Exploring Thermoelectric Property Improvement for Binary Copper Chalcogenides

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Copper chalcogenides have been the subject of extensive research as promising candidates in thermoelectric conversion applications due to their advantageous properties, environmental compatibility, and abundance. The low intrinsic thermal conductivity and high electric conductivity of these materials are born out of the “phonon-liquid electron-crystal” structure between the copper and chalcogens. In this review, strategies for thermoelectric property improvement of copper chalcogenides are discussed. The challenges and the future development of binary copper chalcogenides for further thermoelectric conversion applications are outlined.

Keywords: thermoelectric property, nanostructure, thermal conductivity, carrier concentration, flexible materials

INTRODUCTION

Solid-state thermoelectric (TE) technology, using the Seebeck effect and Peltier effect, can convert directly and simply between heat and electricity (Figure 1A) (Wei et al., 2018). The dimensionless TE figure of merit ($zT$) is the key metric used to evaluate the performance of TE materials: $zT = S^2σT/κ$. Where $S$, $σ$, $κ$, and $T$ are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively (Tan et al., 2016). The earliest studies in TE technology are derived from the 19th century (Shi et al., 2016). Copper sulfides was reported as a promising TE material in 1827. However, there were two main problems unsolved in practical application, which are the stable composition of Cu$_2$S in reheating and contact between the Cu$_2$S and the electrode in the TE generator. When the “phonon-liquid electron-crystal” (PLEC) concept was proposed in 2012, the low thermal conductivity and high TE performance of copper sulﬁdes and copper selenides have been explained. In this review, we discuss the strategies for thermoelectric property improvement of copper chalcogenides based on reducing lattice thermal conductivity of single-component material and tuning compositions for optimizing TE parameters. Challenges for binary copper chalcogenides and perspectives on the flexible copper chalcogenides are outlined.

STRATEGIES FOR THERMOELECTRIC PROPERTY IMPROVEMENT

The fundamental challenge of designing high-performance TE materials stems from the strong correlation of $S$, $σ$, and $κ$, which requires large $S$ and $σ$ values, as well as a low $κ$ value simultaneously
However, these three parameters are strongly interdependent through carrier concentration ($n$). Among three parameters, $\kappa$ comprises the electronic thermal conductivity ($\kappa_e$) and the lattice thermal conductivity ($\kappa_L$) ($\kappa = \kappa_e + \kappa_L$). $\kappa_L$, calculated by $\kappa_L = 1/3C_vvl$, in which $C_v$ is heat capacity, $v$ is speed of sound, and $l$ is mean free path of phonons, is the only one with little dependence on $n$. Therefore, $\kappa_L$ can be minimized through the independent crystal structure and/or microstructure design. This is one strategy for TE property improvement. The other strategy, tuning the composition, such as foreign elements introducing, metal chalcogenides mixing, hybrid compounds building, strongly relates to the $n$ and carrier mobility ($\mu$). Below we will briefly elaborate on these two strategies.

Reducing Lattice Thermal Conductivity of Single Component Material
Reducing $\kappa_L$ can rely on decreasing the mean free path of lattice phonons and eliminating some of the vibrational modes. For example, face-centered cubic (fcc) copper selenide, as a superionic conductor, has two different sub-lattices inside its crystal structure. The sub-lattice frame of Se atoms provides a pathway for the movement of semiconducting electrons, and the highly disordered Cu ions move through the Se lattice frame with "liquid-like mobility" and high diffusivities, which explained as the "PLEC" concept (Figures 1B and 1C) (Qiu et al., 2016; Chen et al., 2018). In addition, the liquid-like mobile Cu ions also introduce extra scattering to lattice phonons to further disrupt heat propagation or alter phonon transfer, and thereby shortening phonon mean free path and suppressing $\kappa_L$.

Now, research on the PLEC Cu-based superionic conductors has become a topic that is very popular in the TE community. A low $\kappa_L$ around 0.4–0.6 W m$^{-1}$ K$^{-1}$ was reported at a high-temperature of 1000 K for Cu$_2$Se, which leads to an enhanced TE performance ($zT = 1.5$) (Liu et al., 2012). This high $zT$ value results from the coexistence of Se and Cu sub-lattices inside the crystal structure of the Cu$_2$Se phase. Introducing nanostructure for defects creation, an effective method to enhance the low-to-high wavelength phonon scattering, results in
a very small value of \( \kappa \). Cu_{2}Se with this low \( \kappa \) (0.34 W m\(^{-1}\)K\(^{-1}\)) reached a high \( zT \) of 2.1 at 973 K (Gaitori et al., 2015).

Copper sulfide and copper telluride are superionic conductors at high-temperatures as well. Thus, they correlate well with the PLEC character that has been observed in Cu_{2}Se. It is reported at high-temperatures as well. Thus, they correlate well with the \( \kappa \) enhancement of TE properties. Carbon brings to high charge the copper chalcogenide bulks has achieved significant improvements in TE properties. For measurement, CdS/Cu_{2}S superlattice nanowires demonstrated the lower \( \kappa \), and the best \( zT \) value is 1.1 at 1000 K (He et al., 2015b).

**Tuning Compositions for Optimizing Thermoelectric Parameters**

Tuning the composition, without the intrinsic restriction from monomers, more depends on the \( n \) and \( \mu \) to optimizing three TE parameters \( S \), \( \sigma \), and \( \kappa \). Firstly, foreign elements introducing by the fabrication process can generate vacancies in material structures which increase the hole concentration at cation positions or electron concentration at cation positions. Furthermore, foreign elements serving as point-defect scattering sources for phonons. These impurity atoms create both force differences (strain field fluctuations) and mass contrast (mass fluctuations) between the host atoms and the impurity atoms and are very effective for scattering high-frequency (short wavelength) phonons. Thus foreign elements, like Na, Ag, I, and Al, can affect TE properties by changing the degree of Cu deficiency. For example, Cu_{2}Se_{1-x}I_{x} presents a \( zT \) value of 2.3 near room temperature as a result of critical scattering, which simultaneously leads to a high \( S \) and high \( \kappa \) (Liu et al., 2013).

Another attractive way is the mixture of homogeneous metal chalcogenides, which not only maintains the PLEC cubic structure of copper chalcogenides but also creates a unique composite structure. He et al. reported a mosaic crystal of mixed Cu_{2}S-Cu_{2}Te bulk nanomaterials, which achieves a \( zT \) value of 2.1 at 1000 K (He et al., 2015a). In this unique microstructure, electrons are freely transferred along with the frames of quasi-single crystals while phonons are strongly scattered by lattice strains or interfaces of mosaic nanograins (Figure 1D). In the Ag_{2}Te-Cu_{2}Te mixed structure, the high \( n \) in pristine Cu_{2}Te is substantially reduced to an optimal range, resulting in much-reduced \( \kappa \) and enhanced power factors over the entire temperature range. Furthermore, the temperature of the last phase transition is significantly lowered when increasing Ag content, which leads to a \( zT \) of 1.8 is achieved at 1000 K in Cu_{2}Te + 50% Ag_{2}Te (Zhao et al., 2019).

Recently, the introduction of different forms of carbon (such as carbon nanotubes, graphene, and carbon encapsulation) into the copper chalcogenide bulks has achieved significant enhancement of TE properties. Carbon brings to high charge \( \mu \) into a composite structure (Zhu et al., 2019), which benefits the \( \kappa \) but increases the \( \kappa \) as well. The introduction of a certain concentration of carbon in composite materials is the key to improve the TE properties. Cu_{2}Se and multi-walled carbon nanotube (CNTs) hybrid materials, with a high degree of homogeneously dispersed molecular CNTs inside the Cu_{2}Se matrix, possess greatly improved \( zT \) of 2.4 at 1000 K for Cu_{2}Se/0.75 wt% CNTs, which is about 30% higher than that of the pristine Cu_{2}Se (Figure 1E) (Nunna et al., 2017). Cu_{2}S matrix and three-dimensional graphene heterointerface composites have created more interfaces between Cu_{2}S−Cu_{2}Te and graphene leading to low energy carrier scattering, which can increase the \( S \) and cut down the \( \kappa \). The \( zT \) value of 1.56 at 873 K is in the Cu_{2}−S with 0.75 wt% graphene (Figure 1F) (Tang et al., 2018). Carbon-encapsulated Cu_{2}−S composites have a 50% improvement of the \( \kappa \) and power factor than that of the pristine Cu_{2}−S. The phase transition from orthorhombic to tetragonal of these composites demonstrated the lower \( \kappa \). A \( zT \) value of 1.04 has been achieved at 773 K in the 0.25 wt% carbon-encapsulated Cu_{2}−S composites (Figure 1G) (Chen et al., 2019).

**CHALLENGES FOR BINARY COPPER CHALCOGENIDES**

Cu ions may migrate from their initial locations to places where electrical potential or chemical potential is low, thus the stabilities of the copper chalcogenides system still worth discussion (Ge et al., 2016). In Dennler’s experiments, it showed that Cu_{2}S is not electrically stable because both cracks and copper whiskers were observed in the sample after extended current stress testing (Figure 2A) (Dennler et al., 2014). Qiu et al. revealed the mechanism for atom migration and deposition in Cu_{2}S-Se materials based on a critical chemical potential difference (Qiu et al., 2018). Constructing a series of electronically conducting but ion-blocking barriers to reset the chemical potential of such conductors to keep it below the threshold for decomposition can remain good stability under high electric currents and/or large temperature differences (Mao et al., 2019a). For example, high \( zT \) and large critical voltage can be decoupled through doping immobile ions into the liquid-like sublattice (Mao et al., 2019b). In recent reports, the Cu_{2}Se/Yb_{0.3}Co_{4}Sb_{12} TE module shows good stability and high energy conversion efficiency of 9.1% (Figure 2B) (Qiu et al., 2019).

Flexible or thin-film TE materials can make up for application limitations from bulk materials, especially for light and portable devices. Several attempts have been made to use the fabrication of flexible or thin-film copper chalcogenide structures. Typically, Cu_{2}Se powder and the organic solution mixing making an ink solution, which was covered on flexible substrates evenly (Figures 2C and D). The Cu_{2}Se thin film fabricated by this route exhibits a power factor of 0.62 mW cm\(^{-1}\) K\(^{-2}\) at 684 K (Lin et al., 2017). Besides, CsS/Cu_{2}S superlattice nanowires showed the enhanced TE performance. For measurement, CsS/Cu_{2}S superlattice nanowires electrically connected to two electrodes that also serve as the temperature sensors. With a temperature gradient (\( \Delta T \)) created by a DC current over a nearby heating electrode, a thermal voltage can be generated along the nanowire and the thermopower can be calculated (Figures 2E and F) (Xiong et al., 2017).
CONCLUSIONS AND PERSPECTIVES

Significant developments and progress have been achieved in TE performance of binary copper chalcogenides. PLEC concept opens up a new situation to explain the low $\kappa$ in copper chalcogenide superlattice structure. Furthermore, tuning compositions optimizes $n$ leading to improved TE parameters. The main challenges for copper chalcogenide TE materials include the electrical and thermal stabilities during high-temperature measurement and the application limitations of the bulk modulus. It is hoped that binary copper chalcogenides will be widely applied in TE generators and device applications.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work, and approved it for publication.

ACKNOWLEDGMENTS

The authors thank the National Natural Science Foundation of China (51702091, 51702046); the College Outstanding Young Scientific and Technological Innovation Team of Hubei province (T201922); and the Special Funding of Preventing the spread of COVID-19, Hubei University of Education (20XGZX20).
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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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