



# The effect of doping on thermoelectric performance of p-type SnSe: Promising thermoelectric material



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## ABSTRACT

Tin selenide (SnSe) based thermoelectric materials are being explored for making inexpensive and efficient thermoelectric devices with improved thermoelectric efficiency. As both Sn and Se are earth abundant and relatively inexpensive and these alloys do not involve toxic materials, such as lead and expensive tellurium. Hence, in the present study, we have synthesized SnSe doped with 2 at% of aluminium (Al), lead (Pb), indium (In) and copper (Cu) individually, which is not reported in literature. Out of these, Cu doped SnSe resulted in enhancement of figure-of-merit ( $zT$ ) of  $\sim 0.7 \pm 0.02$  at 773 K, synthesized employing conventional fusion method followed by spark plasma sintering. This enhancement in  $zT$  is  $\sim 16\%$  over the existing state-of-the-art value for p-type SnSe alloy doped with expensive Ag. This enhancement in  $zT$  is primarily due to the presence of  $\text{Cu}_2\text{Se}$  second phase associated with intrinsic nanostructure formation of SnSe. This enhancement has been corroborated with the microstructural characterization using field emission scanning electron microscopy and X-ray diffraction studies. Also, Cu doped SnSe exhibited a higher value of carrier concentration in comparison to other samples doped with Al, Pb and In. Further, the compatibility factor of Cu doped SnSe alloys exhibited value of  $1.62 \text{ V}^{-1}$  at 773 K and it is suitable to segment with most of the novel TE materials for obtaining the higher thermoelectric efficiencies.

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## 1. Introduction

The ever increasing global energy demand and supply deficit has compelled the world's research community for a paradigm shift leaning towards non-conventional sources of energy [1]. It is required both to search for new renewable sources of energy and to increase the effectiveness of the existing state-of-the-art technologies [2]. As we know that most of the heat generated from the various sources is wasted, so in order to minimize the loss, Thermoelectricity is a small step towards utilization of this unused/waste heat from various resources [3,4]. Thermoelectric materials are being used, since few decades, for heat derived electricity generation and for Peltier refrigeration [2]. Thermoelectric materials in general, are small band gap degenerate semiconductors capable in inter-conversion of heat energy and electrical energy [5]. It is a clean, reliable and environment friendly technology as the

thermoelectric generators (TEGs) are free from any moving parts, liquid fuels and does not emit any greenhouse gases which makes TEG an acoustically silent, durable and a green technology [6].

The performance of TEGs mainly depends on the dimensionless figure-of-merit ( $zT$ ) of materials. Hence, the  $zT$  is expressed mathematically as,  $zT = (\alpha^2 \sigma) T / \kappa$ , where  $\alpha$ ,  $\sigma$ ,  $\kappa$  and  $T$  represents Seebeck coefficient, electrical conductivity, total thermal conductivity and absolute temperature, respectively. This is the key parameter to evaluate the performance of TEGs [2,7,8]. Many strategies had been applied to enhance the thermoelectric performance of materials such as nanostructuring [9], alloying [10] etc. In the view of device applications, TE materials are broadly classified in three categories: (a) low temperature or near-room-temperature ( $\sim 200$  °C or less) TE materials which are mainly  $\text{Bi}_2\text{Te}_3$  and their derivatives [5,11–14], (b) mid-temperature thermoelectrics ( $\sim 500$ – $600$  °C), which are mainly PbTe based alloys or their derivatives [15,16] and (c) high-temperature thermoelectric materials ( $> 800$  °C), which are generally SiGe based alloys [1]. Better thermoelectric performance in the mid-temperature range

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has been observed in group-IV chalcogenides, but these contains expensive Te and toxic Pb which limits their wide scale commercial as well as domestic applicability [6,17]. Hence, Tin is a better candidate material for replacing lead. SnTe has the same crystal structure (rock salt) as that of PbTe and there are many similarities in their band structure and transport properties. However, one disadvantage of SnTe is the defect chemistry. Unlike PbTe, which can be made either p-type or n-type, SnTe is always Sn-deficit. The Sn-defect makes SnTe have too many carriers, so it is difficult to get to the optimal doping for thermoelectric applications. High carrier concentration limits the Seebeck coefficient, and thus, the power factor. However, SnSe, being earth-abundant and non-toxic, exhibits an intrinsically ultralow thermal conductivity has been proven a very stable compound [18,19]. SnSe exhibits layered orthorhombic structure having 8 atoms per unit cell which forms bi-planar layered structure normal to the largest axis [17,20,21]. At room temperature, SnSe belongs to *Pnma* space group (No. 62) and undergoes a phase transition above a temperature of 700 K, where it crystallizes in a higher symmetry *Cmcm* (space group No.63). The transport properties of SnSe showcase strong anisotropy [19], making it suitable for various applications such as thermoelectric generators, detectors and emitters in the infrared spectral region and memory devices [22].

Apart from these, SnSe is a better alternative TE material than Pb Chalcogenides. SnSe alloys affliction with low electrical conductivity, but interestingly exhibits an ultralow thermal conductivity which is required for better thermoelectric performance. Recently, a very high *zT* of  $2.62 \pm 0.3$  was reported by Zhao et al. [19] in SnSe single crystal along a particular crystallographic direction [19]. Further, Chen et al. [20] reported the effect of Te doping on thermoelectric properties of SnSe, according to which there was no improvement in power factor of SnSe after Te doping [20]. In another report by Ananya Banik et al. [23] had also observed a *zT* of  $\sim 0.8$  at 860 K in  $\text{In}_{0.015}\text{Sn}_{0.985}\text{Te}_{0.85}\text{Se}_{0.15}$ , further strengthening the claim of IV-Chalcogenides to be the better TE materials in the mid temperature range [23], but this is doped with expensive Te. Later, Chen et al. reported a *zT* of 0.6 at 750 K for silver doped polycrystalline SnSe [18], but, silver (Ag) is an expensive element to dope with SnSe and it is not commercially viable for TE device fabrication.

In comparison to other state-of-the art thermoelectric materials, a very few reports are available in the literature on synthesis and transport properties of polycrystalline SnSe [24–26]. Because, SnSe possesses lower electrical conductivity resulted from low charge carrier concentrations, many researchers have made significant effort to improve its electrical conductivity by doping with Te [20], In Refs. [23], Ag [18]. Out of these dopants, Ag doped polycrystalline SnSe had reported a *zT* of 0.6 at 750 K. However, Ag is an expensive material to be doped for commercial applications of TE materials. Hence in the current study, we have synthesized p-type polycrystalline  $\text{Sn}_{(1-x)}\text{M}_x\text{Se}$  ( $\text{M} = \text{Al}, \text{Cu}, \text{Pb}$  and  $\text{In}$ ;  $x = 0.02$ ), employing conventional fusion method followed by spark plasma sintering (SPS). The selected dopants are inexpensive compared to Ag and the doping concentration 2 at% has been selected for all the samples uniformly to identify the suitable doping element to increase the thermoelectric performance as that of not reported in literature. Further, the transport properties of doped and un-doped samples have been discussed in correlation with charge carrier concentration. However, Cu doped SnSe alloys resulted in enhancement of *zT* of  $0.7 \pm 0.02$  at 773 K, hence, this could be a potential and cost-effective TE material for mid-temperature applications.

## 2. Experimental section

Sn (99.99%, Alfa Aesar) and Se (99.99%, Alfa Aesar) powders

mixed with 2 at% Pb, In, Al and Cu were grounded separately and vacuum sealed in quartz tubes which were subjected to annealing at 773 K for a time period of  $\sim 72$  h. These annealed powders were then grounded using mortar pestle. Then, these powders were consolidated and sintered under vacuum of  $\sim 6$  Pa using SPS (SPS Syntex, 725) at a pressure of 60 MPa at 773 K, with a heating rate of  $50^\circ\text{C}/\text{min}$  and a soaking time of  $\sim 10$  min, where a 12.7 mm diameter graphite die and punches were used. The sintered pellets were polished to make the disc of 12.7 mm diameter and thickness 2 mm, for thermal diffusivity measurement using laser flash system (Linseis, LFA1023). Seebeck coefficient and electrical conductivity measurements were carried out on sample size of  $3 \times 3 \times 10$  mm (width  $\times$  thickness  $\times$  length) using ULVAC ZEM-3 under helium atmosphere. Phase identification and its purity of all the sintered samples were carried out using X-ray powder diffraction (Rigaku, 40 kV and 30 mA) analysis. Field Emission Scanning Electron Microscope (FESEM, Zeiss, Supra 40VP) was used to study the elemental distribution and EDAX analysis. For calculating specific heat of the samples, Differential Scanning Calorimeter (Netzsch, DSC 404 F3) was employed. The density of pellets were determined using conventional Archimedes principle and were found to be  $>99\%$  of the theoretical density for all the samples. The accuracies in transport measurement are:  $\pm 6\%$  for thermal diffusivity,  $\pm 7\%$  for electrical conductivity,  $\pm 7\%$  for Seebeck coefficient,  $\pm 5\%$  for specific heat and  $\pm 0.5\%$  for density.

## 3. Results and discussions

### 3.1. Microstructural characterization

#### 3.1.1. X-ray diffraction analysis

The X-ray diffraction data of pure and doped SnSe samples are shown in the Fig. 1. All the XRD patterns have been exhibited the single phase of SnSe, except Cu doped SnSe [27]. The Cu doped SnSe shows a minor secondary phase of intrinsically formed  $\text{Cu}_2\text{Se}$  (JCPDS No: 00-046-1129), peaks of which has been marked in the Fig. 1(a). Also, as shown in inset of Fig. 1(a), it has been observed from XRD pattern that the characteristic peak broadening could be attributed to the intrinsic nanostructure formation. Peak shift in XRD spectrum has been observed due to ionic radii mismatch of dopants with Sn leads to strain in terms of tensile or compressive in the matrix depending on the ionic radii of the doping elements [28]. Also, the lattice parameters (a, b and c) for orthorhombic SnSe samples are calculated by employing equation (1) and these results are tabulated in Table 1.

$$\frac{1}{d^2} = \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \quad (1)$$

In order to have the consistency in crystallite size measurements, we have employed Williamson-Hall method, where integral breadth of characteristic XRD peaks will be taken in to consideration for calculating the crystallite sizes of all samples and shown in Fig. 1(b). The polycrystalline grain distribution in SnSe has been observed in the size range of 50–65 nm for all the samples irrespective of their doping.

#### 3.1.2. FESEM analysis

The microstructural analysis and elemental mapping were performed for each sample and it was observed that they exhibits nanoscale features irrespective of doping in SnSe. All the samples show uniformity in grain size distribution over the entire matrix of SnSe. However, Cu doped SnSe alloys exhibited a minor second phase of  $\text{Cu}_2\text{Se}$  as shown in Fig. 1 (a) elemental mapping. Fig. 2 (b) shows the higher magnification image of SnSe alloy exhibiting the

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