\text{Ge}_x\text{Se}_{1-x}$ 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

$$\langle r^2(t) \rangle_{\alpha} = \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \left\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle$$
(12)

where a summed statistical average ($\langle \rangle$) was performed for the three atomic species α . 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 [56]

$$\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle = 6Dt + C \tag{13}$$

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

$$\sigma = \frac{ne^2D}{k_BT} \tag{14}$$

where *n* is the number density of the Ag atoms. Table 3 provides a comparison of the diffusion coefficient and conductivity for the Ag₂₀Ge₂₈Se₅₂ model, Ag_{0.2} (GeSe₃)_{0.8} model [23], and Ag_{0.2} (GeSe₃)_{0.8} experimental data [57]. As shown in Table 3, the D_{Ag} and σ values are less for the Ag_{0.2} (GeSe₃)_{0.8} model as compared to Ag_{0.2}(GeSe₃)_{0.8} (model) and Ag_{0.2} (GeSe₃)_{0.8} (experimental). This discrepancy may be because of the host network of the Ag_{0.2} (Ge₃₅Se₆₅)_{0.8} model is more

Table 3

Self-diffusion coefficient *D* and conductivity σ at T = 1000 K for Ag_{0.2} (Ge₃₅Se₆₅)_{0.8}, Ag_{0.2}(GeSe₃)_{0.8} (model), and Ag_{0.2}(GeSe₃)_{0.8} (experimental).

	D_{Ag} (cm ² /s)	σ (S cm ⁻¹)	Source
$\begin{array}{l} Ag_{0.2} \; (Ge_{35}Se_{65})_{0.8} \\ Ag_{0.2}(GeSe_3)_{0.8} \; (model) \\ Ag_{0.2} \; (GeSe_3)_{0.8} \; (expt) \end{array}$	$2.22X10^{-5}$ $2.53X10^{-5}$	0.330 0.347 0.354	This work Ref. (23) Ref. (57)



— Ag1: most diffusive ion — Ag14: least diffusive ion

Fig. 18. Trajectories of the most (red) and least (blue) mobile Ag atoms in $Ag_{20}Ge_{28}Se_{52}$ structure (T = 1000 K). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 19. Displacement of silver ion A_1 after its initial starting position for T = 1000 K. The shaded regions depict possible non-trapping events.

similar to GeSe₂ than GeSe₃.

We use trajectories of the Ag ions to obtain three-dimensional projections of those trajectories for the most and least mobile Ag atoms in the Ag₂₀Ge₂₈Se₅₂ model. Fig. 18 reveals that the most mobile ion Ag1 has diffused a significant distance in the z direction.

As Ag atoms diffuse through a material they can become trapped by their neighboring atoms; thus, affecting the self-diffusion coefficient *D* and conductivity σ . We have considered the trapping characteristics of the most mobile Ag ion in the Ag₂₀Ge₂₈Se₅₂ model. The non-trapping events for this model, illustrated in Fig. 19, are represented by abrupt changes in displacement. Possible non-trapping events are highlighted by the shaded regions, which have non-trapping times of approximately 1 to 3 ps. These possible events are showing release and capture 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 Abtew and coworkers [58].

5. Conclusion

Several properties, such as structural, electronic, vibrational, and Ag dynamics were considered for evaluation. Interesting substructures (Ag₂Se, Ge₂Se₃) 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.

Acknowledgements

The authors would like to thank Professors M. Mitkova and M.N. Kozicki for valuable discussions and acknowledge the NSF under grants DMR 1507670 and DMR 1506836. We thank the NVIDIA Corporation for donating a Telsa K40 GPU, which was utilized for the calculations.

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