On the high-energy electron beam irradiation-induced defects in Cu$_2$SnSe$_3$ system: an effort towards modifying the structure, microstructure, and thermoelectric transport

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Received: 1 July 2022
Accepted: 26 August 2022
Published online: 7 September 2022

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ABSTRACT

We present report on modulating thermoelectric transport in Cu$_2$SnSe$_3$ system via irradiating high-energy electrons of energy of about 8 MeV. Electrical transport is investigated at near room to mid-temperature regime (300–700 K). A smooth transition from degenerate to non-degenerate type of conductivity is observed in all the samples, which indicates the injection of minority carriers with ionisation of defects at high temperatures. Defects created through the knock-on displacement of the constituent atoms is successful in promoting the power factor in the material. Cu$_2$SnSe$_3$ irradiated with 50 kGy is found to achieve highest power factor of 228 $\mu$W/mK$^2$ at 700 K, which is nearly 20% higher than the power factor of pristine material at the same temperature.

1 Introduction

Thermoelectric (TE) materials have emerged as promising candidates for renewable energy technology that is capable in harvesting electricity by the temperature gradient. Reciprocally dependent electronic and thermal transport parameters can be related to the figure of merit ($ZT$) that defines the thermoelectric performance of a material which is given by [1]

$$ZT = \frac{S^2 \sigma T}{\kappa},$$

where $S$ is Seebeck coefficient, $\sigma$ and $\kappa$ are electrical and thermal conductivities, respectively. Balancing these entangled properties is a major challenge to have a good TE material. The optimal electronic transport depends primarily on the weighted mobility $\mu_w$, which in turn varies with the density of states effective mass $m^*$. Recently, Snyder et al. [2] have proposed an equation which can be used to deduce

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https://doi.org/10.1007/s10854-022-09005-y
temperature-dependent weighted mobility via connecting the electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) which is given by

$$
\mu_w = \frac{3k^3}{8\pi^2(2m_e k_B T)^{3/2}} \left( \frac{\exp\left(\frac{|s|}{k_B T} - 2\right)}{1 + \exp\left(-5\left(\frac{|s|}{k_B T} - 1\right)\right)} + \frac{3}{\pi^2 k_B^2 e^2} \right),
$$

(2)

Here $\mu_w$ is directly related to the thermoelectric quality factor $B$ i.e. $\mu_w \propto B$ which turns out to be an essential factor that decides the superior thermoelectric behaviour in any material. Hence, modulating $\mu_w$ is one of the ways to enhance the power factor [3].

Cu$_2$SnSe$_3$ is a diamond-structured narrow band gap semiconductor of I–IV–VI family of materials in which Cu–Se bond facilitates degenerate electronic transport. Three-dimensional bond network with five possible tetrahedra makes Cu$_2$SnSe$_3$ highly conductive in comparison with the state-of-the-art TE materials systems like SiGe, SiC, etc. [4, 5]. Sn atom residing inside the network of Cu–Se promotes the phonon scattering, thereby fulfilling the criteria of phonon glass electron crystal (PGEC). This facilitates the low thermal conductivity in Cu$_2$SnSe$_3$ as compared to the most of binary chalcogenide systems [6]. Cu$_2$SnSe$_3$ is found to crystallise into different allotropic forms viz. cubic, monoclinic, and rhombohedral [7–9], which depends on the method of synthesis. Since Sn atom in the crystal contributes to the electronic transport, most of the efforts done to optimise the charge transport are at Sn site [5]. In was found to be an effective dopant in enhancing the power factor and hence the highest ZT is reported for In-doped samples [5, 10, 11]. Elemental doping [12, 13], composites [14, 15], and tuning in stoichiometry [16, 17] are promising strategies in promoting the thermoelectric behaviour in these systems. Other than elemental replacement and introducing secondary phases, irradiating the materials is found to show a direct effect on the structure and other electrophysical properties [18–20]. Displacement of constituent atoms via knocking them on to the defect states has been reported using low-energy electrons [21]. Electron beam is used in various carbon-based nanostructured materials to modulate the structural properties [18, 22]. Literature also reports that electron beam irradiation can modify transport properties in perovskite metal oxides [23, 24]. Takashiri et al. [25] have done studies using 0.17 MeV electron beam on Bi–Sb–Te nanocrystalline films. They observed an increase in power factor of the system. Electron irradiation (8 MeV)-induced defects in Bi$_2$Se$_3$ are reported by Saji et al. [26], which demonstrates an increase in the carrier density. It is evident from the literature that the electron beam irradiation is one of the effective ways in modifying the electronic transport in thermoelectric semiconductors. There are not many reports on the influence of electron-induced defects on thermoelectric materials especially in diamond-structured Cu-based materials. The present report deals with a novel ex-situ approach to modify the structure and microstructure so as to improve the TE performance via inducing the crystal distortion through knock-on displacement of atoms by high-energy electrons.

2 Experimental details

Polycrystalline samples of Cu$_2$SnSe$_3$ were synthesised via conventional solid-state reaction route. Highly pure (4 N) elemental powders of Cu (Loba chemie), Se (Sigma Aldrich), and Sn (Sigma Aldrich) were weighed according to the nominal stoichiometry and blended well in agate mortar for about 2 h. The blended powder was compacted into rectangular pellets of dimension 11 mm × 6 mm × 2 mm using a uniaxial hydraulic press with Tungsten carbide die. The pellets were encapsulated inside quartz ampoule at high vacuum ($10^{-6}$ mbar) and then sintered at 773 K for 72 h followed by natural cooling. The metallurgical process was repeated with a sintering temperature of 523 K for 24 h to obtain good quality densified pellets with homogeneity. Samples from the same branch were exposed to electron beam of energy 8 MeV with a fluence of $10^{14}$ cm$^{-2}$ using a Linear accelerator (LINAC). The samples were irradiated with a dosage of 50 kGy, 100 kGy, and 150 kGy. The stopping power and CSDA range of the radiation are calculated using ESTAR program. For Cu$_2$SnSe$_3$ samples with density of 3.80 g/cm$^3$, stopping power is found to be 1.886 MeV g/cm$^2$ and
CSDA range is 5.205 g/cm². To confirm the phase formation, X-ray diffraction was performed at room temperature (Rigaku miniflex 600 5G). Rietveld analysis of the XRD profile was carried to derive crystallographic information of the pure and electron-irradiated samples. Using EVO MA18 Scanning electron microscope, the topographical details of the samples were inspected. Elemental distribution in the samples was analysed using Oxford EDS system attached to the SEM. Simultaneous high-temperature electrical resistivity and Seebeck coefficient measurements were done using Linseis LSR-3 system. Hall effect measurements were performed at room temperature using Ecopia HMS-5500 Hall measurement system employing van der Pauw geometry using InSn alloy ohmic contacts.

3 Results and discussions

3.1 Phase formation and microstructure

The XRD peaks of Cu₂SnSe₃ sample were indexed to JCPDS card #04-002-6015 [7], which shows the crystallisation of the material into cubic sphalerite-type structure consisting of the space group F43m. No changes in the structure were observed due to electron irradiation. The quantitative analysis of the phase was done using Rietveld analysis using Fullprof suite. The line profile was generated for cubic Cu₂SnSe₃ system with Pseudo-Voigt peak profile. The background variation is defined by a set of points with refinable heights. The obtained goodness-of-fit values verify the well fitting of experimental data with the generated line profile (see Fig. 1).

Fig. 1 Rietveld refined graphs of Cu₂SnSe₃ samples irradiated with a 0 kGy, b 50 kGy, c 100 kGy, d 150 kGy

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Crystallographic information with fit parameters is provided in Table 1. Shifting of the XRD peaks towards higher angle is noticed as the irradiation dosage is increased to 50 and 100 kGy beyond which the retrieving up of the peaks could be observed for the sample irradiation dosage 150 kGy as shown in Fig. 2. This behaviour is clearly reflected in the lattice constants, showing the distortion in the lattice with increasing irradiation dosage. The maximum energy transferred, $E_M$, into the constituent atom of mass $m_a$ from an electron of mass $m_e$ with kinetic energy $E$ is given by [25]

$$E_M = \frac{2m_aE(E + 2m_ec^2)}{[(m_a + m_e)c^2 + 2m_aE]}, \quad (3)$$

where $c$ is the speed of light. The evaluated $E_M$ values are listed in Table 2. Since the displacement energy values are found to be high, we presume the formation of knock-on displacement of the atoms thereby creating the point defects [21, 27].

SEM micrographs (Fig. 3) depict the densified microstructure of the synthesised samples with less visible porosities. Irregular growth of the agglomerated grain is identified in all the samples. Elemental distribution in the samples is found to be homogeneous with the recommended stoichiometry as per the EDS analysis as shown in Fig. 4. Even though well-defined changes could not be observed in the microstructure, the nano-level dots noted in the samples bombarded with higher dosage demonstrates the piercing of the high-energy electrons.

### 3.2 Electrical transport

The electrical resistivity of all the samples is measured in the temperature regime 300–700 K, which is shown in Fig. 5a. Electrical resistivity data show that it initially increases with the increase in temperature up to an optimal temperature (~ 450 K), above which it is observed to reduce with further rise in temperature. The slump in the resistivity seen in all the samples at high temperatures signify a smooth transition from degenerate to non-degenerate semiconducting behaviour. Possibility of the diffusion of minority carriers along with ionisation of the defects triggered at high temperatures could be the reason for the observed temperature dependency of charge transport [28, 29]. We suspect the hopping of small polarons at high temperatures where there can be a possibility of rise in phonon hopping rate in an Arrhenius manner. Hence, to explain the intrinsic nature of semiconducting behaviour of $\rho(T)$ Arrhenius equation is used with the assumption of existence of thermally activated carriers which is given by the expression,[30],

$$\rho = \rho_0 \left(\frac{E_a}{2k_B T}\right)^2, \quad (4)$$

where $E_a$ is the activation energy which is calculated from the linear fit of $\ln \rho$ versus $1/T$ plot. Perceiving a linear variation between $\ln \rho$ and $1/T$ beyond 450 K, all the samples confirm a non-degenerate type of behaviour. The $E_a$ value for pristine sample is estimated as 0.34 eV. For the 50 kGy irradiated sample, there is no change in $E_a$ value. Increase in activation energy for the samples irradiated with 100 kGy and 150 kGy can be associated to their higher resistivity.

### Table 1 Crystallographic information by Rietveld analysis of Cu$_2$SnSe$_3$ irradiated with different electron beam dosages

| Irradiation dosage | 0 kGy | 50 kGy | 100 kGy | 150 kGy |
|-------------------|-------|-------|--------|--------|
| System            | Cubic | Cubic | Cubic  | Cubic  |
| Space group       | F$\overline{4}$3m | F$\overline{4}$3m | F$\overline{4}$3m | F$\overline{4}$3m |
| $a = b = c$       | 5.688(6) | 5.683(5) | 5.683(7) | 5.688(1) |
| $\alpha = \beta = \gamma$ | 90 | 90 | 90 | 90 |
| GoF index         | 1.2 | 1.3 | 1.4 | 1.5 |
| $\chi^2$          | 1.3 | 1.6 | 1.9 | 2.3 |
| Maximum energy transferred $E_M$ | Cu | Sn | Se | }

![Fig. 2](image-url) Variation of lattice constants with irradiation dosage. Inset shows the major peak shift of pristine and irradiated Cu$_2$SnSe$_3$ samples.
as compared to the pristine. The \( E_a \) values of pristine and irradiated samples are given in Table 2. Decrease in the resistivity was observed for the lower dose of electrons (50 kGy), which may be connected to the increase in the Cu vacancies as well as Cu to Sn defects created due to the high-energy electrons. Beyond this, an increase in resistivity is found for the samples irradiated with 100 kGy and 150 kGy, indicating the creation of other types of defects that tend to reduce the acceptor levels. Hall measurements were done at room temperature to have a better perception into the electrical transport. Positive Hall coefficient of all the samples has clarified the p-type conductivity in all the samples. Carrier density is found to follow the same trend of electrical conductivity, which is comparable with the earlier reported values [31, 32].

Temperature-dependent Seebeck coefficient was measured in the temperature range, 300–700 K which is shown in Fig. 6a. Increase in Seebeck coefficient \([S (T)]\) with the increase in temperature signifies the existence of degeneracy in the materials. On the other
hand, resistivity shows a reverse trend with temperature. This may be attributed to the existence of partial degeneracy as reported previously in Cu$_2$SnSe$_3$ and isostructural materials [8, 29, 33]. To support the deviation in the thermopower, temperature-dependent Fermi energy and Lorenz number were derived using an algorithm called SPBcal developed by Chang et al. [34] under Java SE runtime environment 1.8.0_131. The equation used for Fermi energy is given by

\[ S = \pm \frac{k_B}{e} \left( \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right) \tag{5} \]

where \( \eta \) is the reduced Fermi energy which is linked to Fermi energy \( E_F \) as \( E_F/k_B T \). \( F_0(\eta) \) and \( F_1(\eta) \) are Fermi integrals of order \( n = 0 \) and \( 1 \), respectively. Fermi energy values [see Fig. 7 (b)] are found to be in the range 0.1–0.2 eV, which is considerably smaller than the activation energy as evaluated by thermal activation, thereby validating extrinsic p-type nature of the materials. The increased conductivity in 50 kGy is directly related with the increased Fermi energy. Considering the degenerate behaviour of all the samples at near room temperature, density of states effective mass \( m^* \) was estimated using Mott’s equation for diffusion thermopower as

\[ S(T > \theta_D) = \frac{\pi^2 k_B^2 2m^*}{e h (3n \pi^2)^{2/3}} T, \tag{6} \]

where \( n \) is the carrier density, \( m^* \) is the effective mass, and \( e \), \( h \), and \( k_B \) are electronic charge, Planck’s constant, and Boltzmann constant, respectively. Reduction in \( m^* \) values is observed with the increase of irradiation dosage thereby signifying the increased carrier mobility. The Lorenz number (\( L_0 \)) was further evaluated to support the partial degenerate behaviour in the materials using two different methodologies [34, 35] given by the following equations:

\[ L_0 = \frac{k_B^2}{e^2} \left( 3F_0(\eta)F_2(\eta) - 4F_1^2(\eta) \right) \frac{\eta}{F_0^2(\eta)} \tag{7} \]

\[ \text{a} \]

\[ L_0 = 1.5 + \exp \left[ - \frac{|S|}{116} \right] \tag{8} \]

where the unit of \( L_0 \) is \( 10^{-8} \) W\( \Omega^{-2} \) and \( S \) is in \( \mu \)V\( \Omega^{-1} \). Calculated values of \( L_0 \) are illustrated in Fig. 7a and b. Both the relations are based on the single parabolic band approximation. The values of \( L_0 \) deduced from both the methods are found to be in proximity within the error limits. \( L_0 \) values are found to lie above 1.9 \( \times 10^{-8} \) W\( \Omega^{-2} \) suggesting the partial degenerate behaviour of the samples.

To assess the total charge transport, weighted mobility (\( \mu_w \)) which is independent of carrier density was computed using Eq. (2). A decrease in \( \mu_w \) was found with increase in temperature witnessing the heavily doped nature of the materials up to a temperature of about 450 K. Beyond this an increase in \( \mu_w \) is observed with increase in temperature which may be caused by the rapid enhancement in number of carriers and hence the DOS effective mass \( m^* \). It can be noted that similar temperature behaviour is observed in electrical conductivity in all the samples indicating weighted mobility is one of the major factors controlling the transport behaviour in the present system. The upsurge in the weighted mobility at higher temperatures can be correlated to the partial degeneracy of Cu$_2$SnSe$_3$ samples. Power factor (\( S^2 \sigma \)) determined from the electrical properties are found to surge with temperature as shown in Fig. 8b. The results suggest that samples with higher weighted mobility were found to show higher power factor values. Zhang et al. [36] recently proposed a single material parameter ‘\( B_E \)’ referred to as ‘electronic quality factor’. For a pair of measurements of Seebeck coefficient (\( S \)) and electrical conductivity (\( \sigma \)) performed simultaneously at a given temperature, \( B_E \) is defined as

\[ B_E = \frac{S^2 \sigma}{1 + \exp[-5(S - 1)]} \left[ \frac{5}{S_\sigma^2/3 + 1 + \exp[5(S - 1)]} \right] \tag{9} \]

where \( S_\sigma = \frac{|S|}{S_\mu/\epsilon} \). This describes the electronic contribution to the power factor. Increased electronic quality factor is accompanied with the increase in power factor. Since the rapid surge in temperature-dependent \( B_E \) values is not observed, the possibility of the band convergence is ruled out. Further, the...
**Fig. 4** X-ray elemental mapping with EDX spectra at selected area of Cu$_2$SnSe$_3$ sample

**Fig. 5**

a) Temperature-dependent resistivity for pristine and irradiated samples. 

b) Linear fit to thermal activation model for (Eq. 4) Cu$_2$SnSe$_3$ samples irradiated with different dosages
bipolar contribution to the electronic transport is not prompt in the samples at high temperature. Cu$_2$SnSe$_3$ irradiated with dosage of 50 kGy is found to achieve the highest power factor of 228 $\mu$W/mK$^2$ at 700 K.

4 Conclusion

A systematic study is done on the effect of electron irradiation on the various properties of Cu$_2$SnSe$_3$ thermoelectric system synthesised by conventional solid state reaction. All the samples are found to crystallise into cubic sphalerite-type structure and no structural changes are observed in the irradiated samples. Electrical transport is investigated at near room to mid-temperature regime (300–700 K). A smooth transition from degenerate to non-degenerate type of conductivity is seen in all the samples indicating the injection of minority carriers with ionisation of defects at high temperature. Enhancement of electrical transport is observed at lower electron dosages. Defects created through the knock-on displacement of the constituent atoms enhance the power factor in the material. Cu$_2$SnSe$_3$ irradiated with 50 kGy of electrons is found to achieve maximum power factor of 228 $\mu$W/mK$^2$ at 700 K which is nearly 20% higher than the power factor of pristine material at 700 K.
Acknowledgements

One of the authors (AR) acknowledges DST-FIST Grant (SR/FIST/PS-1/2017/8) and Council of Scientific and Industrial Research Grant [Sanction No.: 03(1409)/17/EMR-II] for the financial support required for this work.

Author contributions

KG: methodology, measurements, and manuscript preparation. SM: methodology. AR: project administration, resources, supervision, and writing review and editing. PP, manuscript preparation. VCP, resources and methodology. VPV: resources and methodology. JD: resources and methodology.

Funding

Open access funding provided by Manipal Academy of Higher Education, Manipal. This study was funded by DST-FIST Grant (SR/FIST/PS-1/2017/8) and Council of Scientific and Industrial Research Grant [Sanction No.: 03(1409)/17/EMR-II].

Data availability

Data will be made available on reasonable request.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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