Superior intrinsic thermoelectric performance with $zT$ of 1.8 in single-crystal and melt-quenched highly dense Cu$_{2-x}$Se bulks

Lan-ling Zhao$^{1,2}$, Xiao-lin Wang$^1$, Ji-yang Wang$^2$, Zhen-xiang Cheng$^1$, Shi-xue Dou$^1$, Jun Wang$^1$ & Li-qiang Liu$^3$

$^1$Spintronic and Electronic Materials Group, Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, North Wollongong, 2500, Australia, $^2$Institute for Crystal Materials, Shandong University, Jinan, Shandong, P.R. China, $^3$Faculty of Engineering, Shandong Jianzhu University, Shandong, P.R. China.

Practical applications of the high temperature thermoelectric materials developed so far are partially obstructed by the costly and complicated fabrication process. In this work, we put forward two additional important properties for thermoelectric materials, high crystal symmetry and congruent melting. We propose that the recently discovered thermoelectric material Cu$_2$-xSe, with figure of merit, $zT$, over 1.5 at $T$ of $\sim$ 1000 K, should meet these requirements, based on our analysis of its crystal structure and the Cu-Se binary phase diagram. We found that its excellent thermoelectric performance is intrinsic, and less dependent on grain size, while highly dense samples can be easily fabricated by a melt-quenching approach. Our results reveal that the melt-quenched samples and single crystals exhibit almost the same superior thermoelectric performance, with $zT$ as high as 1.7–1.8 at $T$ of $\sim$973 K. Our findings not only provide a cheap and fast fabrication method for highly dense Cu$_{2-x}$Se bulks with superior thermoelectric performance, paving the way for possible commercialization of Cu$_{2-x}$Se as an outstanding component in practical thermoelectric modules, but also provide guidance in searching for new classes of thermoelectric systems with high crystal symmetry or further improving the cost performance of other existing congruent-melting thermoelectric materials.

High temperature thermoelectric (TE) technology has been increasingly significant for a sustainable and environmental friendly supply of clean energy, due to our increasingly severe environmental problems and the energy crisis$^{1,2}$. Thermal energy can be converted into electricity directly when a temperature gradient is formed on TE junctions$^{4–7}$. TE devices can work with high reliability, quiet operation due to the lack of moving parts, and no pollution$^{8–10}$.

Many alloys and nanostructured materials, such as Cu$_x$Sb$_{12}$, β-Zn$_x$Sb$_3$, and PbTe or PbSe-based alloys, have been investigated extensively and developed as high temperature TE materials for power generation$^{11–17}$. Their TE performance has been improved greatly, with the thermoelectric figure-of-merit over 1. It is well known that the energy conversion efficiency of TE materials at a temperature $T$ can be evaluated by the dimensionless thermoelectric figure-of-merit ($zT$) defined as $zT = S^2T/\rho\kappa$, where $S$, $T$, $\rho$, and $\kappa$ are the Seebeck coefficient, absolute temperature, electrical resistivity, and total thermal conductivity, respectively$^{18–23}$. $\kappa$ can be expressed by $\kappa = \kappa_L + \kappa_C$, where $\kappa_L$ and $\kappa_C$ are the lattice thermal conductivity and the charge carrier thermal conductivity, respectively. Lattice or atomic vibrations contribute predominantly to $\kappa$ at high temperatures compared to those of the charge carriers.

Among these parameters, $\kappa$ is the decisive factor ruling the TE performance, as it determines the heat transport capability between the hot and cold sides of the TE modules. Therefore, reducing $\kappa$ has been the main focus of studies aiming to improve $zT$ for various types of high temperature TE materials in particular. The following effective approaches have been commonly used so far to reduce $\kappa$ through phonon refinement: 1) reducing particle sizes to the nanoscale using nano-engineering, which gives rise to both intragrain and intergrain (grain boundary) phonon confinement; 2) fabricating multilayer thin films to reduce the dimensionality of TE materials; and 3) doping with heavy atoms to effectively reduce the phonon vibrations.
Nevertheless, the fabrication methods employed for multilayer thin films and nanoparticles involve costly equipment that is capable of operating under conditions of high vacuum, high temperature, and high pressure, as well as complicated chemical processes. Highly dense polycrystalline TE bulks are commonly synthesized by the hot pressing method under high temperature and high pressure, using expensive spark plasma sintering (SPS) systems. They are all very costly and long heat treatments are needed (usually up to several days), making TE materials less suitable for practical applications. Therefore, it is much more attractive to find an effective fabrication method that is low-cost and time-saving.

In this work, we propose to achieve highly dense samples with excellent TE performance for a certain type of thermoelectric compound by employing a low-cost and time-saving method based on the following facts and analyses: 1). Materials possessing the congruent melting property should maintain the same chemical phase and composition from the homogeneous melt state to the solid state, despite subtle differences in the real chemical compositions of the solid and melt states due to possible loss of volatile element(s) above the melting temperature. This means that highly dense bulks should be easily obtained by the melt-quenching approach. This has been successfully adopted in single crystal growth and casting technology for various materials, giving highly density and excellent performance, although little work has been done on the fabrication of polycrystalline TE materials. 2). Anisotropy plays a significant role in the TE performance of a material with anisotropic crystal structure or low crystal symmetry. It should be noted that the anisotropy is an important or an additional factor that is likely to affect the overall TE performance of polycrystalline bulk samples, and it needs to be taken into account in the consideration of $zT$ improvement.

Materials showing excellent TE performance, such as Bi$_2$Te$_3$, exhibit high anisotropy in their crystal structures, which is likely to be the reason why polycrystalline bulks have lower $zT$ than the corresponding single crystals with certain preferred crystallographic directions. Inspired by the above considerations, for cubic-structured TE materials, their TE performances along the three main crystallographic axes (a, b, and c directions) should be the same due to the identical arrangement of atoms along these equivalent directions. Grain boundaries or particle sizes should have less effect on $\kappa$ and other TE parameters in cubic-structured TE materials compared to those with low crystal symmetry. Therefore, we propose two additional properties for excellent TE materials: congruent melting and high crystal symmetry, or at least less anisotropy.

It has come to our attention that the recently discovered new class of copper ion liquid-like TE material, Cu$_{2-x}$Se, ought to meet these requirements. Cu$_{2-x}$Se bulks prepared by the hot pressing method show high TE performance with $zT > 1.5$ at $T$ of $\sim 1000$ K. Its high temperature β-phase has the cubic crystal structure with space group $Fm\overline{3}m$, and the copper ions can behave like a liquid, which could lead to similar TE performance between single crystals and polycrystalline bulks at high temperatures.

Figure 1 shows the binary phase diagram of the Cu-Se system and the assumed ideal unit cell of the high temperature β-phase Cu$_{2-x}$Se. According to this binary phase diagram, the low temperature α-phase Cu$_{2-x}$Se is transformed to the high-temperature β-phase at $\sim 400$ K and seems to undergo a congruent melting at

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**Figure 1** (a) Binary phase diagram of the Cu-Se system. The inset shows the 3D unit cell of high temperature β-phase Cu$_{2-x}$Se. (b) Unit cell of high temperature β-phase Cu$_{2-x}$Se viewed towards the (100) and (111) planes, respectively.
We anticipate that as long as the Cu$_2$Se samples have 100% density, they should show high TE performance, regardless of grain size. Based on our analysis of the binary phase diagram of the Cu-Se system, the long sintering reported for highly dense Cu$_2$Se bulks seems to be unnecessary. The melt-quenching approach should only take a few minutes to achieve highly dense Cu$_2$Se bulks, in contrast to the conventional hot-pressing method, which requires hours of heat treatment under high pressure and high temperature. Furthermore, there is a lack of information on what the intrinsic TE performance or $zT$ should be for the Cu$_2$Se. Therefore, it is important to carry out experiments using Cu$_2$Se single crystals to investigate their intrinsic TE properties, as well as for comparison purposes.

**Results and Discussion**

Figure 2 presents the XRD patterns of powdered Cu$_2$Se bulks fabricated by the melt-quenching approach (quenched in water and liquid nitrogen (LN)), and of a single-crystal sample prepared by a modified Bridgman method, together with the standard X-ray diffraction (XRD) peaks of low temperature $\alpha$-phase Cu$_2$Se (PDF No. 27-1131). Its XRD pattern indicates that the single-crystal sample only shows (00l) peaks of low temperature $\alpha$-phase Cu$_2$Se, demonstrating that the single crystal sample’s orientation is [00l] at low temperatures. At high temperature, the low temperature $\alpha$-phase is converted to $\beta$-phase. Simultaneously, the (00l) plane becomes the (111) plane, which has been previously reported for Cu$_2$Se single crystals. Therefore, in this work, the TE performance of our single-crystal Cu$_2$Se sample was characterized along the (111) plane of high temperature $\beta$-phase.

We also carried out Rietveld refinements for the powdered single-crystal and polycrystalline bulk samples. The unit cell of monoclinic-structured low temperature $\alpha$-phase Cu$_2$Se is shown in Figure S1 in the Supporting Information (SI). The refined XRD patterns and the values of the Rietveld refinement parameters (lattice parameters, R-factors, and goodness of fit (GOF)) are displayed in Figure S2 and Table S1 (SI), respectively. The results indicate that all samples have the monoclinic structure (space group C2/c) with some differences in the lattice parameters. No visible traces of any secondary phase were detected within the XRD resolution, which is consistent with previous reports.

Field emission scanning electron microscope (FE-SEM) images of the single-crystal, water-quenched, and LN-quenched polycrystalline Cu$_2$Se bulks are shown in Figure 3. The single-crystal surface is extremely smooth, and its edge clearly shows the layered structure. All the melt-quenched samples are highly dense without any visible voids or porosity. The average grain size is ~10 $\mu$m for the water-quenched sample shown in Figure 3(c), which is slightly larger than that of the Cu$_2$Se bulks prepared by the conventional hot-pressing method. The LN-quenched samples also have microscale grains, although they are smaller than those in the water-quenched one. Only in the part near the surface, are there some nanoscale grains. This suggests that Cu$_2$Se can be crystallized quickly and that it is very hard to achieve small grains for thick or large-size samples.

In order to gain insight into the real chemical compositions of our samples, we carried out the chemical analysis using energy dispersive X-ray spectroscopy (EDS), and the results for individual points and EDS mapping are displayed in Figures S3 and S4 (SI), respectively. According to the point EDS analysis, subtle variations in the real chemical composition are detected for different samples. The chemical composition is estimated to be Cu$_{2.01}$Se for the single crystals, Cu$_{1.96}$Se for the water-quenched sample, and Cu$_{1.94}$Se for the LN-quenched one, respectively, which is in good agreement with our XRD refinement results. The EDS mapping for all samples indicate that both Cu and Se are distributed homogeneously inside all the samples. No Cu or Se rich regions are observed, which means that there is no Se or Cu segregation.

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**Figure 2** X-ray diffraction patterns for as-prepared samples: (a) Cu$_2$Se single crystals grown by a modified Bridgman method. (b) water-quenched Cu$_2$Se bulks. (c) LN-quenched Cu$_2$Se bulks. (d) standard XRD peaks of low temperature $\alpha$-phase Cu$_2$Se (PDF No. 27-1131).
The temperature dependence of the electrical resistivity ($\rho$), Seebeck coefficient ($S$), total thermal conductivity ($k$), power factor (PF), lattice thermal conductivity ($k_L$), and thermoelectric figure-of-merit ($zT$) for the single-crystal, water-quenched, and LN-quenched Cu$_2$-xSe samples is plotted in Figure 4. The following facts are observed: 1) The values of $\rho$ and $zT$ for all samples show the same trend of increasing with increasing temperature. 2) $S$ shows almost the same value for all samples over the whole temperature range from 300 to 973 K and increases as the temperature increases. 3) $k$ decreases as the temperature increases for all samples. 4) The power factor, defined as $\text{PF} = S^2/\rho$, is 4-7 x 10$^{-2}$ W m$^{-2}$ K$^{-2}$ for the low temperature $\alpha$-phase and 4-11.5 x 10$^{-2}$ W m$^{-2}$ K$^{-2}$ for the high temperature $\beta$-phase, which is comparable to the previously reported values for conventional hot-pressed Cu$_2$Se samples.$^{30,31}$ Our LN-quenched Cu$_2$-xSe sample has $zT \approx 1.5$ at $T \approx 973$ K, which is as good as what has been reported for hot-pressed samples.$^{30,31}$ Furthermore, the $zT$ for the water-quenched and single-crystal samples exhibits still higher values around 1.7–1.8 at $973$ K.

It is interesting to note that compared to the water-quenched Cu$_2$-xSe, the LN-quenched Cu$_2$-xSe with smaller grain sizes has larger $\rho$ values ($\sim 7 \times 10^{-4} \Omega$m) and lower $k$ values ($\sim 0.48$ W m$^{-1}$ K$^{-1}$ at $973$ K). This seems to be related to the higher density of grain boundaries which could scatter charge carriers. The Seebeck coefficient, however, is almost the same for all samples. Furthermore, the single crystal sample shows an intermediate $\rho$ and $k$ among all the samples. All these data indicates that grain size may not play an important role in the TE performance of the Cu$_2$-xSe system at high temperatures. This is largely due to the liquid-like behavior of the copper ions, which dominates the system’s TE performance at high temperatures. Furthermore, the differences in electrical resistivity and thermal conductivity may also be related to the differences in chemical composition among the samples.

According to the Wiedemann-Franz relationship, the charge carrier thermal conductivity ($k_c$) can be estimated by $k_c = LT/\rho$, where $L$ is the Lorenz number.$^{43-45}$ In this work, we take $L = 1.5 \times 10^{-8}$ V$^2$ K$^{-2}$ to calculate $k_c$ and then subtract it from $k$ to obtain $k_L$. The temperature dependence of the lattice thermal conductivity for all samples is displayed in Figure 4(e). It is interesting to note that the LN-quenched sample does not show the lowest lattice thermal conductivity, even though it has the highest density of grain boundaries compared to the other samples. For conventional TE materials, a high density of grain boundaries can effectively reduce the lattice thermal conductivity, although it seems that this is not applicable to the Cu$_2$-xSe system because its high temperature $\beta$-phase is crystalized in a cubic structure with a rigid fcc sublattice constituted by the Se atoms and kinetically disordered copper ions. It is the liquid-like behavior of the copper ions that dominates the system’s high temperature TE performance. The lattice thermal conductivity of both the LN-quenched and the single-crystal Cu$_2$-xSe samples first decreases and then increases gently. Interestingly, we note that this phenomenon was also reported by Yu et al.$^{31}$ This could be attributed to the liquid-like behavior of the copper ions, which can confine the
lattice vibrations and in turn reduce the lattice thermal conductivity. When the temperature is over the critical temperature (around 773 K), the lattice vibrations are mainly confined by the liquid-like copper ions, and therefore, the lattice thermal conductivity values are almost the same for all samples. As for the temperatures below the 773 K, the crystal sublattices of both the Se and the Cu atoms contribute to the lattice thermal conductivity. Additionally, subtle differences in chemical composition can also lead to different lattice thermal conductivity.

We have conducted measurements on several pieces of samples fabricated by the same method and also them repeated several times for each sample, demonstrating that our data is reproducible. The repeatability of the thermal diffusivity, electrical resistivity, and Seebeck coefficient for water-quenched Cu$_2$-xSe bulks is shown in Figure S5 (SI). Our results indicate that the fast melt-quenching method works well for the fabrication of highly dense Cu$_2$-xSe bulks with excellent TE performance, as the melt-quenching only takes a few minutes. We have also proposed that it is the cubic crystal symmetry and liquid-like behavior of the copper ions that makes Cu$_2$-xSe show superior TE performance. Our findings pave the way for commercialization of Cu$_2$-xSe as an excellent component in TE modules and can also provide guidance in searching for new classes of isotropic TE systems or further improving the cost performance of other congruent-melting TE materials. These investigations are currently underway in our group.

**Methods**

**Sample preparation.** Firstly, polycrystalline Cu$_2$-xSe pellets were synthesized by a conventional solid-state method. A mixture of Cu and Se powders in the molar ratio 2-x:1 (x = 0.02) was pressed into pellets and sealed in evacuated quartz tubes, before being heated to 600°C for 1–5 hours with a heating rate of 5°C/min, followed by a furnace cooling to room temperature. Secondly, the as-sintered Cu$_2$-xSe pellets were used in the melt-quenching approach. In order to achieve fast melting and quenching, the as-sintered samples were placed at one end of the sealed quartz tube and heated up using a flame of acetylene and oxygen until they melted completely. They were then quickly quenched in water or liquid nitrogen to obtain highly dense bulks with different grain sizes. For comparison, single crystals were also prepared using a modified Bridgman method. The as-prepared pellets were sealed in a quartz tube and melted at a temperature above 1150°C for 2 hours to obtain a homogeneous melt, followed by cooling down to 800–900°C at a rate of 1–5°C/h. The samples were then cooled to room temperature at 4°C/min.

Finally, the obtained samples were shaped into disks with dimensions of 10 mm × 1 mm for thermal diffusivity measurements. After the measurements, the same pieces of samples were cut into rectangular bars for measurements of the electrical resistivity and Seebeck coefficient.

**Measurements.** XRD patterns were collected on a GBC MMA system, and the Rietveld refinements were conducted using the Rietica software package. FE-SEM images and energy dispersive X-ray spectroscopy (EDS) for individual points and mapping was conducted with a JEOL JSM-7500FA system. The electrical resistivity and Seebeck coefficient were measured simultaneously in helium atmosphere in the temperature range from 300 to 973 K using a RZ2001i system. The thermal diffusivity (D) was measured by the laser flash method (LINSEIS LFA 1000), and the specific heat ($C_p$) was determined by differential scanning calorimetry (TA Q100). The sample density (dd) was determined by the Archimedes method. The thermal conductivity ($k$) was calculated by $k = D \times C_p \times dd$.

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