Mobile copper ions as heat carriers in polymorphous copper sulfide superionic conductors

Xin Liang

Citation: Appl. Phys. Lett. **111**, 133902 (2017); doi: 10.1063/1.4997501 View online: http://dx.doi.org/10.1063/1.4997501 View Table of Contents: http://aip.scitation.org/toc/apl/111/13 Published by the American Institute of Physics

Articles you may be interested in

How nanobubbles lose stability: Effects of surfactants Applied Physics Letters **111**, 131601 (2017); 10.1063/1.5000831

Quiver-quenched optical-field-emission from carbon nanotubes Applied Physics Letters **111**, 133101 (2017); 10.1063/1.5003004

Origin of high open-circuit voltage in a planar heterojunction solar cell containing a non-fullerene acceptor Applied Physics Letters **111**, 133901 (2017); 10.1063/1.4997502

Variable range hopping electric and thermoelectric transport in anisotropic black phosphorus Applied Physics Letters **111**, 102101 (2017); 10.1063/1.4985333

Room temperature quantum spin Hall insulator: Functionalized stanene on layered Pbl₂ substrate Applied Physics Letters **111**, 072105 (2017); 10.1063/1.4985643

Multiscale identification of local tetragonal distortion in NaNbO₃-BaTiO₃ weak relaxor ferroelectrics by Raman, synchrotron x-ray diffraction, and absorption spectra Applied Physics Letters **111**, 132901 (2017); 10.1063/1.4995009





Mobile copper ions as heat carriers in polymorphous copper sulfide superionic conductors

Xin Liang^{a)}

School of Materials Science and Engineering, Changzhou University, Changzhou, Jiangsu 213164, China

(Received 25 July 2017; accepted 15 September 2017; published online 26 September 2017)

Liquid-like mobile Cu^+ ions are generally considered as phonon scatters in copper chalcogenide superionic conductors, but this is recently disproved by a neutron spectroscopy study on lattice dynamics of Cu_2Se compound [Voneshen *et al.*, Phys. Rev. Lett. **17**, 118 (2017)]. In this work, we provide a different perspective by investigating the thermal transport of three transformable polymorphs of Cu_2S compounds with varying Cu^+ content. We show that the disordered and mobile Cu^+ ions are not the primary factor for suppressing the heat transport. A notable dependence of thermal conductivity on Cu^+ content is observed. By correlating the electrically deducted thermal conductivity with the ion motion behavior for β -Cu₂S superionic phase, we reveal that these fast ionic species Cu^+ are heat carriers instead, which make an appreciable contribution to thermal conduction. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4997501]

Chalcogenide based superionic conductors demonstrate great potential in thermoelectric applications due to their extremely low lattice thermal conductivity.¹⁻³ It has attracted intensive research attention on the thermal transport properties of these superionics, with the key question on understanding the role of fast ionic species. It has been suggested that the dramatically low thermal conductivity of Cu₂Se is attributed to the liquid-like diffusion of copper ions which effectively suppress the transverse phonons and reduce the phonon mean free path close to the minimum wavelength in glass.^{1,4} However, a very recent work⁵ disagrees with this point of view and ascribes the ultralow thermal conductivity of Cu₂Se to the anharmonicity by finding that the copper hopping time scales are too low to influence the lattice vibrations and that transverse phonons persist in both ordered and disordered phases.

Regardless of the fact that mobile ionic species like Cu⁺ and Ag⁺ can or cannot be the primary reason for the dramatically reduced thermal conduction, these charged ions with remarkably high mobility, are potentially heat carriers at the same time, as the same analogy to electrons and holes. The contribution to total thermal conductivity by these "free ions" can be similarly expressed via an "ionic Lorenz number" L_i^6

$$\kappa_{ion} = L_i \sigma_i T = \left(\frac{9\alpha L_0}{2\pi^2 Z^2}\right) \left(\frac{\epsilon_0}{k_B T}\right),\tag{1}$$

where σ_i is the electrical conductivity due to the ionic transport, L_0 is the Sommerfeld electron Lorentz number $L_0 = \left(\frac{\pi^2}{e^2}\right) \left(\frac{k_B^2}{e^2}\right) = 2.45 \times 10^{-8} \text{ J}^2 \text{ K}^{-2} \text{ C}^{-2}$, and ϵ_0 is the binding energy of the localized ion and is regarded as "energy gap" in the free ion model above which free-ion like states exist. *Z* is the charge carried by conducting ionic species, and α is a defined term related to the energy dependence of ion mean free path, which has a typical value of ~1 for

most superionic conductors. k_B is Boltzmann constant, and T is the absolute temperature. This model predicts that ionic thermal conductivity can be quite low, $\kappa_{ion} \sim 10^{-3}$ W/m K, which is insignificant as compared to the phonon or lattice contribution κ_{ph} that is in the order of unit W/m K. However, by working on the Hamiltonian, current operators and transport coefficients based on the lattice gas model, the ionic thermal conductivity κ_{ion} is estimated to be ${\sim}2$ W/m K at 200 °C for a superionic conductor with electrical conductivity of ~ 2 S/cm.⁷ This suggests that the contribution of mobile ions to thermal conductivity is in the same order as that of phonon contribution, making up a nonnegligible portion of the total thermal conductivity. The conclusions drawn from the two theoretical work lead to a controversial issue on whether the amount of heat carried by fast ionic species is appreciable. A recent molecular dynamic (MD) simulation work on Ag₂Te superionic compound shows that thermal conductivity varies as the compound changes from being Ag⁺ deficient to excessive,⁸ which implies the influence of mobile ions on thermal conductivity of superionics. As motivated, the present work experimentally probes into this problem.

Certain phases of binary silver and copper chalcogenides are well-known superionics with Ag⁺ and Cu⁺ as fast ionic species, which are potential model systems for experimental investigations. We note that reasonable allowance for selfnonstoichiometry is desired so that the concentration of fast ionic species can be tuned in a relatively appreciable range while the system still remains the same crystal structure without impurity phases. The other requirement for the model system is that electrons or holes dominated transport is sufficiently low so that the electronic contribution to thermal conductivity κ_{el} is negligible as compared to the total thermal conductivity κ_{tot} . As a consequence, Ag₂Te,⁹ Ag₂Se,¹⁰ Cu₂Se,¹ and Cu₂Te¹¹ binary system which possess electrical conductivity in the order of $\sim 10^3$ S/cm are not appropriate systems for the present purpose. Ag₂S system, albeit with smaller electrical conductivity (~200 S/cm at room temperature and ~ 1000 S/cm at elevated temperatures),¹² is found to

^{a)}Author to whom correspondence should be addressed: liangxin@cczu.edu.cn



FIG. 1. Illustration of atomic models for three Cu₂S polymorphs: low temperature γ phase (monoclinic), intermediate temperature β phase (hexagonal), and high temperature α phase (cubic). The blue and yellow balls represent Cu and S atoms, respectively. The fractional filling of Cu balls illustrates that Cu⁺ ions have partial occupancy and are disordered in β and α phases.

have low tolerance for Ag⁺ content variation. Among all the copper and silver based binary chalcogenides, Cu₂S superionics, with electrical conductivity ~ 10 S/cm from room temperature to 800 K,² appears to be a suitable model system for the present work. In addition, Cu-S binary phase equilibria suggests a reasonable range of stoichiometric modulation for Cu₂S compound,¹³ which provides the room for tuning Cu⁺ content.

Stoichiometric Cu₂S compound has three transformable polymorphs, as shown in Fig. 1. Below 370 K, it crystallizes into low chalcocite (LC) γ phase with a monoclinic lattice, and stabilizes to a high chalcocite (HC) β phase with a hexagonal structure between 370 and 700 K. Above 700 K, Cu₂S transforms to a FCC cubic α phase, which has been long well known as a classic superionic compound that is characteristics of disordered and fast mobile Cu⁺ ions.¹⁴ Also in HC β compound, Cu^+ are distributed over the sites of 2b, 4f and 6g in disorder and mobile through the interstices of hexagonal closed packed S atoms.¹⁵ Recently, it is found that Cu sublattices in β compound (HC) are indeed in liquid phase whereas S sublattices remain solid framework.¹⁶ The LC γ phase, where both cations and anions are ordered in rigid framework, is a typical ionic compound without any superionic characteristics.

 $Cu_{2\pm\delta}S$ powders with varying Cu content (Cu_{1.98}S, Cu_{1.99}S, Cu₂S, Cu_{2.03}S, and Cu_{2.05}S) were prepared by melting the pure substance Cu (shot, 99.9%, Alfa) and S (pieces, 99.99%, Aladdin) in quartz tubes sealed under vacuum. The mixtures were heated to 673 K in 10 h, and then ramped to 1383 K with a rate of 3.5 K/min. After being thermally equilibrated for 10 h, the powders were furnace cooled to room temperature. The samples were ground into fine powders and then densified into solid pellets on a spark plasma sintering system (SPS LABOX-325, Sinter Land[®], Japan), under an axial compressive stress of 65 MPa in vacuum and held at 713K for 5 min. X-ray diffraction patterns were taken at room temperature under a Rigaku D/max 2500 PC X-ray diffractometer using Cu Ka radiation. Temperature dependence of electrical conductivity (σ) and Seebeck coefficient (S) were measured in the argon atmosphere on a Netzsch SBA 458 Nemesis system (Germany). Thermal conductivity (κ) was obtained using the standard relation $\kappa = DC_p \rho$, where D is the thermal diffusivity, C_p is the specific heat capacity, and ρ is the mass density. Thermal diffusivity (D) was measured using the laser flash method on a Netzsch Micro Flash[®] LFA 457 (Germany) with flowing argon gas, and then analyzed using a Cowan model with pulse correction. The heat capacity C_p was measured on a differential scanning calorimetry apparatus (Netzsch STA 449 F3 Jupiter, Germany). Mass densities ρ were measured using the Archimedes method. All sintered samples were well densified with relative mass densities above 96% as compared to the theoretical value of 5.787 g/cm³.

All $Cu_{2\pm\delta}S$ samples remain the pure low temperature LC γ phase (PDF#33-0490), as seen from the room temperature X-ray diffraction patterns in Fig. 2. Thermal diffusivity of $Cu_{2\pm\delta}S$ superionic compounds measured from room temperature to 923 K is presented in Fig. 3(a). There is an abrupt change of thermal diffusivity across the phase boundary at \sim 373 K, while the one at 700 K is less remarkable. These two phase changes are well recorded by measured specific heat capacity with temperature, which is shown in Fig. 3(b). The thermal conductivity of $Cu_{2\pm\delta}S$ compounds is readily obtained, as presented in Fig. 3(c), which has a weak dependence on temperature except across phase boundaries. In each phase region, there is an appreciable variation of thermal conductivity with Cu content. To investigate the ionic contribution of mobile Cu⁺ ions to thermal conduction, it is necessary to carefully deduct the electronic contribution from the measured thermal conductivity which consists of contributions from all types of heat carriers.

The electronic contribution to thermal conductivity κ_{el} can be obtained from the Wiedemann-Franz law

$$\kappa_{el} = L\sigma T,\tag{2}$$

where σ is the electrical conductivity. In Fig. 3(d), we present the measured electrical conductivity from room temperature



FIG. 2. Room temperature X-ray diffraction patterns of $Cu_{2\pm\delta}S$ compounds with varying Cu content.



FIG. 3. Thermal-physical (a)-(c) and electrical transport properties (d)-(f) of $Cu_{2\pm\delta}S$ as a function of temperature covering over three polymorphs. Thermal diffusivity (a), specific heat capacity (b), electrical conductivity (d), and Seebeck coefficient (e) measured from room temperature up to 823 or 923 K. The total thermal conductivity (c) is obtained based on the measured thermal diffusivity and specific heat capacity. The Lorenz number (f) is calculated from the measured temperature-dependent Seebeck coefficient data using a single parabolic model. The dotted orange lines indicate the phase transition temperatures with each phase regime labelled on the top of the figure.

to 823 K. Room temperature electrical conductivity monotonically varies with nominal Cu^+ content, which evidences the changing composition that covers both Cu deficient and excessive ones. The temperature-dependent Lorenz numbers can be calculated using the single parabolic model (SPB) based on solving the Boltzmann transport equations¹⁷

$$L = \frac{(1+\lambda)(3+\lambda)F_{\lambda}(\eta)F_{2+\lambda}(\eta) - (2+\lambda)^{2}F_{1+\lambda}(\eta)^{2}}{(1+\lambda)^{2}F_{\lambda}(\eta)^{2}}\frac{k_{B}^{2}}{e^{2}},$$
(3)

where the Fermi integral is given by

$$F_j(\eta) = \int_0^\infty \frac{x^j \mathrm{d}x}{1 + \exp(x - \eta)}.$$
 (4)

The reduced Fermi energy η is a function of the Seebeck coefficient and for p-type semiconductor¹⁸

$$S_h = \frac{k_B}{e} \left[\frac{(2+\lambda)F_{1+\lambda}(\eta)}{(1+\lambda)F_{\lambda}(\eta)} - \eta \right],$$
(5)

where the Seebeck coefficient measured from room temperature to 823 K is shown in Fig. 3(e). Assuming that carrier relaxation time is limited by acoustic phonon scattering with carrier scattering factor $\lambda = 0$, temperature-dependent Lorenz numbers are obtained by solving Eqs. (3)–(5) based on the measured Seebeck coefficient. As shown in Fig. 3(f), the obtained L values are generally smaller than the free electron limit of $2.45 \times 10^{-8} \text{ J}^2 \text{ K}^{-2} \text{ C}^{-2}$.

In Fig. 4(a), we show the electronic thermal conductivity κ_{el} as a function of temperature, which is contributed by holes in these $Cu_{2\pm\delta}S$ compounds. Subtracting the electronic contribution κ_{el} from the total thermal conductivity κ_{tot} , we obtain the $\kappa_{tot} - \kappa_{el}$ values, which consists of contributions only from phonons and ions, as also presented in Fig. 4(a). The electronic thermal conductivity κ_{el} of $Cu_{2\pm\delta}S$ is in the range of 10^{-4} – 10^{-2} W/m K, which is orders of magnitude smaller than $\kappa_{tot} - \kappa_{el}$, being negligibly small. The Cu_{2± δ}S system we chose then proves to be a proper model system for the present study. Intriguingly, the thermal conductivity $\kappa_{tot} - \kappa_{el}$ of Cu₂S monotonically increases as Cu content decreases, by 20%-40% in a narrow range of non-stoichiometry from 2.5% Cu excess to 1% Cu deficiency for three polymorphs. Point defect scattering induced by excessive or deficient Cu⁺ ions cannot be the reason, since there is no need to the increase the number of defects for such a narrow non-stoichiometric range. The Cu atomic sites are only partially filled in β and α phases, and there are more possible occupations sites than the number of Cu atoms.¹⁶ For instance, the occupancy for the two-fold coordinated 6g Cu sites in β phase is only 0.19.¹⁵ Since the Cu⁺ ions exist in a completely disordered and liquid-like state in β and α phases which possess intrinsically strong anharmonicity,¹⁴ the impact of small stoichiometric modulation on phonon-phonon scattering should be insignificant as well. Eventually, understanding of these experimental observations



FIG. 4. (a) Electronic thermal conductivity κ_{el} and electronically deducted thermal conductivity $\kappa_{tot} - \kappa_{el}$ as a function of temperature for $Cu_{2\pm\delta}S$ compounds. (b) Variation of $\kappa_{tot} - \kappa_{el}$ as a function of Cu^+ content for three Cu_2S polymorphs. The variation of the ion "mean free path" l (right axis) against Cu^+ content for β superionic phase is also superimposed on the figure. The connecting lines are guides to the eye.

requires the examination on the role of Cu^+ ions in thermal conduction.

If fast ionic species Cu^+ act primarily as phonon scatters, it is then expected that the thermal conductivity κ_{tot} $-\kappa_{el}$ would be the lowest for α (cubic) phase where Cu^+ ions are completely disordered in a liquid-like state, followed by β (HC) phase, and then be the highest for γ (LC) phase where Cu^+ ions are ordered in rigid solid sublattices. However, this is not the trend we observed, and α (cubic) phase holds the highest $\kappa_{tot} - \kappa_{el}$ among three polymorphs across the nonstoichiometric range, as seen from Fig. 4(b). Our observations, from a different perspective, are consistent with the recent findings that liquid-like diffusion of mobile Cu^+ ions does not significantly suppress phonon transport.⁵

Based on the hopping mechanisms in ionic conductors and solving the Boltzmann transport equation to ionic flow, and compared with the phenomenological relation according to the laws of irreversible thermodynamics, the heat of transport by ions Q is related to the activation energy for transport E_a by ^{19,20}

$$Q = \frac{2l}{a_0} E_a,\tag{6}$$

where a_0 is the interatomic distance. E_a can be estimated from the measured temperature-dependent electrical conductivity⁶

$$E_a = -\frac{d(\ln\sigma T)}{d(1/k_B T)},\tag{7}$$

l is the average jumping distance of mobile ions that is given by

$$l = \frac{\sum_{i} f_i^2 \tau_i v_i}{\sum_{i} f_i^2},\tag{8}$$

in which f_i , v_i , and τ_i are the weight factor, group velocity and relaxation time of the ion mode with frequency ω_i . l can thus be considered as ion "mean free path." The heat of transport Q is related to the Seebeck coefficient S (also socalled thermopower) according to the equations of irreversible thermodynamics²¹

$$S = -\frac{Q}{eT} + H,\tag{9}$$

where *e* is the charge of mobile ion species and *H* is a correction term due to electrode contact potential. According to Eq. (9), the heat of transport *Q* can be estimated from the slope of the plot of *S* against -1/T.

Among the three polymorphs of Cu₂S, the low temperature γ (LC) phase is well-known as a non-superionic conductor, whereas thermally excited carriers can participate in the conducting process of high temperature α (cubic) phase. In view of that, the intermediate temperature β (HC) superionic phase is the most suitable system for understanding the role of mobile Cu⁺ ions in heat conduction. As shown in Fig. 4(b), the thermal conductivity $\kappa_{tot} - \kappa_{el}$ varies by almost 40% in a narrow nonstoichiometric range. With the Q and E_a assessed from the electrical measurements, the ion "mean free path" *l* for β -Cu_{2± δ}S can be estimated according to Eq. (6), which is plotted against Cu^+ content and superimposed on Fig. 4(b). Physical intuitively, large values of l (or the ratio Q/E_a) suggests an excellent ionic conductor.¹⁹ Since energy barrier for ion jumping basically sits in-middlebetween two adjacent equivalent atomic sites, an ion "mean free path" with a half of the interatomic distance suggests that the ionic flow can readily occur. For stoichiometric β -Cu₂S, we find $l \approx 0.45a_0$, which is consistent with the fact that β -Cu₂S is a good ionic conductor.^{15,16} As shown in Fig. 4(b), the ion "mean free path" l dramatically increases as Cu⁺ content decreases, which suggests that the mobility of liquid-like Cu⁺ ions is largely improved in Cu⁺ deficient samples. It is striking to find that $\kappa_{tot} - \kappa_{el}$ and l vary virtually similarly as a function of Cu^+ content for β phase, which implies the correlation of the thermal conductivity with the ion motion in superionic conductors. Notably, the samples with larger l values have higher thermal conductivity $\kappa_{tot} - \kappa_{el}$, which suggests that the ionic contribution to thermal conduction is enhanced as the mobility of Cu⁺ ions is improved, and that mobile Cu⁺ ions flow as heat carriers in these superionic compounds.

In summary, we have experimentally investigated the role of mobile Cu^+ ions in heat conduction of Cu_2S polymorphous superionic compounds by varying Cu^+ content. The high temperature α phase where Cu^+ ions are completely disordered in a liquid-like sublattices holds the highest

electronically deducted thermal conductivity among the three polymorphs, suggesting that the ultralow thermal conductivity cannot be mainly attributed to the mobile Cu^+ ions as phonon scatters. The electronically deducted thermal conductivity, which has an appreciable dependence on Cu^+ content, is well correlated with the ion "mean free path" which is a measure of ion mobility. Our findings reveal that these fast ionic species Cu^+ are heat carriers that make positive contributions to thermal conduction, instead.

This work was supported by National Natural Science Foundation of China (Grant No. 51502024), Jiangsu Province Distinguished Professorship Endowment and Six Talent Summit Plan of Jiangsu Province (No. 2015XCL037). The author is thankful to D. Jin for laboratory assistance.

- ³Y. He, P. Lu, X. Shi, F. Xu, T. Zhang, G. J. Snyder, C. Uher, and L. Chen, Adv. Mater. **27**(24), 3639 (2015).
- ⁴H. Kim, S. Ballikaya, H. Chi, J.-P. Ahn, K. Ahn, C. Uher, and M. Kaviany, Acta Mater. **86**, 247 (2015).

- ⁵D. J. Voneshen, H. C. Walker, K. Refson, and J. P. Goff, Phys. Rev. Lett. **118**(14), 145901 (2017).
- ⁶M. J. Rice and W. L. Roth, J. Solid State Chem. 4(2), 294 (1972).
- ⁷K. Yonashiro, T. Tomoyose, E. Sakai, M. Yamashiro, and M. Kobayashi, Solid State Ionics 27(3), 157 (1988).
- ⁸T. Ouyang, X. Zhang, and M. Hu, Nanotechnology **26**(2), 025702 (2015).
- ⁹Y. Pei, N. A. Heinz, and G. J. Snyder, J. Mater. Chem. **21**(45), 18256 (2011).
- ¹⁰W. Mi, P. Qiu, T. Zhang, Y. Lv, X. Shi, and L. Chen, Appl. Phys. Lett. 104(13), 133903 (2014).
- ¹¹S. Ballikaya, H. Chi, J. R. Salvador, and C. Uher, J. Mater. Chem. A 1(40), 12478 (2013).
- ¹²C. Xiao, J. Xu, K. Li, J. Peng, J. Yang, and Y. Xie, J. Am. Chem. Soc. 134(9), 4287 (2012).
- ¹³D. J. Chakrabarti and D. E. Laughlin, Bull. Alloy Phase Diagrams 4(3), 254 (1983).
- ¹⁴M. Oliveria, R. K. McMullan, and B. J. Wuensch, Solid State Ionics 28–30, 1332 (1988).
- ¹⁵M. J. Buerger and B. J. Wuensch, Science 141(3577), 276 (1963).
- ¹⁶L.-W. Wang, Phys. Rev. Lett. **108**(8), 085703 (2012).
- ¹⁷H.-S. Kim, Z. M. Gibbs, Y. Tang, H. Wang, and G. J. Snyder, APL Mater. **3**(4), 041506 (2015).
- ¹⁸V. Jovovic and J. P. Heremans, Phys. Rev. B 77(24), 245204 (2008).
- ¹⁹S. Taniguchi and M. Aniya, Thermochim. Acta **532**, 107 (2012).
- ²⁰S. Taniguchi and M. Aniya, Solid State Ionics **180**(6–8), 467 (2009).
- ²¹S. M. Girvin, J. Solid State Chem. **25**(1), 65 (1978).

¹H. Liu, X. Shi, F. Xu, L. Zhang, W. Zhang, L. Chen, Q. Li, C. Uher, T. Day, and G. J. Snyder, Nat. Mater. **11**(5), 422 (2012).

²Y. He, T. Day, T. Zhang, H. Liu, X. Shi, L. Chen, and G. Jeffrey Snyder, Adv. Mater. **26**(23), 3974 (2014).