Cu-Embedded SnSe₂ with a High Figure of Merit at Ecofriendly Temperature

Jiahao Wang, Xianbin Jia, Shiyun Lou, Guihui Li, and Shaomin Zhou*

ABSTRACT: There are many studies concentrated on high-temperature performance of SnSe₂, but few studies were conducted on low-temperature properties of embedded SnSe₂. In this work, a series of SnCuₓSe₂ (x = 0, 0.01, 0.02, and 0.05) layered structures have been successfully synthesized by a melt quenching, mechanical milling process, and spark plasma sintering (SPS) method. Meanwhile, the thermal and electrical transport properties of all synthesized samples are measured. These results suggest that the embedding of Cu into SnSe₂ results in a high carrier concentration (10²⁹/cm³). In addition, the enhancement of defect and interfacial phonon scattering caused by Cu embedding as well as the weak van der Waals force between layers makes a low thermal conductivity (0.81 W/mK) for the SnCu₀.₀₁Se₂ at 300 K. Moreover, the maximum ZT is acquired up to 0.75 for the SnCu₀.₀₁Se₂ sample at 300 K, which is about 2 orders of magnitude higher than the pristine sample (0.009). These features indicate that Cu-embedded SnSe₂ can be a promising thermoelectric material at gentle temperature.

1. INTRODUCTION

Thermoelectric materials based on the Seebeck and Peltier effects can achieve the direct conversion of thermal and electric energy with the advantages of small size, light weight, no noise, environmentally friendly, and long life.¹⁻² Thus, thermoelectricity is playing a very important role in sustainable energy development. The conversion efficiency of a thermoelectric material is determined by the dimensionless figure of merit \(ZT\), defined as

\[
ZT = \frac{\sigma S^2}{\kappa}\frac{T}{L^2} = \frac{\sigma^2 S}{\kappa L}\frac{T}{L^2}
\]

where \(\sigma\), \(S\), \(\kappa\), and \(T\) are the electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature, respectively.³⁻⁵ It is clear and unambiguous that a high thermoelectric performance is achieved for a 1.5 at % Cl-doped SnSe₁.₉₅ pellet at 673 K.¹³ In addition, the thermoelectric figure of merit \(ZT_{max}\) for SnSe₂ obtained by a vacuum-sealed high-temperature melting and SPS process claimed through Luo et al.¹⁴ SnSe₂ is a semiconductor material with an indirect broadband gap, high band degeneracy, and layered structure, which is mainly used in the field of photoelectricity and energy storage.¹⁵ The
atomic model of SnSe₂ is shown in Figure 1, and each layer is covalently bonded by three atomic planes in the sequence of Se–Sn–Se. In addition, the interaction between layers was coupled by a weak van der Waals force, and the spacing was 0.62 nm. In this work, we have successfully synthesized a series of SnCuₓSe₂ (x = 0, 0.01, 0.02, and 0.05) layered structures by a melt quenching, mechanical milling process, and spark plasma sintering (SPS) method. At the same time, we study the thermoelectric properties of the synthesized samples measured from 50 to 300 K. Interestingly, carrier mobility reduce a little with a small amount of Cu embedding compared to the raw sample, but its concentration has nearly increased 2 orders of magnitude than that of raw samples. Otherwise, embedding of Cu leads to enhancement of interfacial phonon scattering, defect phonon scattering, electron—phonon scattering, and the weak van der Waals force between the layers combined to achieve a low thermal conductivity (0.81 W/mK) for the SnCu₀.₀₁Se₂ at 300 K. At the same time, the maximum ZT is achievable at 0.75 for the SnCu₀.₀₁Se₂ sample at 300 K, which is about 2 orders of magnitude higher than the original sample (0.009) and is about 2 times greater than that of the previous work.⁴⁻¹⁰ Therefore, Cu-embedded SnSe₂ becomes a promising thermoelectric material applied widely in the industry at an ecofriendly temperature.

2. RESULTS AND DISCUSSION

Figure 2 shows representative XRD patterns of SnCuₓSe₂ (x = 0, 0.01, 0.02, and 0.05) samples. The XRD spectrum can be well indexed as a SnSe₂ phase without any secondary phase within the detection limit of the laboratory XRD, which is in good agreement with the standard data (PDF #23-0602). No extra peaks related to other crystalline phases are observed in the Cu-embedded samples, indicating that the crystal structure of the low concentration-embedded samples has not change. The lattice parameters are 3.81 × 3.81 × 6.14, and angles α, β, and γ are 90, 90, and 120°, respectively, which indicate that the crystal structure of the synthesized sample is an hexagonal crystal structure. At the same time, the half-peak width of all the samples is narrow, indicating that the crystallization is good. According to Bragg’s law nλ = 2d sinθ, the results show that the characteristic preferred orientation for the (00l) Bragg reflection peaks is due to the lamellar structure. The cell dimension along the c axis of SnCu₀.₀₂Se₂ increases slightly compared with SnSe₂, whereas they have the same distance along the a and b axes, which is consistent with the measurement results of Zhou et al.¹³

The SEM image of the fresh fracture surfaces for the SnCu₀.₀₅Se₂ nanocomposite is shown in Figure 3a. It is obvious from the picture that the synthesized sample has layered structures, and the Cu particles are embedded into the SnSe₂ layer, which is consistent with the deeper observation by TEM in Figure 3b. Moreover, the element mapping diagram of the composition analysis of the SnCu₀.₀₅Se₂ sample measured during TEM imaging shows clearly that Cu elements are uniformly dispersed in layered compound SnSe₂. These extra grain boundaries and defects play an important role in the electrical transport and phonon scattering of samples. The high-resolution TEM (HRTEM) image of the SnCu₀.₀₅Se₂ sample shows an interlayer spacing of 0.62 nm, which is the lattice spacing of the (001) plane (interlayer distance) SnSe₂ (Figure 3c). This result further indicates that each Cu exists between the layers of SnSe₂ without changing the lattice structure.

To further determine the element composition of copper and clarify the chemical state of copper, the SnCu₀.₀₅Se₂ sample is determined by X-ray photoelectron spectroscopy (XPS). Figure 4a shows the full scan of XPS spectra of sample SnCu₀.₀₅Se₂, which shows that the sample is composed of Sn, Se, and Cu elements. All HRXPS data have been processed for peak splitting and fitting. At the same time, Figure 4b shows that the high-resolution peaks of Sn 3d₁/₂, and Sn 3d₃/₂ corresponding to their binding energies were 494.9 and 486.4 eV, respectively, with a splitting of 8.5 eV. Figure 4c shows that peaks due to Se 3d₁/₂ and Se 3d₃/₂ have appeared as a broad peak at 53.91 eV. In addition, the high-resolution XPS of Cu 2p is shown in Figure 4d, and there are two peaks at 931.1 and 951.1 eV corresponding to Cu 2p₁/₂ and Cu 2p₃/₂, respectively, indicating the presence of a simple copper in the SnSe₂ samples.

Thermoelectric properties of the both embedded and pristine SnSe₂ samples are measured as a function of temperature, ranging from 50 to 300 K. The carrier concentration of the embedded sample increases as the amount of embedding rises due to the effective electron injection of the simple copper in Figure 5. At 300 K, the carrier concentration of the SnCu₀.₀₅Se₂ sample is 1 × 10¹⁹ cm⁻³, which is nearly 2 orders of magnitude higher than that of the pristine SnSe₂ sample, which is 3.3 × 10¹⁷ cm⁻³. The carrier mobility with the changing temperature is shown in Figure 6. With the increase of temperature and the Cu-embedded amount, the mobility of all samples decreases to a small extent. The reason is due to electron—phonon scattering, which is where the electron mobility normally increases with decreasing
temperature with the slope of $\mu \sim T^{-3/2}$. At the same time, the enhancement of interfacial scattering leads to decrease the average free path of carriers. The decrease of average free path results in the reduction of carrier mobility.20

Figure 7 shows the temperature dependence of electrical resistivity, the Seebeck coefficient, thermal conductivity, and power factor of SnCu$_{x}$Se$_{2}$ ($x = 0, 0.01, 0.02,$ and $0.05$) samples. Figure 7a shows the electrical resistivity ($\rho$) of the samples as a function of temperature. The electrical resistivity of the samples decreases as temperature increases from 50 to 125 K, showing a semiconducting behavior, and then increases from 125 to 300 K, exhibiting a metal-like behavior. It can be seen from the spectra that the electrical resistivity of SnSe$_{2}$ samples embedded with different concentration of Cu is much lower than that of the pristine sample. The sample of SnCu$_{0.01}$Se$_{2}$ ($2.37$ m$\Omega$cm) is reduced by more than 2 orders of magnitude compared with the pristine SnSe$_{2}$ sample ($506$ m$\Omega$cm) at 300 K.

Figure 3. (a) SEM, (b) TEM, and (c) HRTEM images of the fresh fracture surfaces for SnCu$_{0.05}$Se$_{2}$ and elemental mapping spectra for Sn, Se, and Cu in the SnCu$_{0.05}$Se$_{2}$ during TEM imaging (from the highlighted portion of the TEM image).

Figure 4. Full scan of the (a) XPS spectrum and HRXPS spectra of (b) Sn 3d, (c) Se 3d, and (d) Cu 2p of the SnCu$_{0.05}$Se$_{2}$ sample.
The measured thermal conductivity of all samples of SnCu_xSe_2 (x = 0, 0.01, 0.02, and 0.05) is shown in Figure 7c. The total thermal conductivity (κ) is usually composed of electronic (κ_e) and lattice thermal conductivity (κ_l) with κ_e and κ_l contributed by electrons and phonons, respectively. All the samples of SnCu_xSe_2 (x = 0.01, 0.02, and 0.05) achieve a reduced thermal conductivity than those of Cu-free SnSe_2 in the temperature range of 50–300 K. Especially, the samples of SnCu_0.01Se_2 (x = 0.01 and 0.05) exhibit a significant reduction of thermal conductivity in the entire temperature range because of the increased interfaces, which cause a lattice phonon dissipation as well as carrier scattering at the same time.20,21

The introduction of Cu particles into SnSe_2 did not affect the morphology of the matrix shown in the SEM image. In addition, with the increase of Cu embedding, the phonon scattering from the interface and defects is enhanced, leading to a significant reduction in thermal conductivity.22 At 300 K, it is sure that the SnCu_0.01Se_2 obtained the low thermal conductivity (0.81 W/mK).

Combining the Seebeck coefficient and electrical resistivity measured at different temperatures, the variation trend of power factor PF (S^2/ρ) with temperature can be obtained through formula calculation, as shown in Figure 7d. It can be seen clearly from the picture that the SnCu_0.01Se_2 sample obtained the high power factor PF = 1.96 mWK^-1 m^-1, which is nearly 2 orders of magnitude higher than the PF = 0.03 mWK^-1 m^-1 of pristine SnSe_2 at 300 K.

Combining the results of the electrical and thermal transport properties, the temperature dependence of the ZT value is shown in Figure 8. Obviously, the highest ZT value of ~0.75 is reached in the SnCu_0.01Se_2 sample at 300 K, which is 2 orders of magnitude higher than the pristine sample (0.009). One reason is because the electrical resistivity of SnCu_0.01Se_2 decreases significantly compared with pure SnSe_2 (ρ_0.01 ≈ 0.01ρ_0). Moreover, SnCu_0.01Se_2 obtained the low thermal conductivity (0.81 W/mK). The SnCu_xSe_2 materials achieve high thermoelectric conversion efficiency by optimizing electrical and thermal conductivity.

3. CONCLUSIONS

In summary, a series of the SnCu_xSe_2 (x = 0, 0.01, 0.02, and 0.05) layered structure with uniform size distribution are synthesized by a melt quenching, mechanical milling process, and spark plasma sintering (SPS) method. The effect of SnCu_xSe_2 (x = 0, 0.01, 0.02, and 0.05) on thermoelectric properties of nanocomposites is studied in the temperature range of 50–300 K. The results show that electrical resistivity is reduced by Cu embedding, which is found to have a maximum power factor of 1.96 mWK^-1 m^-1 in SnCu_0.01Se_2 at 300 K. Combining the small thermal conductivity (0.81 W/mK), the maximum ZT value obtained by the formula ZT = PF/κ_T is 0.75, which is 2 orders of magnitude higher than the pristine sample (0.009). These results suggest that Cu-embedded layered compound SnSe_2 can be considered as a promising environmentally friendly and economical thermoelectric material for collecting waste heat to convert into useful electrical energy at gentle temperature.

4. EXPERIMENT

Pure powders Sn, Se (5 N, Aladdin), and Cu (3 N, Aladdin) were used as raw materials and weighed according to an appropriate molar ratio of SnCu_xSe_2 (x = 0, 0.01, 0.02, and 0.05), and the raw materials were all weighed in the vacuum glovebox. After weighing, the reaction materials were
thoroughly mixed and put into a quartz tube, which was sealed by a vacuum. The materials in the tube were heated to 973 K, kept for 6 h, and cooled to room temperature. The obtained ingots were annealed at 773 K for 72 h and naturally cooled to room temperature in argon atmosphere. Afterward, samples were removed and placed in a ball mill for 9 h of milling at 350 r/min under argon atmosphere. The resulting powder was vacuum-sintered for 5 min under pressures of 773 K and 55 MPa by spark plasma sintering (SPS) equipment. After SPS, a cylindrical sample with a height of ≈2 mm and a diameter of 12.7 mm was obtained.

The phase of the as-synthesized products was studied by means of X-ray diffraction (XRD) (X’pert MRD-Philips diffractometer with Cu Kα radiation, λ = 0.154178 Å, a scanning speed of 0.01672°/s in the 2θ range from 10 to 65°, Philips, Holland). The morphology and the element distribution mapping of the powder samples were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). An X-ray photoelectron spectrometer (AXIS ULTRA, London, Britain) was used to analyze the chemical valence and type of the elements of the sample. The disk samples were cut into 2 × 2 × 11 mm³ rectangular shape and polished and used as thermal and electrical transport property tests. In a physical property measurement system (PPMS-9 EverCool), the low-temperature electrical resistivity, thermal conductivity, and Seebeck coefficient of the samples were measured from 50-300 K with the thermal transport option (TTO) mode. According to the Stephen−Boltzmann law, the radiation loss was corrected for the entire measurement temperature range. At 50 K, the numerical error obtained by the system was within 5%. Hall measurements were carried out in the advanced electrical transport option (ETO) mode of the PPMS system from 50 to 300 K using a four-probe method with a magnetic field of up to ±1 T. In addition, the electrical resistivity was confirmed by the ETO model from PPMS.
Enhanced thermoelectric performance of individual Te/TiS2 nanostructures synthesized via chemical route. ACS Appl. Nano Mater. 2018, 1, 3236–3250.

Wang, S.; Hui, S.; Peng, K.; Bailey, T. P.; Liu, W.; Yan, Y.; Zhou, X.; Tang, X.; Uher, C. Low temperature thermoelectric properties of p-type doped single-crystalline SnSe. Appl. Phys. Lett. 2018, 112, 142102.

Zhou, C.; Yu, Y.; Zhang, X.; Cheng, Y.; Xu, J.; Lee, Y. K.; Yoo, B.; Cojocaru-Mireidin, O.; Liu, G.; Cho, S.-P.; et al. Cu intercalation and Br doping to thermoelectric SnSe lead to ultralight electron mobility and temperature-independent power factor. Adv. Funct. Mater. 2018, 30, 1908405.

Luo, Y.; Zheng, Y.; Luo, Z.; Hao, S.; Du, C.; Liang, Q.; Li, Z.; Khor, K. A.; Hippalgaonkar, K.; Xu, J.; Yan, Q.; et al. n-Type SnSe\textsubscript{2} oriented-nanoplate-based pellets for high thermoelectric performance. Adv. Energy Mater. 2017, 1702167.

Shu, Y.; Su, X.; Xie, H.; Zheng, G.; Liu, W.; Yan, Y.; Luo, T.; Yang, X.; Yang, D.; Uher, C.; Tang, X. Modification of bulk heterojunction and Cl doping for high-performance thermoelectric SnSe\textsubscript{2}/SnSe nanocomposites. ACS Appl. Mater. Interfaces 2018, 10, 15793–15802.

Xu, P.; Fu, T.; Xin, J.; Liu, Y.; Ying, P.; Zhao, X.; Pan, H.; Zhu, T. Anisotropic thermoelectric properties of layered compound SnSe\textsubscript{2}. Sci. Bull. 2017, 62, 1663–1668.

Wu, S.; Liu, C.; Wu, Z.; Miao, L.; Gao, J.; Hu, X.; Chen, J.; Zheng, Y.; Wang, X.; Shen, C.; et al. Realizing tremendous electrical transport properties of polycrystalline SnSe\textsubscript{2} by Cl-doped and anisotropy. Ceram. Int. 2019, 45, 82–89.

Li, F.; Zheng, Z.; Li, Y.; Wang, W.; Li, J.-F.; Li, B.; Zhong, A.; Luo, J.; Fan, P. Ag-doped SnSe\textsubscript{2} as a promising mid-temperature thermoelectric material. J. Mater. Sci. 2017, 52, 10506–10516.

Takahashi, H.; Okazaki, R.; Ishiwata, S.; Taniguchi, H.; Okutani, A.; Hagiwara, M.; Terasaki, I. Colossal seebeck effect enhanced by quasi-ballistic phonons dragging massive electrons in FeSb\textsubscript{2}. Nat. Commun. 2016, 7, 12732.

Izadi, Z.; Tabrizchi, M.; Farrokhpour, H. Average drift time and average mobility in ion mobility spectrometry. Int. J. Mass Spectrom. 2017, 412, 20–25.

Lei, J.; Zhang, D.; Guan, W.; Ma, Z.; Cheng, Z.; Wang, C.; Wang, Y. Enhancement of thermoelectric figure of merit by the insertion of multi-walled carbon nanotubes in α-MgAgSb. Appl. Phys. Lett. 2018, 113, No. 083901.

Gong, Y.; Chang, C.; Wei, W.; Liu, J.; Xiong, W.; Chai, S.; Li, D.; Zhang, J.; Tang, G. Extremely low thermal conductivity and enhanced thermoelectric performance of polycrystalline SnSe by Cu doping. Scr. Mater. 2018, 147, 74–78.

Voneshen, D. J.; Walker, H. C.; Refson, K.; Goff, J. P. Hopping time scales and the phonon-liquid electron-crystal picture in thermoelectric copper selenide. Phys. Rev. Lett. 2017, 118, 145901.

Akshay, V. R.; Arun, B.; Suneesh, M. V.; Vasundhara, M. Surfactant-Induced structural phase transitions and enhanced room temperature thermoelectric performance in n-Type Bi\textsubscript{2}Te\textsubscript{3} nanostructures. ACS Appl. Nano Mater. 2018, 1, 3236–3250.

Li, Y.; Wu, M. N.; Ding, T.; Ma, K.; Liu, F. S.; Ao, W. Q.; Li, J. Q. Promising thermoelectric properties and anisotropic electrical and thermal transport of monolayer SnTe. Appl. Phys. Lett. 2019, 114, No. 083901.

Rhyee, J.-S.; Lee, K. H.; Lee, S. M.; Cho, E.; Kim, S. J.; Lee, E.; Kwon, Y. S.; Shim, J. H.; Kotliar, G. Peierls distortion as a route to high thermoelectric performance in In\textsubscript{5}Se\textsubscript{3.5} crystals. Nature 2009, 459, 965–968.