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Synergistic manifestation of band and scattering engineering in single aliovalent Sb alloyed anharmonic SnTe alloy in concurrence with rule of parsimony

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ABSTRACT

Several endeavors were adapted to improve the thermoelectric performance of SnTe as a substitute of toxic PbTe and booming approaches comprise introduction of nanostructuring, resonance states, valence band convergence and interstitial or substitutional defects. In this study, a stratagem was designed to incorporate single aliovalent Sb in SnTe by a one-step approach which successfully modulates the electronic and thermal transport properties by integration of several approaches viz. Energy-filtering effect, valence band convergence and phonon scattering at all length scales synergistically. Here, the alteration of band structure of SnTe incorporated with Sb leads to substantial improvement of Seebeck coefficient, essentially beneficial for the performance of thermoelectric alloy, beyond the designated critical temperature at 473 K which reminiscent the onset of strong contribution of heavy ($\Sigma$) valence band. The experimental finding of band convergence by Sb was for the first time corroborated by the theoretical validation by Density Functional Theory (DFT) calculations. In addition, the presence of mass fluctuation, secondary precipitates, interfaces and the long-range interactions due to resonant bonding leading to optical phonon softening, large phase space available for three-phonon scattering and strong anharmonicity enables a ultralow lattice thermal conductivity of $\sim$ 0.5 Wm\textsuperscript{-1}K\textsuperscript{-1}. Thus, a $zT$ value of $\sim$0.72 at 775 K is recorded for SnTeSb\textsubscript{0.05}.
composition, which is 154% enhancement from our pristine SnTe and is strongly competing with numerous reported $zT$ value using considerably less abundant Ag, Ge, In and highly toxic Pb, Hg, Bi, Cd multiple elements either as a dopant or additive. Thus, the law of parsimony is maintained with reduction in the cost of the thermoelectric module.

**KEYWORDS:**

Tin telluride; Band convergence; Nanostructuring; Thermal conductivity; Sb alloying

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1. INTRODUCTION

Thermoelectric materials deal with the waste heat conversion into the electricity or vice versa. The conversion efficiency depends on the dimensionless figure of merit ($zT$). For many decades, the scientific society worked for the enhancement of the figure of merit, but it rather depends on the three interlinked parameters. The figure of merit can be defined as

$$zT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l} \quad (1)$$

where $S$, $\sigma$, $\kappa_e$, $\kappa_l$ and $T$ stand for the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, lattice thermal conductivity and temperature, respectively[1]. The interlaced kind of the terms demand optimization of $zT$ judiciously. Hence, strategies need to be developed to search for alternate new materials with improved thermoelectric properties or the enhancement of $zT$ of the state-of-art materials by optimizing the power factor ($S^2\sigma$) via tuning the carrier concentration and by engineering the band structure [2]. In the recent past, all-scale nano-mesostructuring [3] and embedded endotaxial nanostructuring in bulk matrix, [4] complex crystal structure,[2] soft phonon modes,[5] lattice anharmonicity due to the presence of lone pairs,[6,7] band nestification,[8] anisotopic layered crystal structure [9-10],
liquid-like cation disordering due to superionic substructures [11-12], band convergence [13-15], resonant bonding [16] and resonant doping [17-20] are some of the ways which proved to be effective for reducing the intrinsic lattice thermal conductivity ($\kappa_{\text{lat}}$) or maximizing the power factor owing to its robustness against structural and temperature variation and grain size.

In the past couple of eras, Pb-chalcogenide, to be specific, PbTe, proved to be a champion material as far as thermoelectricity is concerned. It is highly robust for thermoelectric power generation for mid temperature applications (400-600 K). However, their applications are constrained by reservations about Pb toxicity. Thus, in the search for Pb-free analogue, SnTe has appeared as an ecologically friendly alternative to PbTe for thermoelectric power generation because it exhibits similar rock salt structure and electronic structure calculation shows two-valence band structure analogous to PbTe [22]. Nevertheless, in 1966, Dimmock et al was the first to observe the small band gap of 0.18 eV for SnTe by photoluminescence experiment [23] whereas in 1968 Rogers quantitatively resolved the large energy offset ~0.35 eV at 300 K [24], between the light valence band (L) and the heavy valence (Σ) band, which can be critical due to the remarkable bipolar diffusion and a poor Seebeck coefficient leading to low power factor. He also pointed out that the light hole (L) valence band is forever highly nonparabolic and the heavy hole (Σ) valence band is parabolic. Moreover, the striking characteristics of SnTe unlike PbTe is that due to its characteristic off-stoichiometry (ultra-high hole density ~10^{21} cm^{-3}) associated with Sn vacancies, it shows highly-degenerate transport properties and poor thermoelectric performances. Furthermore, the higher lattice thermal conductivity of SnTe in comparison to PbTe due to the low atomic mass of Sn than Pb leads to higher sound velocity at room temperature, which further lowers the $zT$ [25, 26].

To improve the thermoelectric performance, the hole concentration must be reduced to the required level of the order $10^{19} - 10^{20}$ cm^{-3}[27, 28]. Bhat et al. reported that Sn self-compensation up to 4 mol % would further increase the $zT$ value to ~0.7 in Sn_{1.04}Te by further tuning the carrier concentration [29]. Banik et al reported that presence of Sb by aliovalent cation doping enhances the electronic transport properties and thus optimizes the hole concentration in SnTe. An enhanced $zT$ ~ 1 was obtained for the composition of Sn_{0.85}Sb_{0.15}Te at 800 K [30]. Li et al manipulated the interstitial defect by Ge and Sb codoped SnTe. In this regard, Sn_{0.92}Ge_{0.04}Sb_{0.04}Te-5%Cu_{2}Te was found to exhibit an ultralow lattice thermal conductivity and a remarkably high $zT$ of 1.5 at 873 K [31]. Ma et al integrated several optimization strategies using multi-nanostructure doping in single thermoelectric SnTe material which optimizes the properties and shows an ultralow $\kappa_{\text{tot}}$ ~0.96 Wm^{-1}K^{-1} and a high
$zT \sim 1.56$ at 873 K in SnBi$_{0.03}$Te-1% Mg$_{3.2}$Sb$_{0.6}$Bi$_{1.4}$-0.2% MWCNTs due to the disturbance in electric potential at the interfaces between two dissimilar structures or elements and causes energy dependent scattering of carriers, leading to an energy filtering effect [30, 32]. Kihoi et al reported that Mn and Bi codoped in SnTe leads to an overall $zT$ of $\sim 0.93$ at 773 K and a maximum conversion efficiency of $\sim 8.4\%$ in the temperature range of 293–773 K [33]. In addition, they also doped Sb to tune the carrier concentration leading to a $zT$ of 1 at 773 K, with lattice thermal conductivity of $\sim 0.86$ W/mK due to Mn rich nanoprecipitates [34]. A record high power factor till date of $\sim 47$ $\mu$W/cmK$^2$ was reported by Bhat et al. by co-doping Ca and In in SnTe leading to a $zT$ of 1.65 at 840 K [35]. However, the highest $zT$ of 1.85 was reported by Hussain et al. by introduction of endotaxial nanostructuring leading to a slightly decreased power factor of $\sim 42.2$ $\mu$W/cmK$^2$ and lattice thermal conductivity of 0.75 W/mK [36].

The intentional addition of Sb in SnTe is due to the fact that the aliovalent element i.e. Sb plays a vital role towards optimization of lattice thermal conductivity in PbTe and SnTe based alloys by forming nanostructures via matrix encapsulation. Moreover, it is also reported that group IV-VI, V and V$_2$-VI$_3$ materials exhibit low thermal conductivity owing to their octahedral structure which results in weaker bonding due to the longer bond length [37], resonant bonding, long ranged interaction expected for resonant bonding [38] and softening of transverse optical (TO) phonon mode leading to strong anharmonicity [39]. Thus, the utmost material challenge required for high thermoelectric performance is satisfied and employed to enhance the thermoelectric properties of SnTe using Sb additives. In addition, the theoretical validation of valence band convergence by Sb in SnTe by Density Functional Theory (DFT) is first of its kind in this manuscript.

In this contribution, we report the realization of high thermoelectric performance of Sb-alloyed SnTe, instead of Sb-doped SnTe where the latter shows better performance when doped beyond solubility limit of $x \geq 0.12$. Herein, three separate synergistic approaches, viz., (a) suppression of excess hole concentration, (b) successful energy filtering and valence band convergence to increase the power factor, and (c) diminishing the lattice thermal conductivity were considered to obtain an improved $zT \sim 0.71$ in SnTeSb$_{0.05}$ at 773K. No content of multiple metal doping was envisaged to reduce the cost of thermoelectric modules. This simple and single step methodology is competitive with numerous reported $zT$ value using considerably toxic and expensive elements maintaining the law of parsimony.

2. METHODS

2.1. Experimental details
2.1.1. Starting materials

Chemicals were used as obtained: Sn chunk (99.9999%, Sigma Aldrich), Te shot (99.999%, 5N, Sigma Aldrich), and Sb Chunk (99.999%, 5N, Alfa aesar).

2.1.2. Synthesis

High-purity single elements Sn, Te, and Sb were weighed according to the stoichiometric compositions of SnTeSb\(_x\) (\(x = 0, 0.02, 0.03, 0.04,\) and 0.05) and then put inside 13 mm diameter fused quartz tubes. The tubes were sealed under vacuum (\(\sim 10^{-4}\) Torr) and slowly heated to 900 °C rate of 50 °C per hour. At 900 °C rocked continuously for 3 hours to form uniform composition then soaked for 5h, and slowly cooled down to room temperature with rate of 70 °C per hour. The obtained ingots were then crushed and ground into powders inside the glove box (< 1ppm oxygen level) using a mortar pestle for compaction. The grounded powders were filled in 12mm diameter graphite die and sintered by spark plasma sintering (SPS, M/s. SPS Syntex, 725, Japan) at 773 K for SnTeSb\(_x\) (\(x = 0, 0.02, 0.03, 0.04,\) and 0.05) by maintaining soaking time for 5 minutes under 40 MPa load with a vacuum 10 Pa. Also, during SPS, the DC pulse ratio (current on/off time in milliseconds) 12:2 has been maintained with a high heating rate of 200 °C/min.

2.1.3. X-ray Diffraction, Electron Microscopy, Inductively Coupled Plasma Optical Emission Spectrometry and X-ray photoelectron spectroscopy

The before and after sintered pellets were characterized by X-ray diffraction technique Proto AXRD Benchtop Powder diffractometer), under ambient conditions using CuK\(_\alpha\) radiation (\(\lambda = 1.5418\) Å). Further, a Scanning electron microscope (SEM, M/s. JEOL IT300 operated at 15 kV) is used to study the morphology and the attached EDS analyzer (M/s. EDAX-Octane) is used for elemental analysis and mapping. The transmission electron microscope (JEOL JEM2100F) specimens were created by dispersing the specimen powder onto a copper grid.

Inductively Coupled Plasma Optical Emission Spectrometer with simultaneous solid state detector (ICP-OES, ACTIVA S, Horiba Jobin–Yvon SAS, France) was used for quantification of atom % of Sb, Sn and Te. The samples were digested under controlled temperature and pressure in closed teflon tubes placed inside a microwave digester (Ethos 2, Milestone, Italy). Optimised combination of ultrapure nitric acid, hydrofluoric acid hydrogen peroxide were used for complete dissolution. Emission wavelengths with high sensitivity and
minimum interferences were chosen for analysis. Calibration of the instrument for the determination of concentration was carried out by using Aldrich standard solution.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using Mg-Kα (1253.6eV) source and DESA-150 electron analyzer (Staib Instruments, Germany). The binding energy scale was calibrated to Au-4f7/2 line of 84.0 eV. Data were collected for X-rays with an incidence angle of ~54.7° relative to the analyzer. The other parameters are step size: 38 meV, dwell time: 100ms. Scanning time: 15–20 min depending on the no. of scans. For high resolution, XPS spectra averaging of 15 scans were taken. While fitting the XPS data with two or more peaks the constraint of full-width at half maximum (FWHM) for each peak was applied. The XPS peaks were fitted using a combination of Gaussian and Lorentzian distributions. Baseline corrections of the data were done using Shirley background.

2.1.4. Electrical Transport Properties

The obtained SPS-processed pellets were cut into bars with dimensions of 12 mm × 3 mm × 3 mm that was used for simultaneous measurement of the Seebeck coefficient and the electrical conductivity using M/s. Linseis LSR-3 instrument under a helium atmosphere from room temperature to 823 K. No hysteresis was seen in heating and cooling cycles. Electrical properties measured for different slices cut from the same pellets were similar, corroborating the homogeneity of the samples. The uncertainty of the Seebeck coefficient and electrical conductivity measurements is ±3%.

2.1.5. Thermal Conductivity

Highly dense SPS-processed pellets of diameter 12 mm were polished for thermal diffusivity measurements. The samples were coated with a thin layer of graphite to minimize errors from the emissivity of the material. The thermal conductivity was calculated from \( \kappa = D \times C_p \times \rho \), where the thermal diffusivity coefficient \( (D) \) was measured using the laser flash diffusivity method in a Linseis, LFA-1000, the specific heat capacity \( (C_p) \) was determined by eqn. (2)[40],

\[
C_p = C_{p,300} + C_{p,1} \cdot \left( \frac{T}{300} \right)^\alpha - 1 + \frac{C_{p,1}}{C_{p,300}} \]

where \( T \) is the absolute temperature and \( C_{p,300} \) is the specific heat capacity at 300 K. For SnTe, \( C_{p,300} \) is 0.1973 J g\(^{-1}\) K\(^{-1}\), \( C_{p,1} \) is 0.115 J g\(^{-1}\) K\(^{-1}\), and \( \alpha \) is 0.63 and the density \( (\rho) \) was determined using the dimensions and mass of the sample and found to be >98% of its theoretical density.
The thermal diffusivity data were analyzed using a Cowan model with pulse correction. The uncertainties in transport and other measurements are ± 6% for $D$, ± 3% for $\sigma$, ± 3% for $S$, ± 10% for $C_p$ and ± 0.5% for $\rho$. Unless otherwise mentioned, all the properties described in this study were measured perpendicular to the sintering pressure direction, although no directional anisotropy effects were perceived in the charge transport properties.

2.2. Computational details

First principles density functional theory methods implemented in Quantum ESPRESSO code were used to perform electronic structure calculations of SnTe and Sb incorporated SnTe [41]. Fully relativistic ultrasoft pseudopotentials were used to replace the potential of the ionic core and valence electrons were taken into consideration for the calculation. Inclusion of relativistic pseudopotential was essential to capture the spin orbit coupling interaction. Generalized gradient approximation were used to exchange correlation energy functional with Perdew, Burke and Erzenhoff (PBE) parametrization [42]. SnTe crystallizes in cubic rock salt structure with $Fm\bar{3}m$ space group. A $(\sqrt{2}\times\sqrt{2}\times2)a_o$ supercell with 32 atoms were relaxed and used for the determination of total energies. Electronic wavefunctions were represented using plane wave basis sets, the energies and charge densities of which were terminated with a cutoff of 40 Ry and 320 Ry respectively. Self-consistent field calculations and non-self-consistent field calculations were performed with $7\times7\times5$ and $14\times14\times10$ k mesh. Electronic structure was determined along $\Gamma$-X-$\Sigma$-$R$-$\Gamma$-Z path in the Brillouin zone.

3. RESULTS AND DISCUSSION

Pristine SnTe, being an eco-friendly, highly conducting alloy, possess an extremely low Seebeck coefficient and high electronic thermal conductivity, making it mediocre thermoelectric material. Nevertheless, through proper tailoring, both Seebeck coefficient and electronic thermal conductivity can be optimized to improve its thermoelectric performance. In this manuscript, synergistic efforts were described to increase the power factor by enhancing the Seebeck coefficient by carrier optimization, band convergence and reduction in the lattice thermal conductivity due to the scattering of the wide spectrum of phonons effectively through all-scale-hierarchical architecturing by incorporation of Sb in SnTe. The manuscript also comments about the role of “Critical Temperature “which shows the onset of contribution of heavy valence band ($\Sigma$-band) in the transport properties. Subsequently, the experimental finding was corroborated by DFT calculations and the scope was discussed which makes it suitable for the fabrication of thermoelectric generators.
### 3.1. Analysis of phase compositions and microstructures

The crystalline ingots of Sb incorporated SnTe i.e. SnTeSb$_x$ (x = 0, 0.02, 0.025, 0.03, 0.035 0.04, 0.045 and 0.05) were synthesized via a facile melting reaction in a vacuum sealed-tube at 1173 K. Powder X-ray diffraction (PXRD) of pristine SnTe and SnTeSb$_x$ (x = 0, 0.02, 0.025, 0.03, 0.035 0.04, 0.045 and 0.05) as shown in Fig.1 (a) can be well indexed to rock-salt structure of SnTe ($Fm\overline{3}m$ space group). The pattern shows the absence of secondary phase within the detection limit of the XRD instrument. The diffraction peaks of varied compositions of SnTeSb$_x$ shifts to higher angle with the increase in the concentration of Sb (Fig. 1(b)) suggesting lattice contraction due to the occupancy of large Sn$^{2+}$ vacancies (radius of 0.93 Å) with a smaller radius Sb$^{3+}$(0.76 Å) [31]. The lattice parameter extracted from the PXRD initially decreases linearly following the Vegard’s Law from a = 6.3 Å to a= 6.28 Å with increasing Sb concentration, which indicates the formation of solid solution in SnTeSb$_x$ (up to x=0.045). However, the deviation from the Vegard’s law is prominent for x=0.05(Fig.1(c)). Nevertheless, the non-linear relation between the lattice parameter value and the Sb concentration is not evident in PXRD pattern which can be due to the low concentration of secondary phase or nanostructures which is beyond the detection limit of the apparatus.

Detailed microstructure analysis was performed using scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM) to investigate the underlying mechanism responsible for the experimentally obtained very low $\kappa_{lat}$ of Sb added SnTe.

The morphology of SnTeSb$_x$ characterized by SEM with Energy Dispersive X-Ray Spectroscopy (EDX) are shown in Fig. 2. Addition of Sb shows no apparent change in the surface morphology of the SnTe samples. However, the EDX mapping shows constituent elements are evenly distributed in the matrix when the concentration of Sb lies within the solubility limit. However, when the addition of Sb is high (beyond the solubility limit), both crystalline and amorphous nano precipitates were seen. The quantity of this secondary precipitates enhances with increase in the concentration of Sb. The EDS spectra and the compositional analysis of the nanoprecipitate of the compositions SnTeSb$_x$, (x = 0, 0.04, 0.045 and 0.05) are shown in S1 in the ESI.† In order to gain an understanding of the composition of the material, ICP-OES analysis of SnTeSb$_{0.05}$ shows Sn 50 at%, Te 50 at% and Sb 2 at%.

The detailed nanoscale examination using HRTEM (Fig. 3) for SnTeSb$_x$ shows single phase microstructure when the concentration of Sb lies within x≤0.04, although PXRD pattern shows single phase for all the samples under investigation. Nevertheless, the images of the SPS
samples, SnTeSb$_{0.045}$ and SnTeSb$_{0.05}$ (Fig. 3(b-d)) are of great interest as these compositions reveal that several nanoscale precipitates were formed which shares coherent interfaces with the SnTe matrix and are responsible for low thermal conductivity at higher temperature. The nature of the interface formed between the SnTe matrix and the Sb-nanoprecipitates can be identified from the misfit parameter ($\delta$), which is defined as eqn.(3)[43]:

$$
\delta = \left( d_{\text{SnTe}} - d_{\text{Sb}_2\text{Te}_3} \right) \times 100/d_{\text{SnTe}}
$$

where $d$ stands for the inter-planer distance. The value of $d_{\text{SnTe}}$ estimated from HRTEM image analyses was found to be ~0.315 nm. Similarly, HRTEM images yield the value of $d_{\text{Sb}_2\text{Te}_3}$~0.3218 nm, which is in agreement with the value obtained from the (015) diffraction peak of Sb$_2$Te$_3$[44]. The resultant value of $\delta$ is found to be 2.15%. A low value of $\delta$ (i.e. <25%) implies the formation of coherent interface between matrix SnTe and endotaxial Sb$_2$Te$_3$ nanoparticles [43]. Fig. 3(d), clearly reveals the matching of the lattices resulting in the formation of coherent interface without any dislocations at the grain boundary. Such coherent interface can contribute to scattering of phonons with medium and long wavelengths, meanwhile maintaining required carrier transport without unnecessary scattering. Moreover, the mass fluctuation due to the difference in the molecular mass of the host atom Sn (118.71 g/mol) and Te (127.6 g/mol) and the guest atom Sb (121.76 g/mol) creates atomic defect such as dislocation clusters (as shown in Fig. 3(c)) which contributes to the lattice strain instability and thus reduces the lattice thermal conductivity by scattering the short wavelengths effectively [45]. Thus, these nanoscale features are distinctive in terms of improving the performance of thermoelectric properties of SnTe. On the contrary, when the concentration of Sb is 0.05 at %, the secondary intergrowth is evident in the HRTEM image which is responsible for the overall modification in the chemistry of the SnTe matrix. These nano intergrowths scatter the mid- and long wavelength phonons efficiently through synergistic (i) inter-scattering at the interfaces of the matrix and the nanodomain and (ii) intra-scattering by the intergrowth precipitation. In addition, the point defects due to the presence of Sb, scatters the short wavelength phonons and thus, the $x \geq 0.04$ shows the lowering of the lattice thermal conductivity at high T.

Another evidence of the formation of the Sb$_2$Te$_3$ for the reaction between SnTe and excess Sb beyond solubility limit are the X-ray photoelectron spectroscopy (XPS) results shown in Fig. 4. The survey XPS spectra for the SnTeSb$_{0.05}$ are shown in Fig. 4(a). In the survey XPS spectra, the signal from each element, such as Sn, Te, and Sb are seen. In addition, the sample exhibit the presence of physisorbed oxygen (shown as the O 1s peak). All the XPS
peaks were calibrated with the C 1s peak position at 284.8 eV. It is observed that the Te/Sb spectrum comprises of two characteristics peaks due to spin-orbit splitting, e.g., Te 3d$_{5/2}$ and Te 3d$_{3/2}$, which are fitted for 575.6 eV and 586.0 eV respectively (Fig. 4(b)). The systematic shift of the binding energy for the Te 3d to higher energies can be attributed to the oxidation status of elemental Te (Te$^{4+}$ and Te$^{6+}$), indicating the surface oxidation of Te. However, the systematic shift of the binding energy for Te 3d to lower energies indicates the steadily promoted component of the reduced state for elemental Te (Te$^{2-}$), suggesting the enhanced content of Sb$_2$Te$_3$.

The Sb 3d spectrum shown in Fig. 4(c) refers to the +3 oxidation state, indicating the non-existence of metallic Sb. Nevertheless, the low electron density near Sb$^{3+}$ moves the corresponding peak towards higher binding energy. For example, owing to the oxidation of Sb$_2$Te$_3$, the peaks at 529.5 eV(3d$_{5/2}$ ) contributed by Sb 3d in Sb$_2$Te$_3$ shift upto 530.6 eV (3d$_{5/2}$ ), which corresponds to Sb 3d in Sb$_2$O$_3$. The peak of O 1s at ~532.2 eV corresponds to the adsorbed oxygen. Thus, combining with the presence of oxidation peak in the Te 3d spectrum, the formation of the TeO$_2$ and TeO$_3$ can be rationally deduced subjected to the surface oxidation as follows:

$$2\text{Sb}_2\text{Te}_3+3\text{O}_2=2\text{Sb}_2\text{O}_3+6\text{Te}$$

$$\text{Te}+\text{O}_2=\text{TeO}_2; \quad 2\text{Te}+3\text{O}_2=2\text{TeO}_3$$

Indication of no oxide phase in the XRD indicates the oxidation merely occurs on the sample surface. Therefore, it is believed that the inadequate oxidation would not play any influential role on the thermoelectric properties.

### 3.2. Modification of band structure via Sb incorporation in SnTe

Temperature dependent electrical transport properties are shown in Fig. 5. The trend of electrical conductivity ($\sigma$) vs T (Fig. 5(a)) illustrates degenerate semiconducting behavior, which primarily originates due to intrinsic Sn vacancies [22]. In the entire investigating temperature range, the $\sigma$ reduces with increase in T and shows the typical characteristic of metallic conduction. The value of $\sigma$ drastically decreases from 7740.5 Scm$^{-1}$ to 4877.6 Scm$^{-1}$ for the composition SnTeSb$_{0.04}$ at room temperature. The gradual reduction of the $\sigma$ with the increase of the donor Sb content is due to systematic reduction of the p-type carrier concentration ($n_H$). In other words, the reduction of the hole concentration (which are primarily responsible for the high conductivity of SnTe) is attributed to their neutralization by aliovalent Sb$^{3+}$ which are supposed to donate surplus electron to the system from the chemical valence count [30]. However, at room temperature, with the increase of the secondary nanoprecipitates,
the $\sigma$ value increases and shows a value of 6400 S/cm for $x=0.05$. The observation can be endorsed to the increase in the hole concentration due to the precipitation of the Sb-rich nanodomains. The finding can also be interrelated with the alteration of the chemical composition of the matrix and thereby the change in the hole carrier density. Tan et al and Banik et al explicitly mentioned that Sb doping in PbTe and Sb doping in SnTe induces strained endotaxial nanoprecipitates Pb$_m$Sb$_{2n}$Te$_{m+3n}$ and Sn$_m$Sb$_{2n}$Te$_{3n+m}$ respectively [30,46]. Using the similar analogy, it is worth to mention that the non-linearity in the Vegard’s law and the presence of nanoprecipitates in the matrix with $x \geq 0.04$, is due to the formation of intergrowth nanostructures of quasi-binary composition of (SnTe)$_m$(Sb$_2$Te$_3$)$_n$. However, for Banik et al, since the Sb was doped at Sn site, the formation of the secondary intergrowth was evident for Sb content $\geq 0.12$ [30] and the concentration of the secondary intergrowth precipitate is within the detection limit of XRD. In this study, since the Sb was added in excess to the SnTe matrix, the presence of the nano-intergrowth was manifested at a much lower concentration of Sb ($x \geq 0.04$) in electron microscopy observation, however, the concentration was beyond the detection limit of PXRD. Measurement of Hall carrier density at room temperature shows positive Hall coefficient value ($R_H$) which indicates the p-type conduction. The hole carrier density reduces drastically in Sb-doped SnTe($x \geq 0.04$) from $1.01 \times 10^{20}$ /cm$^3$ to $6.4 \times 10^{19}$ /cm$^3$, due to the quenching of the holes. Nevertheless, the hole density shows enhancement for $x=0.05$ (Fig. 5(b)), which is correlated to the change in the matrix system due to the nanostructured intergrowth as mentioned earlier. The hole mobility measured by $\mu = \frac{\sigma}{n_e}$ were plotted as a function of Sb concentration (Fig. 5(c)). As described by Banik et al, not much variation is seen in the carrier mobility especially at lower Sb addition, which indicates the nanoprecipitates are endotaxial in nature, and so the interfaces are transparent for the electrons [30].

Fig. 6(a) shows the temperature dependence of Seebeck coefficient ($S$) of SnTeSb$_x$ ($x=0, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045$ and $0.05$). The positive value of $S$ indicates the dominating p-type conduction in the investigated temperature range of 300-800 K, which is consistent with the sign of Hall carrier concentration. The pristine SnTe i.e. $x=0$ sample possesses a low Seebeck coefficient of $\sim 34$ $\mu$V/K at room temperature because of its high hole concentration as stated above. Remarkably, the room temperature Seebeck coefficient decreases gradually with the increase in $x$ i.e. with the alloying of Sb, despite being the reduction of hole concentration, which is contradictory from the typical behavior expected for a p-type semiconductor. This strange variation in Seebeck coefficient is related to the
distinctive character of the two non-degenerate valence bands (at the $L$ and $\Sigma$ points of the Brillouin zone) of SnTe. For the two-valence band case, the total Seebeck coefficient is given by eqn.(4),

$$S = \frac{\sigma_{lh}S_{lh} + \sigma_{hh}S_{hh}}{\sigma_{lh} + \sigma_{hh}}$$

where $S_{lh}$ and $S_{hh}$ denote the Seebeck coefficient of the light hole band and heavy hole band respectively, while $\sigma_{lh}$ and $\sigma_{hh}$ denote the electrical conductivity from light hole band and heavy hole band contribution, respectively [14]. Due to the high hole density in pristine SnTe, the Fermi level lies in the valence band, closer to the heavy-hole band and is energetically low. However, with decreasing hole concentration in SnTeSb$_x$ ($x= 0, 0.02, 0.025, 0.03, 0.035 0.04, 0.045$ and $0.05$), the Fermi level rises and gradually shifts away from the heavy-hole band. Thus, only the light-hole band contributes to the Seebeck coefficient [28] with feeble participation of the heavy hole band in the transport properties. In accordance of the statement, the $S$-$T$ plot depicts that at lower temperature, the Seebeck coefficient is maximum for the pristine SnTe and shows the minimum value for $x= 0.05$ at%. To further clarify the reduction of Seebeck coefficient, $S$, the effective mass ($m^*$) of the carriers were calculated for SnTeSb$_x$ using the experimental $S$ and carrier density ($n_H$) measured at 300 K, by the following expressions (eqs. 5-7):

$$m^* = \frac{\hbar^2}{2k_B^2} \left[ \frac{n}{4\pi F_{1/2}(\eta)} \right]^{2/3}$$

$$S = \pm \frac{k_B}{e} \left[ \frac{(r+3/2)F_{r+3/2}(\eta) - \eta}{(r+3/2)F_{r+1/2}(\eta) - \eta} \right]$$

$$F_{n}(\eta) = \int_{0}^{\infty} \frac{x^n}{1 + e^{-x}} dx$$

Where, $r$, $e$, $\hbar$, $k_B$, $\eta$ and $F_{n}(\eta)$ are the scattering factor, electron charge, Planck’s constant, the Boltzmann constant, reduced fermi energy and $n^{th}$ order Fermi integral respectively. The reduced Fermi energy was computed by fitting the resultant experimental Seebeck data. The $m^*$ values were evaluated based on the single parabolic band model, where, for simplicity, the $r= -1/2$ was considered for acoustic phonon scattering. The estimated $m^*$ value of pristine SnTe was $0.36m_0$, which reduces to $0.15m_0$ for the composition SnTeSb$_{0.05}$ and thereby indicates the participation of predominantly light ($L$) valence band at 300K for the Sb added SnTe [47].

Surprisingly, the SnTeSb$_x$ samples with lower Seebeck coefficients at lower temperature shows higher Seebeck coefficient when temperature is ~ 473 K (designated as critical temperature here) (Fig. 6(a)). The brisk rise of the Seebeck coefficient at $T > 473$ K is evocative of the similar but more noticeable behavior of p-type PbTe, and is attributed to the
enhanced contribution of the heavy hole $\Sigma$ band at higher temperatures due to the thermal excitations. Aggarwal et al have explicitly mentioned in an article that in the temperature range of 300-473 K, SnTe alloys exhibit local ferroelectric domain. However, the concrete vindication of the relation between the critical temperature and the local ferroelectric instability has not been understood [48]. Similar to PbTe in SnTe, the valence band is formed by the Te orbital, while Sn constitutes the conduction band due to the difference in the electronegativity, $\chi$, of Sn ($\chi_{Sn}=1.96$, in Pauling electronegative scale) and Te ($\chi_{Te}=2.10$) [18]. Aliovalent dopant Sb, forms the donor impurity states immediately below the conduction band, because of the slightly lower values of the electronegativity, $\chi_{Sb}=2.05$, than Te, which thus, reduces the principal band gap [49].

However, the contribution of the heavy hole $\Sigma$ band in the high temperature properties of SnTe is better demonstrated once a substantial number of Sn vacancies has been removed. In other words, alloying of Sb in SnTe alters the electronic structure of SnTe as explained using DFT calculations in later section. Sb reduces the band offset ($\Delta E_{L-S}$) and thereby causes the band convergence and beyond critical temperature, promotes the conduction of heavy hole valence band and enhances $S$ with increasing $x$ at higher temperature [49,50]. Moreover, the participation of the heavy ($\Sigma$) valence band is validated by the thermal bandgap calculation as a function of Sb concentration using Goldsmid-Sharp equation $E_g = 2e|S| \Delta E_{L-S}$ (Fig. 5(b)). The plot indicates that the thermal band gap increases at high temperature without any signature of bipolar conduction in the $S$ vs $T$ plot. This can be attributed to the fact that with the onset of the band convergence, the majority carriers can undergo seamless transmission from the $L$-valence band to the $\Sigma$-valence band. Consequently, at higher $T$, the carriers undergo transition from the $\Sigma$-valence band to the conduction band and thus, shows opening of the thermal band gap. The understanding of the effect of weak band convergence by Sb is in good agreement with X. Tan et al, where Bi and Sb were classified as elements contributing to band convergence in SnTe and PbTe [51]. A similar observation in Sn- self compensated SnTe was reported by Tan et al, where the support for the contribution of heavy hole $\Sigma$ band at higher temperature was shown in Hall coefficient measurement as a function of time. The $R_H$-$T$ plot shows a peak at the critical temperature (~500 K) as observed in the $S$-$T$ plot and is probably due to the onset of the $\Sigma$-band contribution in the transport properties [28]. This anomaly has also been observed in p-type skutterudites and other Pb-chalcogenides [13, 52-54].

Fig. 6(b) depicts the power factors (P.F.$s'$) for all SnTeSbx samples. The pristine SnTe has relatively high P.F. $\sim 9\mu W \text{ cm}^{-1} \text{ K}^{-2}$ at 300 K mainly benefitting from its very high electrical
conductivity. The P.F.s’ deteriorate upon Sb addition in the low temperature range \(T < 470\,\text{K}\) due to the simultaneously decreased electrical conductivities and Seebeck coefficients, but above 470 K, there is a greatly enhanced Seebeck coefficient for the hole compensated Sb added SnTe samples and the P.F.s’ improve with respect to SnTe itself. At 775 K, the P.F. of SnTeSb\(_{0.05}\) shows 71% enhancement as compared to the pristine SnTe.

Room temperature Pisarenko plot of Seebeck coefficient \((S)\) as a function of carrier concentration \((n_H)\) of SnTeSb\(_x\) samples is shown in Fig. 6(c). Theoretical Pisarenko plot was constructed as a function of carrier density (the solid line in the curve) based on the two-valence band model (VBM) of SnTe by Zhang et al which considers the nonparabolicity of the light-hole band. The model was calculated using a light-hole band \((L)\) effective mass of \(\sim 0.168\,m_e\), a heavy-hole band \((\Sigma)\) effective mass of \(\sim 1.92\,m_e\) and an energy offset, \(\Delta E_{L,\Sigma}\), between the two valence bands of 0.35 eV, respectively [19]. For comparison, the present \(S\) vs \(n_H\) data of SnTeSb\(_x\) samples at room temperature were considered with previously reported that of Cd [28], Mg [55], Cu [56], Bi [57], Mn [58], In [19] doped SnTe. The results obtained indicates the validity of the VBM of SnTe. The \(S\) value reported by Zhang et al lies far above the theoretical prediction and is claimed to appear due to the resonant state formation near the Fermi level induced by the indium dopant. Other SnTe samples are in good agreement with the VBM model, indicative of conventional doping behavior. The experimental room temperature \(S\) values of Sb-added SnTe samples reside slightly above the Pisarenko curve. This originates probably due to the mass fluctuation which causes disturbance in electric potential at the interfaces between two dissimilar structures or elements and causes energy dependent scattering of carriers, leading to an energy filtering effect and weak valence band convergence [32, 59]. This enhances the Seebeck coefficient, the similar trend has been earlier observed for Sb doped SnTe and Sb and Ge co-doped SnTe alloys [30, 60].

In order to elucidate the role of incorporation of Sb comprehensively on the band structure of SnTe, DFT calculations were performed on its electronic band structure and was subsequently compared with pristine SnTe. Pristine SnTe is known to possess principal band gap between the light hole valence and conduction bands at L point which folds on to \(\Gamma\) point (Fig. 7(a)) in the current tetragonal supercell [61]. This band gap is estimated to be 0.08 eV which agrees well with the previous results, although with a typical underestimation compared to the experimental band gap of 0.18 eV due to the existence of discontinuity in the derivative of energy with respect to number of electrons [17,18]. The projected density of states (pDOS) reveals that the valence band is typically formed by the Te ‘p’ states while the conduction band is formed by the Sn ‘p’ states (Fig. 7(b)). One of the reasons for the poor performance of SnTe
is the large separation between the light hole and heavy hole valence sub-bands [62]. The heavy hole valence sub-band which typically occurs at $\Sigma$ point of Brillouin zone of the primitive cell occurs at $Z+\delta$ point in $Z\rightarrow R$ direction in the current supercell due to folding of the bands [61]. An energy offset of 0.30 eV is observed between the light hole valence band at $\Gamma$ point and heavy hole valence band at $Z+\delta$ point in the present case preventing the participation of heavy hole valence band in the transport properties at lower temperatures [63]. On the other hand, the energy offset between the light hole (at $\Gamma$ point) and heavy hole (at $Z+\delta$ point) conduction bands is observed to be 0.24 eV. Incorporation of Sb in SnTe matrix leads to the direct band gap at $\Gamma$ point reducing to 0.038 eV (Fig. 7(c)). This reduction in band gap is due to the 8 fold degenerate conduction bands losing degeneracy to form 4 sets of doubly degenerate bands and splitting off of the lower most doubly degenerate band, capping the top of the valence band as seen previously in the case of Bi resonant dopant [63]. Up until now, Sb was known to optimize the hole carrier concentration and reduce the thermal conductivity [30,64]. The interesting feature here is the reduction in the energy offset between the light hole and heavy hole valence as well as conduction bands leading to the band convergence phenomenon by Sb which was not reported previously by Banik et al. [30]. The energy difference in the valence band area reduces to 0.26 eV while the heavy hole conduction band appears 0.1 eV above the lowest point in the light hole region. The convergence of the valence sub-bands is clearly observed as the increase in the DOS at the valence band edge (Fig. 7(d)). Such increase in the DOS is previously seen in the case of convergence caused due to Mg and Ca dopants [29,35]. In Sb incorporated SnTe the valence band is contributed by Te ‘p’ orbitals while the conduction band has contributions from ‘p’ orbitals of Sn and Sb. The pDOS reveals that the hybridization of Sb ‘p’ orbitals with Sn ‘p’ orbitals in the conduction band region leads to the reduction in the band gap and the conduction band convergence. The hybridization also gives rise to hyper deep defect states within the valence band region. Although the convergence value of 0.04 eV seems too small to have any effect on the transport properties at lower temperatures, as the temperature increases this value increases as the heavy hole band further rises in energy as seen previously in the case of PbTe to cause considerable effect [14]. The number of degenerate valleys contributing at the higher temperature increase from 4 contributed by the light hole valence bands at $\Gamma$ point to 16 due to the addition of 12 valleys contributed by the heavy hole valence band at $Z+\delta$ point in $Z\rightarrow R$ direction in the Brillouin zone. The result of this is the increase in the density of states effective mass which is directly proportional to the Seebeck coefficient [35]. The contribution by the heavy hole valence band further increases with the
increase in the amount of dopant added [49]. Hence, at higher temperature, experimentally an increase in the Seebeck value is observed with increase in the Sb content.

3.3. Analysis of thermal transport properties and \( zT \) of Sb added SnTe

The other problem, which needs to be resolved, is the high thermal conductivity induced by the intrinsic Sn vacancies, which also provoke high electrical conductivity. Fig. 8(a) represents the temperature dependent total thermal conductivity \( (\kappa_{\text{total}}) \) of SnTeSb \( x \) \((x = 0, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045 \text{ and } 0.05) \) which is essentially a combination of two components: the lattice contribution \( (\kappa_{\text{lat}}) \) and the electronic contribution \( (\kappa_{\text{ele}}) \) which also includes the bipolar conduction. The electronic contribution can be estimated by the Wiedemann–Franz relation
\[
\kappa_{\text{ele}} = L \sigma T,
\]
where \( L \) is the Lorenz number, \( \sigma \) is the electrical conductivity, and \( T \) is the absolute temperature. In this report, the \( L \) value was obtained from the accepted methodology of fitting the Seebeck data to the reduced chemical potential and the details is shown in Supporting Information, S2 [65]. The lattice thermal conductivity \( (\kappa_{\text{lat}}) \) is then computed by subtracting the electronic contribution of the thermal conductivity from the \( \kappa_{\text{total}} \) and the results are shown in Fig. 8(b). Alloying of Sb in SnTe, reduces the \( \kappa_{\text{total}} \) from 7.33 Wm\(^{-1}\)K\(^{-1}\) to 6.09 Wm\(^{-1}\)K\(^{-1}\) for SnTeSb\(_0.3\) at 300 K, which is \(-17\%\) as compared to pristine SnTe. However, the compositions, \( x = 0.045 \text{ at}\% \) and \( 0.05 \text{ at}\% \) shows higher \( \kappa_{\text{total}} \) at room temperature. This can be attributed to the dominating nature of the electronic part of the thermal conductivity at low \( T \). With increasing temperature, the \( \kappa_{\text{total}} \) decreases rapidly without indicating any bipolar effect, and is in harmony with the behavior of the \( S \) vs \( T \) plot. No onset of the bipolar diffusion also corroborate the fact that Sb incorporation opens the thermal band gap and reduces the value of bipolar thermal conductivity \( (\kappa_{\text{bip}}) \). This is logical because \( \kappa_{\text{bip}} \) is related to the band gap \( (E_g) \) through the eqn. (8) [66]:

\[
\kappa_{\text{bip}} = AT^n \exp\left(-\frac{E_g}{2\kappa_B T}\right)
\]

Here, \( A \) and \( n \) are the two variable parameters and \( \kappa_B \) is the Boltzmann constant. The total thermal conductivities of all Sb-added SnTe are lower than the undoped sample. Moreover, at high temperature, when the acoustic phonon scattering is high, the \( \kappa_{\text{total}} \) of 0.05 at\% Sb reduces substantially from 6.95 Wm\(^{-1}\)K\(^{-1}\) at 300 K to 2.56 Wm\(^{-1}\)K\(^{-1}\) at 800 K which is 63\% reduction as compared to pristine SnTe which shows a reduction of \(-47\%\). This enormous reduction in \( \kappa_{\text{total}} \) is due to the reduction of \( \kappa_{\text{el}} \) caused due to the quenching of the intrinsic Sn-vacancies and simultaneously the reduction of \( \kappa_{\text{lat}} \) due to the increased phonon scattering at different length scales. The various mechanisms that were successfully implemented to scatter the wide
spectrum of phonons within the working temperature range and are responsible for the ultralow lattice thermal conductivity of the Sb-added SnTe are discussed below:

(i) Grain Boundary scattering
Grain boundaries were employed as phonon scatterers in scheming the TE materials. The association between the grain size (characterized length), phonon coherencies, the wavelength, and mean free path, have influence on dispersion of phonons. Thermal conductivity reduces when the actual phonon mean free path is greater than the crystal or grain size [67]. Since mean free path of the phonon is a function of wavelength, and wavelength itself is related to temperature by Wien's displacement law i.e. $\lambda_{\text{max}}T=$constant, thus, grain boundaries are the important scattering sources at low T [59]. The microstructural analysis in the present study reveals the presence of several secondary nano precipitates both crystalline and amorphous. This precipitates form both coherent and incoherent interfaces which scatter the phonons effectively and thus reduces the lattice thermal conductivity.

(ii) Point defect scattering
Aliovalent or isovalent ion doping are advantageous for the modulation of electronic transport property by band engineering and thermal properties by reducing the thermal conductivity [61,63]. They are expected to be the first and foremost contributors of charge carriers whereby they usually slash the formation energies of the vacancies propelled by the compensation of the charge carriers [68]. Thus, the vacancies are stabilized either near the dislocations or at the interfaces [69,70]. Moreover, any dopants or additives with different atomic sizes and masses, trigger the stress-strain and mass fluctuations. With the increase in temperature, the wavelength of the phonon decreases and so the short wavelength phonons are scattered effectively by mass fluctuation defects such as presence of impurities, vacancies, dislocations and alloy atoms. In addition, the mass fluctuation also shows impact on the group velocities. In accordance to equation (9), the group velocity decreases for high atomic mass impurity elements/dopants/weak chemical bonds is given by:

$$V_s = \frac{E}{\sqrt{\rho}} \text{------------------------ (9)}$$

where $V_s$ is the speed of the sound in solids and is also considered as the group velocity of phonons, $\rho$ is the density and $E$ is the strength of the chemical bonding [68]. The HRTEM analysis shows the presence of dislocation clusters due to the excess addition of aliovalent Sb in SnTe. These clusters are responsible for the scattering of the short wavelength phonons.

(iii) Lattice anharmonicity
Lattice anharmonicity exists in all materials as an intrinsic scattering character due to phonon-phonon Umklapp scattering which lowers the relaxation time for phonons with entire range of frequencies. According to the Slack, thermal conductivity is given by eqn. (10) [66,68]:

$$\kappa_{}\text{lat} = A \frac{M\theta_D^3}{\gamma^2 n^{1/3} T^{2/3}}$$

where $M$ is the average atomic mass (in amu), $\theta_D$ is the Debye temperature, $V$ is the average atomic volume (in cubic angstrom), $T$ is the absolute temperature, $\gamma$ is the Gruneisen parameter measuring the strength of lattice anharmonicity, $n$ is the number of atoms in primitive cell, and $A$ is a collection of physical constants ; $A \approx 3.04 \times 10^{-6}$ and $\kappa_L$ is in W m$^{-1}$ K$^{-1}$.This implies that a large number of atoms in the primitive cell ($n$) and a strong anharmonicity ($\gamma$) are effective for maintaining low $\kappa_{}\text{lat}$, and that $\kappa_{}\text{lat}$ decreases with rise in temperature. Thus, the strength of lattice anharmonicity is crucial as it reduces the lattice thermal conductivity and empowers the performance of thermoelectric materials. Experimental and theoretical analysis shows that SnTe exhibit strong anharmonicity and is strongly correlated to the ferroelectric instability [48,68], which causes robust coupling of acoustic and optical phonons and thus reduces the phonon relaxation time significantly. The coupling effect originates from the presence of soft transverse optical (TO) mode predominantly at the $\Gamma$ point in the Brillouin zone [16, 68]. This optical phonon modes contain very low group velocities which, if, neglected, leads to underestimation of $\kappa_{\text{lat}}$. However, the optical phonons contribute in three-electron process and cause added scattering with acoustic phonons and thus reduces the lattice thermal conductivity. Alloying of Sb in SnTe, reduces the $\kappa_{\text{lat}}$ further and is attributed to the lone pair of the 5s orbital of the Sb atom. Moreover, Lee et al explicitly mentioned that in addition to IV-VI alloys, Group V elements such as Bi and Sb also shows resonant bonding which leads to long range interaction and consequently lowers the lattice part of the thermal conductivity [16]. Infact, the experimental $\kappa_{\text{lat}}$ obtained in the present study shows ultra low $\kappa_{\text{lat}}$ value which is in proximity to the theoretical limit of the $\kappa_{\text{lat}}=0.4$ Wm$^{-1}$K$^{-1}$ for SnTe when calculated by the model proposed by Cahill et al [71]. Surprisingly, the minimum $\kappa_{\text{lat}}$ value obtained for higher Sb content SnTe is lower than the value reported for Hg-, Mn-, In-, Mg-, Cd- doped SnTe, several co-doped SnTe system Fig.8(c) [19,55,72-79]. This is endorsed by the precipitation of Sb$_2$Te$_3$ (as seen in microstructural analysis) which also demonstrate the existence of resonant bonding [16].

The temperature dependence of figure of merit values ($zT$) of the SnTeSbx ($x=0, 0.02, 0.03, 0.04,$ and $0.05$) samples shown in Fig. 9(a). The $zT$ at high temperatures increases with
the concentration of Sb. The highest $zT$ of ~ 0.71 is obtained in SnTeSb$_{0.05}$ at 773K, due to the synergism of band convergence and ultra-low lattice thermal conductivity. A significant improvement in $zT$ was seen for SnTeSb$_{0.05}$ which was calculated to be ~154% increment from our pristine SnTe. Finally, the $ZT$ of the TE device was computed using the equation, having a finite, temperature difference $\Delta T = T_h - T_c$, is expressed from the maximum efficiency ($\eta$) of a single thermoelectric leg, is presented by eqn. (10) [80,81]:

$$ZT = \left( \frac{T_h - T_c (1 - \eta)}{T_h (1 - \eta) - T_c} \right)^2 - 1 \quad \text{-------------------------- (10)}$$

where the highest conversion efficiency ($\eta$) was calculated by using the eqn. (11):

$$\eta_{max} = \frac{\Delta T \left( \frac{ZT + 1}{\sqrt{ZT + 1 + \frac{T_c}{T_h}}} \right)}{T_h \left( \frac{ZT + 1}{\sqrt{ZT + 1 + \frac{T_c}{T_h}}} \right)} \quad \text{-------------------------- (11)}$$

using the temperature-dependent parameters $S(T)$, $\sigma(T)$, and $\kappa(T)$ between $T_h$ and $T_c$. Further, Fig. 9(b) shows the temperature-dependent efficiency and calculated device $ZT$ of SnTeSb$_x$ and all the samples have shown an improvement of device $ZT$ with increasing Sb incorporation in SnTe. However, the highest device $ZT$ was shown when the Sb addition is within the solubility limit (Fig. 9(c)). Finally, the device $ZT$ value of 0.14307 at 775 K has been obtained for SnTeSb$_{0.03}$ and SnTeSb$_{0.035}$, which is ~44.5 % higher than the value 0.09903 at 775 K of pristine SnTe. The exact calculation of maximum efficiency is explained in the spreadsheet S.3.1 to S.3.7 for download in ESI. Finally, the maximum conversion efficiency has been observed to be increased to 2.9% for SnTeSb$_{0.03}$. The significant improvement of 45% in device efficiency is promising for considering these materials as an appropriate substitute to Pb-based chalcogenides. This is the first study to achieve eco-friendly and cost effective SnTe based alloys having moderate $zT$ via facile and controllable single step methodology without the utilization of any toxic or precious element doping. The high performance benefits the potentials of the realization of proficient thermoelectric modules with SnTe as a p-type thermoelement. Nevertheless, the actual application of the device should exhibit genuine feasibility for energy claims such as output voltage, current density, power density, actual device illustrations, etc. [82]. Table 1 summarizes some of the recent advances of mid-temperature based thermoelectric materials, particularly those with band convergence or resonant states having high $zT$ values. Thermoelectric generators based on these alloys ought to be explored in future.

4. CONCLUSIONS
In conclusion, a simple methodology was adapted to synthesize inexpensive, eco-friendly Sb-added SnTe via single-step melting route. Sb causes carrier optimization along with induction of band convergence by favorably altering the band structure. Mass contrast causes disturbance in electric potential at the interfaces between two dissimilar elements leading to an energy filtering effect which altogether enhances the Seebeck coefficient. Incorporation of Sb in excess leads to the precipitation of intergrowth which forms coherent interface with the matrix. The lattice thermal conductivity reduces remarkably and is in proximity to the amorphous limit owing to scattering by grain boundaries, point defects and lattice anharmonicity. Integration of the approaches synergistically modulates the electronic and thermal transport properties of polycrystalline SnTe with no addition of precious and toxic dopants. This kind of cost-effective high-performance material is suitable for the fabrication of budget thermoelectric modules and makes it a suitable alternative to the conventional PbTe based alloys.

5. Conflict of Interest:
There is no conflict of interest.

6. Acknowledgments:
The author RB would like to acknowledge Dr. K.P. Muthe and entire Thin Film Devices Section (TFDS) for providing their support and valuable inputs for this article. SN acknowledge the FRGS (Grant No. GGSIPU/DRC/FRGS/2020/1988/9). The author (USS) acknowledges the grant in the form of DST INSPIRE Faculty award from Department of Science and Technology, Government of India. The authors also thank the National Physical Laboratory, New Delhi for consolidation of the sample using Spark Plasma Sinter and founder Chancellor Bhagawan Sri Sathya Sai Baba and Trustees/Administrators for providing characterization facilities at Central Research Instruments Facility (SSSIHL-CRIF).

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