Enhanced Stability and Thermoelectric Figure-of-Merit in Copper Selenide by Lithium Doping

Stephen Dongmin Kang1,2, Jan-Hendrik Pöhls3, Umut Aydemir1,2, Pengfei Qiu4, Constantinos C. Stoumpos2, Riley Hanus2, Mary Anne White3, Xun Shi4, Lidong Chen4, Mercouri G. Kanatzidis2 and G. Jeffrey Snyder1,2

1Department of Applied Physics and Materials Science, California Institute of Technology, CA 91125, USA
2Department of Materials Science and Engineering, Northwestern University, IL 60208, USA
3Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS, Canada
4Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Superionic thermoelectric materials have been shown to have high figure-of-merits, leading to expectations for efficient high-temperature thermoelectric generators. These compounds exhibit extremely high cation diffusivity, comparable to that of a liquid, which is believed to be associated with the low thermal conductivity that makes superionic materials good for thermoelectrics. However, the superionic behavior causes cation migration that leads to device deterioration, being the main obstacle for practical applications. It has been reported that lithium doping in superionic Cu2-xSe leads to suppression of the Cu ion diffusivity, but whether the material will retain the promising thermoelectric properties had not yet been investigated. Here, we report a maximum \( zT \) > 1.4 from Li0.09Cu1.9Se, which is higher than what we find in the undoped samples. The high temperature effective weighted mobility of the doped sample is found higher than Cu2-xSe, while the lattice thermal conductivity remains similar. We find signatures of suppressed bipolar conduction due to an enlarged band gap. Our findings set forth a possible route for tuning the stability of superionic thermoelectric materials.

Thermoelectric generators produce electrical energy from a heat flux through the device. Having been proven for their reliability from stable implementations in space missions, the technology is now drawing interest for terrestrial applications. For example, using thermoelectric technology to convert waste industrial heat into electricity could deliver a significant alleviation to the energy crisis. However, wide-spread use of the technology is limited by the energy conversion efficiency, which is bottlenecked by what thermoelectric materials can offer. The maximum efficiency obtainable from a material is characterized by the figure-of-merit:

\[
zT = \frac{S^2 \sigma}{\kappa} T,
\]

where \( S \) is the Seebeck coefficient, \( \sigma \) is electrical conductivity, and \( \kappa \) is thermal conductivity. Thermoelectric materials research is thus heavily focused on the search for high \( zT \) materials.

In the search for new material families for thermoelectrics, the revisit to superionic compounds as thermoelectric materials [1] has sparked great interest because of their inherently low thermal conductivity [2] which is advantageous in obtaining a high \( zT \). In the superionic phase, cations exhibit liquid-like diffusivity [3, 4] and this disordered nature typically results in a very low lattice thermal conductivity (<1 W m\(^{-1}\) K\(^{-1}\)). Many of the superionic compounds, particularly those that are also good electric conductors, indeed show promising thermoelectric properties as exemplified by Cu\(_2\)Se [1, 5], Cu\(_2\)S [6, 7], Ag\(_2\)Se [8, 9], and Zn\(_4\)Sb\(_3\) [10].
Figure 1: Activation energy for ionic conduction in the high-temperature phase (solid circles, left axis) and ionic conductivity at 617 K (open circles, right axis) as a function of lithium content in Li\textsubscript{x}Cu\textsubscript{2-x}Se. Cation movement is seen to be suppressed with the addition of lithium. Data from Ref.[16].

Unfortunately, these superionic compounds suffer from long-known reliability issues where the diffusive cation is prone to thermo- and electromigration [11–13]. The cation-induced instability has been an obstacle in earlier development efforts [14, 15], hence raising skepticism regarding applications of superionic thermoelectrics [12]. It is a general belief that a solution to cation migration is one of the most essential requirements for superionic materials to compete with other state-of-art materials.

On the positive side, Balapanov et al. have previously reported suppressed ionic conductivity and cation diffusivity in Cu\textsubscript{2-x}Se by substituting copper with lithium [16] (Fig.1). This behavior indicates that it might be possible to chemically tune the cation diffusivity in Cu\textsubscript{2-x}Se to a level where it could be countered by using longer leg segments (which will decrease the thermal or electric potential gradients driving migration). Whether such cation-suppressed compositions could maintain good thermoelectric properties has remained an unanswered question. Cu-S based tetrahedrites have recently been implemented in industrial power generation products [17, 18], but the details remain undisclosed.

Li doping is expected to help suppress bipolar conduction in Cu\textsubscript{2-x}Se at high temperatures by increasing the band gap since pure Li\textsubscript{2}Se is an ionic compound with a wide gap >2.8 eV [19, 20] and it has the identical average crystal structure as Cu\textsubscript{2}Se with a similar lattice constant [21].

Here, we report the first investigation on the thermoelectric properties of Li-doped Cu\textsubscript{2-x}Se up to 1000 K, showing an improved $zT$ at 1000 K compared to the parent compound due to suppressed bipolar conduction.

In our stoichiometry-controlled Cu\textsubscript{2-x}Se, the optimal composition for thermoelectrics is experimentally found to lie in the range of 0.01 ≤ $x$ ≤ 0.02 (which is similar to the composition of nominal-Cu\textsubscript{2}Se in some other reports [1, 5], according to transport property comparison). Since lithium cations (Li\textsuperscript{+}) are isovalent to the copper cations (Cu\textsuperscript{+}) in Cu\textsubscript{2-x}Se, good thermoelectric properties are expected in a similar range of off-stoichiometry. We thus investigated the composition Li\textsubscript{0.09}Cu\textsubscript{1.9}Se in an attempt to stay close to the optimal composition.

Figure 2 compares the transport properties of the high-temperature cubic phases of Li-doped and parent compounds. It is best seen from the thermopower (Fig.2b) that Li\textsubscript{0.09}Cu\textsubscript{1.9}Se indeed has values similar to the parent compound with comparable off-stoichiometry. As thermopower indicates the electron chemical potential (with respect to the band edge), the thermopower result is a strong indication that Li is incorporated in the structure substituting for Cu.

The maximum $zT$ is improved upon Li-doping, reaching > 1.4 at 1000 K, compared with the best value 1.2 obtained in Cu\textsubscript{1.985}Se (Fig.2d). While the lattice thermal conductivity remains at similarly low values upon Li-doping (Fig.2c), the improved electronic property accounts for the increase in $zT$. Particularly, it is seen from the thermopower at >900 K that the Li-doped sample does not show as much of the saturation
Figure 2: High temperature transport properties of Li$_{0.09}$Cu$_{1.9}$Se compared with Cu$_{2-x}$Se. (a) Electrical resistivity (b) Seebeck coefficient (c) Total thermal conductivity (solid points) and lattice + bipolar thermal conductivity (open points) estimated by subtracting the electronic portion (see Methods). The glassy limit for thermal conductivity, calculated from speed of sound measurements, is shown together for comparison. (d) Thermoelectric figure-of-merit. Gray dashed lines are data from Ref.[1] (nominal sample composition given as Cu$_2$Se) for comparison. Square data points in (b) are from separate measurements on the same sample. Solid lines in (b) and (c) are guides to the eyes.
behavior seen in the parent compound, indicating suppressed bipolar transport. This point will become more apparent with the weighted mobility analysis.

The minimal change in lattice thermal conductivity with Li doping is consistent with the understanding that the thermal conductivity of the Cu$_{2-x}$Se is already around the glassy limit [22]. From Cu$_{1.985}$Se, we measure longitudinal and transverse speed of sounds of $v_L = 3086$ and $v_T = 1381$ m/s, respectively, with a 5 MHz pulse-echo method. From $\kappa_{\text{glass}} = 0.5(\pi/6)^{1/3}k_B N^{2/3} (v_L + 2v_T)$, where $N$ is the number density of atoms, we calculate $\kappa_{\text{glass}} = 0.49 \text{W m}^{-1}\text{K}^{-1}$ (Fig.2c).

While sample variation has been an issue in the recent reports of Cu$_{2-x}$Se, we find stable results in the composition control and property measurements from our current synthesis method of the parent compound. The most critical step is to fully reduce the raw copper material before reaction (see Methods). Repeated measurements from multiple samples (see SI) indicate the establishment of a good reference for the parent compound properties. Therefore, the difference achieved by Li-doping is considered significant when compared to the sample variance of the parent compound.

The electronic properties of Li-doped samples can be quantitatively addressed by comparing the weighted mobility $U = \mu_0(m^*/m_e)^{3/2}$ of the samples (Fig.3). Here, $m^*/m_e$ is the effective mass relative to the electron mass and $\mu_0$ is the mobility parameter $\mu_0 = \tau_0 e/m^*$, where $e$ is the elementary charge and $\tau_0$ defines the relaxation time of free carriers through $\tau = \tau_0(E/k_B T)^{-0.5}$ (the exponent for energy in $\tau$ describes carriers scattered by acoustic phonons [23]). Here, we first demonstrate that it is not necessary to individually determine $\mu_0$ and $m^*$—which requires a Hall measurement—for the evaluation of $U$; a pair of thermopower and conductivity could be used instead. From thermopower, one can solve for the reduced chemical potential ($\eta = E_F/k_B T$ where $E_F$ is the electron chemical potential) using:

$$S(\eta) = \frac{k_B}{e} \left[ \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right].$$

Here, $F_i$ is the Fermi-Dirac integral ($F_i = \int_0^\infty x^i/(1 + \exp[x - \eta])dx$). Then, $\eta$ and measured conductivity $\sigma$ yields the transport coefficient $\sigma_{E_0}$ from the following equation:

$$\sigma = \sigma_{E_0} \cdot F_0(\eta).$$

Finally, $\sigma_{E_0}$ can be converted to $U$ at a given temperature:

$$U = \sigma_{E_0} \cdot \frac{3\hbar^3}{8\pi e(2m_e k_B T)^{3/2}}.$$

This approach for evaluating weighted mobility $U$ could be especially helpful in analyzing the transport in materials like Cu$_{2-x}$Se where it is not straightforward to interpret (or sometime hard to obtain) Hall measurements at high temperatures.

The evaluation of weighted mobility $U$ (Fig.3) shows that the Li-doped sample has a higher effective $U$ (which includes any discounts from bipolar) than the parent compound at $>800$K. This difference is attributed to the suppression of bipolar transport in the Li-doped samples. In the Cu$_{2-x}$Se samples, additional contribution from the minority electrons cancels the thermopower from hole carriers at $>800$K, effectively yielding a diminished $U$ value. The onset of bipolar conduction is clearly manifested in the departure from the linear region in the $U$ vs. $T^{-1.5}$ plot (compare dotted lines and solid lines in Fig.3). In the Li-doped sample, signature of this bipolar effect is not apparent until reaching 1000K.

Another difference for Li-doped samples found from the weighted mobility analysis is the shallower slope of the $U$ vs. $T^{-1.5}$ curve when compared with the non-bipolar region of Cu$_{2-x}$Se, which indicates a slower decrease in $U$ with temperature. The linearity of this curve is an indication that the charge carriers are scattered by acoustic phonons, the case in which $\mu_0$ is described as [24]:

$$\mu_0 = \frac{3\sqrt{\pi}}{4} \mu_{cl} = \frac{\pi e^4 C_I}{\sqrt{2m^* k_B T}^{3/2}}.$$

$$\mu_{cl} = \frac{\pi e^4 C_I}{\sqrt{2m^* k_B T}^{3/2}}.$$
Here, $C_l$ is the longitudinal elastic constant and $\Xi$ is the deformation potential from acoustic phonons ($\mu_d$ is the drift mobility in the non-degenerate limit, the classical limit in which the scattering model is originally defined). The shallower slope in the Li-doped sample would thus indicate either a larger effective mass or deformation potential ($C_l$ would be similar as indicated by similar lattice thermal conductivities). Since $m^*$ would typically increase when Li-doping induces a larger band gap [25], it is possible to find the upper bound of the increase in $\Xi$. Assessing values for $\Xi$ requires estimates of the effective mass and elastic constants. The effective mass of Cu$_{2-x}$Se is estimated as $m^* = 2m_e$, which can be obtained from $|S|$ together with either the nominal composition or a low temperature Hall measurement (which agree with each other). $C_l = 64$ GPa is evaluated from the longitudinal speed of sound measurement. We thus find $\Xi = 5.9$ eV for Cu$_{2-x}$Se. Estimate for $\Xi$ of the Li-doped sample follows to be $<7.2$ eV.

We note the anomalous behavior found by analyzing one of the earlier reports on Cu$_2$Se (nominal) [1], shown as a dashed line in Fig.3. The unusual departure from the typical trend of acoustic-phonon scattering is associated with the steep increase in thermopower measurements at high temperature above 750 K (Fig.2b). We tentatively attribute this anomalous behavior to uncertainties in the ZEM measurement method, where thermopower is often overestimated at high temperatures due to cold-finger effects [26–29] (overestimation could be as large as $>10\%$ [26, 29, 30]) and the high temperature reactivity of Type S thermocouples with chalcogenides [28]. We use a measurement method where such artifacts are avoided (see Methods).

![Figure 3: Weighted mobility $U$, evaluated from the thermopower and conductivity data, as a function of temperature.](image)

When the transport of charge carriers is limited by acoustic-phonon scattering, $U$ scales linearly with $T^{-1.5}$. When bipolar conduction becomes non-negligible, the $U$ evaluated with this method apparently decreases, causing a departure from the linear relation. Therefore the solid lines for Cu$_{2-x}$Se represent overall effective values in the high temperature bipolar region, while the linearly extrapolated dotted lines represent $U$ of the p-type carriers. The slope in the linear regime is related to the deformation potential. The gray dashed line is an evaluation using the data reported in Ref.[1], showing anomalous behavior at high temperatures.

While the quality of the electronic properties is well characterized by the weighted mobility $U$ (or, alternatively, $\sigma_{E_0}$), the overall material quality for thermoelectrics is characterized by the material quality factor $B$ which additionally takes into account the lattice thermal conductivity [31]:

$$B = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_{E_0}}{\kappa_L} T.$$  \hspace{1cm} (6)

Recall that $\sigma_{E_0}$ is proportional to $U$ (Eq.4). $B$ determines the $zT$ vs $\eta$ curve, where $B > 0.4$ is a good reference value for good thermoelectrics that gives a curve with a peak at $zT > 1$. 

5
Figure 4: Quality factor analysis. (a) Quality factor $B$ of each compound as a function of temperature (solid lines). $B$ of only the p-type carriers is shown together (dotted lines) which was obtained by extrapolating $U$ in Fig.3. The reduced $B$ at >800 K reflects the effect of bipolar conduction, showing that the $zT$ of Cu$_{2-x}$Se is band-gap limited at high temperatures. (b) $zT$ vs. reduced chemical potential curves predicted by the quality factor at 1000 K (solid lines) and 930 K (dotted lines), shown together with the points experimentally determined from the sample. It is seen that, most samples are close to the optimum doping, having a $zT$ close to that predicted to be the maximum.

The quality factor curve for each sample is plotted in Fig.4a, showing a peak of $B \approx 0.65$ at 1000 K in Li$_{0.09}$Cu$_{1.9}$Se which is higher than the maximum value of $B \approx 0.5$ around 930 K found in Cu$_{1.985}$Se. The maximum $zT$ predicted by these quality factors (lines in Fig.4b) corresponds well to the experimental $zT$ values observed, indicating that the chemical potential is very close to the optimum for thermoelectrics. Furthermore, the agreement also supports the assumption of acoustic-phonon scattering and the use of an effective band model for the analysis.

In the last part of the paper, we discuss the phase transition behavior which changes significantly with Li-doping. In the parent compound Cu$_{2-x}$Se, the superionic transition happens across a temperature range (380-410 K for $x \approx 0.01$) in which the low temperature phase (complete structure remains unknown) and high temperature phase (cubic, $Fm\overline{3}m$) is mixed. The transition shows strong hysteresis even at the slowest practical ramping rates, showing behavior characteristic of a first order transition. The detailed nature of this phase transition was extensively investigated in a previous report [32].

The biggest change upon substituting Cu with Li is the splitting of the phase transition into two transitions, involving an additional intermediate phase. This is most easily seen in the heat capacity results (Fig.5a), where the large transformation enthalpy peak (measured $\Delta H = 30.9$ J/g) is split into two back-to-back peaks (measured $\Delta H = 5.1$ and 21.1 J/g, for the lower and higher temperature transition, respectively). The high temperature superionic phase is reached at a higher temperature of around 500 K upon heating. The total transformation enthalpy ($i.e.$ integrated area of the peaks) remains large indicating that the cation-sublattice melting nature [33] of the transition still persists with Li doping. The distribution of the transformation enthalpy over a wide range of temperatures in both peaks likely indicates that both transitions happen gradually through a phase mixture region in the phase diagram, where the peak shape reflects the shape of the phase boundaries [32].

The resistivity curve obtained upon cycling around the two transitions (Fig.5b) in Li$_{0.09}$Cu$_{1.9}$Se shows a change that is even more dramatic than in the parent compound. In the parent compound, the resistivity increase with the onset of the transformation is due to the composition change of the main phase towards smaller off-stoichiometry $x$, causing a decrease in the native hole carrier density [32]; an analogous effect would explain the trend in Li$_{0.09}$Cu$_{1.9}$Se, although knowing the details of the ternary phase diagram of Li-Cu-Se is beyond the scope of this study.

Powder X-ray diffraction (Fig.5c) also shows the existence of the intermediate phase. At 425 – 450 K,
when the peak characteristic of the low temperature phase ($Q \approx 0.92 \, \text{Å}^{-1}$) is almost diminished, some peaks that are not present in the high temperature phase persist ($Q \approx 2.54, 2.70, 3.23 \, \text{Å}^{-1}$). These peaks can be indexed together with the other strong peaks using a monoclinic unit cell ($a = 6.379 \, \text{Å}, b = 5.815 \, \text{Å}, c = 6.155 \, \text{Å}, \beta = 97.91^\circ$), which is similar to what has been suggested from an earlier study on $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ [34]. However, we were not able to confirm further information about the structure of this intermediate phase with our data.

The lower temperature phase transition ($< 400 \, \text{K}$) progresses with a shift of peaks to smaller $Q$, a characteristic also seen in the phase transition of the parent compound. In $\text{Cu}_{2-x}\text{Se}$, the transformation progresses by gradually increasing the fraction of the high temperature phase with increasing temperature, which causes a gradual decrease in the off-stoichiometry $x$ of the original phase that dominates the diffraction pattern at most temperatures except at the close vicinity of the completion temperature; decrease in off-stoichiometry shifts the peaks to smaller $Q$ due to lattice expansion. The transition in $\text{Li}_{0.09}\text{Cu}_{1.9}\text{Se}$ can be understood with a parallel picture, which is also consistent with the features found in heat capacity and resistivity across the transition.

The high temperature cubic phase is identical to that of the parent compound, which is expected since $\text{Li}_2\text{Se}$ has the same average structure (anti-fluorite) [21] as $\text{Cu}_2\text{Se}$ at high temperature with a very similar lattice constant ($< 3 \%$ difference). By refining the 490 K pattern with the crystal structure of the $\text{Cu}_{2-x}\text{Se}$ cubic phase ($Fm\overline{3}m$) and only accounting for Cu and Se atoms (Li is almost transparent to X-rays), we obtain a lattice constant of 5.82 Å and Cu ion distribution very similar to the parent compound (see SI for Rietveld refinement results).

Overall, the Li-doped compounds show improved thermoelectric properties with maximum $\alpha T > 1.4$ due to suppressed bipolar conduction, which sets forth some promising aspects for superionic compounds because the result implies possible tuning of cation diffusivity to ensure stability while retaining the good thermoelectric properties of superionic compounds. Our results motivate further investigation on the cation diffusion change due to Li doping. Preliminary investigation indeed shows increase in the ionic diffusion activation energy with Li doping (see Supporting Information), consistent with previous reports. Neutron diffraction and quasi-elastic scattering experiments [3, 4] could help study the Li doping effect more systematically and lead to mechanistic understandings. We anticipate that such studies will be a key for practical implementation of superionic materials in thermoelectrics. On the other hand, it should be noted that material sublimation and other stability tests over extended periods under operating conditions (as high as 1000 K) should be conducted to qualify the material for use in a thermoelectric device.
Figure 5: The phase transition in Li_{0.09}Cu_{1.9}Se. (a) Heat capacity measured using differential calorimetry upon heating (2 K/min), comparing Li_{0.09}Cu_{1.9}Se (red) and Cu_{1.985}Se (green). A second transition is observed in the Li-doped sample. Lines are guides to the eyes. (b) Resistivity cycle of Li_{0.09}Cu_{1.9}Se (2 K/min) showing steep changes in resistivity during the transformation and strong hysteresis. Transformation curves of the parent compound (from ref.[32]) are shown for comparison. Note that the Cu_{2-x}Se curves are measured at a much slower heating rate (0.1 K/min). (c) Powder X-ray diffraction patterns of Li_{0.09}Cu_{1.9}Se obtained upon heating. The broad peak around $Q \approx 1.5 \text{ Å}^{-1}$ is from the polyimide capillary.

Methods

Sample preparation

Cu_{2-x}Se samples were synthesized by reacting the raw elements. Copper shots (Alfa Aesar Puratronic, 99.999% metals basis) were reduced at 700 °C in a 1% H$_2$-Ar atmosphere. We find this reduction step to be critical for controlling the stoichiometry of the product compound. Selenium shots (Alfa Aesar, 99.999% metals basis) and the reduced copper shots were sealed in a carbon-coated fused silica ampoule under a vacuum level of $1 \times 10^{-4}$ Torr. The sealed ampoule was placed in a vertical furnace in which it was maintained at 1170 °C for 12 h, followed by annealing at 700 °C for 72 h. After the reaction, the furnace was naturally cooled to room temperature. The resulting ingot (typically $\approx 25$ g) was ball-milled in a steel vial (sealed under Ar) for 20 min to obtain fine-grain powder of the parent compound Cu_{2-x}Se. The extended ball milling time results in lower thermal conductivity while minimally changing the electronic transport properties in this compound. For lithium-doped samples, lithium granules (Alfa Aesar, 99% metals basis) were placed in a steel vial after removing surface oxygen layers, together with fine-powder of Cu_{1.9}Se. After sealing the vial under Ar, the lithium was reacted by mechanical alloying using a ball miller for 90 min. To
consolidate the powder into a pellet, the power was hot-pressed at 45 MPa and 700°C for 1 h under an Ar atmosphere using a high-density graphite die in an induction furnace. The densities of the pellets were typically 6.7 and 6.2 g/cm³ for Cu₂-xSe and Li₀.₀₀Cu₁.₀₉Se, respectively. All compositions noted in the text refer to the nominal composition.

Transport property characterization

Electrical conductivity was measured with the van der Pauw four-probe method while ramping (1.5 K/min) under high vacuum. The Seebeck coefficient was measured under vacuum with W/Nb thermocouples, using an apparatus as described in Ref.[28]. In this setup, thermocouples were embedded in heater blocks to avoid cold-finger effects. In addition, the thermocouples were spring loaded from opposite sides, counter balancing the contact forces, and avoiding contact issues related to soft materials. Thermal diffusivity was measured using the laser flash method with a Netzsch LFA457 instrument. Measured thermal diffusivity values were converted to thermal conductivity using the measured densities and heat capacities. A constant high temperature heat capacity, rather than a decreasing one used in the recent literature[1], was used, thus giving conservative estimates of the thermal conductivity. To estimate the lattice and bipolar portion of thermal conductivity κ_{lattice} + κ_{bipolar}, the electrical portion κ_{e} was subtracted using κ_{e} = LσT where L is the Lorenz number calculated by: 

\[ L = \left( \frac{k_B}{e} \right)^2 \frac{3F_2F_3-4F_4^2}{F_0^2}. \]

Temperature-dependent X-ray diffraction measurements

High resolution synchrotron powder diffraction data were collected at the beamline 11-BM, Advanced Photon Source, Argonne National Laboratory using an average wavelength of \( \lambda = 0.4592 \) Å. Discrete detectors covering an angular range of \( 2\theta = 6^\circ \) were scanned up to \( 2\theta = 30^\circ \), with data points collected every \( 2\theta = 0.001^\circ \) at a scan speed of 0.1° s⁻¹. The sample was mounted on a magnetic base and spun at about 5400 RPM to eliminate any preferred orientation effects. An Oxford Cryosystems Cryostream Plus device allowed for the sample environment to be controlled under a nitrogen gas flow over the 300 – 500 K temperature range.

The measured sample was prepared as follows. A piece of the consolidated material was chipped off and ground using a mortar and pestle. The powder material (0.1 mmol, 20 mg) was transferred into a mortar and ground together with fused SiO₂ (0.9 mmol, 54 mg) into a homogeneous gray powder. The resulting powder was transferred into a 0.5 mm outer-diameter polyimide capillary that had the bottom part filled with epoxy. The capillary was filled up to about 2 cm in height and, importantly, the powder was tightly packed using a hex key of suitable diameter, followed by a layer of clay to contain the powder. Mixing of the Li₀.₀₀Cu₁.₀₉Se with SiO₂ was deemed necessary to reduce the absorption coefficient of the sample relative to the neat Li₀.₀₀Cu₁.₀₉Se material.

Heat capacity measurements

The heat capacity was measured with a differential scanning calorimeter (TA Instruments, Q200) using the enthalpic method. Intervals of 10 K were recorded with constant scanning rates of 2 K/min under N₂ atmosphere. Before and after each interval the calorimeter was held isothermally for 5 min. The samples were polished prior to the experiments to a thickness of 0.8 – 1.0 mm to get a smooth surface and remove potential surface oxidation. Hermetically sealed aluminum pans were used for the measurement. Three experiments were combined to calculate the heat capacity of each material. In the first run, an empty pan with known mass, \( m_0 \), was recorded to measure the background signal. In the next two runs, a thin sapphire crystal (\( m = 10 – 20 \) mg) (as a standard sample) and the test sample (\( m = 10 – 36 \) mg) were measured. For each temperature interval the background heat flow, \( \delta Q_0 \), was subtracted from the sapphire or test sample heat flow (\( \delta Q_{\text{sample+pan}} \)):

\[ \delta Q_{\text{sample}} = \delta Q_{\text{sample+pan}} - \frac{m_{\text{sample}}}{m_0} \cdot \delta Q_0. \]
The specific heat of the sample was calculated by integrating $\delta \dot{Q}_{\text{sample}}$ over each time interval ($F$) and scaling relative to the sapphire reference:

$$C_{P,\text{sample}} = \frac{F_{\text{sample}}}{F_{\text{sapphire}}} \cdot \frac{m_{\text{sapphire}}}{m_{\text{sample}}} \cdot C_{P,\text{sapphire}}.$$  

The heat capacity of the reference sapphire $C_{P,\text{sapphire}}$ was taken from Ref.[35]. To ensure good thermal contact between the sample, pan, and stage, loading positions were adjusted so that the $F$ of the room temperature interval was maximized.

**Acknowledgments**

We acknowledge D. R. Brown for discussion and ideas in the early stage of the project. The authors would like to acknowledge support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences through the following programs: the Solid-State Solar-Thermal Energy Conversion Center (S3TEC), an Energy Frontier Research Center (DE-SC0001299); the Advanced Photon Source at Argonne National Laboratory (DE-AC02-06CH11357); grant for C. C. S. and M. G. W. (DE-SC0014520). J. -H. P. and M. A. W. would like to acknowledge funding from the Natural Sciences and Engineering Research Council of Canada.

**References**


Enhanced Stability and Thermoelectric Figure-of-Merit in Copper Selenide by Lithium doping

Stephen Dongmin Kang\textsuperscript{1,2}, Jan-Hendrik Pöhls\textsuperscript{3}, Umut Aydemir\textsuperscript{1,2}, Pengfei Qiu\textsuperscript{4}, Constantinos C. Stoumpos\textsuperscript{2}, Riley Hanus\textsuperscript{2}, Mary Anne White\textsuperscript{3}, Xun Shi\textsuperscript{4}, Lidong Chen\textsuperscript{4}, Mercouri G. Kanatzidis\textsuperscript{2} and G. Jeffrey Snyder\textsuperscript{1,2}

\textsuperscript{1}Department of Applied Physics and Materials Science, California Institute of Technology, CA 91125, USA
\textsuperscript{2}Department of Materials Science and Engineering, Northwestern University, IL 60208, USA
\textsuperscript{3}Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS, Canada
\textsuperscript{4}Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Supporting Information

Figure S1: Transport properties of Cu\textsubscript{2-x}Se and Li\textsubscript{δ}Cu\textsubscript{2-x}Se. Multiple samples and measurements are shown together, showing that the variation is significantly less than the difference achieved by changing the compositions.
Figure S2: Comparison of the activation energy for ionic diffusion measured by fitting ionic relaxation times. The relaxation times were measured by a method described by Yokota [1] at the Shanghai Institute of Ceramics. A DC current is stressed on the sample to induce a polarized Cu ion profile. Two Pt wire leads were placed on the sample with a distance of \( \approx 5 \) mm, which were used to record the potential variation induced by the DC current. The relaxation time represents the time to revert to 0 V after turning off the current. Measurements were done under static Ar atmosphere.

Figure S3: Rietveld refinement of Li\(_{0.09}\)Cu\(_{1.9}\)Se at 490 K. The refined parameters are shown in Table S1. Only the main phase was taken into account for the refinement.

Table S1: Parameters for the refinement of Li\(_{0.09}\)Cu\(_{1.9}\)Se at 490 K. Space group is \( Fm\bar{3}m \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.8205</td>
</tr>
<tr>
<td>Cu (8c)</td>
<td>0.710</td>
</tr>
<tr>
<td>U(_{iso}) (Å(^2))</td>
<td>0.0613</td>
</tr>
<tr>
<td>x in (x,x,x)</td>
<td>0.3846</td>
</tr>
<tr>
<td>Cu (32f)</td>
<td>0.0605</td>
</tr>
<tr>
<td>U(_{iso}) (Å(^2))</td>
<td>0.084</td>
</tr>
<tr>
<td>Se (4a)</td>
<td>0.0319</td>
</tr>
<tr>
<td>U(_{iso}) (Å(^2))</td>
<td>0.084</td>
</tr>
<tr>
<td>( R_p ) (%)</td>
<td>6.2</td>
</tr>
<tr>
<td>( R_w ) (%)</td>
<td>6.1</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>1.21</td>
</tr>
</tbody>
</table>

References