Research Article

Synthesis and Thermoelectric Properties of C$_{60}$/Cu$_2$GeSe$_3$ Composites

Degang Zhao, Jiai Ning, Shuyu Li, and Min Zuo

School of Materials Science and Engineering, University of Jinan, Jinan 250022, China

Correspondence should be addressed to Degang Zhao; mse_zhaodg@ujn.edu.cn

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Nanosized C$_{60}$ powder was sufficiently incorporated with Cu$_2$GeSe$_3$ powder by ball milling and C$_{60}$/Cu$_2$GeSe$_3$ composites were prepared by spark plasma sintering. C$_{60}$ distributed uniformly in the form of clusters and the average size of cluster was lower than 1 μm. With the addition of C$_{60}$ increasing, the electrical resistivity and Seebeck coefficient of C$_{60}$/Cu$_2$GeSe$_3$ composites increased while the thermal conductivity decreased significantly which resulted from the phonon scattering by C$_{60}$ clusters locating on the grain boundaries of Cu$_2$GeSe$_3$ matrix. The maximum ZT of 0.20 was achieved at 700 K for 0.9% C$_{60}$/Cu$_2$GeSe$_3$ sample.

1. Introduction

Thermoelectric (TE) material which directly converts electricity to heat (and vice versa) has attracted increasing worldwide attention due to their potential applications in electronic cooling, waste heat recovery, and special power supplies [1, 2]. The conversion efficiency of TE material is determined by the dimensionless figure of merit, $ZT = \alpha^2 T/\rho \kappa$, where $\alpha$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $T$ is the absolute temperature, and $\kappa$ is the total thermal conductivity. The total thermal conductivity consists of an electron part ($\kappa_e$) and a phonon part ($\kappa_v$). Therefore, to maximize $ZT$ value of TE material, low $\kappa$ and $\rho$ as well as large $\alpha$ are required. In recent years, several classes of bulk materials with high $ZT$ have been developed, such as lead telluride, skutterudite, clathrates, and Cu-based chalcogenide semiconductors [3–5]. 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 systems, the Cu$_2$GeSe$_3$ structure has partial “phonon glass electron crystal” (PGEC) characteristic which is possible to achieve high TE performance. The Cu-Se bond network dominates the electron conduction while the contribution from the element Ge is very weak; thus the Ge site is suitable for optimizing TE property. Various attempts including doping by partial substitution have been made to improve the thermoelectric properties of Cu$_2$GeSe$_3$ compound [6–8]. Cho et al. synthesized the Cu$_2$Ga$_{1−x}$Ga$_x$Ge$_{1−x}$Se$_3$ samples and achieved the $ZT$ value of 0.50 for Cu$_2$Ga$_{0.97}$Sn$_{0.03}$Se$_3$ sample [9]. Chetty et al. reported the maximum $ZT$ value of in-doped Cu$_3$In$_{0.1}$Ga$_{0.9}$Se$_3$ was 0.23 at 700 K for Cu$_3$In$_{0.1}$Ga$_{0.9}$Se$_3$ sample [10]. Besides doping, the dispersion of nanostructure phases into thermoelectric matrix is also an attractive approach to improve the performance of TE materials. However, Cu$_2$GeSe$_3$-based thermoelectric composites are scarcely investigated because the enhancement of $ZT$ is unapparent compared with the doping. Although significant reduction in $\kappa_v$ can be achieved via enhanced phonon scattering at matrix/inclusion interfaces, the electrical resistivity of TE composites maybe also increases resulting in a marginal improvement of the overall $ZT$ value. Therefore, effective enhancement of $ZT$ for TE composites depends on the good selection of dispersed nanophase and the control of microstructure of composites [11].

Fullerene C$_{60}$ has ultra high elastic module and is a chemically stable nonpolar molecule. Nanosized C$_{60}$ maybe provide an effective phonon scattering which decreases $\kappa_v$. Meanwhile, the scattering of the charge carriers by C$_{60}$ molecules could be ineffective due to the large value of electron (hole) wavelength compared to a fullerene size. Blank et al. ever reported that the addition of 0.5 vol%...
C$_{60}$ improved the TE properties of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and the maximum $ZT$ of 1.17 was obtained at 450 K [12, 13]. Shi et al. found that adding 6.5 mass% C$_{60}$ into the binary CoSb$_3$ can increase the $ZT$ while adding amounts between 0.5% and 4.8% into CoSb$_3$ decreased the $ZT$ [14]. Nandihalli et al. also reported the $ZT$ value of C$_{60}$/Ni$_{0.05}$Mo$_{0.05}$Sb$_{1.5}$Te$_{1.5}$ composites was enhanced in the whole temperature range due to the large decrease of $\kappa_L$ [15]. In this contribution, we attempted to introduce C$_{60}$ into Cu$_2$GeSe$_3$ system and expect to achieve larger reduction in $\kappa_L$ of C$_{60}$/Cu$_2$GeSe$_3$ composites.

In the present work, C$_{60}$ powder was incorporated into Cu$_2$GeSe$_3$ matrix using ball milling (BM) and C$_{60}$/Cu$_2$GeSe$_3$ composites were fabricated by spark plasma sintering (SPS). Effects of C$_{60}$ particles on the thermoelectric properties of C$_{60}$/Cu$_2$GeSe$_3$ composites were discussed.

### 2. Experimental Procedures

The polycrystalline samples Cu$_2$GeSe$_3$ were synthesized by melting method. The stoichiometric amounts of starting materials Cu (powder, 99.95%), Ge (powder, 99.999%), and Se (shot, 99.999%) were first placed in carbon crucible and then cooled to room temperature. To increase the homogeneity and crystallinity, the samples were annealed at 823 K for 72 h. The resulting ingots were then ground into fine powder using mortar and pestle. Commercially available C$_{60}$ powder with average particle size of 500 nm (Figure 1, XFNANO, China) was chosen as the nanoinclusions. C$_{60}$ purity is 99.98% and the other 0.02% refers to impurities of C$_{70}$ and other carbon structures. C$_{60}$ particles were added to the Cu$_2$GeSe$_3$ powder at fractions of 0.3, 0.6, 0.9, and 1.2 vol%, respectively. Then C$_{60}$-added Cu$_2$GeSe$_3$ powders were mechanically ground with planetary ball milling equipment at 200 rpm for 300 min in an argon atmosphere. Steel balls of 0.5 mm were charged as the milling media. The as-milled powders were sintered by spark plasma sintering (SPS 2040) at around 850 K for about 8 min under uniaxial pressure of 50 MPa in vacuum.

The densities of the sintered C$_{60}$/Cu$_2$GeSe$_3$ composites were measured using the Archimedes method. The constituent phases of composites were determined by X-ray diffractometry (Cu K$_\alpha$, Rigaku, Rint2000). The chemical compositions of bulk samples were characterized using electron probe microanalysis (EPMA, JEOL, and JXA-8100) with a wavelength dispersive spectrometer (WDS). The compositions were calculated by averaging five spots. The microstructure of all C$_{60}$/Cu$_2$GeSe$_3$ composites was observed by high-resolution transmission electron microscopy (HREM, JEM2100F). The thermal diffusivity ($\lambda$) was measured by laser flash method (Netzsch LFA427) in a flowing Ar atmosphere. The thermal diffusivity was calculated from the relationship $\kappa = \rho C_p \lambda$, where $\kappa$ is the density of the sintered sample and $C_p$ is the specific heat capacity. $\rho$ (taken as 0.33 J/gK) was determined by the ratio method with a sapphire reference using a Netzsch Differential Scanning Calorimetry. The electrical resistivity and Seebeck coefficient were measured simultaneously using commercial equipment (ZEM-3, ULVAC-RIKO) on the bar-type sample with a dimension of $2 \times 2 \times 10$ mm. The Hall coefficient ($R_H$) was measured using the van der Pauw’s method in vacuum with the magnetic field of 2 T. The carrier concentration ($p_H$) and mobility ($\mu_H$) were estimated from the relations of $p_H = 1/(e R_H)$ and $\mu_H = R_H / \rho$ based on the single band model, where $e$ is the electronic charge. All the measurements were performed in a temperature range of 300–700 K.

### 3. Results and Discussion

#### 3.1. Microstructure and XRD Analysis

Figure 2 displays the SEM image of 0.9 vol% C$_{60}$-added Cu$_2$GeSe$_3$ powder after ball milling. It can be observed that the average size of milled C$_{60}$/Cu$_2$GeSe$_3$ powder was about 100 nm. Figure 3 shows the XRD patterns of $x$C$_{60}$/Cu$_2$GeSe$_3$ composites ($x = 0$, 0.3, 0.6, 0.9, and 1.2 vol%) after SPS. The measured relative densities for all C$_{60}$/Cu$_2$GeSe$_3$ composites after SPS are above 97% of the theoretical value. The diffraction peaks in Figure 3 are well indexed based on the JCPDS 65-2533 of Cu$_2$GeSe$_3$ (1mm2 group). However, no diffraction peak of C$_{60}$ is found in the XRD of all C$_{60}$/Cu$_2$GeSe$_3$ samples,
or interfaces between the second phase and matrix in the composites, the carrier mobility can be expressed as \[\mu_H = \frac{el}{\sqrt{8k_BTm^*}e^{-E_a/k_BT}}, \quad (1)\]

where \(k_B\) is the Boltzmann constant, \(m^*\) is the carrier effective mass, \(l\) is the average grain size, and \(E_a\) is the activation energy characterizing the barrier height between the matrix and second phase. As the relative density of \(xC_{60}/Cu_2GeSe_3\) composite is higher than 97\%, the porosity effect could be eliminated. Table 1 lists some physical parameters of \(C_{60}/Cu_2GeSe_3\) composites at room temperature. It can be noted that the carrier mobility (\(\mu_H\)) decreases with the content of \(C_{60}\) increasing. Therefore, \(\rho\) of \(C_{60}/Cu_2GeSe_3\) composites increases compared with \(\rho\) of \(Cu_2GeSe_3\) matrix.

Figure 8 displays the Seebeck coefficient (\(\alpha\)) of \(xC_{60}/Cu_2GeSe_3\) composites as a function of temperature. All composites have a positive \(\alpha\) over the whole temperature range, indicating the holes are major carriers. With rising temperature, \(\alpha\) of all \(xC_{60}/Cu_2GeSe_3\) composites increases and \(\alpha\) of 1.2\% \(C_{60}/Cu_2GeSe_3\) composite reaches 183 \(\mu V/K\) at 700 K. In addition, \(\alpha\) of \(C_{60}/Cu_2GeSe_3\) composites increases with the content of \(C_{60}\) increasing. At room temperature, \(\alpha\) increases from 58 \(\mu V/K\) for \(Cu_2GeSe_3\) matrix to 101 \(\mu V/K\) for 1.2\% \(C_{60}/Cu_2GeSe_3\) composite. The enhancement of \(\alpha\) of \(xC_{60}/Cu_2GeSe_3\) composites should be related with the “energy filter” effect. The Seebeck coefficient can be expressed as \[\alpha = -\frac{\pi}{3} \frac{k_B}{e} \frac{d}{dE} \ln \sigma(E) \bigg|_{E=E_f} = -\frac{T}{n(E)} \frac{d}{dE} \ln n(E) \bigg|_{E=E_f}, \quad (2)\]

where \(k_B\), \(n(E)\), and \(\sigma(E)\) are Boltzmann constant, value of density of states (DOS), and electrical conductivity, respectively. When nanophases or nano-inclusions are incorporated into a semiconducting matrix, the band bending at inclusion/matrix interface will produce potential energy barrier which could effectively block low energy electrons, while transmitting high energy electrons [20]. This “electron energy filter” could enhance the Seebeck coefficient by moving the Fermi level \(E_F\) to an energy level with larger local DOS.

### 3.3. Thermal Transport Properties

Figure 9 displays the temperature dependence of total thermal conductivity (\(\kappa\)) and lattice thermal conductivity (\(\kappa_L\)) for \(C_{60}/Cu_2GeSe_3\) composites. \(\kappa_L\) is estimated by subtracting the electronic contribution via the Wiedemann-Franz law \(\kappa_T = L_0\sigma T\), where the Lorenz number \(L_0\) is taken as a constant of 2.0 \(\times 10^{-8} V^2/K^2\) from the total thermal conductivity. \(\kappa\) for all samples declines with increasing temperature. Moreover, \(\kappa\) of \(xC_{60}/Cu_2GeSe_3\) composites decreases with the content of \(C_{60}\) increasing. The achieved \(\kappa\) of 1.2\% \(C_{60}/Cu_2GeSe_3\) composite at room temperature is 1.43 W/mK, which is 45\% lower than that of \(Cu_2GeSe_3\) matrix. The minimal \(\kappa\) of 1.2\% \(C_{60}/Cu_2GeSe_3\) composite is 0.65 W/mK at 700 K. As known to all, the grain boundary, wide or point defects, porosity, and impurity could contribute to the decrease of \(\kappa\). Owing to the high relative density of \(C_{60}/Cu_2GeSe_3\) composites, the
reduction of $\kappa$ originated from the porosity is negligible. Meanwhile, the calculation of $\kappa_L$ shows that the reduction of $\kappa_L$ has a limited contribution to the decrease of $\kappa$. Therefore, the decrease of $\kappa$ for C$_{60}$/Cu$_2$GeSe$_3$ composites mainly originates from the depression of $\kappa_L$ due to the enhancement of phonon scattering by C$_{60}$ inclusions or nanoparticles in the composite. Figure 9(b) is the temperature dependence of $\kappa_L$ of C$_{60}$/Cu$_2$GeSe$_3$ composites. $\kappa_L$ of C$_{60}$/Cu$_2$GeSe$_3$ composites drastically decreases with the content of C$_{60}$ increasing. The minimal $\kappa_L$ achieved in the present work is 0.58 W/mK at
Table 1: Chemical composition and some physical parameters of \( xC_{60}/Cu_2GeSe_3 \) composites at room temperature.

<table>
<thead>
<tr>
<th>( x ) (vol%)</th>
<th>Relative density (%)</th>
<th>( \rho ) (mΩcm)</th>
<th>( \rho ) (( 10^{19} ) cm(^{-3} ))</th>
<th>( \mu_{|} ) (cm(^2)/Vs)</th>
<th>( \alpha ) (( \mu )V/K)</th>
<th>( \kappa_L ) (Wm(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>97.6%</td>
<td>2.85</td>
<td>13.8</td>
<td>15.7</td>
<td>58</td>
<td>2.37</td>
</tr>
<tr>
<td>0.3</td>
<td>98.1%</td>
<td>3.53</td>
<td>12.4</td>
<td>14.2</td>
<td>67</td>
<td>1.49</td>
</tr>
<tr>
<td>0.6</td>
<td>97.5%</td>
<td>4.26</td>
<td>12.1</td>
<td>12.0</td>
<td>80</td>
<td>1.46</td>
</tr>
<tr>
<td>0.9</td>
<td>98.3%</td>
<td>6.37</td>
<td>10.7</td>
<td>9.1</td>
<td>93</td>
<td>1.40</td>
</tr>
<tr>
<td>1.2</td>
<td>97.8%</td>
<td>8.02</td>
<td>9.5</td>
<td>8.2</td>
<td>101</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Figure 6: HRTEM image of \( C_{60} \) particle in \( C_{60}/Cu_2GeSe_3 \) composite.

Figure 7: The electrical resistivity (\( \rho \)) as a function of temperature for \( C_{60}/Cu_2GeSe_3 \) composites.

Figure 8: The Seebeck coefficient (\( \alpha \)) as a function of temperature for \( C_{60}/Cu_2GeSe_3 \) composites.

Before [9, 10, 21], the \( ZT \) value of \( C_{60}/Cu_2GeSe_3 \) composites increases approximately linearly with increasing temperature. Compared with the \( ZT \) of \( Cu_2GeSe_3 \) sample, the \( ZT \) value of \( C_{60}/Cu_2GeSe_3 \) composites is enhanced. The inset in Figure 10 shows the \( ZT \) value as a function of volume fraction of \( C_{60} \) at different temperature. For 0.9% \( C_{60}/Cu_2GeSe_3 \) composite, the maximum \( ZT \) is 0.20 at 700 K which is almost three times higher than that of pure \( Cu_2GeSe_3 \) sample. The enhancement of \( ZT \) for \( C_{60}/Cu_2GeSe_3 \) composites is mainly attributed to the reduced \( \kappa_L \) and the enhanced \( \alpha \). The addition of nano-\( C_{60} \) into the \( Cu_2GeSe_3 \) matrix through BM method improves the TE properties, which provides a novel process to 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 obtained.

4. Conclusions

In this study, \( C_{60} \) was incorporated into \( Cu_2GeSe_3 \) matrix and \( C_{60}/Cu_2GeSe_3 \) composites were fabricated using BM-SPS method. \( C_{60} \) phase distributed uniformly in the form of clusters and the average size of cluster was lower than 1\( \mu \)m. With the content of \( C_{60} \) increasing, the electrical resistivity increased, and the Seebeck coefficient decreased, which led to the enhancement of the \( ZT \) value. The \( ZT \) value of \( C_{60}/Cu_2GeSe_3 \) composites is higher than that of pure \( Cu_2GeSe_3 \) sample, and it increases approximately linearly with increasing temperature. This work provides a new approach for designing high-\( ZT \) Cu-based TE materials.
resistivity and Seebeck coefficient of C₆₀/Cu₂GeSe₃ composites increased. The thermal conductivity of C₆₀/Cu₂GeSe₃ composites decreased significantly which originated from the phonon scattering by C₆₀ clusters locating on the grain boundaries of Cu₂GeSe₃ matrix. The highest ZT value for 0.9% C₆₀/Cu₂GeSe₃ composite was 0.20 at 700 K.

Competing Interests
The authors declare that they have no competing interests.

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References


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