Tuning of thermoelectric properties with changing Se content in Sb$_2$Te$_3$

D. Das$^{1}$, K. Malik$^{2}$, A. K. Deb$^{3}$, V. A. Kulbachinski$^{4}$, V. G. Kytin$^{4}$, S. Chatterjee$^{5}$, D. Das$^{5}$, S. Dhara$^{6}$, S. Bandypadhyay$^{1,7}$ and A. Banerjee$^{1,7(a)}$

1 Department of Physics, University of Calcutta - 92 A P C Road, Kolkata-700009, India
2 Department of Physics, Vidyasagar Evening College - 39 Sankar Ghosh Lane, Kolkata-700006, India
3 Department of Physics, Raiganj University - Uttar Dinajpur 733134, India
4 Department of Low Temperature Physics and Superconductivity, Physics Faculty, M.V. Lomonosov Moscow State University - 119991, Moscow, Russia
5 UGC-DAE Consortium for Scientific Research, Kolkata Centre, Sector III, LB-8 - Salt Lake, Kolkata-700098, India
6 Surface and Nanoscience Division, Indira Gandhi Centre for Atomic Research - Kalpakkam 603102, India
7 Center for Research in Nanoscience and Nanotechnology, University of Calcutta, JD-2, Sector-III Salt Lake, Kolkata-700098, India

received 16 December 2015; accepted in final form 24 February 2016
published online 9 March 2016

PACS 72.20.Pa – Thermoelectric and thermomagnetic effects
PACS 72.20.-i – Conductivity phenomena in semiconductors and insulators
PACS 61.05.cp – X-ray diffraction

Abstract – Polycrystalline Sb$_2$Te$_{3-x}$Se$_x$ (0.0 ≤ x ≤ 1.0) samples were synthesized by the solid-state reaction method. The structural analysis showed that up to the maximal concentration of Se, the samples possess rhombohedral crystal symmetry (space group R3m). The increase of Se content increases the resistivity of the samples. The variation of phonon frequencies, observed from the Raman spectroscopic study, depicts an anomalous behaviour around x = 0.2. The sample Sb$_2$Te$_{2.8}$Se$_{0.2}$ also shows maximum Seebeck coefficient, carrier concentration and thermoelectric power factor. The nature of the scattering mechanism controlling the thermopower data has been explored. The thermoelectric properties of the synthesized materials have been analyzed theoretically in the frame of the Boltzmann equation approach.

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Introduction. – The thermoelectric (TE) effect refers to the phenomenon of direct conversion of heat to electric voltage and vice versa [1,2]. The efficiency of a TE material can be quantitatively expressed by the dimensionless term figure of merit $ZT = S^2T/(\rho\kappa)$, where $S$, $\rho$ and $\kappa$, are, respectively, the Seebeck coefficient, the electrical resistivity and the thermal conductivity of the TE material and $T$ is the absolute temperature. By maximizing the power factor ($PF = S^2/\rho$) and/or lowering the thermal conductivity, $ZT$ can be improved [3,4]. Antimony telluride (Sb$_2$Te$_3$) is a well-known $p$-type TE material for near room temperature applications [5–8]. The incorporation of Se atoms into a Sb$_2$Te$_3$ lattice modifies the nature of defect states, which, in principle, should lead to interesting changes in its TE properties. Efforts were thus devoted to study the effect of Se doping on the structural [9], transport [10], electronic band structure [5] and TE [11] properties of Sb$_2$Te$_3$ alloys. Some anomalous behaviour was reported in the range x = 0.0–1.0 for the Sb$_2$Te$_{3-x}$Se$_x$ system, which needs further attention. On the contrary, Bi$_2$Te$_3$-based chalcogenides, viz., Bi$_2$Te$_{1-x}$Se$_x$, including the most compensated compound Bi$_2$Te$_2$Se, are well explored [12,13].

Here we investigate different compositions of the Sb$_2$Te$_{3-x}$Se$_x$ (0.0 ≤ x ≤ 0.1) alloy. Room temperature powder X-ray diffraction (XRD) and thermal variation of resistivity, $\rho(T)$ data show a systematic variation with the Se content. However, the $S$, $PF$, Hall carrier concentration of the charge carriers ($n_H$), and the Raman spectroscopic study show some anomalous behaviour around x = 0.2. In this report, an attempt has been made to elucidate the origin of this anomalous behaviour. In addition, the $S(T)$, $\rho(T)$, $n_H(T)$ and $PF$ data have also been theoretically simulated. The evaluation of the band energy spectrum with the Se content is predicted.

(a)E-mail: arbphy@caluniv.ac.in (corresponding author)
Table 1: Rietveld refinement parameters, viz., lattice parameters, unit cell volume, position coordinates, site occupancy, Debye-Waller factor ($B_{	ext{iso}}$), reliability parameters ($R_w$ (%), $R_b$ (%), and $R_{	ext{exp}}$ (%)), and goodness of fit (Gof or $\chi^2$) value, as obtained using MAUD software for the samples Sb$_2$Te$_{3-x}$Se$_x$ ($x = 0.0, 0.2, 0.6, \text{and} 1.0$). The corresponding values of the estimated errors are also provided.

| Phase | Sb$_2$Te$_3$ [R$^3m$] | Sb$_2$Te$_2$S$_{0.2}$ [R$^3m$] | Sb$_2$Te$_4$S$_{0.6}$ [R$^3m$] | Sb$_2$Te$_2$Se [R$^3m$] |
|-------|-------------------|-----------------|-----------------|-----------------|
| Cell (Å) | $a$: 4.2558 (4.3 \times 10^{-4}) | $a$: 4.2403 (1.2 \times 10^{-4}) | $a$: 4.2096 (1.1 \times 10^{-4}) | $a$: 4.1781 (1.6 \times 10^{-4}) |
| | $c$: 30.3629 (7.4 \times 10^{-4}) | $c$: 30.3134 (1.1 \times 10^{-3}) | $c$: 30.1278 (1.1 \times 10^{-3}) | $c$: 29.8964 (1.6 \times 10^{-3}) |
| Cell volume | 476.25 | 472.02 | 462.36 | 451.97 |
| Sb$_2$/Sb$_2$/Sb$_2$ | 0.0 / 0.0 / 0.3994 | 0.0 / 0.0 / 0.6027 | 0.0 / 0.0 / 0.3962 | 0.0 / 0.0 / 0.3943 |
| (4.1 \times 10^{-5}) | (6.2 \times 10^{-5}) | (4.3 \times 10^{-5}) | (4.7 \times 10^{-5}) | |
| Te$_{1x}$/Te$_{1y}$/ | 0.0 / 0.0 / 0.0 | 0.0 / 0.0 / 0.0 | 0.0 / 0.0 / 0.0 | 0.0 / 0.0 / 0.0 |
| Te$_{1x}$ | 0.7874(2.4 \times 10^{-5}) | 0.7879(4.0 \times 10^{-5}) | 0.7867(2.9 \times 10^{-5}) | 0.7860(3.5 \times 10^{-5}) |
| Se$_{1x}$/ Se$_{1y}$/ | Te$_2$/ Se$_2$: 0.0 / 0.0 / 0.0 | Te$_2$/ Se$_2$: 0.0 / 0.0 / 0.0 | Te$_2$/ Se$_2$: 0.0 / 0.0 / 0.0 | Te$_2$/ Se$_2$: 0.0 / 0.0 / 0.0 |
| Se$_{1x}$ | |
| $B_{\text{isoSe/Te1/Se1}}$ | Sb: 2.619 (0.026) | Sb: 1.1917 (0.021) | Sb: 1.8722 (0.020) | Sb: 1.544 (0.024) |
| Te$_1$: 1.522 (0.032) | Te$_1$: 1.917 (equal), Te$_2$: 0.147 (0.029) | Te$_2$/Se$_2$: 1.1917 (equal) | Te$_2$/Se$_2$: 1.8722 (equal) | Te$_2$/Se$_2$: 1.544 (equal) |
| $R_w$ (%) | 3.941 | 5.967 | 5.171 | 4.814 |
| $R_b$ (%) | 3.091 | 4.617 | 4.089 | 3.819 |
| $R_{\text{exp}}$ (%) | 2.104 | 4.602 | 4.115 | 3.886 |
| Gof or $\chi^2$ | 1.873 | 1.296 | 1.257 | 1.239 |

Fig. 1: (Color online) (a) X-ray diffraction patterns of the samples Sb$_2$Te$_{3-x}$Se$_x$ ($x = 0.0, 0.2, 0.6, \text{and} 1.0$). (b) X-ray diffraction pattern of the sample Sb$_2$Te$_2$S$_{0.2}$ after Rietveld refinement. The inset shows the variation of the lattice constants, $a$ and $c$, with the Se composition for all the samples.

**Experimental.** Polycrystalline Sb$_2$Te$_{3-x}$Se$_x$ ($x = 0.0, 0.2, 0.6, \text{and} 1.0$) samples were synthesized by the solid-state reaction method [6]. The details of the structural characterization, the $\rho(T)$, $S(T)$ measurements and room temperature Raman spectroscopic studies can be found elsewhere [6]. The temperature-dependent Hall coefficient $R_H(T)$ measurements were performed by the van der Pauw method on similar bar samples in a closed cycle refrigerator (CCR)-based 15 T magnet supplied by Cryogenic Ltd., UK.

**Results and discussion.** Phase purity and structure of the Sb$_2$Te$_{3-x}$Se$_x$ (0.0 $\leq x \leq 1.0$) mixed crystals have been identified by XRD and the corresponding spectra are shown in fig. 1(a). We have performed Rietveld refinement utilizing the Materials Analysis Using Diffraction (MAUD) program) using atomic positions and substitutions of all the synthesized Sb$_2$Te$_{3-x}$Se$_x$ ($x = 0.0, 0.2, 0.6, \text{and} 1.0$) samples. The space group $R^3m$ and point group $D_{4d}$ were used for the refinement [14–16]. The refinement parameters are provided in table 1. Figure 1(b) shows a typical refinement result for the Sb$_2$Te$_2$S$_{0.2}$ sample. The variation of the lattice constant with the Se content for the samples are shown in the inset. The linear contraction of the lattice parameters with increased Se concentration closely follows Vegard’s law. The atomic radii of Te and Se are 142 pm and 100 pm, respectively [17]. Thus, substitution of Se at the Te position should lead to a decrease in the lattice parameter and hence the cell volume (table 1). According to Vegard’s law, the crystallographic parameters of a continuous substitutional solid solution vary linearly with the concentration when the nature of the bonding is similar in the constituent phases. The XRD results thus confirm that synthesized Sb$_2$Te$_{3-x}$Se$_x$ alloys are single phase in nature and a complete solid solution has been formed with Se, substituting Te. However, a close observation reveals that the variation of the lattice parameter $a$ with the Se concentration is exactly linear, i.e., strictly following Vegard’s law. However, the variation of the lattice parameter $c$ with the Se content shows a little deviation from linearity around $x = 0.2$. This might be related to the anomaly observed in $S(T)$, $R_H(T)$ or $n_H(T)$ and $PF$ data of the Sb$_2$Te$_2$S$_{0.2}$ sample discussed later.

Figure 2 shows room temperature Raman spectra (RS) for all the synthesized samples. The Sb$_2$Te$_3$ alloy exhibits
the higher wave number side. The unit cell of Sb$^{1.0}$, the observed phonon frequencies gradually shift to Raman active $A_g$, $E_g$, $A_{2g}$ modes. The inset summarizes the observed Raman shifts of different vibrational modes with the Se($x$) content for the synthesized Sb$_{2}$Te$_{3-x}$Se$_{x}$ ($0.0 \leq x \leq 1.0$) samples.

Four Raman active modes: $E^1_g$ (46 cm$^{-1}$), $A^1_{1g}$ (62 cm$^{-1}$), $E^2_g$ (113 cm$^{-1}$) and $A^2_{2g}$ (166 cm$^{-1}$) [18–20]. The RS (fig. 2) for Se-doped Sb$_2$Te$_3$ alloys depict three peaks at around 69 cm$^{-1}$, 112 cm$^{-1}$ and 166 cm$^{-1}$, that can be attributed to Raman active $A^1_{1g}$, $E^2_g$, and $A^2_{2g}$ vibrational modes, respectively. The active Raman mode $E^2_g$ (around 46 cm$^{-1}$) is out of the range measured in this work [6].

Although the Se atom is iso-electronic with Te, it is more electro-negative than Te. The incorporation of Se in the Sb$_2$Te$_3$ lattice will change its lattice dynamics. The inset in fig. 2 summarizes the observed Raman shifts of different vibrational modes with the Se content and reveals that all the observed Raman active modes have a very small shift with the Se doping. Since the atomic masses of Sb and Te are comparable, the observed slight variation in $A^1_{1g}$, $E^2_g$ and $A^2_{2g}$ modes with the Se($x$) content is anticipated for Sb$_2$Te$_{3-x}$Se$_x$ ($0.0 \leq x \leq 1.0$) mixed crystals, where the Se concentration is not significantly higher. However, a close observation of fig. 2 (inset) divulges that, initially, for low Se content ($x = 0.2$), the phonon frequencies shift to the lower wave number side. But with a further increase of Se, i.e., for $x = 0.6$ and 1.0, the observed phonon frequencies gradually shift to the higher wave number side. The unit cell of Sb$_2$Te$_3$-like compounds has five quintuple layers (Te$^3$-Sb-Te$^2$-Sb-Te$^3$) weakly bound by the van der Waals force in which Te atoms exhibit two different environments, i.e., Te$^3$ and Te$^2$. Te$^2$ atoms are the centre of mass of the lattice vibration [12] and the Raman active modes directly manifest the vibrational properties of the Sb-Te(2)/Te(1) bonds. The Sb-Te$^2$ bond is more polar than the Sb-Te$^3$ bond. Initially for a low concentration ($x = 0.2$), Se preferentially replaces Te at the Te$^2$ site, and, subsequently, for a higher concentration ($x = 0.6, 1.0$) the Se atoms continue to replace Te at Te$^3$/Te$^2$ sites in a random manner [21]. This might lead to the observed anomaly in phonon frequency for the Sb$_2$Te$_{2.8}$Se$_{0.2}$ sample (inset in fig. 2, marked with an arrow).

The $\rho(T)$ data of the polycrystalline Sb$_2$Te$_{3-x}$Se$_x$ samples depict that $\rho$ increases with increasing Se concentration (fig. 3(a)). Pristine Sb$_2$Te$_3$ always possesses over-stoichiometric Sb atoms along with native point defects, viz., $V_{\text{Te}}$ and segregated Te [6,22,23]. The over-stoichiometric Sb atoms occupy prevalingly the Te$^2$ sites in the Te sublattice, giving rise to antisite (AS) defects of Sb$_{Te}$ type. Due to such AS defects, Sb$_2$Te$_3$ always shows a $p$-type conductivity with hole concentration around $10^{20}$ cm$^{-3}$ [9]. With increasing Se concentration, the formation energy of these AS defects increases. As a consequence the formation probability of AS defects decreases, which, in turn, leads to the decrease of the carrier (hole) concentration in Sb$_2$Te$_{3-x}$Se$_x$ samples with increasing $x$. Thus, $\rho$ increases with increasing Se content for the reported Sb$_2$Te$_{3-x}$Se$_x$ alloys.

Figure 3(a) further depicts that while Sb$_2$Te$_3$ and Sb$_2$Te$_{2.8}$Se$_{0.2}$ samples exhibit weakly metallic $\rho$, but an
activated $\rho(T)$ behaviour is observed for higher-Se-content samples. The observed metallic $\rho(T)$ data, arising due to the increase of the intrinsic carrier concentration at high temperatures, are typical for these heavily doped narrow band semiconductors [24]. In order to extract the nature of carrier scattering in Sb$_2$Te$_{3-x}$Se$_x$ ($x = 0.0, 0.2$) samples, the $\rho(T)$ curve is fitted with the power-law expression $\rho = \rho_0 + AT^n$. For both the samples, the obtained best-fit value of $n$ is 1.66. Recently Dutta et al. reported the same $n$ value for Sb$_2$Te$_3$ crystals [8]. On the other hand, a similar value of $n$ (= 1.3) for the Sb$_2$Te$_{3-x}$Se$_x$ system was also reported earlier by Kulbachinskii et al. [5]. For bulk Sb$_2$Te$_3$ and the related TI systems, the transport properties of the surface state are often mixed with the bulk state, which probably gives rise to the unusual value of the exponent in the low-Se-content Sb$_2$Te$_{3-x}$Se$_x$ samples [6,8].

The $S(T)$ data depict that all the reported samples are of $p$-type in nature (fig. 3(b)). $S(T)$ initially increases with increasing $x$ from $x = 0.0$ to 0.2. But for $x \geq 0.2$, $S(T)$ decreases. The compositional dependence of the scattering parameter ($r$) is estimated from the $S(T)$ data. For a heavily doped semiconductor (for a single valley in the isotropic case), $S$ is given by [13]

$$ S = \pm \frac{k_B}{e} \left[ \eta_F - \left( \frac{r + 5/2}{r + 3/2} \right) \frac{F_{r+3/2}(\eta_F)}{F_{r+1/2}(\eta_F)} \right]. $$

Here $\eta_F = E_F/(k_B T)$ is the reduced Fermi energy; the parameter $r$ describes the energy dependence of the scattering temperature, and

$$ F_n = \int_0^\infty \frac{d\eta}{1 + \exp(n - \eta_F)} $$

is the Fermi integral. Now, $r = -0.5$ corresponds to the acoustic phonon scattering, $r = 0.5$ is the scattering due to optical phonons and $r = 1.5$ denotes the scattering by ionized impurities. We estimate the Fermi energy ($E_F$) in two samples, viz., Sb$_2$Te$_3$ and Sb$_2$Te$_{2.8}$Se$_{0.2}$, exhibiting metallic behaviour by a simple model,

$$ E_F = \frac{h^2}{2m^*} \left[ 3\pi^2 n_{1H} \right]^{2/3}, $$

where $n_{1H}$ is the carrier concentration (fig. 3(c)). Reasonable values of $E_F \approx 100$ meV and 120 meV are obtained, respectively, for $x = 0.0$ and 0.2 samples [25,26]. Using these Fermi energies and formulae (1) and (2) we may estimate the scattering parameter $r$. Such procedure yields $r = -0.5$ and $r = 0.1$, respectively for $x = 0.0$ and $x = 0.2$ alloys. The obtained best-fit value of $r = -0.5$ for Sb$_2$Te$_3$ alloy (i.e., $x = 0.0$) corroborates the reported results [13]. The $S(T)$ data thus reveal that in SbTeSe-based degenerated semiconductors, the increase of the Se content shifts the scattering from the preferentially acoustic phonon closer to impurity scattering.

For the Sb$_2$Te$_{2.8}$Se$_{0.6}$ and Sb$_2$Te$_2$Se samples, the activation energy ($E_{act}$) is estimated from the $\rho(T)$ data using the relation

$$ \rho = \rho_0 \exp \left( \frac{E_{act}}{2k_B T} \right), $$

where $\rho_0$ is a constant. The estimated $E_{act}$ values, 9.24 meV and 12.30 meV respectively for Sb$_2$Te$_{2.8}$Se$_{0.6}$ and Sb$_2$Te$_2$Se, indicate that the estimated transport gap ($E_g$) is such smaller than the reported band gap ($E_g$) [27]. $E_g$ arises due to the difference between the lower conduction band (LCB) and the upper valance band (UVB) [22]. However, according to Akrap et al., while $E_g$ is determined by the band structure, $E_{act}$ is actually linked to the presence of point defects [13]. Sb$_2$Te$_3$ hosts various kinds of defects, viz., AS defects of Sb$_{12}$ type, $V_{\text{Tm}}$ and segregated Te. Increasing the Se content in the Sb$_2$Te$_3$ matrix enhances the interplay between these defects with Se atoms initially replace Te$^2$ atoms, but for a higher concentration it continues to replace Te$^1$/Te$^2$ atoms randomly. This might lead to the observed change from a metallic to an activated behaviour in the $\rho(T)$ data for $x > 0.2$. The energy state due to the native defects in the Sb$_2$Te$_{3-x}$Se$_x$ system probably lies between LCB and UVB and leads to a smaller $E_{act}$ in the activated samples. Further, when the composition is tuned from Sb$_2$Te$_3$ to Sb$_2$Te$_2$Se, the concentration of holes in the system decreases. Around the composition $x = 1$ (Sb$_2$Te$_2$Se), the Se/Te sublattice is expected to be ordered with an almost complete compensation of donor and acceptor impurities [13]. Therefore, around $x = 1$ the bulk conductivity should be minimum, which is correctly reflected in our $\rho(T)$ data (see fig. 3(a)).

Figure 3(c) represents the thermal variation of $n_{1H}$ data for all the Sb$_2$Te$_{3-x}$Se$_x$ samples, measured in a magnetic field of 12 T. Like the $S(T)$ data initially with increasing $x$, $n_{1H}$ increases for Sb$_2$Te$_3$ and Sb$_2$Te$_{2.8}$Se$_{0.2}$, but for $x \geq 0.2$, it decreases, indicating that the apparent hole concentration is highest in Sb$_2$Te$_{2.8}$Se$_{0.2}$. Here we would like to present a plausible explanation for such anomalous behaviour of $n_{1H}$ in Sb$_2$Te$_{3-x}$Se$_x$. The band structure calculation indicates that the UVB of Sb$_2$Te$_3$ consists of six ellipsoids and the lower valence band (LVB) is known to be multivalleyed [5,24]. While explaining the Shubnikov-de Haas (SdH) and transient thermoelectric effect (TTE) data for the Sb$_2$Te$_{3-x}$Se$_x$ (0.0 $\leq x \leq 1.0$) system Kulbachinskii et al. indicate the presence of another valence band (NVB) for $x \geq 0.2$ and clearly predict two different regions, viz., $0 \leq x \leq 0.2$ and $0.2 < x \leq 1.0$ in the band structure [5]. In the first region $0 \leq x \leq 0.2$, only UVB and LVB contribute. But in the second region $0.2 < x \leq 1.0$ the contribution comes from UVB, LVB and NVB, where NVB moves up and UVB moves down due to Se doping. It should be mentioned that UVB and LVB are not equally populated, the ratio of the density of holes in LVB to that of UVB is around 390 [28]. In view of this large ratio, LVB contributes mostly in the conduction mechanism. The evaluation of the band structure with the Se content in the Sb$_2$Te$_{3-x}$Se$_x$ (0.0 $\leq x \leq 1.0$) alloy as predicted by Kulbachinskii et al. [5], and correspondingly
Table 2: The simulated parameters of the investigated Sb$_2$Te$_3$ and Sb$_2$Te$_{2.8}$Se$_{0.2}$ alloys obtained by fitting the experimental temperature dependences of the Seebeck coefficient, the resistivity, and the Hall carrier concentration.

|                  | Sb$_2$Te$_3$ [R3m] | Sb$_2$Te$_{2.8}$Se$_{0.2}$ [R3m] |
|------------------|--------------------|----------------------------------|
| Bandgap (eV)     | 0.25               | 0.25                             |
| Second valance band (eV) | 0.19               | 0.08                             |
| Effective masses ($m_0$) |                   |                                  |
| Light Holes      | 0.043              | 0.043                            |
| Heavy Holes      | 0.15               | 0.15                             |
| b1               | 0.705              | 0.705                            |
| b2               | 0.615              | 0.615                            |
| Light Holes      |                   |                                  |
| b3               | 0.615              | 0.615                            |
| b2               | 0.534              | 0.534                            |
| Heavy Holes      |                   |                                  |
| b2               | 0.341              | 0.341                            |
| b3               | 0.341              | 0.341                            |
| Acceptor concentration (cm$^{-3}$) | 2.0 x 10$^{19}$ | 2.3 x 10$^{19}$ |
| Scattering parameters |                   |                                  |
| Density (kg/m$^3$) | 6500               | 6500                             |
| Sound velocity (m/s) | 1780               | 1780                             |
| Deformation potential (eV) | 3                  | 3                                |
| Grain boundaries |                   |                                  |
| Grain size (nm)  | 15.3               | 10                               |
| Scattering constant | 0.3                | 0.3                             |
| Dielectric constant |                   |                                  |
|                  | 101                | 101                              |

The net contribution of the carrier from UVB, LVB, and NVB might be related to the experimentally observed $n_H$ behaviour.

In the framework of the Boltzmann equation approach, we simulated simultaneously (with the same parameters) $\rho(T)$ (see fig. 3(a)), $S(T)$ (see fig. 3(b)), and $n_H(T)$ (see fig. 3(c)) for the samples with $x = 0.0$ and 0.2. Theoretical dependences are shown in fig. 3(a)–(c) by solid lines. However, we were unable to reproduce a small value of the Seebeck coefficient in samples with $x = 0.6$ and $x = 1.0$ Se content without an unrealistic change of the band parameters. We suggest that part of holes in the material is localized and to fit data for samples with high Se content the localization of part of the holes should be taken into account. The theoretical model and the method of calculation are described in ref. [5].

Figure 4 shows the compositional dependence of PF for the Sb$_2$Te$_{3-x}$Se$_x$ ($x = 0.0$, 0.2, 0.6, and 1.0) samples estimated from the measured quantities. The theoretical values of PF for the Sb$_2$Te$_3$ and Sb$_2$Te$_{2.8}$Se$_{0.2}$ alloys, calculated from the simulated $S(T)$ and $\rho(T)$ data, are also plotted in fig. 4. The PF increases with increasing temperature and reveals a non-saturating behaviour around room temperature. Similar to the behaviour observed for the $S(T)$ and $n_H(T)$

\[
\rho(T) \text{ data, which has an activated character (see fig. 3(a)). These samples have too large value of the Hall coefficient and a small value of the Seebeck coefficient. One of the reasons may be (probably) due to modification of the band structure with high Se content [5] and localization of the part of the holes.} 
\]
data, the maximum value of $PF$ is also observed for the Sb$_2$Te$_3$-xSe$_x$ alloy. This further indicates that increasing the Se content in Sb$_2$Te$_3$ does not always contribute a positive role in increasing the thermoelectric performances of Sb$_2$Te$_3$-xSe$_x$ samples. However, conclusive evidence can be drawn only after estimating $ZT$. It should be recalled that Sb$_2$Te$_3$-xSe$_x$ possesses the highest $\eta_{11}$ ($\sim 10^{12}$/cc). It is thus quite justified to assume that tuning of the carrier concentration as well as band structure engineering including the optimization of the band parameters in the Sb$_2$Te$_3$-xSe$_x$ system should play a crucial role in obtaining a good TE material.

**Conclusion.** – XRD data and Raman spectra confirm that all the synthesized Sb$_2$Te$_3$-xSe$_x$ samples exhibit rhombohedral crystal geometry. It has been realized that the surface states are often mixed with the bulk state, giving rise to the observed metallicity in the Sb$_2$Te$_3$ and Sb$_2$Te$_3$-xSe$_x$ samples. The transport gap ($E_{\text{gap}}$), estimated in high-Se-content samples showing an activated behavior, is smaller than the reported band gap ($E_g$) probably due to the presence of point defects and the tail of the density of state. Acoustic phonon scattering dominates the $S(T)$ data for the synthesized host Sb$_2$Te$_3$. However, with increasing Se concentration, impurity scattering gradually dominates the $S(T)$ data. The theoretical calculation, based on a four-band model, demonstrates that the position of the second valence band as well as the acceptor concentration are sensitive to the Se concentration and to the part of the holes in high-Se-content samples is localized.

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The work is supported by DST, Government of India-RFBR, Government of Russia (DST reference No.: INT/RUS/RFBR/P-183; RFBR grant: IND-a 15-52-45037). The financial grant, including the fellowship of the first author DD, received from the UGC-DAE Consortium for Scientific Research, Kalpakkam node (Project reference No.: CSR-KN/CRS-65/2014-15/505) is also gratefully acknowledged. The authors would also like to thank the DST, Government of India, for low-temperature high-magnetic-field facilities at UGC-DAE CSR, Kolkata Centre.

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