Enhanced Thermoelectric Performance of Cu$_2$SnSe$_3$-Based Composites Incorporated with Nano-Fullerene

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Abstract: In this study, nano-sized fullerene C$_{60}$ powder was sufficiently mixed with Cu$_2$SnSe$_3$ powder by ball milling method, and the C$_{60}$/Cu$_2$SnSe$_3$ composites were prepared by spark plasma sintering technology. The fullerene C$_{60}$ distributed uniformly in the form of clusters, and the average cluster size was less than 1 µm. With increasing C$_{60}$ content, the electrical conductivity of C$_{60}$/Cu$_2$SnSe$_3$ composites decreased, while the Seebeck coefficient was enhanced. The thermal conductivity of composites decreased significantly, which resulted from the phonon scattering by the C$_{60}$ clusters located on the grain boundaries of the Cu$_2$SnSe$_3$ matrix. The highest figure of merit ZT of 0.38 was achieved at 700 K for 0.8% C$_{60}$/Cu$_2$SnSe$_3$ composite.

Keywords: thermoelectric alloy; composites; Cu$_2$SnSe$_3$; C$_{60}$

1. Introduction

Thermoelectric (TE) materials have attracted increasing worldwide attention due to their potential application in electronic cooling, waste heat recovery, and power generation [1–4]. The conversion efficiency of TE materials is determined by the dimensionless figure of merit, $ZT = \alpha^2 \sigma T / \kappa$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the total thermal conductivity. The total thermal conductivity is composed of an electron part ($\kappa_E$) and a phonon part ($\kappa_L$). Therefore, to maximize the $ZT$ value of TE materials, a large $\alpha$ and $\sigma$, as well as a low $\kappa$ are required. In recent years, several classes of bulk materials with high $ZT$ have been discovered and developed, such as skutterudites, clathrates, and Cu-based chalcogenide semiconductors.

Cu-based chalcogenide compounds with a diamond-like structure, such as ternary Cu$_2$MSe$_3$ (M = Sn, Ge) and Cu$_3$SbSe$_4$, have attracted a lot of attention recently, due to their quite low thermal conductivity. In several Cu-based chalcogenide compound systems, the Cu$_2$SnSe$_3$ structure has partial “phonon glass electron crystal” (PGEC) characteristic, which makes it possible to achieve high TE performance. The Cu-Se bond network dominates the electron conduction, while the contribution from the element Sn is very weak; thus, the Sn site is suitable for optimization of the TE property. Various attempts, including doping by partial substitution, have been made to improve the thermoelectric properties of Cu$_2$SnSe$_3$ compound [5–7]. Shi et al. have reported the In-doped Cu$_2$In$_{1-x}$Sn$_{1.5}$Se$_3$ and the maximum $ZT$ value reaches 1.14 at 850 K for Cu$_2$In$_{0.1}$Sn$_{0.9}$Se$_3$ sample [8]. Fan et al. fabricated the Cu$_2$Ga$_{0.5}$Sn$_{1.5}$Se$_3$ samples using hot-press sintering technique and achieved the $ZT$ value of 0.43 for Cu$_2$Ga$_{0.075}$Sn$_{1.925}$Se$_3$ sample [9]. In addition, Skoug, et al. also confirmed that doping with isoelectronic Ge on the Sn site is also effective in enhancing the $ZT$ value [10]. Aside from doping, the dispersion of nanostructure phases into the thermoelectric matrix is also an attractive approach to improving the performance of TE materials. However, the Cu$_2$SnSe$_3$-based thermoelectric composites are scarcely
investigated, because the enhancement of $ZT$ is unapparent compared with the doping. Although significant reduction in the lattice conductivity can be achieved via enhanced phonon scattering at grain boundaries or matrix/inclusion interfaces, the electrical conductivity of TE composites also decreases, resulting in a marginal improvement of the overall $ZT$ value. In addition, good selection of the dispersed phase and the control of microstructure are also required for TE composite [11–14]. Therefore, effective enhancement of $ZT$ for TE composites depends on the microstructure of composites—i.e., the distribution or the shape of the component.

Fullerene $C_{60}$ has very high elastic modulus and is a chemically-stable nonpolar fullerene molecule. $C_{60}$ and $C_{60}$-decorated grain boundaries may provide an effective phonon scattering, which could decrease the lattice thermal conductivity. Meanwhile, the scattering of charge carriers (electrons or holes) by the $C_{60}$ could be ineffective due to the large value of electron (hole) wavelength compared to a fullerene molecule size. Blank and Kulbachinskii, et al. reported that the addition of 0.5 vol % $C_{60}$ improved the TE properties of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ material, and the $ZT$ value obtained was 1.17 at 450 K [15,16]. Shi, et al. found that adding 6.5 mass% $C_{60}$ into pure CoSb$_3$ can increase the $ZT$ value, while adding amounts between 0.5% and 4.8% into CoSb$_3$ decreased the $ZT$ value [17]. The similar results of Itoh, et al. showed that the maximum $ZT$ value for the 1% $C_{60}$/Co$_{0.92}$Ni$_{0.08}$Sb$_{2.96}$Te$_{0.04}$ composite was 0.62 at 800 K, which is evidently higher than that of $C_{60}$-free sample [18]. Nandihalli, et al. also reported that the $ZT$ value of $C_{60}$/Ni$_{0.05}$Mo$_{0.5}$Sb$_{5.4}$Te$_{1.6}$ composites was enhanced in the whole temperature range due to the large decrease of $\kappa_L$ [19]. In this contribution, we attempted to introduce the $C_{60}$ into a Cu$_2$SnSe$_3$ system and expected to achieve a larger reduction in the thermal conductivity of $C_{60}$/Cu$_2$SnSe$_3$ composites.

In the present work, the fullerene $C_{60}$ powder was incorporated into Cu$_2$SnSe$_3$ matrix using ball milling (BM), and $C_{60}$/Cu$_2$SnSe$_3$ composites were fabricated by spark plasma sintering (SPS) technology. Effects of $C_{60}$ particles on the thermoelectric properties of $C_{60}$/Cu$_2$SnSe$_3$ composites were discussed, and the results are beneficial to the development of Cu$_2$SnSe$_3$-based composites with high performance using BM-SPS technology.

2. Experimental Procedures

The polycrystalline Cu$_2$SnSe$_3$ samples were synthesized by melting method. The stoichiometric amount of starting materials Cu (powder, 99.95%), Sn (powder, 99.999%), and Se (shot, 99.999%) were first placed in a carbon crucible enclosed in evacuated fused-silica ampoules. The ampoules were slowly heated to 1173 K and held for 12 h in a vertical furnace. Then, the ampoules were slowly cooled to 873 K in 24 h, followed by annealing at this temperature for 2 days. Finally, the obtained ingots were ground into fine powder. Commercially available fullerene powder with average particle size of 500 nm (XFNANO, Nanjing, China) was chosen as the nanoinclusion, as shown in Figure 1. The fullerene $C_{60}$ purity is 99.98%, and the other 0.02% refers to impurities of $C_{70}$ and other carbon structures. The fullerene $C_{60}$ powder was added into the Cu$_2$SnSe$_3$ powder at fractions of 0.4, 0.8, 1.2, and 1.6 vol %, respectively. Then, the $C_{60}$-added Cu$_2$SnSe$_3$ powders were mechanically ground with planetary ball milling equipment at 150 rpm for 240 min. The as-milled powders were sintered by spark plasma sintering (SPS 2040) at around 860 K for about 8 min under uniaxial pressure of 50 MPa in vacuum.

The density of the sintered $C_{60}$/Cu$_2$SnSe$_3$ composites was measured using the Archimedes method. The constituent phases of the samples were determined by X-ray diffractometry (Cu K$_{\alpha}$, Rigaku, Rint2000, Tokyo, Japan). The chemical composition of bulk samples was characterized using electron probe micro-analysis (EPMA, JEOL, JXA-8100, Tokyo, Japan) with a wavelength dispersive spectrometer (WDS). The composition was calculated by averaging five spots. The microstructure of all $C_{60}$/Cu$_2$SnSe$_3$ composites was observed by high-resolution transmission electron microscopy (HRTEM, JEM2100F, JEOL, Tokyo, Japan). The thermal diffusivity ($\lambda$) was measured by laser flash method (Netzsch LFA427) in a flowing Ar atmosphere between 300 and 700 K. The thermal conductivity was calculated from the relationship $\kappa = \rho \lambda C_p$, where $\rho$ is the density of the sintered sample and
C_p is the specific heat capacity. The electrical conductivity and Seebeck coefficient were measured simultaneously using commercial equipment (ZEM-3, ULVAC-RIKO, Tokyo, Japan) on a bar-type sample with a dimension of 2 \times 2 \times 10 \text{ mm}^3. The Hall coefficient (R_H) was measured using the van der Pauw’s method in vacuum with a magnetic field of 2 T. The carrier concentration (p_H) and mobility (\mu_H) were estimated from the relations of p_H = 1/(\epsilon R_H) and \mu_H = \sigma R_H, based on the assumption of single band model, where \epsilon is the electronic charge. All measurements were performed in a temperature range of 300–700 K.

![Figure 1](image1.png)

**Figure 1.** SEM image of fullerene powder with average particle size of 500 nm.

3. Results and Discussion

3.1. Microstructure and XRD Analysis

Figure 2 shows the SEM image of the 1.6 vol % C_{60}-added Cu_2SnSe_3 powder after ball milling. It can be observed that the average particle size of milled C_{60}/Cu_2SnSe_3 powder was about 100 nm. Figure 3 shows the X-ray diffraction patterns of xC_{60}/Cu_2SnSe_3 composites (x = 0, 0.4, 0.8, 1.2, and 1.6 vol %) after SPS. The measured relative densities for all C_{60}/Cu_2SnSe_3 composites after SPS are above 97% of the theoretical value. The diffraction peaks in Figure 3 are well-indexed based on the JCPDS 65-4145 (Joint Committee on Powder Diffraction Standards) of Cu_2SnSe_3. As the content of C_{60} in the composites is very low, the diffraction peak of C_{60} is not found in the XRD pattern of all C_{60}/Cu_2SnSe_3 samples. Therefore, all C_{60}/Cu_2SnSe_3 samples show the same XRD patterns with the pure Cu_2SnSe_3 sample.

![Figure 2](image2.png)

**Figure 2.** SEM image of the 1.6 vol % C_{60}/Cu_2SnSe_3 powder after ball milling.
Figure 3. XRD patterns of sintered C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composites.

Figure 4a,b show the SEM microstructure of the sintered pure Cu\textsubscript{2}SnSe\textsubscript{3} sample and 1.6 vol % C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composite, respectively. The fullerene C\textsubscript{60} distributed uniformly in the form of clusters, and the average cluster size was lower than 1 μm. Shi, et al. reported that in the CoSb\textsubscript{3} material, most of the C\textsubscript{60} molecules agglomerate into irregular micrometer-size clusters located at the grain boundaries [17]. The smaller size of clusters in this study should be due to the ball milling technology. The chemical composition of C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composites was characterized by SEM and energy-dispersive X-ray spectroscopy (EDS), as shown in Figure 5. The results of EDS also confirm that the matrix was analyzed to be composed of 33.53 at. %; Cu, 16.85 at. %; Sn, and 49.62 at. %; Se, corresponding to the Cu\textsubscript{2}SnSe\textsubscript{3} phase. The black phase only contains C element, indicating C\textsubscript{60} phase. To further analyze the C\textsubscript{60} clusters in the C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composite, HRTEM of C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composite was carried out, as shown in Figure 6. The size of C\textsubscript{60} is about 80 nm, which means the ball milling process decreases the average size of C\textsubscript{60} particles. According to the theory proposed by Faleev and Zebardaji, et al. [20,21], nano-phases that distribute in the thermoelectric matrix can result in strain fields, which could cause some changes in the band structure of the material and then greatly influence its thermoelectric properties.

Figure 4. (a) SEM microstructure of the sintered pure Cu\textsubscript{2}SnSe\textsubscript{3}; (b) SEM microstructure of sintered 1.6 vol % C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composite.
Figure 5. (a) SEM image of the sintered 1.6% C<sub>60</sub>/Cu<sub>2</sub>SnSe<sub>3</sub> composite; (b) energy-dispersive X-ray spectroscopy (EDS) results of Cu<sub>2</sub>SnSe<sub>3</sub> matrix and C<sub>60</sub> phase.

Figure 6. High-resolution transmission electron microscopy (HRTEM) image of a C<sub>60</sub> particle in the C<sub>60</sub>/Cu<sub>2</sub>SnSe<sub>3</sub> composite.
3.2. Electrical Transport Properties

Figure 7 shows the temperature dependence of electrical conductivity (σ) for C_{60}/Cu_{2}SnSe_{3} composites with different vol % C_{60}. It can be seen that the σ of the Cu_{2}SnSe_{3} matrix decreases approximately linearly with rising temperature over the measured temperature range, indicating a typical behavior of a heavily-doped semiconductor. The similar tendency of σ was also observed in C_{60}/Cu_{2}SnSe_{3} composites. In addition, the σ of C_{60}/Cu_{2}SnSe_{3} composites decreases with increasing C_{60} content, which should be attributed to the enhanced carrier scattering at the incoherent interfaces between well-dispersed C_{60} clusters and the Cu_{2}SnSe_{3} matrix. Generally, in the case of carriers primarily scattered by grain barriers or interfaces between the second phase and matrix in the composites, the carrier mobility can be written as [22]

\[ \mu_H = \frac{e b}{\sqrt{8 k_B T m^*}} e^{-\frac{E_B}{k_B T}} \]  

(1)

where \( b \) is the average grain size, \( k_B \) the Boltzmann constant, \( m^* \) the carrier effective mass, and \( E_B \) the activation energy characterizing the barrier height between the matrix and the second phase. As the relative density of the xC_{60}/Cu_{2}SnSe_{3} composite is higher than 97%, the porosity effect can be eliminated. Table 1 lists some physical and structural parameters of xC_{60}/Cu_{2}SnSe_{3} composites at room temperature. As the C_{60} could act as an electron acceptor in the p-type C_{60}/Cu_{2}SnSe_{3} composite, the carrier concentration increases with increasing C_{60} content, which is consistent with the results of Blank [15]. In addition, it can be noted that the carrier mobility decreases with increasing C_{60} content. Therefore, the σ of xC_{60}/Cu_{2}SnSe_{3} composites decreases compared with the σ of the Cu_{2}SnSe_{3} matrix.

![Figure 7. Temperature dependence of electrical conductivity (σ) of C_{60}/Cu_{2}SnSe_{3} composites.](attachment:figure7.png)

| \( x \) (vol %) | Relative Density (Ω^{-1} cm^{-1}) | \( p \) (10^{19} cm^{-3}) | \( \mu_H \) (cm^{2}/Vs) | \( \alpha \) (µV/K) | \( k_L \) (Wm^{-1} K^{-1}) | \( m^* \) (m_0) |
|---|---|---|---|---|---|---|
| 0  | 98.7% | 127 | 3.74 | 21.2 | 131 | 2.77 | 2.6 |
| 0.4 | 97.2% | 110 | 4.81 | 14.3 | 165 | 2.22 | 2.8 |
| 0.8 | 98.9% | 90 | 5.01 | 11.2 | 188 | 2.06 | 2.9 |
| 1.2 | 98.2% | 75 | 4.98 | 9.4 | 225 | 1.96 | 3.1 |
| 1.6 | 97.9% | 62 | 5.09 | 7.6 | 252 | 1.81 | 3.2 |
Figure 8 displays the Seebeck coefficient ($\alpha$) of xC$_{60}$/Cu$_2$SnSe$_3$ composites as a function of temperature. All composites have a positive $\alpha$ across the whole temperature range, indicating that the holes are major carriers. With rising temperature, the $\alpha$ of all xC$_{60}$/Cu$_2$SnSe$_3$ composites increases approximately linearly and the $\alpha$ of 1.6% C$_{60}$/Cu$_2$SnSe$_3$ composite reaches 314 $\mu$V/K at 700 K. Moreover, the $\alpha$ of xC$_{60}$/Cu$_2$SnSe$_3$ composites significantly increases with the increasing content of C$_{60}$. At room temperature, the $\alpha$ increases from 130 $\mu$V/K for the Cu$_2$SnSe$_3$ matrix to 252 $\mu$V/K for the 1.6 vol % C$_{60}$/Cu$_2$SnSe$_3$ composite. The enhancement of $\alpha$ of xC$_{60}$/Cu$_2$SnSe$_3$ composites should be related to the “energy filter” effect. The Seebeck coefficient can be expressed as [23],

$$\alpha = -\frac{\pi}{3} \frac{k_B T}{e^2} \frac{d\ln\sigma(E)}{dE}\bigg|_{E=E_F} - \frac{T}{n(E)} \frac{d n(E)}{dE}\bigg|_{E=E_F}$$  \hspace{1cm} (2)

where $k_B$, $\sigma(E)$, and $n(E)$ are Boltzmann constant, electrical conductivity, and value of density of states (DOS), respectively. Many studies have confirmed that when nano-phases or nano-inclusions are incorporated into a semiconducting matrix material, the band bending at the inclusion/matrix interface will produce a potential energy barrier which could effectively block low energy electrons, while transmitting high energy electrons [24]. This “electron energy filter” could evidently increase the local density of states near the Fermi level ($E_F$) and enhance the Seebeck coefficient.

![Figure 8. Temperature dependence of Seebeck coefficient ($\alpha$) of C$_{60}$/Cu$_2$SnSe$_3$ composites.](image)

The $\mu_H$ of xC$_{60}$/Cu$_2$SnSe$_3$ composites is shown in Figure 9. The $\mu_H$ of xC$_{60}$/Cu$_2$SnSe$_3$ composites decreases with increasing C$_{60}$ content. In addition, the $\mu_H$ of xC$_{60}$/Cu$_2$SnSe$_3$ composites was in the order of 10 cm$^2$/V$^{-1}$s$^{-1}$ at room temperature, which was close to that of skutterudites [25,26]. It may be caused by the similar carrier effective mass of Cu$_2$SnSe$_3$ and CoSb$_3$ compounds. The $m^*$ can be estimated in the single parabolic band model using the following equations,

$$m^* = \frac{\hbar^2}{2k_B T} \left(\frac{n}{4\pi F_1 (\eta)}\right)^{2/3}$$  \hspace{1cm} (3)

$$\alpha = -\frac{k_B}{e} \left[\frac{(r+2)F_{r+1} (\eta)}{(r+1)F_r (\eta)} - \eta\right]$$  \hspace{1cm} (4)

where $F_r$, $\hbar$, and $r$ are Fermi integral, Planck's constant, and scattering parameter of relaxation time, respectively. The evaluated equivalent carrier effective mass of xC$_{60}$/Cu$_2$SnSe$_3$ composites at room temperature is listed in Table 1. It can also be seen from Figure 9 that the $\mu_H$ of pure Cu$_2$SnSe$_3$ shows a temperature dependence of $T^{-1.5}$ above 500 K, indicating that the acoustic phonon scattering is
dominant in the temperature range from 500 to 700 K. Below 500 K, the $\mu_H$ of pure Cu$_2$SnSe$_3$ has a weak temperature dependence relationship and the relationship of $\mu_H \propto T^{-0.5}$ is observed, suggesting that a dominative mechanism is alloy scattering. However, the $\mu_H$ of $x$C$_{60}$/Cu$_2$SnSe$_3$ composites deviates from the $T^{-1.5}$ or $T^{-0.5}$ dependence over the entire temperature range, indicating that a mixed scattering mechanism dominates these samples.

![Image](https://via.placeholder.com/150)

**Figure 9.** Temperature dependence of carrier mobility ($\mu_H$) of C$_{60}$/Cu$_2$SnSe$_3$ composites.

### 3.3. Thermal Transport Properties

Figure 10 displays the temperature dependence of total thermal conductivity ($\kappa$) and lattice thermal conductivity ($\kappa_L$) for C$_{60}$/Cu$_2$SnSe$_3$ composites. The $\kappa_L$ is estimated by subtracting the electronic contribution via the Wiedmann–Franz law ($k_F = L_0\sigma T$, where the Lorenz number $L_0$ is taken as a constant of $2.0 \times 10^{-8} \text{V}^2/\text{K}^2$) from the total thermal conductivity. The $\kappa$ for all samples declines with increasing temperature. Moreover, the $\kappa$ of $x$C$_{60}$/Cu$_2$SnSe$_3$ composites decreases with increasing C$_{60}$ content. The achieved $\kappa$ of 1.6 vol % C$_{60}$/Cu$_2$SnSe$_3$ composite at room temperature is 1.85 W/mK, which is 34% lower than that of pure Cu$_2$SnSe$_3$. The minimal $\kappa$ of 1.6 vol % C$_{60}$/Cu$_2$SnSe$_3$ composite is 0.71 W/mK at 700 K. It is well-known that the grain boundary, wide or point defects, porosity, and impurity could contribute to the decrease of $\kappa$. Owing to high relative density of C$_{60}$/Cu$_2$SnSe$_3$ composites, the reduction of $\kappa$ originating from the porosity is negligible. Meanwhile, the calculation of $\kappa_F$ shows that the reduction of $\kappa_F$ has a limited contribution to the decrease of $\kappa$. Therefore, the decrease of $\kappa$ for C$_{60}$/Cu$_2$SnSe$_3$ composites mainly originates from the depression of $\kappa_L$ due to the enhancement of phonon scattering by the C$_{60}$ inclusions or nano-particles in the composite. Just as shown in Figure 10b, the $\kappa_L$ of C$_{60}$/Cu$_2$SnSe$_3$ composites drastically decreases with the content of C$_{60}$ increasing. The minimal $\kappa_L$ achieved in the present work is 0.68 W/mK at 700 K for the 1.6 vol % C$_{60}$/Cu$_2$SnSe$_3$ sample, which is 43% lower than that of pure Cu$_2$SnSe$_3$. According to the kinetic theory [27], the minimum lattice thermal conductivity $\kappa_{L\text{min}}$ can be obtained when the phonon mean free path reaches the shortest interatomic distance. The $\kappa_{L\text{min}}$ can be estimated from the formula $\kappa_L = 1/3C_v\nu_ml$, where $C_v$ is heat capacity per unit volume of the system using Dulong and Petit value, $\nu_m$ the mean sound velocity, and $l$ the mean free path of phonon. The $\nu_m$ comes from the data in reference [28]. If we assume the minimum $l$ to be the interatomic distance for Cu$_2$SnSe$_3$ (0.238 nm), the $\kappa_{L\text{min}}$ is calculated as 0.52 Wm$^{-1}$K$^{-1}$, just as shown by dashed line in Figure 10b. The $\kappa_L$ of 1.6 vol % C$_{60}$/Cu$_2$SnSe$_3$ composites approaches the $\kappa_{L\text{min}}$ of Cu$_2$SnSe$_3$ at high temperature.
3.4. Figure of Merit

The conversion efficiency of TE materials depends on the maximum dimensionless figure of merit (ZT). Figure 11 shows the dimensionless figure of merit (ZT) of C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composites as a function of temperature. Like other doped Cu\textsubscript{2}SnSe\textsubscript{3} investigated before [8,29,30], the ZT value of C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composites increases approximately linearly with increasing temperature. Compared with the ZT of the Cu\textsubscript{2}SnSe\textsubscript{3} sample, the ZT value of C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composites is enhanced. For the 0.8 vol % C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} sample, the maximum ZT value is 0.38 at 700 K, which is 45\% higher than that of the pure Cu\textsubscript{2}SnSe\textsubscript{3} sample. The enhancement of ZT for C\textsubscript{60}/Cu\textsubscript{2}SnSe\textsubscript{3} composites is mainly attributed to the reduced \( \kappa \)\textsubscript{l} and the enhanced \( \alpha \). The addition of C\textsubscript{60} into the Cu\textsubscript{2}SnSe\textsubscript{3} matrix could improve the TE properties, which is a promising process to the design Cu-based chalcogenide compounds with high TE performance. When the material with optimized carrier concentration is selected as the matrix, the higher ZT value of TE composite could be achieved.
Acknowledgments:

Author Contributions:

Jiai Ning performed the experiments. Degang Zhao wrote the paper. Jiai Ning and Min Zuo contributed to the data analysis.

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Figure 11. Temperature dependence of the dimensionless figure of merit of (ZT) of C_{60}/Cu_{2}SnSe_{3} composites.

4. Conclusions

In this study, C_{60} was incorporated into a Cu_{2}SnSe_{3} matrix, and C_{60}/Cu_{2}SnSe_{3} composites were fabricated using BM-SPS method. The C_{60} phase distributed uniformly in the form of clusters, and the average cluster size was less than 1 μm. With increasing C_{60} content, the electrical conductivity of C_{60}/Cu_{2}SnSe_{3} composites decreased, while the Seebeck coefficient of C_{60}/Cu_{2}SnSe_{3} composites increased due to the “electron energy filter” of the C_{60} nano-phase. The thermal conductivity of C_{60}/Cu_{2}SnSe_{3} composites decreased significantly, which originated from the phonon scattering by the C_{60} clusters located on the grain boundaries of the Cu_{2}SnSe_{3} matrix. The maximum ZT of 0.38 was obtained at 700 K for 0.8 vol % C_{60}/Cu_{2}SnSe_{3} composite.

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