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Giant enhancement of the figure-of-merit over a broad temperature range in nano-boron incorporated Cu₂Se

Abstract

Superionic conductors in the chalcogenide-based copper selenide family have been considered as a promising class of thermoelectric materials, which offer great prospects for converting ubiquitous waste heat into highly demanded electrical energy. Further improvement of the thermoelectric figure-of-merit, zT , for Cu₂Se is very desirable for its practical applications. Since any enhancement in electrical conductivity is often accompanied by a reduction in the Seebeck coefficient or thermal power or vice versa, a significant reduction of thermal conductivity becomes an important strategy for improvement of zT . In this work, we demonstrate that insulating-boron nano-particle inclusion in Cu₂Se has little effect on the overall power factor but can significantly reduce the thermal conductivity, resulting in great improvement in zT , by a factor of 1.6-2.6 compared to undoped samples over a wide range of temperatures. Microstructure studies by high resolution transmission electron microscopy revealed that boron nanostructures interspaced between Cu₂Se microscale grains are responsible for the great reduction in thermal conductivity and, in turn, the significantly enhanced zT . The enhancement of thermal boundary resistance ascribed to the strong acoustic mismatch between Cu₂Se and boron is responsible for the low thermal conductivity of the microstructured composite. Our findings offer an effective approach of using insulating nano-particles to significantly improve the Seebeck coefficient and significantly reduce lattice thermal conductivity for achieving high zT in Cu₂Se and many other similar thermoelectric composites.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Nazrul Islam, S., Li, M., Aydemir, U., Shi, X., Chen, L., Snyder, G. Jeffrey. & Wang, X. (2018). Giant enhancement of the figure-of-merit over a broad temperature range in nano-boron incorporated Cu₂Se. *Journal of Materials Chemistry A*, 6 (38), 18409-18416.

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Giant enhancement of the figure-of-merit over a broad temperature range in nano-boron incorporated Cu₂Se[‡]

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Abstract

Superionic conductors in the chalcogenide-based copper selenide family have been considered as a promising class of thermoelectric materials, which offer great prospects for converting ubiquitous waste heat into highly demanded electrical energy. Further improvement of the thermoelectric figure-of-merit, zT , for Cu₂Se is very desirable for its practical applications. Since any enhancement in electrical conductivity is often accompanied by a reduction in the Seebeck coefficient or thermal power or *vice versa*, a significant reduction of thermal conductivity becomes an important strategy for improvement of zT . In this work, we demonstrate that insulating-boron nano-particle inclusion in Cu₂Se has little effect on the overall power factor but can significantly reduce the thermal conductivity, resulting in great improvement in zT , by a factor of 1.6-2.6 compared to undoped samples over a wide range of temperature. Microstructure studies by high resolution transmission

electron microscopy revealed that boron nanostructures interspaced between Cu₂Se microscale grains are responsible for the great reduction in thermal conductivity and, in turn, the significantly enhanced zT . The enhancement of thermal boundary resistance ascribed to the strong acoustic mismatch between Cu₂Se and boron is responsible for the low thermal conductivity of the microstructured composite. Our findings offer an effective approach of using insulating nano-particles to significantly improve the Seebeck coefficient and significantly reduce lattice thermal conductivity for achieving high zT in Cu₂Se and many other similar thermoelectric composites.

Introduction

Thermoelectric (TE) technology offers a simple and environment-friendly solution for directly recovering waste heat as usable electricity leading to reduction in the global energy crisis.¹⁻³ These devices operate with high reliability, with no moving parts or emission of greenhouse gasses.⁴ TE materials are classified with respect to their intended operating temperature range, with applications varying from spacecraft⁵ to harvesting waste heat from industrial appliances⁶ and automobile exhaust systems.⁷ The figure of merit, $zT = (\sigma S^2)/(\kappa_{Lat} + \kappa_{ele})T$, is the key factor for the energy conversion efficiency of thermoelectric generators, where σ , S , κ_{lat} , κ_{elec} , T are the electrical conductivity, Seebeck coefficient, lattice thermal conductivity, charge carrier thermal conductivity, and absolute temperature, respectively. The total thermal conductivity (κ) expressed by $\kappa = \kappa_{lat} + \kappa_{ele}$, is mainly dominated by lattice vibrations compared to those of the charge carriers at high temperature. Since there are strong correlations between thermal and electrical transport in solids, achieving high zT is extremely challenging. So, optimizing the interdependent transport coefficients κ , σ , and S has been the key focus in research to improve zT . The following techniques have been successfully implemented so far to enhance zT in a wide range of high-temperature TE materials: 1) substitution that changes σ due to carrier

concentration as well as κ due to different atomic masses; 2) reduction of particle size by a nano-engineering approach, which gives rise to confinement of both intragrain and intergrain phonons; 3) reducing the dimensionality of TE materials by creating multilayer thin films; and 4) introducing inclusion of a secondary phase that does not change the carrier concentration, but does reduce κ due to the blocking of phonons.

Among all the Cu-based TE materials, Cu_2Se has received great attention recently, as it has good thermoelectric performance. To date, the electronic structures and thermal conductivity of Cu_2Se have been modified by doping using Al, Sn, Sb, Ag, and Li in the Cu sites⁸⁻¹², and Te, S, I, and Br in the Se sites.¹³⁻¹⁶ Recently, it has been reported that various types of carbon incorporated Cu_2Se composites exhibited high zT of $\sim 1.8\text{-}2.4$ at 850 K¹⁷⁻¹⁹ using a melt fabrication process above the melting point of Cu_2Se .²⁰ The key factor for the great enhancement of zT by carbon incorporation is the giant reduction of thermal conductivity. Since any enhancement in electrical conductivity is often accompanied by a reduction in the Seebeck coefficient or thermal power or *vice versa*, a significant reduction of thermal conductivity becomes an important strategy for improvement of zT . In this work, we propose to use another non-toxic, lightweight, but insulating dopant, boron nano-particles, to incorporate into Cu_2Se . It is also well known that boron (B) doping provides remarkable stability in corrosive and acidic environments and improves mechanical stability.²¹⁻²⁶

In this Communication, we report that using the light element boron as a second nanophase in the Cu_2Se can give significantly enhanced thermoelectric performance. We demonstrate that boron addition can remarkably reduce κ and enhances S preserving high power factor over a wide range of temperatures, leading to the enhancement of zT by a factor of 1.6 - 2.6 compared to undoped samples over a wide temperature range (450-850 K).

Results and discussion

The fabrication process for the boron doped Cu_2Se is illustrated by schematic representation in Fig. 1 and details are mentioned in sample preparation section. Fig. S1 in the ESI† shows the Cu_2Se structure, with the monoclinic α -phase (left side) at room temperature and the cubic β -phase (right side) at high temperature, respectively. Powder X-ray diffraction (XRD) patterns (Fig. 2b) shows that the boron doped samples at room temperature is α -phase. We noted that peak positions slightly change with boron nanoparticle inclusions. They all shifted to small 2-theta values (Fig. 2b) indicating that the lattice parameters are likely to decrease due to boron inclusion. The peak intensity at 37 deg (2-theta) decreases and disappears at high boron contents. There is another remarkable change in peaks as shown in the middle and right figures of Fig. 2c. The shoulder peaks gradually disappear with B addition. These results may suggest that higher boron contents tend to stabilize another crystal structure.²⁷ A Synchrotron high temperature (HT) experiment was performed on both the undoped and boron doped samples (Fig. S3a-h†). Overall this may indicate that B doping may stabilize the HT cubic phase (Fig. S3b†). A further detailed study using high temperature TEM is needed to identify the possible boron-stabilized phases.

Temperature-dependent synchrotron powder X-ray diffraction was performed in order to further investigate the boron doping effect over the change of phase transition with temperature and to identify the change in lattice parameters with temperature. Heat-map images with respect to temperature of undoped Cu_2Se and a 0.42 wt% nano-boron doped Cu_2Se sample from room temperature to 774 K are shown in Fig. 3a and b, respectively. The mapping shows that there are α to β phase transitions for both undoped and boron doped Cu_2Se within this temperature range. This transformation can also be observed in differential scanning calorimetry (DSC) measurements (Fig. 3c), where the phase transition takes place at

400 K for undoped Cu₂Se and 417 K for 0.42 wt% boron doped Cu₂Se. Possible boron substitution effect and any atom deficiency might contribute to the phase transition shift.

The Rietveld refinements and high-resolution synchrotron XRD data of undoped and 0.42 wt% boron doped Cu₂Se samples are shown in Fig. S2 and S3,[†] respectively. The lattice parameters and R-factors of the undoped and boron doped Cu₂Se samples deduced from the Rietveld refinement of the synchrotron XRD patterns are listed in Tables S1[†], respectively. We found that lattice parameter for the boron doped Cu₂Se has 5.8507 Å, 5.8388 Å, 5.8277 Å whereas it was observed to be 5.8611 Å, 5.8427 Å and 5.8316 Å at 624 K, 512 K and 403 K, respectively for the undoped sample. From this result, we can see that lattice parameter variations with boron doping is obvious and it further indicates that there is a boron doping effect in Cu₂Se. We note that the XRD patterns recorded before and after heating and cooling are almost identical for both undoped and doped samples (Fig. 3d), indicating that the phase transformation process is reversible. This also confirms that the boron doped samples have good thermal stability, which is in conformity with the reproducibility of σ , S , and the thermal diffusivity (D) (Fig. S7[†]).

Field emission scanning electron microscope (FE-SEM) images of the boron doped Cu₂Se and pure Cu₂Se bulks are shown in Fig. S4[†]. All the samples were found to be highly dense with no porosity. The processed high-angle annular dark field – scanning transmission electron microscope (HAADF-STEM) images of monoclinic Cu₂Se, their ball models and selected area electron diffraction (SAED) pattern are presented in Fig. 4.

Fig. 4a shows the structure of boron doped Cu₂Se as determined from the HAADF-STEM image (Fig. 4b). The signal-to-noise ratio of the image was improved by using an average filter. The top inset (Fig. 4b) is the distance profile of Se-Se along the marked dotted yellow lines A and B in the image, showing that the space between Se and Se is around 0.899 nm. The bottom inset (Fig. 4b) shows the corresponding atomic model, indicating a perfect

monoclinic structure along the [0 -1 0] orientation. Due to the very much lower Z contrast of B (atomic number contrast), it is impossible to distinguish B atoms in the HAADF-STEM image from the [0 -1 0] orientation. Fig. 4c presents the SAED pattern along the [0 -1 0] orientation. Transmission electron microscope (TEM) images and the high resolution TEM images show (Fig. 4d-e) the boron regions, which appear as black patches and dots embedded inside the Cu₂Se grains, as determined by energy dispersive spectroscopy (EDS) mapping. The presence of boron inclusions across the grain boundary is also shown in Fig. S5†. We can see that the average boron particle sizes are as small as 80 nm. This may indicate that most of the boron precipitates at the grain boundaries but it is likely that a small amount of boron goes into the lattice for causing the lattice parameter to reduce. These nano-boron inclusions are expected to play a significant role in blocking the phonons.

We studied the effects of nano-boron addition on the σ , S , and κ , as well as the microhardness. The temperature dependence of σ , S , κ , and zT for an undoped and boron doped Cu₂Se samples is shown in Fig. 5. The σ of all samples decreases with increasing temperature over the whole temperature range (Fig. 5a). We can see that the boron-doped Cu₂Se sample shows lower electrical conductivity than the undoped sample for both α - and β -phases. This trend becomes more obvious for high boron doping levels. The electrical conductivity is reduced from $\sim 458 \text{ S cm}^{-1}$ for the undoped sample to 207 S cm^{-1} for the 0.42 wt% boron doped Cu₂Se at 852 K. The carrier concentration p and mobility μ_H were determined using Hall effect measurements using the formula: $p = 1/(eR_H)$, where e represents the elemental charge and R_H the Hall coefficient. We found from the Hall effect measurements that hole concentration (p) for the pure Cu₂Se, 0.28 wt% B and 0.42 wt% B is $6.17 \times 10^{20} \text{ cm}^{-3}$, $5.6 \times 10^{20} \text{ cm}^{-3}$ and $3.92 \times 10^{20} \text{ cm}^{-3}$, respectively. The mobility (μ_H) for the pure Cu₂Se, 0.28 wt% B and 0.42 wt% B are $11.11 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, $5.73 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ and $\sim 5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, respectively. The hole carrier concentration decreases

with the amount of boron and for the 0.42 wt% boron doped samples it is ~37% lower than that of the pure Cu₂Se. This result is consistent with the electrical conductivity and Seebeck coefficient measurements. This may indicate that either B dope into the Cu sites or fill the Cu vacancies. Both can lead to a decrease in the carrier concentration. The carrier mobility μ_H for the 0.42 wt% B doped sample is $\sim 5 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$, which is about 54% lower than for the undoped Cu₂Se (Fig. 5d). As $\sigma = ne\mu_H$, where n is the carrier concentration, the overall reduction in σ is mainly caused by the decreased hole concentration as well as carrier mobility in the B added sample. In addition, the electron scattering occurring at the boron/Cu₂Se interface may also play an important role in reducing the σ .

The reduction in electrical conductivity is often accompanied by enhancement of the Seebeck coefficient. Fig. 5b shows the temperature dependence of the Seebeck coefficient for both boron doped and undoped samples. It can be seen that S increases with boron doping over a wide range of temperatures. For the 0.42 wt% boron doped Cu₂Se, the maximum S value is $245 \text{ } \mu\text{V K}^{-1}$ at 852 K, which is about 48 % higher than that of the undoped sample.

The power factor (PF) = σS^2 is $6 - 10 \times 10^{-4} \text{ Wm}^{-1} \cdot \text{K}^{-2}$ for the undoped α -phase and $6.6 - 12.7 \times 10^{-4} \text{ Wm}^{-1} \cdot \text{K}^{-2}$ for the β -phase, which is almost same as in the previously reported results (Fig. 5c).^{13, 28} All the boron-doped samples show the same trend in the power factor with increasing temperature, and the highest values obtained were $10 - 12 \times 10^{-4} \text{ Wm}^{-1} \cdot \text{K}^{-2}$ for the α -phase and $9 - 12.4 \times 10^{-4} \text{ Wm}^{-1} \cdot \text{K}^{-2}$ for the β -phase of 0.42 wt% B doped Cu₂Se. Although there was no significant difference at high temperature, the latter one is about 39 % larger as compared to the pristine Cu₂Se sample at 456 K. In this case, our expectations of any enhancement in zT completely rely on whether or not the thermal conductivity can be reduced by the boron nano-inclusions.

Remarkably, the boron doped Cu₂Se samples exhibit greatly reduced thermal conductivity compared to the boron-free sample, as displayed in Fig. 5e over a temperature range from

300-850 K. The κ for the undoped sample is $1.4\text{-}1.08 \text{ W m}^{-1} \cdot \text{K}^{-1}$ from 456 K - 852 K, while the value is as small as $\sim 0.66 \text{ W m}^{-1} \cdot \text{K}^{-1}$ for the 0.42 wt% boron doped Cu_2Se over the whole temperature range. This value is half of the value for the undoped sample and is also the lowest among almost all the undoped Cu_2Se samples reported so far.^{12, 14, 15, 28-30} The microstructure and phonon transport property of the boron precipitated microcomposite Cu_2Se samples (average grain size $0.4 \mu\text{m}$) are illustrated in Fig. 5f. The reduction of thermal conductivity and enhancement of the thermoelectric figure-of-merit are absolutely due to boron.

The zT is found to increase with boron doping concentration for all temperatures (Fig. 6a). The zT is 1.0 at $T = 600 \text{ K}$ and reaches 1.6 at 852 K for the 0.42 wt% boron doped sample as compared to the zT of 0.46 at 600 K and 0.99 at 852 K for the undoped sample. It is remarkable that the overall zT enhancement ratio is 1.6 to 2.6 for the optimum boron doped sample compared to the undoped one (Fig. S6†). The efficiency is calculated according to the literature.³¹ It was found that efficiency is $\sim 15 \%$ at 852 K for the 0.42 wt% B sample, whereas it is only 9.4% for the undoped Cu_2Se at 852 K (Fig. 6b).

We calculated κ_{ele} according to the Wiedemann-Franz law ($\kappa_{ele} = L\sigma T$), where L represents the Lorentz number. In this work, L is calculated according to the equation $L = 1.5 + \exp[-|S|/116]$, where L is in $10^{-8} \text{ W}\Omega \cdot \text{K}^{-2}$ and S in $\mu\text{V} \cdot \text{K}^{-1}$.^{32, 33} The calculated results show that L varies in the range of $(1.6 - 2) \times 10^{-8} \text{ W}\Omega \cdot \text{K}^{-2}$ with different types of boron doping and with the temperature increasing from 350 to 852 K (Fig. 7a). The total κ in Fig. 7b shows a decrease to $\sim 0.66 - 0.73 \text{ W m}^{-1} \text{ K}^{-1}$ with temperature for the 0.42 wt% boron doped Cu_2Se , while it was $\sim 1.08\text{-}1.40 \text{ W m}^{-1} \text{ K}^{-1}$ for the undoped Cu_2Se . The calculated κ_{ele} was $0.68 - 1 \text{ W m}^{-1} \text{ K}^{-1}$ for the undoped Cu_2Se , and it decreased to $0.27\text{-}0.39 \text{ W m}^{-1} \text{ K}^{-1}$ for the 0.42 wt% boron doped Cu_2Se . The dependence of κ_{lat} of all samples on temperature is shown in Fig. 7c. The κ_{lat} value is significantly lower than for most the

reported polycrystalline samples at $0.23 \text{ W m}^{-1} \text{ K}^{-1}$,^{12, 28, 34-36} as shown in Fig. 7c and d. The reduced transmission of heat is most obviously correlated with extremely low κ_{lat} along with κ_{ele} and is due to the decreased number of charge carriers as well as the lattice vibrations through the complex heterogeneous microstructure of our boron doped polycrystalline Cu_2Se with boron nano-inclusions at the grain boundaries. The κ_L of a polycrystalline solid can be determined using the following relation³⁷:

$$\kappa_p^{-1} = \kappa_b^{-1} + \frac{R_\kappa}{\bar{d}}$$

Where, κ_b , κ_p , $1/\bar{d}$ and R_κ are the intrinsic thermal conductivity of Cu_2Se , the change in thermal conductivity of a doped sample, the inverse average grain size, and the grain boundary resistance, respectively. The reduction of transmission of heat observed using this model is due to the thermal resistance developed across the interface, and it becomes more strengthened as the number of interfaces increase in microcrystalline solids. The key parameter R_κ represented the percentage of grain boundary covered by the boron inclusions and the reflection of phonons instead of transport through the edge of the grain. A negligible R_κ value of $\sim 1 \times 10^{-9} \text{ m}^2 \cdot \text{K} \cdot \text{W}^{-1}$ is found in the intrinsic Cu_2Se solid due to the large crystalline grain size, while micro- and nanograins have almost the same κ_p ,²⁰ whereas it becomes significant with the boron inclusions near the edge, in conformity with other thermoelectric results.³⁷ The average grain size of the boron doped sample was found to be $0.4 \text{ } \mu\text{m}$ with κ_b and κ_p of $1.41 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $0.73 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively, which results in the ultra-high R_κ value $2.63 \times 10^{-7} \text{ m}^2 \cdot \text{K} \cdot \text{W}^{-1}$. This value is comparable to the results for recently reported graphene doped thermoelectric materials.³⁷

Thermoelectric materials with good mechanical properties can better sustain strong mechanical and thermal stresses and improve the reliability of segmented thermoelectric modules.³⁸⁻⁴⁰ Fig. 8 shows the microhardness values of the pure Cu_2Se and boron doped

Cu₂Se bulks. The hardness value of the pure Cu₂Se bulk is found to be ~0.38 GPa, and this mechanical performance gradually increases with increasing content of boron. The measured hardness values are 0.40, 0.43, and 0.45 GPa for the 0.14 wt% B, 0.28 wt% B, and 0.42 wt% B doped Cu₂Se samples, respectively. These values are comparable to those for reported polycrystalline Cu₂Se solids (~0.40 GPa) prepared using melt-quenching approach.¹³

Conclusions

We have demonstrated that nano-boron particles can significantly enhance the zT of Cu₂Se. Our studies indicate that boron inclusion can considerably reduce the thermal conductivity, while preserving high power factor, resulting in enhancement of zT by a factor of 1.6-2.6 over a wide temperature range compared to undoped samples. The mechanism for this improvement of zT is that the reduction of heat conduction by boron-decorated microstructure edges increases the boundary resistance with decreasing carrier concentration. Our findings offer an effective approach of using insulating nano-particles to achieve high zT in Cu₂Se and many other types of thermoelectric composites.

Experimental

Synthesis

Firstly, the polycrystalline Cu₂Se powders were milled in a high energy ball-mill to mix with amorphous boron (B) powders. The balls to powder weight ratio was 10 : 1. The rotation conditions were set to 500 rpm for 4 hours. The weight ratios of Cu₂Se and B are 1: x ($x = 0.14\%$, 0.28% , and 0.42%). The highly dense 20 mm diameter and 2 mm thick solids were formed by spark plasma sintering (SPS; Thermal Technology SPS model 10-4) at 773 K for just 10 min under a pressure of 40 MPa in vacuum. Finally, the samples were shaped into a rectangular bar and round disks using a cutting machine (Struers Accutom-50) for electrical and thermal transport measurements, respectively. The boron-doped Cu₂Se samples are

denoted by their boron weight percent, so that the sample with 0.14 wt% boron was denoted as 0.14 B, *etc.*

Measurement summary

The room temperature powder diffraction patterns were determined by X-ray diffractometry (Cu K α , GBC MMA) ($\lambda=1.5418$ Å), $10^\circ \leq 2\theta \leq 60^\circ$, in step scan mode with a step size of 0.014° and speed of 1 degree per min. The Australian Synchrotron was used to collect high resolution data using a wavelength of $\lambda = 0.58973$ Å, where the detectors covered an angular range of $2.5^\circ \leq 2\theta \leq 80^\circ$, simultaneously every 30 seconds and the sample was rotated at ~ 1 Hz with a heating rate of 4 deg./min under helium gas flow over the 300–774 K temperature range. The sample morphologies and microstructures were investigated with field emission scanning electron microscopy (FE-SEM, JEOL 7500), and transmission electron microscopy (TEM, JEOL ARM200F) was used to investigate the phase composition and microstructure of the undoped and boron doped Cu₂Se samples. The thin TEM specimens were prepared using focused ion beam milling (FIB, FEI Helios Nanolab) after being mounted in Polyfast[®] using Struers Citopress-20 equipment and polished with Struers Tegamin-20 water equipment, before they were used for scanning transmission electron microscopy/X-ray spectroscopy (STEM/X-ray mapping) investigations. Room temperature Hall coefficient measurements were performed to determine the carrier concentration and carrier mobility using a physical properties measurement system (Quantum Design PPMS-9). The σ and S were simultaneously measured from room temperature to 852 K under vacuum using a commercial RZ2001i system. The laser flash method (LINSEIS LFA 1000) was used to measure thermal diffusivity under vacuum conditions. The heat capacity (C_p) was measured by differential scanning calorimetry (DSC-204F1 Phoenix) under argon atmosphere. The weight and dimensions were used to measure the sample density (dd) and found 6.480, 6.375, 6.255, and 6.161 g/cm³ for the undoped, 0.14, 0.28 and 0.42 B. The total thermal conductivity

(κ) was calculated using the formula $\kappa = D \times C_p \times dd$. The Vickers Hardness measurements of the undoped and boron doped Cu₂Se samples were carried out under 0.245 N load in Lens (60x) using Struers Emco-Test DuraScan-70. All the transport measurements were repeated several times to check the consistency of the polycrystalline samples.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by the Australian Research Council (ARC) through a Discovery Project DP 130102956 (XLW), an ARC Professorial Future Fellowship project (FT 130100778, XLW), and a Linkage Infrastructure Equipment and Facilities (LIEF) Grant (LE 120100069, XLW). This research also used equipment funded by the Australian Research Council (ARC) FEI NanoLab G3 CX: LE160100063 and ARM- LE120100104. We are thankful to Mitchell Nancarrow, David Cortie and Michael Cortie for assistance with sample preparations for SEM/TEM analysis and Synchrotron experiments.

Figures and Captions:

Fig. 1 Schematic illustration showing the formation mechanism of the B-doped Cu_2Se bulks with the fabrication process.

Fig. 2 (a) Schematic illustration of the crystal structure of α -phase Cu_2Se , and (b) X-ray diffraction patterns of pure Cu_2Se and boron doped Cu_2Se ($\text{Cu}_2\text{Se}-x\text{wt}\% \text{ B}$ samples ($x = 0, 0.14, 0.28$, and 0.42)) showing that the peak intensity at 37° 2θ disappears at high B contents, (c) enlarged peaks for the undoped and boron doped Cu_2Se samples showing that all the peaks shift to the left with boron doping and one peak in the right (c) disappears with the boron.

Fig. 3 Synchrotron radiation X-ray diffraction (SR-XRD) profiles of (a) pure Cu_2Se and (b) 0.42 wt% boron doped Cu_2Se obtained upon heating to different temperatures; (c) Temperature dependence of the heat capacity (C_p) for the undoped and boron doped Cu_2Se samples; (d) XRD patterns for $\text{Cu}_2\text{Se}/0.42$ wt% boron obtained at 300 K at the beginning of the measurement (1) and after the measurement (2), respectively.

Fig. 4 Structural characterization of 0.42 wt% boron-doped Cu_2Se polycrystals. (a) Ball model of the monoclinic unit cell of Cu_2Se representing the dashed square of the main panel of (b). (b) Atomic resolution HAADF image at room temperature along the $[0 -1 0]$ zone axis, where the Se atoms are represented by the yellow balls and the weak contrast Cu atoms among Se layers are represented by the red balls in the bottom inset; Top inset: the line profile along the dotted line AB in the main panel, showing the spacing between two Se. (c) The SAED pattern along the $[0 -1 0]$ orientation. (d) HAADF STEM image of the FIB milled sample, showing boron-rich precipitates within the Cu_2Se -rich matrix along with the corresponding EDS elemental mapping for Cu, Se and B. Average Boron particle sizes are 80 nm. (e) Magnified observation of boron-rich precipitates within the Cu_2Se -rich matrix.

Fig. 5 Temperature dependence of the thermoelectric transport properties of the samples: (a) electrical conductivity (σ), (b) Seebeck coefficient (S), (c) Power factor (PF); (d) Carrier concentration and carrier mobility for the pure, 0.28 wt% boron and 0.42 wt% boron doped Cu₂Se samples; (e) Thermal conductivity (κ) as a function of temperature; and (f) Schematic diagram of B-doped Cu₂Se composite, showing the microstructure and phonon transportation.

Fig. 6 Thermoelectric figure of merit zT for the undoped and B-doped Cu₂Se with different wt% B. b) Thermoelectric efficiency of the undoped and B-doped Cu₂Se samples, in comparison with the previously reported Cu₂Se data.⁴¹

Fig. 7 Temperature dependence of the thermal transport properties for the undoped and boron doped polycrystalline samples: (a) The calculated Lorenz number (L) of undoped and boron doped Cu_2Se ; (b) total thermal conductivity (κ) and electronic thermal conductivity (κ_e); (c) lattice thermal conductivity (κ_L) with total thermal conductivity (κ); (d) comparison of the boron doped κ_{lat} values and κ_{tot} values (dotted lines) with those of state-of-the-art Cu_2Se ,^{12, 28, 34} PbTeSe ,³⁵ PbTe ,³⁶ polycrystals.

Fig. 8 Hardness of the undoped and boron doped Cu_2Se polycrystalline samples in comparison with data for Cu_2Se polycrystalline bulks.¹³

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Footnote

† Electronic supplementary information (ESI) available: figures, table

Supporting Information

Giant enhancement of the figure-of-merit over a broad temperature range in nano-boron incorporated Cu₂Se

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Fig. S1 Low-temperature monoclinic phase (left) and high-temperature cubic phase (right) of the Cu₂Se crystal structure

Fig. S2 Rietveld refinement of 0.42 wt% boron doped Cu_2Se (a-c) and undoped Cu_2Se (d-f) at 624 K, 512 K, and 403 K, respectively. The refined parameters are shown in Table S1.

Table S1 Parameters for the refinement of boron doped and undoped Cu₂Se at 624 K, 512 K, and 403 K. R_p and R_{wp} are the profile and weighted profile R-factors, respectively, and χ^2 is the goodness-of-fit.

Temp (K)	Lattice parameter	a (Å)	R _p	R _{wp}	χ ²
	Sample				
624	(a) 0.42 wt% Boron	5.85070	9.867	13.313	2.609
512	(b) 0.42 wt% Boron	5.83880	8.560	11.077	1.853
403	(c) 0.42wt% Boron	5.82770	9.858	12.999	2.579
624	(d) Cu ₂ Se	5.86110	9.777	12.962	1.242
512	(e) Cu ₂ Se	5.84270	9.325	12.175	1.157
403	(f) Cu ₂ Se	5.83160	9.517	12.165	1.283

Fig. S3 Synchrotron powder diffraction patterns over the entire measured temperature range of ~300–773 K for 2θ = (a) 2.5° – 30° (Undoped), (b) 2.5° – 30° (0.42 wt% Boron) (c) 9.5° – 10.5° (Undoped), (d) 16° – 17° (Undoped), (e) 18.75° – 19.75° (Undoped), (f) 9.5° – 10.5° (Boron), (g) 16° – 17° (Boron), (h) 18.75° – 19.75° (Boron). The wavelength is $0.5897313 \text{ \AA}$.

Fig. S4 SEM images of fractured surface morphology of (a) pure Cu₂Se, and b) 0.14 wt%, (c) 0.28 wt% and (d) 0.42 wt% boron-doped polycrystalline Cu₂Se fabricated by the spark plasma sintering (SPS) method.

Fig. S5 Low magnification TEM image of the boron doped Cu₂Se bulk sample showing the presence of boron across the grain boundary

Fig. S6 Temperature dependence of (a) $\sigma/\sigma_{0.0}$, (b) $S/S_{0.0}$, (c) $\kappa/\kappa_{0.0}$, and (d) $zT/zT_{0.0}$ for the boron doped Cu_2Se samples with doping levels of 0.14, 0.28, and 0.42 wt%.

Fig. S7 The electrical and thermal transport properties with respect to temperature during heating up and cooling down for a 0.42 wt.% Boron doped Cu_2Se sample: (a) electrical conductivity (σ); (b) Seebeck coefficient (S); (c) thermal diffusivity (D).