Thermoelectric properties of copper selenide with ordered selenium layer and disordered copper layer

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<td>As Published</td>
<td><a href="http://dx.doi.org/10.1016/j.nanoen.2012.02.010">http://dx.doi.org/10.1016/j.nanoen.2012.02.010</a></td>
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<td>Version</td>
<td>Author's final manuscript</td>
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<td>Accessed</td>
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Thermoelectric properties of copper selenide with ordered selenium layer and disordered copper layer

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Abstract

Thermoelectric figure of merit (ZT) of \(\sim 1.6\) at 700 °C is achieved in \(\beta\)-phase copper selenide (Cu\(_2\)Se) made by ball milling and hot pressing. The \(\beta\)-phase of such material possesses a natural superlattice-like structure that combines ordered selenium (Se) and disordered copper (Cu) layers in its unit cell, resulting in a low lattice thermal conductivity of 0.4-0.5 W m\(^{-1}\) K\(^{-1}\). A \(\lambda\)-shaped specific heat peak indicates a phase transition from cubic \(\beta\)-phase to tetragonal \(\alpha\)-phase at around 140 °C upon cooling and vice versa. An abnormal decrease in specific heat with increasing temperature was also observed due to the increased random motion of disordered Cu atoms. These features indicate that \(\beta\)-phase Cu\(_2\)Se could be potentially an interesting thermoelectric material, competing with other conventional thermoelectric materials.

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1. Introduction

A good thermoelectric material has high dimensionless figure-of-merit $ZT$: defined as $(S^2 \sigma/\kappa)T$, where the $S$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Normally, $\kappa$ is composed of three components, i.e., electronic contribution ($\kappa_{\text{car}}$), lattice contribution ($\kappa_{\text{lat}}$), and bipolar contribution ($\kappa_{\text{bipolar}}$). As reducing $\kappa_{\text{lat}}$ was proven to be the easiest and most straightforward way to improve $ZT$, numerous efforts have been devoted in the last two decades in order to increase the $ZT$ value from the longstanding 1.0 in thermoelectric bulk materials to higher values by minimizing $\kappa_{\text{lat}}$ through the concept of nanocomposite [1-4]. The key idea of nanocomposite is to create grains or inclusions that scatter the phonons without deteriorating the electron transport. More generally, a good thermoelectric material should behave as a “phonon-glass-electron-crystal” with a high charge carrier mobility and low lattice thermal conductivity [5]. Structures with strong phonon scatters, such as skutterudites [6] and clathrates [7] were first demonstrated to have “phonon glass electron crystal” type of behavior resulting in low $\kappa_{\text{lat}}$. Other materials with complex unit cells [8], such as Zn$_4$Sb$_3$ and Zintl compounds also have low $\kappa_{\text{lat}}$.

Another direction in reducing the lattice thermal conductivity is to use layered structures, both artificial ones such as superlattices [9,10], and naturally formed superlattices [11,12]. In the artificially grown superlattices, it was known that interface roughness reduces the thermal conductivity [13,14]. We noted that lamella crystals---natural superlattices---usually have higher lattice thermal conductivity for in-plane direction than out-of-plan direction. Increasing the disturbance at the interfaces of layers and reducing the thickness of the crystalline layers therefore can potentially lead to further reduction in thermal conductivity. A distorted lattice has
recently been reported in the lamella-structured In₄Se₃₋δ crystals with only 2 atomic layers in the ordered lamella, which has even a lower in-plane lattice thermal conductivity than that of the out-of-plane direction, resulting in a \( ZT \) of 1.4 at 708 K [15]. Motivated by these facts, \( \beta \)-phase Cu₂Se crystalized in layered cubic structure, as shown in Figure 1a and b, could very likely have a low thermal conductivity and good thermoelectric properties since these polycrystals have monoatomic Se layers acting as ordered lamella, and Cu atoms randomly distribute at several lattice sites as the disordered lamella (Fig. 1a, b), if one views along the (111) plane directions [16]. In this paper, we show that a \( ZT \) of about 1.6 at 700 °C could be obtained in \( \beta \)-phase Cu₂Se polycrystals with such structure features.

2. Material and Methods

2.1. Sample fabrication

In our synthesis, Cu₂Se nanopowders were firstly prepared from Cu (99.5%, Alfa Aesar, USA) and Se (99.99%, 5N PLUS, Canada) elements through high-energy ball milling (Spex 8000M Mixer/Mill). Bulk samples were fabricated by consolidating the as-prepared nanopowders in a graphite die (1/2 or 1 inch in diameter) via a conventional hot pressing method.

2.2. Structure characterizations

PANalytical multipurpose diffractometer with an X’celerator detector (PANalytical X’Pert Pro) was used for lattice structure characterizations at both room temperature and high temperature. We studied the grain size of bulk samples on a scanning electron microscope (SEM, JEOL-6340F). The structural change versus temperature was monitored by in situ heating experiments inside a high-resolution transmission electron microscope (HRTEM, JEOL-2010F). The bulk
sample was first hand polished and then fixed on a Mo grid with epoxy (stable up to 1000 °C). Subsequently, the polished sample was ion milled with a Precision Ion Polishing System (model 691, Gatan) till electron transparent and loaded on the heating holder (model 652, Gatan) for in situ observation.

2.3. Transport property measurements

We used a commercial four-probe system (ULVAC ZEM-3) to simultaneously measure electrical resistivity and Seebeck coefficient. A laser flash system (NETZSCH LFA 457) was used for the thermal diffusivity characterization. Specific heat \( (C_p) \) data was obtained on a differential scanning calorimetry (NETZSCH DSC 404C) station.

3. Results

3.1. Structural properties

Conventionally, \( \beta \)-phase \( \text{Cu}_2\text{Se} \) has been known as a superionic conductor [17,18] that crystallizes in an \( Fm\overline{3}m \) type of lattice with Se atoms occupying the (0, 0, 0) site while the knowledge of Cu sites still remains controversial due to its variation with temperatures. Figure 1b shows a possible three-site model for the location of Cu atoms in \( \beta \)-phase \( \text{Cu}_2\text{Se} \) at 160 °C where Cu fractionally locates at \((0.25, 0.25, 0.25)\), \((0.315, 0.315, 0.315)\), and \((0.5, 0.5, 0.5)\) sites as was mostly reported [16]. It should also be pointed out that in those models all the Cu sites fall in the \(<111>\) direction. If one views along the \((111)\) plane direction, a lamella structure is clearly seen, in which the monoatomic Se layer is separated by a two randomly distributed Cu layers. During cooling process, \( \beta \)-phase turns into \( \alpha \)-phase at temperatures lower than 140 °C and this phase transition was reported to be reversible [16]. Compared to \( \beta \)-phase that has an FCC
structure, the structure of $\alpha$-phase Cu$_2$Se is much more complicated since it could crystallize in three possible ways: monoclinic, tetragonal, and cubic. Figure 1c shows that the $\alpha$-phase Cu$_2$Se nanopowders we obtained from high-energy ball milling are tetragonal phase (PDF# 29-0575) at room temperature. After being consolidated into bulk form via hot pressing, those $\alpha$-phase Cu$_2$Se polycrystals show an increase of $\{111\}$ texturing (see the intensity of planes (111) and (222) relatively to that of (404) in Fig. 1c) with the pressing temperature from 400 to 700 °C. It is noted that similar XRD patterns were obtained when we measure along both vertical and parallel directions (to the hot pressing force direction) on those bulk samples. High temperature XRD measurements (Fig. 1d) were also done at 200, 400, and 600 °C for the samples pressed at 700 °C where we could clearly see the phase transformation between 25 and 200 °C and the high-temperature $\beta$-Cu$_2$Se phase shows the texturing in $\{111\}$ planes as well. We want to point out that the cubic $\beta$-phase has smaller unit cell (e.g., 200 °C, $a=b=c=5.8639$ Å) than the low-temperature tetragonal $\alpha$-phase ($a=b=11.52$ Å and $c=11.74$ Å at room temperature), which makes the (111) plane of $\beta$-phase corresponds directly to the (222) plane of $\alpha$-phase. Furthermore, we found through the XRD study that the lattice parameter of the cubic $\beta$-phase Cu$_2$Se changed from 5.8639 to 5.8918 to 5.9172 Å when the measurement temperature increased from 200 to 400 to 600 °C, respectively, indicating a possible change in Cu sites with a large thermal expansion of $22 \times 10^{-6}$ K$^{-1}$.

Figure 2a is a room temperature HRTEM image of a typical as-prepared bulk sample, where the ordered tetragonal (111) lattice planes are clearly seen. As the sample temperature reached 200 °C, we also observed the (111) lattice planes in $\beta$-phase (Fig. 2b), however, they now belong to the FCC crystals instead and correspond to the (222) planes in tetragonal $\alpha$-phase lattice as we discussed above. This observation suggests the phase change and possible
disordering of Cu sites at elevated temperature, which agrees well with our XRD results above. Figure 2c shows that the grains are typically within a few micrometers.

### 3.2. Thermoelectric transport properties

Figure 3 shows the temperature dependent thermoelectric properties of Cu$_2$Se$_{1.01}$ samples that were hot pressed at different temperatures. The extra Se was used to compensate the potential Se loss during hot pressing due to its high vapor pressure. Electrical resistivity (Fig. 3a) of a typical Cu$_2$Se$_{1.01}$ sample is around 6-8 μΩm at room temperature and increases quickly to about 55 μΩm at 700 °C. With Seebeck coefficient (Fig. 3b) increasing from 75 to 250 μV K$^{-1}$, these samples have moderate power factor (Fig. 3c) of 750–950 μW m$^{-1}$ K$^{-1}$ at room temperature and peaked around 1125–1250 μW m$^{-1}$ K$^{-1}$ at 600 °C. The temperature dependent $C_p$ data was shown in Fig. 3d where we could see a λ-shape peak at around 140 °C as a symbol of the phase transition discussed above. Besides this feature, one may also notice that the $C_p$ value is slightly decreasing with the temperature at above 200 °C. Those β-phase Cu$_2$Se samples also possess low total and lattice thermal conductivities (Fig. 3e) as we initially expected from their natural superlattice-like structures, where the lattice thermal conductivity is around 0.4 W m$^{-1}$ K$^{-1}$ and a total thermal conductivity of less than 1 W m$^{-1}$ K$^{-1}$ at 700 °C. Overall, $ZT$s of ~1.6 at 700 °C were obtained (Fig. 3f), which are competitive to other traditional medium temperature thermoelectric materials, such as skutterudites [19] and PbTe [20-22], but using abundant and environment-friendly elements. Due to the aforementioned phase transition between tetragonal α-phase and cubic β-phase, a clear change could be observed in all the curves of Fig. 3 and this sudden change was found to happen at around 140 °C which is slightly higher than the reported value of 130 °C [16].
Furthermore, one may also conclude from Fig. 3 that the thermoelectric properties of as-prepared 
\( \text{Cu}_2\text{Se}_{1.01} \) are not sensitive to hot pressing temperature (400 to 700 °C).

We also studied the composition effect on the thermoelectric properties of \( \text{Cu}_2\text{Se}_{1+x} \) by 
changing the amount of Se in the initial compositions (Fig. 4). For all these samples, we used 
700 °C for hot pressing to make sure that the samples are mechanically strong as the hot-pressing 
temperature is insensitive to the thermoelectric properties as shown in Fig. 3. At any given 
temperature, both electrical resistivity and Seebeck coefficient (Fig. 4a, b) decrease with higher 
selenium content indicating an increased hole concentration due to more Cu vacancies. 
Accordingly, the \( \text{CuSe}_{1.02} \) sample has the highest power factor (Fig. 4c) due to its lowest 
electrical resistivity. Figure 4d shows the data of temperature dependent thermal conductivity \( \kappa \) 
while the lattice thermal conductivity \( \kappa_{\text{latt}} \) (Fig. 4e) was calculated by subtracting the carrier 
contribution \( \kappa_{\text{carr}} \) from the total \( \kappa \). The \( \text{Cu}_2\text{Se}_{1.02} \) sample shows not only the highest \( \kappa_{\text{carr}} \) due to 
high carrier concentration, but also the highest \( \kappa_{\text{latt}} \) in this series. As for the \( ZT \) (Fig. 4f), the 
\( \text{Cu}_2\text{Se}_{1.01} \) sample shows the highest peak value of \( \sim 1.65 \) at 700 °C, while the highest average \( ZT \) 
appears in \( \text{Cu}_2\text{Se} \) benefiting from its lowest lattice thermal conductivity. From practical 
application point of view, \( \text{Cu}_2\text{Se} \) is the preferred composition because of the higher average \( ZT \).

4. Discussion

The good thermoelectric performance of \( \beta \)-phase \( \text{Cu}_2\text{Se} \) is a direct result of its unique crystal 
structure as it possesses low lattice thermal conductivity and good power factor at the same time. 
The disordered Cu atoms at multiple lattice positions in the high temperature \( \beta \)-phase would be a 
highly efficient phonon scattering mechanism, which is similar to the role of Zn in \( \text{Zn}_4\text{Sb}_3 \) [23]. 
On the other hand, the monoatomic Se ordered layer may also introduce disturbance to the
phonon propagation. Besides the structure disorder, the abnormal decreasing $C_p$ value at above 200 °C is also worth thinking. Normally, the $C_p$ should approach a constant at high temperatures according to Dulong-Petit law or slight increase with temperature due to the thermal expansion of the materials [24]; however, what we observed in our experiments is different: a slightly decreasing $C_p$ with temperature (Fig. 3d), where similar phenomena were also reported in Ag$_2$S [25] and AgCrSe$_2$ [26]. Anharmonic phonons usually lead to increasing specific heat with increasing temperature although theoretically they can also reduce the specific heat [27,28]. In the other extreme, many liquids have shown a reducing specific heat as a function of increasing temperature [29-31]. The random distribution of Cu in β-phase Cu$_2$Se among several sites along <111> direction could also be considered as a partial melting of Cu atoms, similar to the reported “molten sublattice” in other superionic conductors [32]. Thus it is reasonable to attribute the decreasing specific heat to the increasing anharmonicity in the Cu-Se bonds due to increased random motion of the Cu atoms at high temperature. It is also the reason for the low total and lattice thermal conductivities (Fig. 3e) in the β-phase Cu$_2$Se sample.

From the Archimedes’ method we found that the volumetric densities of all the β-phase Cu$_2$Se samples are similar at ~6.8 g cm$^{-3}$, close to the theoretical value of 6.9~7.0 g cm$^{-3}$, and the SEM study also showed that their typical grain sizes are all in the range of 1~3 µm (Fig. 2c), which are the reasons for their similar thermoelectric properties regardless the hot pressing temperature. Different from other techniques [3,4] utilizing nano-inclusions or nano-grains, the good thermoelectric properties of the β-phase Cu$_2$Se sample mainly relies on its own intrinsic structure features.

5. Conclusions
In conclusion, low lattice thermal conductivity of 0.4-0.5 W m\(^{-1}\) K\(^{-1}\) from room temperature to 700 °C was obtained in β-phase Cu\(_2\)Se polycrystals due to a unique combination of monoatomically ordered Se layer and disordered Cu layer in their crystal structure. The increased random motion of Cu atoms results in a slightly decreasing \(C_p\) values at above 200 °C. A phase transition from a tetragonal α-phase to the FCC β-phase was indicated at around 140 °C in the plots of their thermoelectric transport properties, which was also confirmed by our XRD and HRTEM study at different temperatures. Finally, \(ZT\) values of ~1.6 in Cu\(_2\)Se and Cu\(_2\)Se\(_{1.01}\) were achieved in our study, which competes well with other medium temperature thermoelectric materials.

**Acknowledgements**

This work is supported by “Solid State Solar-Thermal Energy Conversion Center (S3TEC)”, an Energy Frontier Research Center funded by the U. S. Department of Energy, Office of Science, Office of Basic Energy Science under award number DE-SC0001299 (G. C. and Z. F. R.).

**References:**


Figure Captions:

**Figure 1** Crystal structure of cubic $\beta$-phase Cu$_2$Se. (a) View of (111) plane. (b) FCC unit cell with proposed possible Cu distribution at (0.25, 0.25, 0.25), (0.315, 0.315, 0.315), and (0.5, 0.5, 0.5) along <111> direction. (c) Room temperature XRD patterns of Cu$_2$Se nanopowders and bulk samples hot pressed at 400 °C (HP400 bulk), 500 °C (HP500 bulk), 600 °C (HP600 bulk), and 700 °C (HP700 bulk). (d) Temperature dependent XRD patterns of hot pressed (700 °C) Cu$_2$Se bulk samples measured at 25, 200, 400, and 600 °C.

**Figure 2** Microstructure images of as-prepared (pressed at 700 °C) Cu$_2$Se$_{1.01}$ sample. (a) and (b) HRTEM images at room temperature, and 200 °C, respectively. (c) Typical SEM image taken from the same sample to show the grain size.

**Figure 3** Temperature dependent thermoelectric properties of Cu$_2$Se$_{1.01}$ bulk samples prepared with different hot pressing temperatures. (a) Electrical resistivity. (b) Seebeck coefficient. (c) Power factor. (d) Specific heat ($C_p$), and thermal diffusivity (HP700 bulk). (e) Total thermal conductivity (filled symbols) and lattice thermal conductivity (open symbols). (f) Figure-of-merit, $ZT$.

**Figure 4** Temperature dependent thermoelectric properties of Cu$_2$Se$_{1+x}$ with varying selenium content. (a) Electrical resistivity. (b) Seebeck coefficient. (c) Power factor. (d) Thermal conductivity. (e) Lattice thermal conductivity. (f) Figure-of-merit, $ZT$. 
Figure 1. B. Yu et al.
Figure 2. B. Yu et al.
Figure 3. B. Yu et al.
Figure 4. B. Yu et al.
Title: Thermoelectric properties of copper selenide with ordered selenium layer and disordered copper layer

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Keywords: Copper selenide, Thermoelectrics, Ordered and disordered layers, Natural superlattice, Specific heat

Graphic Abstract:

Research Highlights:

- \( \beta \)-phase Cu\(_2\)Se with a combination of ordered and disordered layers in its unit cell was studied.
- The natural superlattice like structure promises to achieve low lattice thermal conductivity.
- Increased random motion of disordered Cu atoms at high temperature results in reducing \( C_p \) values.
- High thermoelectric figure-of-merit (\( ZT \)) values of \(~1.6\) at 700 °C were obtained.