Thermoelectric and mechanical properties of spark plasma sintered Cu3SbSe3 and Cu3SbSe4: Promising thermoelectric materials

Kriti Tyagi, Bhasker Gahtori, Sivaiah Bathula, Vijaykumar Toutam, Sakshi Sharma, Niraj Kumar Singh, and Ajay Dhar

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Thermoelectric and mechanical properties of spark plasma sintered 
Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$: Promising thermoelectric materials

Kriti Tyagi, Bhasker Gahtori, Siviah Bathula, Vijaykumar Toutam, Sakshi Sharma, 
Niraj Kumar Singh, and Ajay Dhara

CSIR-Network of Institutes for Solar Energy, Materials Physics and Engineering, CSIR-National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi 110012, India

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We report the synthesis of thermoelectric compounds, Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$, employing the conventional fusion method followed by spark plasma sintering. Their thermoelectric properties indicated that despite its higher thermal conductivity, Cu$_3$SbSe$_4$ exhibited a much larger value of thermoelectric figure-of-merit as compared to Cu$_3$SbSe$_3$, which is primarily due to its higher electrical conductivity. The thermoelectric compatibility factor of Cu$_3$SbSe$_4$ was found to be $\sim$1.2 as compared to 0.2 V$^{-1}$ for Cu$_3$SbSe$_3$ at 550 K. The results of the mechanical properties of these two compounds indicated that their microhardness and fracture toughness values were far superior to the other competing state-of-the-art thermoelectric materials. © 2014 AIP Publishing LLC.

Electricity can be produced directly by harnessing waste-heat employing thermoelectric (TE) power generation; however, the limited efficiency of the existing TE materials limits their usage for commercial applications.\(^1\) The efficiency of TE devices is strongly associated with the dimensionless figure-of-merit (ZT) of its constituent n- and p-type TE materials and can be increased by enhancing the ZT, which is defined as, $ZT = (\alpha^2 \sigma / \kappa) T$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, and $\kappa$ is the total thermal conductivity ($\kappa = \kappa_l + \kappa_e$, the lattice and electronic contributions, respectively). A high electrical conductivity, a large Seebeck coefficient, and low thermal conductivity are desired in order to realize a high-performance TE material.\(^2\) It is well known that the best TE materials are narrow bandgap semiconductors,\(^3\) and recently, several Cu–Sb–Se based ternary compounds have been found to exhibit promising thermoelectric properties.\(^4\) Among these, Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$ exhibit interesting electronic and thermal transport properties as both of these are narrow bandgap semiconductors.\(^6\) Moreover, Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$ have received considerable attention as potential TE materials, since experimental measurements have recently shown that Cu$_3$SbSe$_3$ exhibits an ultra-low and nearly temperature-independent lattice thermal conductivity.\(^5\) Recently, many reports\(^5\) have also appeared in literature on the thermoelectric properties of Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$.\(^10\) On the other hand, apart from the ZT, the mechanical properties of these TE materials are also equally important especially for device fabrication wherein these TE materials have to withstand thermal stresses created due to rapid temperature cycling and gradients across its module TE elements. Hence, apart from their TE properties there is a need to determine their mechanical properties as well. Therefore, the objective of the current work is to study the TE properties of Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$ compounds and to provide an insight into their mechanical properties, both of which are equally important for their use for TE device applications in the mid-temperature range.

Experimental synthesis of Cu$_3$SbSe$_3$ has been reported elsewhere\(^5\) and a similar methodology has been adopted for the synthesis of Cu$_3$SbSe$_4$. The density of both the samples, was measured using the conventional Archimedes principle and was found to be $\sim$98.6% of their theoretical density. The high densifications in both the samples are due to the rapid heating rates generated by Spark Plasma Sintering (SPS) used for synthesizing the materials. Further, nano-indentation on these samples was carried out employing Berkovich indenter using Multi-mode Atomic Force Microscope (AFM) (Bruker Ltd.,) with Nanoscope 5 controller. The deflection sensitivity was measured on sapphire surface after performing Force–Displacement (F-D) spectroscopy on the samples. In order to use a maximum set load, the AFM tip was engaged with an x-rotation of 12° with a small amplitude of 300 mV. To minimize the errors, all the measurements were carried out without disturbing the laser alignment on the cantilever. Indentation–fracture toughness analysis was carried out employing Vickers’s micro hardness tester (Model: FM-17, Make: Future Tech Corp., Japan).

Figs. 1(a) and 1(b) show the X-Ray Diffraction (XRD) patterns of Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$ samples at room temperature. The actual composition of Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$ samples was determined using Flame atomic absorption spectrometry technique (Analytik Jena, Vario-6) and both the samples exhibited almost the same stoichiometry as the starting composition. Cu$_3$SbSe$_3$ crystallize in single-phase with orthorhombic structure with Pnma (62) space group with lattice constants\(^6\) of $a = 7.98$ Å, $b = 10.61$ Å, $c = 6.83$ Å, and $\alpha = \beta = \gamma = 90^\circ$. On the other hand, Cu$_3$SbSe$_4$ crystallize in a tetragonal structure with I42m(121) space group with lattice constants of $a = 5.7$ Å, $b = 5.7$ Å, $c = 11.2$ Å, and $\alpha = \beta = \gamma = 90^\circ$.\(^5\) The high intensity peaks in the XRD patterns clearly indicate the high crystallinity of both the
is consistent with the picture of a degenerate semiconductor where carrier mean free path is nearly equal to inter-atomic distance. Further, as is evident from Fig. 2(a), the Seebeck coefficient of Cu$_3$SbSe$_4$ is higher than Cu$_3$SbSe$_3$ sample in the entire temperature range. This higher magnitude of Seebeck coefficient of Cu$_3$SbSe$_4$ can be attributed to its crystal structure, consisting of a three-dimensional Cu/Se framework [Cu$_3$Se$_4$] acting as the hole conduction pathway and the [SbSe$_4$] tetrahedral that is a distorted diamond-like structure, thus, providing a relatively large Seebeck coefficient. The magnitude of the Seebeck coefficient of the Cu$_3$SbSe$_4$ sample is comparable to earlier reported values (Table I). Whereas, no such reports for Cu$_3$SbSe$_3$ is available in literature. Fig. 2(b) shows that the electrical conductivity of Cu$_3$SbSe$_4$ is higher than the Cu$_3$SbSe$_3$, throughout the temperature range of measurement. Further, in contrast to the Cu$_3$SbSe$_3$ sample, the Cu$_3$SbSe$_4$ sample exhibits an increase in electrical conductivity with increasing temperature indicating a semiconductor behavior. The electrical conductivity of Cu$_3$SbSe$_4$ sample is 3 times higher at 300 K and around an order of magnitude higher at 550 K than that of Cu$_3$SbSe$_3$ (Fig. 2(b)).

The variation of thermal conductivity with temperature for both, Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$ samples, has been shown in Fig. 2(c), which clearly exhibits a discontinuity at $\sim$450 K in case of Cu$_3$SbSe$_3$ due to a order-disorder transition. The value of thermal conductivity for Cu$_3$SbSe$_3$ was found to be 0.26 W m$^{-1}$ K$^{-1}$ as compared to 0.761 W m$^{-1}$ K$^{-1}$ for Cu$_3$SbSe$_4$ at 550 K. This ultralow value of thermal conductivity in Cu$_3$SbSe$_3$ has been attributed to a combination of its complex crystal structure, very low Debye temperature, and extreme anharmonicity of the lattice vibrational spectrum that gives rise to a large value Gruneisen parameter in this compound. On the other hand, Cu$_3$SbSe$_4$ sample exhibits the value of $\kappa$, which is much lower than reported earlier by Wei et al. and Yang et al. of 1.35 and 1.1 W m$^{-1}$ K$^{-1}$, respectively. After combining the results of electrical conductivity, Seebeck coefficient and thermal conductivity, the calculated ZT has been displayed in Fig. 2(d). Despite the intrinsically low value of thermal conductivity in case of Cu$_3$SbSe$_3$, a drastic decrease in its electrical conductivity is the main reason for its low value of ZT as compared to Cu$_3$SbSe$_4$, which shows a value of 0.3 at 550 K. For better evaluation of our results, we have compared the ZT data of Cu$_3$SbSe$_4$ with the recent reports literature, as shown in Table I.

Nanoindentation on Cu$_3$SbSe$_3$ and Cu$_3$SbSe$_4$ compounds was carried out using Berkovich indenter. Hardness and modulus of elasticity (E) measurements were done using Oliver and Pharr method, in which the Sneddon’s elastic solution

<table>
<thead>
<tr>
<th>Material</th>
<th>T (K)</th>
<th>Seebeck (µV/K)</th>
<th>$\kappa$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\sigma$ ($\times 10^5$ S/m)</th>
<th>ZT</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_3$SbSe$_4$</td>
<td>550</td>
<td>214</td>
<td>0.761</td>
<td>9.1</td>
<td>0.30</td>
<td>Current Study</td>
</tr>
<tr>
<td>Cu$_3$SbSe$_4$</td>
<td>527</td>
<td>347</td>
<td>1.42</td>
<td>4.6</td>
<td>0.20</td>
<td>[15]</td>
</tr>
<tr>
<td>Cu$_3$SbSe$_4$</td>
<td>575</td>
<td>270</td>
<td>1.1</td>
<td>5</td>
<td>0.19</td>
<td>[4]</td>
</tr>
</tbody>
</table>
for the indentation of an isotropic sample\textsuperscript{17} is used to relate the contact stiffness and the projected contact area between indenter and sample to the indentation modulus, and is given by

\[ E = \frac{s}{2\beta} \sqrt{\pi A}, \]

(1)

where \( \beta = 1.034 \) for Berkovich indenter and \( A \) is the area of indentation, which is given by

\[ A = 3\sqrt{3}h_c^2 \tan^2 \theta, \]

(2)

where a semi-angle \( \theta = 65.3^\circ \) for diamond tip is used. AFM images of Cu\textsubscript{3}SbSe\textsubscript{3} and Cu\textsubscript{3}SbSe\textsubscript{4} sample after fine polishing and surfaces with indentation marks at different loads given in volts (2 V, 2.5 V, and 3 V) has been shown as an inset of Figs. 3(a) and 3(b). From Figs. 3(a) and 3(b), the unloading curve of load vs distance plot for a trig threshold of 1.5 V, the maximum load \( P_{\text{max}} \), and maximum depth of indentation \( h_{\text{max}} \) is estimated for both Cu\textsubscript{3}SbSe\textsubscript{3} and Cu\textsubscript{3}SbSe\textsubscript{4} systems. The plastic deformation depth \( h_c \) is measured from the point of no load. From the F-D plot, the slope near maximum load \( S = dP/dh \) gives the contact stiffness. The contact depth \( h_c \) is given by

\[ h_c = h - \frac{P}{S}, \]

(3)

where \( \varepsilon = 0.75 \) is for Berkovich\textsuperscript{16} indenter. From the F-D plot, considering the elastic deflection of the surface, the critical depth of indentation, \( h_c \), is calculated. The hardness of the sample is given by

\[ H = \frac{P}{24.5h_c^2}. \]

(4)

From the above analysis of F-D curves, the hardness and modulus of elasticity for Cu\textsubscript{3}SbSe\textsubscript{3} and Cu\textsubscript{3}SbSe\textsubscript{4} was found to be 0.85 GPa, 0.63 GPa and 0.39 GPa, 1.06 GPa, respectively. The measured Vickers hardness (VHN) found to be 0.9 GPa and 0.65 for Cu\textsubscript{3}SbSe\textsubscript{3} and Cu\textsubscript{3}SbSe\textsubscript{4}, respectively. This suggests that the hardness values measured by AFM were in fair agreement with the Vickers hardness values. Further, the hardness of Cu\textsubscript{3}SbSe\textsubscript{3} samples is much higher than Cu\textsubscript{3}SbSe\textsubscript{4} as well as to those of reported for other state-of-the-art TE materials\textsuperscript{18,19} as shown in inset of Fig. 4(a). All these reported values are within 5% of uncertainty.
Fracture toughness was estimated by a method proposed by Niihara et al., which is quite accurate and successful for a range of brittle materials. According to this method, the fracture toughness \( K_{IC} \) as measured by Vicker's indentation-crack technique with Palmqvist crack model is given as

\[
K_{IC} = 0.0089 \left( \frac{E}{H} \right)^{2/3} \times \frac{P}{a^{1/2}}, \quad 2.5 \geq \frac{l}{a} \geq 0.25,
\]

where \( P \) is the load, \( l \) is the crack length, \( a \) is half-diagonal of Vicker's indentation, \( E \) is the Young's modulus, and \( H \) is the hardness. In the present work, dimensions “\( a \)” and “\( l \)” were measured using FESEM for better accuracy of the results (Figs. 4(a) and 4(b)). The calculated fracture toughness of \( \text{Cu}_3\text{SbSe}_3 \) and \( \text{Cu}_3\text{SbSe}_4 \) found to be \( 0.63 \pm 0.05 \) and \( 0.80 \pm 0.03 \) MPa m\(^{1/2}\), respectively, which are comparable with the other state-of-the-art TE materials (as shown in inset of Fig. 4(b)). Moreover, it is well known that the fine grain size in nanostructured alloys helps to minimize the dislocation pile-up stresses resulting in improvement in fracture toughness. In the present study, it has been observed that the intrinsically nanostructure of \( \text{Cu}_3\text{SbSe}_3 \) and \( \text{Cu}_3\text{SbSe}_4 \) sample is expected to assist in localized fracture processes, which generally occurs during crack extension in many nanostructured materials and which in turn improves the fracture toughness. Furthermore, fracture toughness of the materials could also be improved by the addition of nanosized secondary reinforcements without losing its transport properties, where these reinforcements act as crack bridging and crack deflection.

It is well known that in order to enhance the efficiency of TE devices the segmentation of the thermoelectric elements is desirable, which is judged by the thermoelectric compatibility factor of the material, given as

\[
S = \frac{\sqrt{1 + ZT} - 1}{\alpha T}.
\]

where \( \alpha \) is Seebeck coefficient in Volts and \( T \) is temperature in Kelvin.

The thermoelectric compatibility of thermoelectric materials is currently of technological interest in TE device fabrication for enhancement of their efficiency. However, in order to derive a maximum TE efficiency benefit of employing segmentation in TE devices, the difference in compatibility factor \( S \) for the two TE materials should be less than a factor of \( 2^{26,28} \). The temperature dependence of TE compatibility factor for \( \text{Cu}_3\text{SbSe}_3 \) and \( \text{Cu}_3\text{SbSe}_4 \) sample are shown in Fig. 5. It is clear from this figure that the compatibility factor of \( \text{Cu}_3\text{SbSe}_3 \) is quite low as compared to \( \text{Cu}_3\text{SbSe}_4 \) at 550 K. In comparison to other state-of-the-art p-type TE materials, \( \text{Cu}_3\text{SbSe}_4 \) is reasonably good thus making it a suitable candidate for segmentation with other TE materials to derive enhanced efficiency benefit. However, the compatibility factor of these materials can further be enhanced by increasing their \( ZT \) employing suitable doping and adopting nanostructuring.

In summary, \( \text{Cu}_3\text{SbSe}_3 \) and \( \text{Cu}_3\text{SbSe}_4 \) thermoelectric compounds were synthesized by conventional fusion method followed by spark plasma sintering. \( \text{Cu}_3\text{SbSe}_4 \) exhibits a much higher \( ZT \) compared to \( \text{Cu}_3\text{SbSe}_3 \), which is due to its large electrical conductivity. Mechanical properties, in terms...
of hardness and fracture toughness, were measured using both Berkovich and Vickers indentors. Hardness and fracture toughness values for Cu₃SbSe₄ and Cu₃SbSe₃ were found to be 0.9 GPa, 0.65 GPa and 0.63 MPa m¹/₂, 0.80 MPa m¹/₂, respectively, which are superior compared to the existing state-of-the-art TE materials. The TE compatibility factor of Cu₃SbSe₄ was found to be 1.2 V, which is much higher than 0.2 V for Cu₃SbSe₃, which is mainly due to its higher ZT, owing to its higher electrical conductivity in comparison to Cu₃SbSe₃. Thermoelectric and mechanical properties of these materials can be improved further by suitable doping and nanostructuring methodology.

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