

Available online at www.sciencedirect.com

ScienceDirect Acta Materialia 86 (2015) 247–253



Ultralow thermal conductivity of β -Cu₂Se by atomic fluidity and structure distortion

Hyoungchul Kim,^{a,b,*} Sedat Ballikaya,^{c,d} Hang Chi,^c Jae-Pyung Ahn,^e Kiyong Ahn,^b Ctirad Uher^c and Massoud Kaviany^a

^aDepartment of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109, USA

^bHigh-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

^cDepartment of Physics, University of Michigan, Ann Arbor, MI 48109, USA

^dDepartment of Physics, University of Istanbul, Vezneciler, Istanbul 34134, Turkey

^eAdvanced Analysis Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

Received 5 September 2014; revised 2 December 2014; accepted 5 December 2014

Abstract—We demonstrate a prototype thermal evolution path for liquid thermal conductivity in solids. Thermal evolution of β -Cu₂Se shows large interstitial displacement of constituent atoms marked by glass-like transitions and an asymptotic liquid thermal transport. Using ab initio molecular dynamics (AIMD), we identify these transitions, and confirm them with in situ transmission electron microscopy and electron energy loss spectroscopy. The thermal disorder of the Cu⁺ ions forms homopolar Cu–Cu bonds under a rigid Se framework, and at yet higher temperatures the Se framework undergoes thermal distortion. The non-equilibrium AIMD prediction of lattice thermal conductivity shows significant suppression of the phonon transport, in agreement with experiments and molecular behavior. © 2014 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Structure evolution; Thermal conductivity; Thermophysical property; Thermoelectrics; Phonon engineering

1. Introduction

Thermal structure evolution is ubiquitous in solids, including expansion, phase transformation and melting; as well as amorphous and crystalline morphologies, transitional superionics, macromolecules and quasi-crystals exist. These have attracted interest due to the possibility of being able to tune properties via structural anomalies. In thermoelectrics, structure evolution approaching liquid behavior has led to the "phonon-glass electron-crystal" paradigm.

Copper selenide, a chalcogenide, is a mixed conductor (electronic-ionic) that exhibits a phase transition [1-6]. It undergoes a $\alpha-\beta$ transition (at $T_{tr,\alpha-\beta} \sim 410$ K) from the low-temperature monoclinic α -phase to the high-temperature β -phase (face-centered cubic (fcc) structure, Fm3m; β -Cu₂Se) [1-6]. Its critical electron and phonon scatterings during the second-order phase transition have been

explored [7], however, its relevant thermoelectric (TE) properties suffer from structural instability and a narrow temperature domain. The β -phase also offers a high TE figure-of-merit over unity, due to abnormal Cu migration reducing lattice thermal conductivity (κ_L) [6,7]. Fig. 1a and b show the β -Cu₂Se structure consisting of eight cations (Cu⁺) and four anions (Se²⁻) and several near-neighbor interstitial sites [3,5,8].

Since the crystallinity of fcc β -Cu₂Se is maintained for $T > T_{tr,\alpha-\beta}$ and the thermophysical properties are controlled by the Se framework, no significant property changes are expected. However, measurements show dramatic changes, surprisingly without any distinct phase transitions. The β -Cu₂Se liquid-like behavior includes reduced specific heat (c_v) approaching the theoretical limit for liquid (i.e. $c_v = 2k_B$ per atom, where k_B is the Boltzmann constant) and a colossal linear thermal expansion coefficient (α_l) of 10.7×10^{-5} K⁻¹ above 800 K [5]. Another anomaly has been associated with the significant scattering of lattice phonons, i.e. glassy behavior close to the amorphous limit [5,6,9,10], as desired for "phonon-glass electron-crystals" of superior TE materials [11]. So far, clarifying the related physics and predicting the phonon transport have not been successful due to the theoretical and experimental (especially at high temperature) challenges.

^{*} Corresponding author at: High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea; e-mail: hyoungchul@kist.re.kr

http://dx.doi.org/10.1016/j.actamat.2014.12.008

^{1359-6462/© 2014} Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.



Fig. 1. Crystal structure of β -Cu₂Se. (a) The β -Cu₂Se crystal structure (blue and green are Cu and Se atoms). (b) Multiple atomic sites for Cu⁺ and Se²⁻ ions, with designations. The Se atoms form a rigid framework (fcc site, 4*a*) and Cu⁺ ions readily drift among the different sites (octahedral, 4*b*; tetrahedral, 8*c*; trigonal site, 32*f*). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We report the heterogeneous structure evolution of β -Cu₂Se at elevated temperatures, which explains the anomalous thermophysical properties and significant suppression of phonon transport, close to a liquid-state behavior, without any phase changes. Using the density-functional theory (DFT) including ab initio molecular dynamics (AIMD) simulations, we predict the temperature-dependent lattice dynamics and thermal conductivity changes due to the atomic fluidity and homopolar Cu–Cu bonds. We use in situ transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) techniques to test our theoretical predictions.

2. Methodology

2.1. Sample preparation

Cu₂Se was synthesized via a solid-state reaction method by mixing Cu (99.9999% shot) and Se (99.999% powder), in their respective stoichiometric ratios, in a glovebox. The charge was then loaded into a carbon-coated quartz tube and sealed under a vacuum of 10^{-3} torr. The quartz tube was placed in a furnace and heated to 1423 K at a rate of 1 K min⁻¹ with a subsequent soak for 12 h to ensure thorough mixing of the constituents. The temperature of the furnace was then decreased to 1073 K at a rate of 4 K min^{-1} and held for 10 days to complete the reaction. The furnace was finally turned off and allowed to cool to room temperature. The resulting ingot was ground into a fine powder in a glovebox and loaded into a cylindrical graphite die for spark plasma sintering under a dynamic vacuum. The powders were first cold pressed under a pressure of 50 MPa, and then the pressure was reduced to 10 MPa. The samples were heated under this reduced load at a rate of 50 K min^{-1} to a final temperature of 823 K at which point the uniaxial pressure was increased to 50 MPa, with a subsequent isothermal/isobaric hold. The ingot was cut with a diamond-blade saw into disks for thermal diffusivity measurements and into rectangular bars for transport characterization.

2.2. Property measurements

The low- and high-temperature AC Hall effect measurements shown in Fig. 2a were performed to determine the carrier type, and concentration of the charge carriers and their mobility. The Hall coefficient $(R_{\rm H})$ measurements were performed on a Hall bar with typical thickness of 1 mm in a Quantum Design Magnetic Property Measurement System (2–300 K) using silver epoxy contacts and/or in a customized air-bore Oxford Instruments superconducting magnet (300-850 K) using pressure contacts. The signal was recorded using an AC resistance bridge (LR 700, Linear Research), magnetic fields of ± 1 T were applied in order to eliminate probe misalignment. All high-temperature transport properties in Fig. 2b and c were observed under the dynamic flow of argon in the temperature range 300-900 K. The electrical conductivity (σ_e) was measured using a home-built apparatus with a standard four-probe potentiometric configuration, and the results are shown in Fig. 2b. We have repeated the measurements for each sample at least twice and in each of these have repeated a heating-cooling cycle. After the first measurement, the sample was removed and all surfaces polished to make a new contact with new thermocouples. As shown in Fig. 2b, the thermal hysteresis becomes negligible and there were no material losses. However, Brown et al. [12] report that under normal operating conditions material loss does occur (mostly due to vaporization of Se) and innovative methods should be developed to avoid this. The total thermal conductivity (κ) was calculated from $\kappa = D\rho c_p$, where D is the thermal diffusivity, ρ is the bulk density and c_p is the specific heat capacity at constant pressure. Thermal diffusivity was measured using a Flashline 5000 laser-based apparatus (Anter Corporation). Specific heat was measured by a differential scanning calorimeter (DSC 404 Pegasus, Netzsch), and density at room temperature was obtained by Archimedes' method, indicating a value corresponding to 98% of the theoretical density. Linear thermal expansion was measured using a horizontal pushrod dilatometer (DIL 402E, Netzsch). The sample was heated with 5 K min⁻¹ to 1143 K under argon atmosphere. For analysis of structural and electronic properties, a transmission electron microscope (Tecnai F20, FEI) operating at 200 kV and equipped with a CCD imaging system (GIF 866, Gatan) was used. Electron energy loss spectra were acquired with a dispersion of 0.05 eV/channel, a 2 mm GIF entrance aperture and parallel illumination.

2.3. First-principles calculations

We investigated the high-temperature electronic structure and the lattice dynamics of β -Cu₂Se using the DFT method (including equilibrium and non-equilibrium AIMD) implemented in the Vienna Ab initio Simulation Package (VASP) [13]. The PBE parameterization of the GGA for the exchange-correlated functional [14] and the PAW method for modeling core electrons (energy cutoff = 355.2 eV) [15,16] were used. High-temperature lattice dynamics were investigated by equilibrium AIMD. These simulations were performed on supercells consisting of 324 atoms (3 × 3 × 3 conventional cells). To consider the thermal expansion in the high-temperature simulations, we prepared supercells with the lattice parameter (a = 5.864 Å at T = 453 K) [5,6] using our measured linear



Fig. 2. Variations of the measured β -Cu₂Se properties with respect to temperature. (a) Hall coefficient, (b) electrical conductivity (including thermal hysteresis) and (c) total thermal conductivity. The electrical conductivity measurements where repeated during heating and cooling of the specimen, and these measurements were repeated twice, as marked.

thermal expansion coefficient. The Brillouin zone is sampled at the gamma point. After constant-temperature simulations with the Nosé thermostat for 1 ps (0.5 fs time step) reaching equilibrium, we collect atomic trajectories for 20 ps (1 fs time step).

To predict the lattice thermal conductivity of β -Cu₂Se, we use non-equilibrium ab initio molecular dynamics (NEAIMD). The VASP code was modified to perform the NEAIMD-energy exchange [17,18] as reported in the literature [19,20]. The non-equilibrium method is one of the computational techniques used to predict the lattice thermal conductivity. It is derived from Fourier's law: the time rate of heat transfer is proportional to the negative gradient in the temperature and to the area [21,22]. The lattice thermal conductivity using NEAIMD simulations is computed as the ratio of an applied heat flux to the resulting temperature gradient [19,20], i.e.

$$\kappa_L = -\left[\overline{Q(t)}/A\right] \left(\overline{\mathrm{d}T/\mathrm{d}z}\right)^{-1},\tag{1}$$

where the overbar indicates time average and O(t) is the heat flow rate. The heat flux is imposed by dividing the simulation cell into sections of equal width, and exchanging kinetic energy between hot and cold sections. The temperature gradient along the z axis is computed from the mean temperature of adjacent sections. Simulations were performed on supercells consisting of 192 ($4 \times 2 \times 2$ conventional cells), 288 ($6 \times 2 \times 2$) and 384 ($8 \times 2 \times 2$) atoms. Structure preparations were the same as the equilibrium AIMD simulations. We used the constant-temperature simulations with the Nosé thermostat for 1 ps (0.5 fs time step) and, after reaching equilibrium, non-equilibrium calculations were performed for 20 ps (1 fs time step). Because the exchange of kinetic energy results in non-Newtonian dynamics in the hot and cold sections, only the linear portion of the temperature gradient is considered in calculating the lattice thermal conductivity.

3. Results and discussion

3.1. Anomalies in thermophysical properties

From the various measurements shown in Fig. 2a-c, we observe an abrupt change in the transport properties



Fig. 3. Thermophysical properties of β -Cu₂Se as a function of temperature. (a) Measured lattice parameter and linear thermal expansion coefficient. (b) Measured density and the predicted bulk modulus. (c) Measured specific heat capacity at constant pressure, predicted specific heat capacity at constant volume and the Grüneisen parameter. The predicted glass transition temperatures, $T_{g,I}$ and $T_{g,II}$, are also shown. Shaded areas show temperature regimes.

resulting from the distinct structural transition between the α - and β -phase at $T_{tr,\alpha-\beta} \sim 410$ K. For the $T > T_{tr,\alpha-\beta}$ regime, the β -Cu₂Se has a stable thermophysical structure due to the rigid Se framework and the negligible anomalies in high-temperature transport properties. However, several anomalies in the thermophysical properties of the β -Cu₂Se (without any phase transition) are observed from the detailed experimental and computational analyses. Fig. 3 presents the temperature dependence of the thermophysical properties of β -Cu₂Se. The low-temperature linear thermal expansion coefficient is nearly constant and consistent with the reported value, 2.3×10^{-5} K⁻¹ for $T \sim 773$ K [5], while the high-temperature results have two distinct peaks. Constructing tangent lines to the lattice parameter (a) curve, there are two distinct temperatures, ~ 800 and ~ 1000 K, where the tangents intersect. Such transition temperatures in the thermal expansion are commonly observed in the glass transitions of amorphous materials. While the glass transition theory generally applies to amorphous phases, the glass transition temperature (T_g) signifies the glass to rubber transition. Noting the β -Cu₂Se crystallinity (fcc for $T > T_{tr,\alpha-\beta}$) up to the melting point $(T_m \sim 1380 \text{ K})$, here we suggest its glass transition, i.e. thermal structure heterogeneity, at two distinct temperatures. Based on the measured thermal expansion coefficient and the specific heat capacity at constant pressure, we use a lattice parameter relation ($a = a_{\circ} + a_{\circ} \alpha_{l} \Delta T$, where a_{\circ} is the reference lattice parameter of a sample at T_{\circ}), the bulk density ($\rho = m/a^3$, where m is sample mass), specific heat capacity at constant volume $[c_v = c_p - c(3\alpha_l)T/\rho$, where c is constant], bulk modulus $[B = \rho(c_p - c_v)/(3\alpha_l)^2 T]$, and the Grüneisen parameter ($\gamma_G = 3\alpha_l B/\rho c_v$), as shown in Fig. 3a–c. Above the Debye temperature (~292 K [10]), B is obtained from the thermodynamic properties and the quasi-harmonic model, and its product with the volumetric thermal expansion is constant [23]. These thermophysical properties undergo noticeable changes at two distinct temperatures, without notable phase changes. Below T = 800 K, denoted as the "first glass transition point", B, c_v and γ_G are nearly constant. For 800 < T < 1000 K, B and c_v decrease, and the $\gamma_{\rm G}$ increases with temperature. Above T = 1000 K, the "second transition point", most properties reach a plateau. These three distinct regimes explain the evolution of structural heterogeneity, and the associated significant phonon scatterings are discussed later.

3.2. Heterogeneous structure evolution

To elucidate this thermal structure evolution leading to heterogeneous glass transitions, we use lattice dynamics analyses based on the DFT to reveal the unique vibrational behavior of β -Cu₂Se as a function of temperature (see calculation details in Section 2). Fig. 4 shows the temperature-dependent atomic trajectories of Cu and Se atoms in β -Cu₂Se obtained from the equilibrium AIMD simulations. Unique lattice dynamics features reported in the literature [5-7,9,10] are successfully reproduced: the Cu atoms are highly disordered, while the Se atoms remain approximately in their rigid framework. Based on these AIMD results, the temperature-dependent bond length (r) of various atoms in β -Cu₂Se atoms are calculated (Fig. 5a). For the Cu atoms, multiple interstitial sites are accessed, and their bond lengths are much reduced (at T = 500 K, r_{Cu-Cu} is 2.94 and 2.60 Å for ideal symmetry and distorted structure, respectively) and decreases with temperature (at T = 1100 K, r_{Cu-Cu} is 2.56 Å). This feature is also observed in another Cu-related bond length, $r_{\text{Cu-Se}}$, while $r_{\text{Se-Se}}$ follows the pure thermally expanded symmetrical structure. The atomic trajectories of Cu atoms become random and some migration among sites occurs, but for the Se atoms below 900 K this is very limited (because of the larger ion size and lack of interstitial sites). Such findings are consis-



Fig. 4. Atomistic trajectories of β -Cu₂Se sampled with AIMD atomic trajectories for 3 ps, for four different temperatures: (a) 500, (b) 700, (c) 900 and (d) 1100 K.

tent with the qualitative understanding of β -Cu₂Se lattice dynamics. Also, we expect the formation of homopolar Cu–Cu bonds with high-temperature structural distortions because the predicted $r_{\text{Cu-Cu}}$ is surprisingly in agreement with that of Cu metal (2.56 Å at 500 K [24], dash-dotted line in Fig. 5a).

This supports the hypothesis we stated above, and will be verified with TEM-EELS studies in the following section. Quantitatively, we also analyze the structural transitions of β -Cu₂Se using the structure factor S(q), i.e.

$$S(\boldsymbol{q}) = \sum_{n=1}^{N_{u.c.}} f_n \exp(i\boldsymbol{q} \cdot \boldsymbol{r}_n), \qquad (2)$$

where q is the wave vector, r is the position vector and f is the atomic scattering factor, calculated from equilibrium AIMD (Fig. 5b). As expected, the S(q) of a perfect crystal is represented as a series of sharp peaks at the designated wave vectors, while the thermally disordered structure gives broad and shifted (to lower q) peaks. The peaks associated with Cu–Cu and Cu–Se bonds are observed at 3 $Å^{-1}$, while Se–Se correlations give $\sim 1.9 \text{ Å}^{-1}$. The second sharp diffraction peak (at 3 Å⁻¹) in $S_{Cu-Cu}(q)$ and $S_{Cu-Se}(q)$ is reduced to unity close to its asymptotic limit. These changes suggest significant alteration of the spatial periodicity of Cu-related bonds in the β -Cu₂Se structure. We suggest marking this Cu thermal disorder, as $T_{g,I} \sim 800$ K was observed in the expansion measurement and becomes more pronounced for T > 700 K (Cu–Cu panel in Fig. 5b). The Se–Se correlations among the nearest neighbors persist in $S_{\text{Se-Se}}(q)$, and Se-Se framework persists up to 1000 K. Similarly, we find a close relation between the Se atom thermal disorder and mark $T_{g,II} \sim 1000$ K, by interpreting the peak transitions in Fig. 5b (Se–Se panel). Since the logarithm of the intensity of the diffraction peaks is proportional to the Debye-Waller factor and decreases linearly with temperature [25], we use the squared modulus of S(q) to analyze this transition [26]:

$$|S_i'(\boldsymbol{q})|^2 = \frac{1}{f_i^2 N^2} \Biggl\{ \Biggl[\sum_{n=1}^N f_i \cos(\boldsymbol{q} \cdot \boldsymbol{r}_n) \Biggr]^2 + \Biggl[\sum_{n=1}^N f_i \sin(\boldsymbol{q} \cdot \boldsymbol{r}_n) \Biggr]^2 \Biggr\}.$$
(3)

This structural amplitude is strictly unity only at 0 K and has a clear linearity in a single-phase system, while it is



Fig. 5. Thermal evolution of β -Cu₂Se structure. (a) Temperature variations of three bond lengths (Cu–Cu, Cu–Se and Se–Se) in disordered Cu₂Se from AIMD simulations. The vertical arrows demonstrate the extent of structural disorder. (b) Temperature-dependent partial and total structure factors. (c) The temperature dependence of the amplitude of the structure factor with a linear approximation between two glass transition points. Total and projected quantities are also shown. The straight dotted guideline shows the general trend for each. The shaded areas shows temperature regimes.

close to zero for the liquid phase and its linearity is deflected at the phase transition temperature. The thermal evolution of $|S'_i(q)|^2$ confirms the heterogeneous phase transition of β -Cu₂Se (for Cu- and Se-related bonds, $T_g \sim 800$ and 1000 K), as observed in Fig. 5c.

3.3. Chemical and electronic state analysis

The presence of these thermal structural heterogeneities was verified by analysis of the chemical and electronic states by (i) in situ TEM with sample-temperature control and (ii) EELS. Before TEM-EELS characterization, the sample was a bulk slab, and its crystal orientation was identified by electron backscatter diffraction (EBSD). The {111} cubic plane, a layered structure owing to alternating segregation of Cu and Se atoms, is most relevant for the TEM-EELS analyses of β -Cu₂Se (see Fig. 6a). The final EBSD mapping results shown in Fig. 6b provide the crystal orientations of all the grains. The circled blue region corresponds to the normal direction parallel to {111} with an error of 12.5°. This region was milled with a focused ion beam to prepare samples for in situ TEM-EELS and Fig. 6c shows the images at two elevated temperatures. Other than carbon deposited on the ultra-thin sample edges, no significant physical change is observed, which is required to reduce uncertainties.

As we expected, Cu and its compounds show distinct EELS spectra [7,27,28]. Our EELS characterizations detect changes in the L₂ and L₃ core-loss edges of β -Cu₂Se, as shown in Fig. 6d. (i) As temperature increases, the EELS spectra above 980 eV show diminishing decay and reach a plateau for $T \ge 773$ K. This abnormal decay can be associated with the multiple scattering of the high-temperature structure, while single scattering occurs in the low-temperature structure. (ii) Broader L₃ and L₂ peaks (or larger shoulders) are observed, while the L₃/L₂ magnitude ratio becomes smaller, with increase in temperature. (iii) The magnitude of the Cu⁰ peak (i.e. the right edges of the L₃ and L₂ shadow region) becomes stronger as temperature increases. Comparing these thermal evolutions with the



Fig. 6. TEM-EELS experimental results on β -Cu₂Se. (a) The {111} cubic plane showing a layered structure. (b) Inverse pole figure map showing the crystal orientation (parallel to the sample normal) of individual grains. The rolling direction of the circled area is close to {221}, not exactly normal to {111}. (c) In situ TEM images taken at 300 and 773 K. (d) Temperature dependence of L₂ and L₃ core-loss edges in EELS for four temperatures. Distinct peak positions of each ionic state of Cu atom are shaded with dashed lines and color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Predicted lattice thermal conductivity from NEAIMD simulations. (a) Variation of the inverse of the predicted κ_L with respect to the inverse of the supercell size, for three different temperatures. (b) The predicted κ_L variations with respect to temperature, and comparison with our and available experimental results [5], and with amorphous-solid minimum [29], liquid thermal conductivity [21,30,31], and the Slack relation [21]. All predictions use the relevant, temperature-dependent properties from our measurements and predictions in Fig. 3 and the literature [5,10]. κ_{\min} is decomposed into the longitudinal (L) and transverse (T) components. κ_{liquid} is $3k_{\text{B}}u_f/l_f^2$, where u_f is the speed of sound $(B/\rho)^{1/2}$, l_f is the mean intermolecular distance ($V_{u.c.}/4$)^{1/3} and λ_p is $3l_f$ [21,30,31].

conventional EELS observations of different Cu ionic states [27,28], we draw close analogies between them. The fine structure of the low-temperature structure and the Cu ions (e.g. Cu⁺ or Cu²⁺) [7,27,28] result in relatively sharp edges for L₃ and L₂, while the weak (or broad) L₃ and L₂ ionization edges appear in the high-temperature structure and Cu metal [27,28]. The changes in Cu ionic states result in similar variations in the white-line ratio L₃/L₂. From these analogies we conclude that the ionic states of Cu in β -Cu₂Se depend on temperature for Cu disorder, i.e. the presence of Cu⁰ (Cu–Cu direct bond) for $T > T_{g,I}$, and Cu⁺ for $T < T_{g,I}$.

3.4. Lattice thermal conductivity

The homopolar Cu-Cu bonds, two structural transitions and the related anomalous thermophysical properties of β -Cu₂Se result in significant suppression of lattice thermal conductivity κ_L , reaching the limit of liquid thermal conductivity (κ_{liquid}). As noted in Section 2, we use NEAIMD simulations and verify this observed suppression of lattice thermal conductivity. Computational details are presented in Section 2. Using three different simulation cell lengths *l*, we verify the expected size effect and extrapolate the lattice thermal conductivity for an infinite structure with the linear extrapolation of their reciprocal relation, $1/\kappa_L = 1/\kappa_{L,\infty} + c/l$, where c is a constant [19]. Fig. 7a shows the l dependence of the calculated κ_L and their extrapolation to very large l, for several temperatures. Due to the extensive computation time for NEAIMD simulations, we use limited cell volumes. The uncertainties associated with the linear extrapolation of the limited data sets are shown by error bars in Fig. 7b.

The variations of the predicted lattice thermal conductivity, as a function of temperature, are shown in Fig. 7b, and are in favorable agreement with experiments [5,6,9]. The predicted lattice thermal conductivity is constant for $T < T_{g,I}$, and decreases for $T > T_{g,I}$, while the bulk, homogeneous crystal is expected to be dominated by the interphonon scattering and follow the T^{-1} dependence [32]. The minimum (amorphous-solid) thermal conductivity

 κ_{\min} based on the phonon mean-free-path (λ_p) of one-half of its phonon wavelength [29] is also shown in Fig. 7b, with its decomposition. The NEAIMD κ_L for $T < T_{g,I}$ is in general agreement with the total κ_{\min} , indicating significant Cu⁺ disorder and homopolar Cu-Cu bond formation noted in the above. Despite the stable Se framework, the interstitial random distribution of Cu⁺ ions and reduction in bond length, reaching the interatomic separation of metallic Cu, result in large suppression of phonon transport, approaching κ_{\min} . Applying the Bridgman theory for κ_{liquid} based on liquid analogy to the lattice [30,31,21], another lower limit to phonon transport is κ_{liquid} . As shown in Fig. 7b, the κ_{liquid} model predicts a value slightly lower than κ_{\min} for $T < T_{g,\text{II}}$ and close to $\kappa_{\min,\text{L}}$ for $T > T_{g,\text{II}}$. We consider this as an additional phonon suppression due to the atomic fluidity of β -Cu₂Se beyond $T_{g,I}$. This is consistent with the principle of sound waves in fluids having a longitudinal component only (not supporting shear stress). The NEAIMD results approach $\kappa_{\min,L}$ and κ_{liquid} and supports this fluidity limit. The suggested two glass transitions of β -Cu₂Se, correlate well with the anomalous changes in lattice thermal conductivity toward these limits.

4. Conclusions

In summary, the temperature-dependent lattice dynamics and the measured thermal expansion of β -Cu₂Se show large interstitial displacement of the Cu⁺ ions and the presence of two distinct glass transition temperatures associated with the two elements. These heterogeneous evolutions result in significant suppression of the phonon transport (i.e. temperature-independent lattice thermal conductivity approaching κ_{liquid}). These results provide new strategy and direction for achieving superior thermal insulators, thermal data storage devices and TE materials.

Acknowledgements

The work at the University of Michigan is supported as part of the Center for Solar and Thermal Energy Conversion at the University of Michigan, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0000957. Work at the Korea Institute of Science and Technology (KIST) was supported by the institutional research program of the KIST (2E24691). S.B. kindly acknowledges financial support by Scientific Research Projects Coordination Unit of Istanbul University with project number of 43041 and 43053 and would also like to thank the Scientific and Technological Research Council of Turkey (TUBITAK) for financial support. We are thankful to Dr. Dong-Ik Kim of KIST for the EBSD analysis.

References

- W. Borchert, Gitterumwandlungen im system Cu_{2-x}Se, Z. Kristallogr. 106 (1945) 5–24.
- [2] A. Stevels, F. Jellinek, Phase transformations in copper chalcogenides: I. The copper–selenium system, Recl. Trav. Chim. 90 (1971) 273–283.
- [3] R. Heyding, R. Murry, The crystal structure of Cu_{1.8}Se, Cu₃Se_{2, α}- and γ-CuSe, CuSe₂, and CuSe₂ II, Can. J. Chem. 54 (1976) 841–848.
- [4] S. Danilkin, M. Avdeev, T. Sakuma, R. Macquart, C. Ling, Neutron diffraction study of diffuse scattering in Cu_{2-δ}Se superionic compounds, J. Alloys. Compd. 509 (2011) 5460– 5465.
- [5] H. Liu, X. Shi, F. Xu, L. Zhang, W. Zhang, L. Chen, et al., Copper ion liquid-like thermoelectrics, Nat. Mater. 11 (2012) 422–425.
- [6] B. Yu, W. Liu, S. Chen, H. Wang, H. Wang, G. Chen, et al., Thermoelectric properties of copper selenide with ordered selenium layer and disordered copper layer, Nano Energy 1 (2012) 472–478.
- [7] H. Liu, X. Yuan, L. Ping, X. Shi, F. Xu, Y. He, et al., Ultrahigh thermoelectric performance by electron and phonon critical scattering in $Cu_2Se_{1-x}I_x$, Adv. Mater. 25 (2013) 6607–6612.
- [8] M. Oliveria, R. McMullan, B. Wuensch, Single crystal neutron diffraction analysis of the cation distribution in the high-temperature phases α-Cu_{2-x}S, α-Cu_{2-x}Se, and α-Ag₂Se, Solid State Ion. 28–30 (1988) 1332–1337.
- [9] S. Ballikaya, H. Chi, J. Salvador, C. Uher, Thermoelectric properties of Ag-doped Cu₂Se and Cu₂Te, J. Mater. Chem. A 1 (2013) 12478–12484.
- [10] Y. He, T. Day, T. Zhang, H. Liu, X. Shi, L. Chen, et al., High thermoelectric performance in non-toxic earth-abundant copper sulfide, Adv. Mater. 26 (2014) 3974–3978.
- [11] G. Slack, New materials and performance limits for thermoelectric cooling, CRC Handbook of Thermoelectrics, CRC Press, Boca Raton, FL, 1995.
- [12] D. Brown, T. Day, T. Caillat, G. Snyder, Chemical stability of (Ag,Cu)₂Se: a historical overview, J. Electron. Mater. 42 (2013) 2014–2019.

- [13] G. Kresse, J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186.
- [14] J. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [15] P. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979.
- [16] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59 (1999) 1758–1775.
- [17] F. Müller-Plathe, A simple nonequilibrium molecular dynamics method for calculating the thermal conductivity, J. Chem. Phys. 106 (1997) 6082–6085.
- [18] P. Jund, R. Jullien, Molecular-dynamics calculation of the thermal conductivity of vitreous silica, Phys. Rev. B 59 (1999) 13707–13711.
- [19] S. Stackhouse, L. Stixrude, B. Karki, Thermal conductivity of periclase (MgO) from first principles, Phys. Rev. Lett. 104 (2010) 208501–1–4.
- [20] D. Wang, L. Tang, M. Long, Z. Shuai, Anisotropic thermal transport in organic molecular crystals from nonequilibrium molecular dynamics simulations, J. Phys. Chem. C 115 (2011) 5940–5946.
- [21] M. Kaviany, Heat Transfer Physics, Cambridge University Press, New York, 2008.
- [22] M. Kaviany, Essentials of Heat Transfer, Cambridge University Press, New York, 2011.
- [23] Anderson O, Isaak D. Mineral Physics and Crystallography: A Handbook of Physical Constants. Washington DC: AGU; 1995.
- [24] M. Straumanis, L. Yu, Lattice parameters, densities, expansion coefficients, and perfection of structure of Cu and of Cu-In α phase, Acta Cryst. A25 (1969) 676–682.
- [25] C. Kittel, Introduction to Solid State Physics, Wiley, New York, NY, 1971.
- [26] K. Govers, S. Lemehov, M. Hou, M. Verwerft, Comparison of interatomic potentials for UO₂. Part II: Molecular dynamics simulations, J. Nucl. Mater. 376 (2008) 66–77.
- [27] C. Ahn, O. Krivanek, EELS Atlas, Gatan Inc., Warrendale, PA, 1983.
- [28] F. Hofer, P. Golob, New examples for near-edge fine structures in electron energy loss spectroscopy, Ultramicroscopy 21 (1987) 379–384.
- [29] D. Cahill, S. Watson, R. Pohl, Lower limit to the thermal conductivity of disordered crystals, Phys. Rev. B 46 (1992) 6131–6140.
- [30] P. Bridgman, The Physics of High Pressures, Bell, London, 1931.
- [31] J. Horrocks, E. McLaughlin, Thermal conductivity of simple molecules in the condensed state, Trans. Faraday Soc. 56 (1960) 206–212.
- [32] G. Slack, The thermal conductivity of nonmetallic solids, Solid State Physics, Academic Press, New York, 1979.