

Cu–Se Bond Network and Thermoelectric Compounds with Complex Diamondlike Structure

Xiaoya Shi,^{†,‡} Lili Xi,^{†,‡} Jing Fan,[‡] Wenqing Zhang,* and Lidong Chen*

State Key Laboratory of High Performance Ceramics and Superfine Microstructure and CAS Key Laboratory for Energy-conversion Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

[†] Those authors contributed equally to the work.

[‡] Also at Graduate University of Chinese Academy of Sciences, Beijing, China

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Thermoelectric (TE) power generation and cooling may arouse a revolution in energy saving and environmental protection if inexpensive materials of high performance can be discovered, which has been a focus for materials science for decades and becomes even more urgently needed in recent years. Generally speaking, the slow progress of the performance improvement of TE materials, even with extremely strong efforts incorporating both extensive materials exploration and sophisticated nanotechnology,^{1–6} originates from the strongly but reversely intercorrelated electrical and thermal transports in one TE material, whose performance is characterized by figure of merit ($ZT = S^2\sigma T/\kappa$). The electrical transport (numerator) is determined by Seebeck coefficient S and electrical conductivity σ , and thermal transport (denominator) is determined by total thermal conductivity κ . T is the absolute temperature. The correlation results in a very limited choice of the currently state-of-the-art TE materials.

By following G Slack's general criterion of selecting high-performance TE materials, i.e., the so-called "phonon-glass-electron-crystal" (PGEC)⁷ that requires glasslike thermal transport and crystal-like electron transport inside one material, a lot of work has focused primarily on compounds of special structures, especially those with

intrinsic voids in crystal structures such as CoSb₃ and clathrates.^{8,9} Those open-structure compounds are presumed to be able to decouple, to a large extent, the electrical and thermal transport properties, as demonstrated in filled skutterudites, for efficient TE performance optimization.^{10,11} The structures of these compounds could be divided into the framework part and the fillers. Usually, the framework atoms build up the skeleton of the system and the network-like bonds between them not only act as the key factor to stabilize the whole structure but also dominate the carrier transport. The filler atoms exhibit relatively weak bond with the framework and donate extra carriers for tuning carrier concentration for performance optimization. Therefore, based on such a structural analysis, it seems reasonable to expect that a material, as long as it holds a bond network with the similar functionality to the caged framework in CoSb₃ and some constituent species for carrier donation, should be able to show a good TE performance, whereas its crystal structure may be different from those of the caged compounds. The recently reported quaternary diamondlike compounds Cu₂MSnQ₄ ($M = \text{Zn, Cd}$; $Q = \text{S, Se}$),^{12–15} even without an open structure but with a reasonably strong interlayer interactions, still show a relatively high p-type ZT at intermediate temperature, which seems to support the above-mentioned idea.

In fact, the structures of copper-containing diamondlike compounds are quite similar. Investigating different compounds may result in a deeper understanding of the structural and functional relationship in these compounds. In this paper, the ternary diamondlike compound Cu₂SnSe₃ was studied and we were going to show that a special bond network exists in both the quaternary and ternary copper-containing diamondlike compounds using *ab initio* calculations. The work reported here also shows that a good TE performance could truly be realized in a 3D non-open-structure system Cu₂SnSe₃ with a distorted diamondlike structure.^{16,17} The maximum ZT obtained is 1.14, even higher than that for Cu₂MSnQ₄ systems of layered diamondlike

*Correspondence author. E-mail: wqzhang@mail.sic.ac.cn (W.Z.); cld@mail.sic.ac.cn (L.C.).

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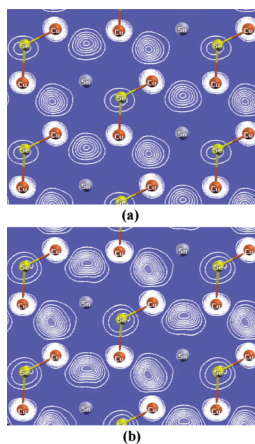


Figure 1. Contour plots of the partial charge density of the states close to upper valence-band of Cu_2SnSe_3 on (100) crystal face. The solid lines represent charge density accumulation. The VBM was set to be 0 eV. The given energy window for the partial charge density distribution is (a) 0 to -0.1 eV and (b) -0.1 to -0.2 eV.

structures.^{12,13} The latter has a two-dimensional layer-like bond network partly similar to the 3D pattern in Cu_2SnSe_3 . Our analysis demonstrates that a Cu–Se conductive network exists in these p-type diamondlike compounds. Furthermore, the existence of the Cu–Se bond network, if undisturbed or only weakly disturbed when optimizing electrical transport properties by selective doping, makes the Cu_2SnSe_3 a good thermoelectric material, probably also be similar to that was observed in the caged PGEC material.

We first discuss the conductive network based on the *ab initio* calculated partial electron charge density distribution in Cu_2SnSe_3 (CTS) system, which displays the primary bond network in the material in real space. As a comparison, result for $\text{Cu}_2\text{ZnSnSe}_4$ (CZTS) system is also discussed. Computational details are given in the Supporting Information. The partial charge density contour plots for CTS are plotted in Figure 1, whereas the result of CZTS is shown in Supporting Information (Figure S3). For CTS, as shown in Figure 1, the partial charge densities, determined by the electronic states falling in a given energy window (e.g., 0.0 to -0.1 eV or -0.1 to -0.2 eV from VBM), accumulate mainly in the line linking Cu and Se atoms, thus, as a p-type material, the Cu–Se bonds play the dominant role in controlling hole transport. In addition, the Sn atoms exhibit little charge density accumulation in the area linking with Se, which indicates that the Sn orbitals do not contribute much for the p-type carrier transport but just offer electrons to the system. Analysis on the density of states also shows that the p-d hybridization from Cu–Se bonds dominates a large parts of the occupied valence bands close to VBM, substantiating the essential role of the Cu–Se bond network in stabilizing the whole structure. The influence of Sn orbitals on the occupied states is so weak that could be almost neglected. Instead, Sn s states contribute primarily to the states at the conduction band minimum. Therefore, in the 3D scale, the Cu–Se bond network fabricates a 3D electrically conductive framework of this complex dia-

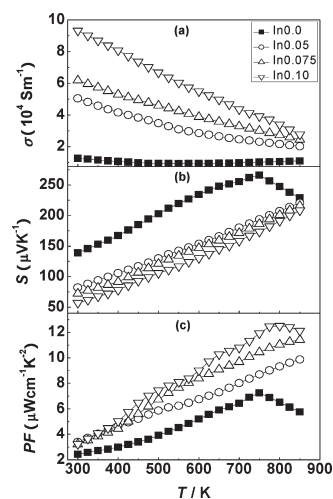


Figure 2. Temperature dependence of (a) electrical conductivity σ , (b) Seebeck coefficient S , and (c) power factor PF of $\text{Cu}_2\text{Sn}_{1-x}\text{In}_x\text{Se}_3$ ($x = 0, 0.05, 0.075, 0.10$).

mondlike compound while Sn atoms provide electrons to tune carrier concentration. Although the compositions or structures of the compounds among copper-containing diamondlike family, especially for the multication contained systems, are very complicated, the underlying relationship of structure/function was observed to be similar. This could be demonstrated from the charge density result of the quaternary diamondlike compound Cu_2MSnQ_4 (e.g., CZTS, see Figure S3 in the Supporting Information) with a relatively simple layered structure. The partial carrier density distribution in CZTS also shows a similar Cu–Se charge accumulation, whereas Zn and Sn atoms have little contribution to the partial charge density close to valence band maximum but donate electrons to the whole system. From this point of view, the CZTS can be regarded as the layered compound with conductive bond layers and electron-offering layers.

Now that the Cu–Se bonds show the dominant place in the p-type electrical transport while Sn exhibits weak contribution to the conductive framework, in principle, the Sn sites should be good choice to make property optimization in CTS. Thus, the doping method with In/Sn partial substitution was investigated in CTS. Although a structure change from monoclinic to cubic type was observed after In substitution (see Figure S1 in the Supporting Information), the dominant Cu–Se hybridization near the VBM keeps unaltered. Also, as expected, In/Sn substitution does not change the distribution of the partial charge density, as shown in Figure S4 in the Supporting Information. Thus, all the samples exhibit the similar picture as we described in Figure 1. Figure 2 shows the temperature dependence of electrical transport properties of In-doped $\text{Cu}_2\text{Sn}_{1-x}\text{In}_x\text{Se}_3$. The electrical conductivity (Figure 2a) is greatly enhanced after In/Sn substitution, changing from 12600 S m^{-1} (matrix) to 93200 S m^{-1} ($\text{Cu}_2\text{Sn}_{0.90}\text{In}_{0.10}\text{Se}_3$) at room temperature, which results in the improvement of power factor (Figure 2c) within the whole temperature range. The

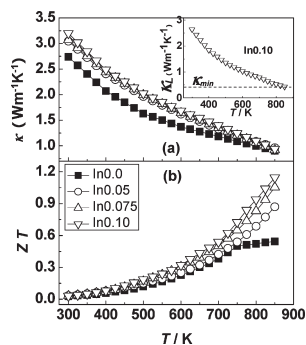


Figure 3. Temperature dependence of (a) thermal conductivity κ (inset is the temperature dependence of lattice thermal conductivity for $\text{Cu}_2\text{Sn}_{0.90}\text{In}_{0.10}\text{Se}_3$ and the dashed line represents the minimum lattice thermal conductivity), and (b) figure of merit ZT of $\text{Cu}_2\text{Sn}_{1-x}\text{In}_x\text{Se}_3$ ($x = 0, 0.05, 0.075, 0.10$).

improved electrical property can be mainly attributed to the enhanced carrier concentration (see Table S1 in the Supporting Information), which could be easily tuned by In/Sn doping in the p-type materials. Furthermore, Ga/Sn substitution was also investigated and the result is listed in Table S1 in the Supporting Information. Again, the improved electrical property was obtained by Ga/Sn partial substitution as we expected. These results show that, as p-type material, the electrical performance could be optimized through the A/Sn doping method, here A represents different cations with lower valence-electron number than Sn.

Figure 3a shows the thermal conductivity κ for In-doped samples. The κ for all the samples decrease rapidly with rising temperature and reach around $1.0 \text{ W m}^{-1} \text{ K}^{-1}$ at 850 K, which is a relatively low level among thermoelectric materials. The detailed data of κ_L for all the samples is plotted in Figure S5 in the Supporting Information and we only use the κ_L of the sample $\text{Cu}_2\text{Sn}_{0.90}\text{In}_{0.10}\text{Se}_3$ in the insert figure to show how low the lattice thermal conductivity could be. The minimum lattice thermal conductivity of the CTS, as shown by dashed line in the insert figure, is calculated from the formula $\kappa_L = 1/3 C_V v l$ when the phonon mean free path reaches the shortest interatomic distance in the CTS,¹⁸ where $l = 0.235 \text{ nm}$. The velocity of sound comes from the data in ref 19. C_V is the heat capacity per unit volume of the system using Dulong and Petit value. The κ_L of $\text{Cu}_2\text{Sn}_{0.90}\text{In}_{0.10}\text{Se}_3$ approaches minimum lattice thermal conductivity (around $0.4 \text{ W m}^{-1} \text{ K}^{-1}$) of CTS at high temperature. The most likely reason for the extremely low lattice thermal conductivity, which needs to be confirmed by further research, may be the structure distortion caused by different cations and the point defects from In/Sn partial substitution. The intercross-linked distribution of different bonds (Cu–Se and Sn–Se) will affect the phonon transportation, which is decided by lattice vibration, between different element sites in the diamondlike

compounds. On the contrary, some unitary (e.g., diamond) and binary (e.g., ZnSe) diamondlike compounds, whose thermal conductivities are extremely high,²⁰ do not possess different bond relationship but the uniform bond. Thus, the multication diamondlike compounds exhibit much more complicated structures and larger unit cells than the unitary and binary compounds, which could be one of the most important reasons for the relatively low lattice thermal conductivity.

Although the complex distorted diamondlike structure of CTS does not contain open structures, the similar effect could be realized in the Cu–Se networks. If the conductive Cu–Se bond network was considered as the 3D framework of the compound, the behavior of the differently bonded Sn atoms is pretty much like the filler atoms in filled skutterudites. Thus, great potential emerges for the Sn atoms to form phonon scattering centers inside the diamondlike structures. As a result, the multication copper-containing diamondlike compounds always possess relatively low thermal conductivity, even without any optimization.

The figure of merit ZT for $\text{Cu}_2\text{Sn}_{1-x}\text{In}_x\text{Se}_3$ was calculated in Figure 3b. In-doped samples exhibit higher ZT value than the matrix CTS within the whole temperature range. The most important reason is the improved electrical performance by In/Sn substitution. The highest ZT reaches 1.14 at 850 K for the sample $\text{Cu}_2\text{Sn}_{0.90}\text{In}_{0.10}\text{Se}_3$. The high ZT value deserves further investigation on these new systems of complex diamondlike crystal structure together with a Cu–Se bond network for electrical conduction as well as for structure stabilization.

To sum up, the partial charge density calculation shows the dominant conductive bond network in the p-type copper containing compounds of complex diamondlike structure. The Sn atoms, which donate electrons to balance the structure, reside in the framework formed by Cu–Se bond in CTS. The matrix and the doped compounds exhibit extremely low thermal conductivity, especially at high temperature, as well as tunable electrical property. These materials are similar to the traditional caged “PGEC” compounds, such as CoSb_3 and clathrate, whose structures are built up by the open-structure framework and the different bonded filler atoms. This work may make an extension to the “PGEC” family and pave the way for the further study of these diamondlike compounds with different bond network.

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Supporting Information Available: Experimental and calculational details and thermoelectric properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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