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Tuning the thermoelectric properties by manipulating copper in Cu$_2$SnSe$_3$ system

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Abstract: Cu$_{2+x}$SnSe$_3$ (0 $\leq$ x $\leq$ 0.08) compounds were synthesized by conventional solid-state reaction followed by spark plasma sintering (SPS) technique. Transport properties of the samples were measured as a function of temperature in the temperature range 323-773 K. As compared to Cu$_2$SnSe$_3$ sample, the electrical resistivity ($\rho$) is increased for the sample with $x$ = 0.04, thereafter a decrease is seen with further increase in copper content. Analysis of electrical resistivity indicates that small polaron hoping model is operative in the entire temperature range for all samples. The positive Seebeck coefficient ($S$) for the samples in the entire temperature range indicates that the majority charge carriers are holes. The highest figure of merit, $ZT$ ( = 0.32) was achieved at 773 K for the sample Cu$_{2.06}$SnSe$_3$ which is about 3 times that of Cu$_2$SnSe$_3$ sample. Maximum thermoelectric compatibility factor ($\approx 1.28$ V$^{-1}$) was observed at 673 K for the sample Cu$_{2.08}$SnSe$_3$.

KEYWORDS: A. alloys, C. X-ray diffraction, D. electrical properties, D. thermal conductivity, D. thermoelectrics
1. Introduction:

The unprecedented economic and societal growth has attributed to supplies of the ‘Big Three’ energy sources; viz. oil, coal and natural gas [1]. It may be noted that more than 60% of the energy generated is wasted as heat. Even a small amount of utilizing this waste heat can perhaps have great effect on global energy issues. In this context, thermoelectric materials play important role in converting waste heat into electricity. Thermoelectricity is the phenomenon of the direct conversion of temperature difference to electricity and vice versa. The efficiency of thermoelectric materials is given by a dimensionless quantity known as figure of merit (ZT), which is given by the expression \( ZT = \frac{S^2 T}{\kappa \rho} \), where \( S \) is the Seebeck coefficient, \( \rho \) is the electrical resistivity, \( \kappa \) is the total thermal conductivity and \( T \) is the absolute temperature. Good thermoelectric materials should have high ZT, which means high Seebeck coefficient, low electrical resistivity and low thermal conductivity [2-5].

Generally, thermoelectric materials are classified on the basis of the temperature range of their applications. The classification is (a) Cryogenic range (4-250 K): Materials in this range are primarily used for Peltier cooling. CsBi₄Te₆ is a good example for such low temperature applications [6]. By modifying the band structure or by doping, these materials exhibit ZT values of about 0.8 at 225 K. The major heat sources in this temperature range include air compressors, refrigerators, furnace doors and electronic circuits. (b) Near room-temperature applications (300-500 K): Bi₂Te₃ is the best material in this temperature range and it was the first thermoelectric material to have high ZT value in 1950s [7-9]. The heat sources for this temperature range include gas turbine exhaust, steam boiler exhaust, ovens and automotive exhaust. (c) High-temperature applications (>900 K): These are typically used in power generators. PbS-CdS is a good example for high temperature power generation [10]. The heat sources for this temperature range are hydrogen plant, steel heating furnaces and metal refining furnaces.

There are two ways of enhancing ZT, viz. either by increasing Power factor \( (PF = \frac{S^2}{\rho}) \) or by reducing thermal conductivity (κ). There are several methodologies which have been used to enhance ZT. One of the most effective accomplishments in the improvement of high performance thermoelectric materials is the theory of “Phonon-Glass-Electron-Crystal” (PGEC) [11, 12]
which suggests that an ideal thermoelectric material must possess good electrical transport properties as that of crystals and low thermal conductivity as observed in glasses. During last two decades, optimization of thermoelectric properties via PGEC methodology has led to substantial enhancement in $ZT$ values of several thermoelectric materials [13,14]. Lately, the concept of PGEC has also been extended to “Phonon-Liquid-Electron-Crystal” (PLEC) which elucidates the enormously low lattice thermal conductivity which is witnessed in superionic materials like Cu$_2$Se [15].

The semiconductors which belong to the family I$_2$-IV-VI$_3$ found to have applications in various field of thermoelectrics. In particular, Cu$_2$SnSe$_3$ is a p-type semiconductor with band gap in the range 0.8-1.7 eV and has high optical absorption coefficient ($10^4$-$10^5$ cm$^{-1}$) [16]. The properties for Cu$_2$SnSe$_3$ can be modified by doping. Many attempts have been made by researchers in enhancing the $ZT$ value of Cu$_2$SnSe$_3$ system by doping elements like In, Mn, Ga, Sb and Pb at Sn site [15, 17-20].

Literature suggests that stoichiometry plays an important role as far as $ZT$ of thermoelectric materials is concerned. It has been well realized that tiny deviations in the chemical composition from stoichiometry can affect the physical properties of thermoelectric materials like band gap, carrier concentration, and mobility which in turn effect the thermoelectric properties [21, 22]. Yu et al. [23] reported the thermoelectric properties of Cu$_{2-x}$Se (0.05≤$x$≤0.25) binary compounds, and observed an increase in electrical conductivity and decrease in Seebeck coefficient with decrease in Cu content. This is attributed due to increase in Cu vacancies which leads to an increase in hole concentration and they observed highest $ZT = 0.46$ at 750 K for the compound Cu$_{1.95}$Se. Li et al. [24] studied the thermoelectric properties of Cu$_{2+\delta}$SnSe$_4$ (-0.01≤$\delta$≤0.1) system and reported low lattice thermal conductivity of 0.6 W/mK for the compound Cu$_{1.99}$SnSe$_4$. This is attributed to vacancies created on cation site. The maximum $ZT$ (= 0.6) at 700 K was observed for the compound Cu$_{1.99}$SnSe$_4$. Kumar et al. [25] studied the copper deficiency in Cu$_{3-\delta}$SbSe$_4$ (0≤$\delta$≤0.04) system and reported maximum $ZT = 0.59$ at 650 K, for the compound Cu$_{2.98}$SbSe$_4$. Wei et al. [26] studied the thermoelectric properties of Cu deficient in Cu$_{3-x}$SbSe$_4$ (0≤$x$≤0.075) samples. They observed that increase in Cu deficiency increases the hole concentration which in turn enhances the electrical conductivity. However, Seebeck coefficient retained its large value. The maximum $ZT$ (0.5 at 673 K) was reported for the
compound Cu$_{2.925}$SnSe$_4$. Huang et al. [27] studied the thermoelectric properties of Cu deficient Cu$_{2-x}$GeSe$_3$ ($0 \leq x \leq 0.2$) system, and it was observed that Cu deficiency leads to increase in hole concentration and reported highest ZT (0.65 at 758 K) for the compound Cu$_{1.95}$GeSe$_3$.

There are perhaps no reports on manipulation of Cu site in Cu$_2$SnSe$_3$ system. This motivated us to undertake studies on optimization of Cu content in Cu$_2$SnSe$_3$ system. In the present communication, we explore the high temperature thermoelectric properties of Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) compounds. It is anticipated that an increase in Cu content might decrease the carrier concentration which in turn may increase Seebeck coefficient. In the present work, we aim to estimate optimum concentration of Cu which may provide higher ZT values.

2. Experimental details

Polycrystalline samples with nominal composition Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) were synthesized by conventional solid state reaction method. High purity powders of Cu (99.7%, Lobo Chemi), Se (99.999%, Alfa Aesar), and Sn (99.999%, Alfa Aesar) in stoichiometry proportion were mixed homogeneously in an agate mortar and ground. The powder was pelletized and vacuum sealed in quartz tube. The sealed ampoules were annealed at 450°C and allowed to cool naturally room temperature. The obtained pellets were crushed and the powder was pressed uniaxially in a graphite die at a pressure of 60 MPa at 300 °C for 5 minutes at a heating rate of 250 °C/min in vacuum conditions (≈ 4 Pa) using spark plasma sintering (SPS; SPS Syntex-725). The room temperature X-ray diffraction (XRD) was recorded to reveal the structure and lattice parameters of prepared samples using Rigaku Miniflex diffractometer. To further analyze the XRD data, Rietveld refinement technique was employed using Fullprof program. The surface morphology of the samples was imaged using Scanning Electron Microscopy (SEM) attached with Energy Dispersive X-ray (EDAX) analyzer (EVO MA18 with Oxford EDS (X-act)). EDAX measurement was carried out to ascertain the elemental composition of dopants in the prepared samples. The Seebeck coefficient (S) and electrical resistivity (ρ) measurements were carried out simultaneously with an ULVAC-RIKO ZEM3 from room temperature to 773 K under low-pressure helium atmosphere. The thermal conductivity was calculated using the equation $\kappa = \lambda DC_p$ (where $\lambda$, $D$ and $C_p$ are the thermal diffusivity, density and specific heat capacity, respectively). The thermal diffusivity was measured under vacuum in a NETZSCH LFA-457 laser flash system. Differential Scanning Calorimeter (Netzsch, DSC 404 F3) was used to
measure the specific heat $C_p$ of the samples. Density of samples was determined using Archimedes principle. Thermal diffusivity, electrical conductivity, Seebeck coefficient were respectively measured with inaccuracy of $\pm 6\%$, $\pm 10\%$ and $\pm 7\%$ and the inaccuracies in the measurement of specific heat and density were $\pm 8\%$ and $\pm 0.5\%$ respectively.

3. Results and discussion

3.1 Structural properties

3.1.1 XRD

The room temperature powder X-ray diffraction patterns for Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) samples were recorded and the data was analyzed using Rietveld refinement. Fig. 1 shows the Rietveld refined pattern for Cu$_2$SnSe$_3$ as well as excess Cu compounds. From the analysis of Rietveld refinement, we observe that all the samples exhibit cubic structure (space group $P\bar{4}3m$), indicating that variation in Cu stoichiometry in Cu$_2$SnSe$_3$ does not introduce any phase change within the experimental limits of XRD setup. In all the samples a small amount (<1 %) of SnSe impurity phase is observed at 29.7$^\circ$ of 2-theta which is revealed from power XRD analysis. This amount is very negligible, it is expected that it will not affect the electrical properties of prepared samples [28]. From the refinement, we have estimated the lattice parameters, unit cell volume and goodness of the fit which are presented in table 1. It is observed that the lattice parameters and cell volume increase monotonically with increase in Cu content. This behavior may be attributed to disorder in cation site in which either increasing Cu$_{Sn}$ or decreasing Sn$_{Cu}$ defects leads to an increase in cell volume. It may also be noted that the atomic radii of Sn$^{4+}$ (0.64 Å) is smaller than Cu$^{1+}$ (0.77 Å) which perhaps may be one of the reasons for increase in cell volume with increase in Cu content.

3.1.2 Scanning electron microscopy (SEM)

The surface morphology of Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) samples was investigated using SEM and SEM pictures are presented in Fig. 2. The morphologies of the samples exhibit similar features. Homogeneous and continuous large grain growth in conjunction with low porosity confirms the densification of all the prepared samples. In order to estimate the chemical composition of the samples, EDS studies were done which reveal that the chemical composition of prepared samples match well with the nominal composition and the results are tabulated in table 2.
3.2 Electrical resistivity (ρ)

The temperature dependent electrical resistivity for Cu$_{2+x}$SnSe$_3$ (0≤x≤0.08) samples is shown in Fig. 3(a). The electrical resistivity for the samples is observed to increase with increase in temperature, which indicates degenerate semiconducting behavior and the results are consistent with earlier reports [28, 29]. Now we describe the effect of Cu content on electrical resistivity in Cu$_{2+x}$SnSe$_3$ system. It is observed that by increasing Cu content in Cu$_{2+x}$SnSe$_3$ system, the electrical resistivity is greatly increased for the sample with x=0.04. The decrease in carrier concentration may be one of the reason for this kind of behavior. However, with further increase in x, a systematic decrease in electrical resistivity is observed. The lowest electrical value is observed for the Cu$_2$SnSe$_3$ sample (7.89 µΩ-m) at 773 K. To check the temperature dependence of electrical resistivity for Cu$_{2+x}$SnSe$_3$ (0 ≤ x ≤ 0.08) samples, we have used small polaron hopping (SPH) model which is given by [30, 31],

\[ \rho = \rho_0 T \exp \left( \frac{E_A}{k_B T} \right) \]  

where, \( \rho_0 \) is the pre-exponential factor which is independent of temperature, \( E_A \) is the activation energy, \( k_B \) is the Boltzmann constant. To validate this model a plot of \( \ln(\rho/T) \) versus \( 1/T \) is expected to be a straight line. Fig. 3(b) shows such a plot for Cu$_{2+x}$SnSe$_3$ (0 ≤ x ≤ 0.08) samples, which suggests that SPH can explain the conduction mechanism in the temperature range 330-476 K. From the slope of the graph activation energy \( (E_A) \) was determined. The evaluated activation energy \( (E_A) \) for the samples is given in table 3.

3.3 Seebeck coefficient (S):

The Seebeck coefficient for Cu$_{2+x}$SnSe$_3$ (0 ≤ x ≤ 0.08) samples as a function of temperature is plotted in Fig. 4(a). The positive values of Seebeck coefficient over the whole measured temperature range indicates that holes are majority charge carriers. The Seebeck coefficient for the samples increases with increase in temperature which demonstrates that the samples show heavily doped semiconducting behavior [17-20]. Now we describe the effect of Cu content on Seebeck coefficient in Cu$_{2+x}$SnSe$_3$ system. It is observed that the Seebeck coefficient has greatly increased for x=0.04, with further increase in x, there is a systematic decrease in Seebeck coefficient. The variation of Seebeck coefficient has a correlation with electrical resistivity i.e. it shows similar trend. The maximum value of Seebeck coefficient (244.8µV/K) is
observed for $x=0.04$ which is approximately 3.4 times that of Cu$_2$SnSe$_3$ sample. The increase in Seebeck coefficient for the sample with $x=0.04$ as compared to Cu$_2$SnSe$_3$ sample. This may be due to decrease in carrier concentration. One can roughly estimate the carrier concentration using Mott’s formula for the diffusion of thermopower of a free electron gas at the temperature above the Debye temperature ($\theta_D$) which is given by [28, 29, 32],

$$S(T > \theta_D) = \frac{8k_B^2n^2}{3e\hbar^2} m^* \left(\frac{\pi}{3n}\right)^{2/3} T$$  \hspace{1cm} (2)

where $m^*$ being the charge mass, $e$ is the carrier charge, $k_B$ the Boltzmann constant, $\hbar$ is the Planck’s constant, $T$ is the absolute temperature, and $n$ is the carrier concentration respectively. For the estimation of $n$, $S(T)$ data was fitted with temperature by considering $m^* = m_e$. The fitted plots are represented in Fig. 4(b). From the slope of the linear fit, we have calculated the values of carrier concentration ($n$). The estimated values of carrier concentration for all the samples are given in table 3. It may be noted that the variation of $n$ is consistent with that of $S(T)$ data and this variation can be explained in terms of defects caused by the non-stoichiometry of Cu$_2$SnSe$_3$ samples. It is observed that pure sample has the highest value of $n$, this is because of the acceptor defects (energy levels near to the valence band will accept the electron known as acceptor) V$_{Cu}^{1-}$ & Cu$_{Sn}^{3-}$ created by the moving Cu$^{1+}$ ion to the Sn$^{4+}$ site. The minimum value of $n$ is observed for $x=0.04$, which is mainly because of Sn$_{Cu}^{2+}$ donor defect (energy level located near the conduction band may donate electrons to the conduction band and is considered as Donor). With further increase in $x>0.04$, the value of $n$ is observed to increase. This may be because of minor Cu$_{Sn}^{3-}$ antisite defect which usually increases with increase in Cu concentration. Thus, the carrier concentration and electronic transport properties are strongly correlated with variation in Cu content and induced defects.

We have also computed of Hall mobility ($\mu_H$) at room temperature for all the samples using the well-known equation [28],

$$\mu_H = \frac{1}{nep}$$  \hspace{1cm} (3)

where, $n$ is carrier concentration and $\rho$ is the electrical resistivity and $e$ is the electron charge. Table 2 presents the values of Hall mobility for the samples under present investigation. It is observed that Hall mobility of Cu$_2$SnSe$_3$ sample is $2.9 \times 10^{-3} \text{ m}^2/\text{V}s$ which is higher than the reported value in literature [15] which may be due to different sample preparation conditions. It
may be noted that the variation of Hall mobility is consistent with carrier concentration.

3.4 Thermal conductivity \((\kappa)\)

The temperature dependence of thermal conductivity for Cu\(_{2+x}\)SnSe\(_3\) \((0 \leq x \leq 0.08)\) samples is shown in Fig. 5(a). The thermal conductivity decreases with increase in temperature for the samples in the entire temperature range in a similar manner as reported for ternary diamond like semiconductors [17, 18, 20]. This is essentially due to the dominance of phonon scattering at high temperatures. The observed value of thermal conductivity at room temperature for Cu\(_2\)SnSe\(_3\) samples is 7.11 W/mK. Now we discuss the effect of Cu content on thermal conductivity in Cu\(_{2+x}\)SnSe\(_3\) system. It is observed that thermal conductivity is reduced for the sample with \(x=0.04\), however with further increase in \(x\), a systematic increase in thermal conductivity was observed. This is kind of behavior is attributed to the enhanced phonon scattering and intrinsic complex bonding. The lowest thermal conductivity \((\sim 1.5\) W/mK) is observed for the sample Cu\(_{2.04}\)SnSe\(_3\) which is mainly because of large grain boundary with low porosity is observed in this sample, this is confirmed by scanning electron microscope images.

The total thermal conductivity is expressed as sum of electronic thermal conductivity \((\kappa_e)\) and lattice thermal conductivity \((\kappa_L)\), i.e., \(\kappa = \kappa_e + \kappa_L\). The electronic contribution was calculated from the electrical resistivity by applying Wiedemann-Franz law which is given by,

\[
\kappa_e = \frac{L_0 T}{\rho} \tag{4}
\]

where, \(L_0 = 2.44 \times 10^{-8} \ V^2/K^2\) (called Lorenz number) and \(\rho\) is electrical resistivity. From Eq. 4 one can conclude that \(\kappa_e\) varies inversely with electrical resistivity. We have estimated \(\kappa_e\) from Eq. 4 and observed that the contribution from \(\kappa_e\) is about 45% to the total thermal conductivity for Cu\(_2\)SnSe\(_3\) sample whereas for higher Cu concentration, it is less than 1%. This is because of lowest electrical resistivity observed for the Cu\(_2\)SnSe\(_3\) sample than other samples with higher Cu concentrations. Thus we conclude that measured thermal conductivity for the Cu\(_2\)SnSe\(_3\) sample is associated with both phonons as well as charge carriers and for higher Cu concentrations it is mainly with the lattice phonons rather than charge carriers. The temperature dependence of estimated lattice thermal conductivity for the sample is which shown in Fig. 5(b). The \(1/T\)
dependence of lattice thermal conductivity for the samples indicates a dominant Umklapp phonon-phonon scattering at high temperatures which is shown in the insets of Fig. 5(b) [28,33].

3.5 Power factor and Figure of merit:

Power factor can be enhanced by different approaches such as doping, band engineering [34, 35], heavy valence/conduction band convergence [36, 37], quantum confinement effect and electron energy barrier filtering [38, 39]. The power factor (\(PF\)) can be estimated using the expression

\[
PF = \frac{\sigma^2}{\rho} \tag{5}
\]

The temperature dependence of \(PF\) for \(\text{Cu}_{2+x}\text{SnSe}_3\) (0≤\(x\)≤0.08) is shown in the insets of Fig. 6. It is observed that \(PF\) is reduced for the sample with \(x=0.04\), however, with further increase in \(x\), \(PF\) is observed to increase. The maximum \(PF\) (7.71 µW/cmK²) is observed for the sample \(\text{Cu}_{2.08}\text{SnSe}_3\) at 670 K, which is approximately 1.5 times that of \(\text{Cu}_2\text{SnSe}_3\) (5.02 µW/cmK²) at the same temperature. Fig. 6 shows the thermoelectric figure of merit (\(ZT\)) for the \(\text{Cu}_{2+x}\text{SnSe}_3\) (0≤\(x\)≤0.08) samples as a function of temperature. The \(ZT\) for all the samples increases slowly with increase in temperature till 500 K, beyond this, a sharp increase can be seen in \(ZT\) for all the samples. The maximum \(ZT\) (0.32) was observed for \(\text{Cu}_{2.06}\text{SnSe}_3\) sample at 773 K which perhaps is due to balanced conditions of \(PF\) and thermal conductivity. The value of \(ZT\) for the sample \(x=0.06\) is approximately three times that of \(\text{Cu}_2\text{SnSe}_3\) sample.

3.6 Compatibility factor:

Usually the efficiency of a thermoelectric generator is governed by the thermoelectric properties of the material and the temperature drop across the generator. The temperature difference, \(\Delta T = T_h - T_c\) where \(T_h\) and \(T_c\) are temperatures at the hot side and cold side respectively, sets the upper limit of efficiency through Carnot efficiency which is given by,

\[
\eta = \frac{\Delta T}{T_h} \tag{5}
\]

To attain the maximum efficiency for any material, large temperature differences as well as high figure of merit for materials are required. But the thermoelectric properties of the materials (\(S\), \(\rho\) and \(\kappa\)) vary with temperature and one cannot use the same material throughout the temperature range. However, the material with high efficiency at high temperature can be segmented with a different material which has high efficiency at low temperature. In this way both materials are operating only in their most efficient temperature range. The thermoelectric
compatibility of several thermoelectric materials are currently possessing technological interest in the device fabrication for the development of segmented TE generators for obtaining maximum efficiency [40]. The thermoelectric compatibility factor can be calculated from the data of $S(T)$ and $ZT$ which is given by,
\[
C = \frac{\sqrt{T+ZT-1}}{ST} \quad (6)
\]
where $S$ is Seebeck coefficient and $T$ is temperature [41]. To fabricate a TE device using segmented method, the compatibility of TE material is to be considered in order to draw maximum power from TE devices. The compatibility factor for the materials used for segmentation should be less than 2 in order to obtain maximum efficiency from the device. In the present work, we have calculated the thermoelectric compatibility factor for all the samples and its temperature dependence is represented in Fig. 7. It is observed that the compatibility factor increases with increasing temperature for all the samples. The highest compatibility (1.2 V$^{-1}$) factor is observed for the sample with $x=0.08$ at 673 K.

4. Conclusions:

We have investigated the high temperature thermoelectric properties of Cu excess Cu$_{2+x}$SnSe$_3$ $(0 \leq x \leq 0.08)$ system in the temperature range 300 -773 K. The powder XRD Reitveld analysis confirms that the samples are crystalline in nature with cubic structure (space group $F43m$). The electrical transport properties for all the samples demonstrate heavily doped semiconducting behavior. From the electrical resistivity data we have validated the small polaron hopping model in the entire temperature region and the positive values of Seebeck coefficient indicates holes are the majority carriers. The thermal conductivity for all the samples exhibits a similar temperature dependent characteristic, i.e. $\kappa(T)$ decreases with increase in temperature. The electronic thermal conductivity is estimated using Wiedeman-Franz law and it is found that the total thermal conductivity is predominantly due both electronic and lattice thermal conductivity. The highest value of $ZT$ ($= 0.32$) is achieved for the sample Cu$_{2.06}$SnSe$_3$ at 773 K, this value is 3 times that of Cu$_2$SnSe$_3$ sample. The highest value of thermoelectric compatibility (1.28 V$^{-1}$) factor is reported for the sample Cu$_{2.06}$SnSe$_3$ at 673 K.

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Table 1. Rietveld refined parameters of X-ray diffraction data of Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) samples.

<table>
<thead>
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<th>$x$</th>
<th>system</th>
<th>Space group</th>
<th>$a=b=c$ (Å)</th>
<th>$\alpha=\beta=\gamma$</th>
<th>Cell volume (Å$^3$)</th>
<th>Bragg R-factor</th>
<th>RF-Factor</th>
<th>$\chi^2$</th>
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<td>0</td>
<td>cubic</td>
<td>$F43m$</td>
<td>5.686 (0.003)</td>
<td>90°</td>
<td>183.83 (0.020)</td>
<td>2.92</td>
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<td>90°</td>
<td>184.02 (0.02)</td>
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<td>184.99 (0.01)</td>
<td>5.96</td>
<td>5.58</td>
<td>2.81</td>
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Table 2. EDS results for Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) samples.

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<td>3.02</td>
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<td>Se</td>
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Table 3. From $S(T)$ fit data, estimated values of $n$ and $\mu_H$ at room temperature along with activation energy $E_A$ obtained by the best fit of electrical resistivity plot using SPH model for Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) samples.

<table>
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<tr>
<th>$x$</th>
<th>$n$ ($10^{26}$/m$^3$)</th>
<th>$\mu_H$ ($10^{-3}$) m$^2$/Vs</th>
<th>$E_A$ (meV)</th>
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<tr>
<td>0</td>
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<td>1.7</td>
<td>1.3</td>
<td>19.3</td>
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<td>0.08</td>
<td>2.2</td>
<td>1.6</td>
<td>15.2</td>
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Fig. 1. Rietveld refinement plots of Cu$_{2+x}$SnSe$_3$ (0 ≤ x ≤ 0.08) samples.
Fig. 2. SEM images of (a) Cu$_2$SnSe$_3$ (b) Cu$_{2.04}$SnSe$_3$ (c) Cu$_{2.06}$SnSe$_3$ and (d) Cu$_{2.08}$SnSe$_3$ samples
Fig. 3. (a) Temperature dependence of electrical resistivity of Cu$_{2+x}$SnSe$_3$ (0≤x≤0.08) compounds, (b) Plot of ln(ρ/T) versus 1/T for the resistivity data of Cu$_{2+x}$SnSe$_3$ (0≤x≤0.08) system fitting of SPH in the high temperature regime.
Fig. 4. (a) Temperature dependence of Seebeck coefficient for Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) compounds, (b) Plot of $S$ versus $T$ by fitting Mott’s equation to thermopower data of Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) system.
Fig. 5. (a) Temperature dependence of thermal conductivity plot of Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) compounds, (b) lattice thermal conductivity ($\kappa_L$) for all the sample in the entire temperature range and inset shows the $1/T$ dependence of lattice thermal conductivity.
Fig. 6. Temperature dependence of figure of merit ($ZT$) of Cu$_{2+x}$SnSe$_3$ ($0 \leq x \leq 0.08$) compounds and inset shows the variation of power factor for presently investigated samples in the entire temperature range.
Fig. 7. Compatibility factor of p-type polycrystalline Cu_{2+x}SnSe_3 (0 ≤ x ≤ 0.08) samples in the entire temperature range.
Highlights

- All the samples are in single phase
- Electrical resistivity and Seebeck data follow Variable hopping model at low temperatures
- $ZT = 0.32$ was achieved at $773 \, K$ for the sample $Cu_{2.06}SnSe_3$
- Compatibility factor $\sim 1.28 \, V^{-1}$ was observed at $673 \, K$ for the sample $Cu_{2.08}SnSe_3$. 