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Electronic tuning of the transport properties of off-stoichiometric Pb$_x$Sn$_{1-x}$Te thermoelectric alloys by Bi$_2$Te$_3$ doping

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The recent energy demands affected by the dilution of conventional energy resources and the growing awareness of environmental considerations have motivated many researchers to seek for novel renewable energy conversion methods. Thermoelectric direct conversion of thermal into electrical energies is such a method, in which common compositions include IV-VI semiconducting compounds (e.g., PbTe and SnTe) and their alloys. For approaching practical thermoelectric devices, the current research is focused on electronic optimization of off-stoichiometric $p$-type Pb$_x$Sn$_{1-x}$Te alloys by tuning of Bi$_2$Te$_3$ doping and/or SnTe alloying levels, while avoiding the less mechanically favorable Na dopant. It was shown that upon such doping/alloying, higher $ZT$s, compared to those of previously reported undoped Pb$_{0.5}$Sn$_{0.5}$Te alloy, were obtained at temperatures lower than 210–340°C, depending on the exact doping/alloying level. It was demonstrated that upon optimal grading of the carrier concentration, a maximal thermoelectric efficiency enhancement of $\sim$38%, compared to that of an undoped material, is expected.

INTRODUCTION

PbTe and SnTe are narrow band gap semiconductors, with energy gap, $E_G$, values of 0.217 and 0.360 eV, respectively, at 77 K. They form single phase pseudo-binary Pb$_{1-x}$Sn$_x$Te (PST$_x$) alloys, which are widely employed in far-infrared applications at wavelengths beyond 7 µm. In such alloys, the configuration of the valence and conduction bands is modified by increasing the Sn content, $x$, which reduces the energy gap of the alloys compared to pure PbTe, and a zero-band gap is reached for $x = 40\%$ at 77 K. At higher $x$ values, an inverted band structure is obtained, which is commonly referred to a negative gap, and it is characterized by valence band states originating from the cations and conduction band states from the anions. IV-VI compounds exhibit inherent high carrier concentration, in the range of $10^{19} - 10^{20}$ cm$^{-3}$, which is optimal for thermoelectric heat to electricity conversion applications. Due to this fact and the recent energy demands affected by the dilution of conventional energy resources and the growing awareness of environmental considerations, novel PbTe and SnTe based thermoelectric alloys, capable of an effective direct conversion of waste heat into electricity, are constantly developed. Such recently developed alloys include the nano-structured $p$-type Pb$_x$Sn$_{1-x}$Te, Pb$_x$Mg$_{1-x}$Te, Pb$_x$Te$_{1-y}$Se$_y$, and Pb$_x$Cd$_{1-x}$Te (Ref. 9) compositions, in which sodium was employed as an acceptor (while substituting Pb) for optimizing the electronic properties, and Pb$_x$Ge$_{1-x}$Te (Refs. 10–12) and (Pb$_x$Sn$_{1-x}$)$_y$Ge$_{1-y}$Te (Refs. 13 and 14) compositions, which were electronically tuned by the donor Bi$_2$Te$_3$. Na was involved in cases where an increase of the carrier concentration was required while Bi$_2$Te$_3$ was involved for highly degenerated $p$-type compositions, for compensating higher than optimal holes concentration toward lower more optimal values. In all of these compositions, thermoelectric figure of merit ($ZT = z^2\sigma T/k$, where $T$ is the temperature; $z$ is the Seebeck coefficient; and $\sigma$ and $k$ are the electrical and thermal conductivities, respectively) values much higher than 1 were obtained, mainly due to reduced lattice thermal conductivity, attributed to an effective phonon scattering by embedded nano-features. Due to the fact that thermoelectric materials are subjected to high temperature gradients and cycles as well as thermal stresses due to non-matched coefficients of thermal expansion to the other device’s components, during operation conditions, the mechanical properties are also of a major practical interest. Previous studies of the mechanical properties of $p$-type undoped and Na-doped PST, thermoelectric compositions clearly indicated that Na doping degrades the mechanical properties of such alloys. This finding was concluded by the establishment that non- Na doped PST, alloys are more favorable for practical uses compared to Na-doped alloys from a mechanical point of view in spite of the higher $ZT$s of the latter. An off-stoichiometric single-phase non-nano-structured Te-rich (Pb$_{0.5}$Sn$_{0.5}$Te)$_{0.4955}$Te$_{0.5045}$ (PST$_{0.5}$) composition, exhibiting improved stability characteristics compared to Pb$_{0.99}$Na$_{0.01}$Te, was recently reported as a possible $p$-type candidate for practical thermoelectric applications, although exhibiting a limited maximal $ZT$, $ZT_{\text{max}}$, of only 0.5, compared to 0.8 of the latter (see red and black curves of Fig. 1), due to improved mechanical properties. Yet, as can be seen by the red curve in Fig. 1, the $ZT_{\text{max}}$ of this composition was obtained at 450°C, which is close to the upper allowed temperature limit of PbTe based materials. Due to the fact that PbTe based thermoelectric devices operate at temperatures ranging from 50 to 100°C at the cold side up to 450–500°C at the hot side, $ZT$ enhancement at temperatures lower than...
450 °C is highly desired for maximizing the thermoelectric efficiency of the device over the entire operating temperature range. Since no single thermoelectric composition enables maximization of ZT over the wide temperature ranges required in practical applications, due to the strong temperature dependence of the transport properties, generating functionally graded materials (FGMs) based on stacking of several segments, each with an optimal carrier concentration at its local temperature range, is a reasonable option for enhancement of the average ZT over the entire operating temperature range. This approach was successfully applied for n-type (Pb,Sn)Te,Si−1−x, with graded PbI2 (donor) doping levels and for p-type stoichiometric PSTx compositions with varied x values in the range of 0.1 < x < 0.5.10 Due to the fact that, for the latter, the stoichiometric PST0.5 composition exhibited a lower ZTmax of ~0.35 (Ref. 19) than the 0.5 value of the off-stoichiometric PST1.05 composition, shown in Fig. 1, the current research was dedicated to the investigation of grading possibilities of the latter. The grading was approached by various Bi2Te3 doping levels of off-stoichiometric (Pb1−xSnx)Te0.4955Te0.5045, PSTTx, alloys with x values in the 0.5 < x < 0.8 range. As was mentioned above, Bi2Te3 had been extensively used as a donor dopant in GeTe rich (Pb,Sn)1−x,Ge1−yz,Te alloys10–14 but was never applied before for electronic tuning of PST, and PSTT alloys, although a similar role is expected. The maximal ZT envelope of the currently investigated 0.01–5 mol. % Bi2Te3 doped PSTT0.5 alloys is shown by the blue curve of Fig. 1, while that of the 0.1 mol. % Bi2Te3 doped PSTT0.5 alloys with x values of 0.5 (5–6 segment), 0.7 (6–7 segment), and 0.8 (7–8 segment) is shown by the pink curve in this figure. Comparing both of these curves to the previously reported undoped PSTT0.5 composition17 (the red curve of Fig. 1) clearly indicates higher ZTs upon Bi2Te3 doping of PSTT0.5 (blue curve) at temperatures lower than 340°C and for the 0.1 mol. % Bi2Te3 doped PSTT0.5<x<0.8 (pink curve) at temperatures lower than 300°C. This highlights the potential of grading the Bi2Te3 doping levels or the x values of such alloys for enhancing the average ZTs over the entire operating temperature range. It is interesting to note, referred to Fig. 1, that even compared to the previously reported more efficient but less mechanically favorable Pb0.99Na0.01Te composition17 (the dashed black curve), the currently investigated compositions exhibit higher ZTs at temperatures lower than ~200°C.

EXPERIMENTAL DETAILS

0.01–5 mol. % Bi2Te3 doped (Pb1−xSnx)Te0.4955Te0.5045 (PSTT0.5) alloys with x values in the range of 0.5 < x < 0.8 were synthesized from pure elements (purity of 5N) in evacuated quartz ampoules under vacuum of 10−6 Torr. The ampoules were placed in a rocking furnace (Thermcraft Inc.) for 15 min at 950 °C, then water quenched. Milling of the cast ingots to a maximal powder particle size of 60 mesh was performed using agate mortar and pestle. The sieved powder was subsequently cold pressed under a mechanical pressure of 766 MPa, and sintered in an argon atmosphere for 3h at 625 °C which was subsequently raised to 720°C for additional 15 min, resulting in high density values of >95% of the theoretical density. Seebeck coefficient, z, and the electrical resistivity, ρ, were measured by Linseis LSR-3/800 Seebeck coefficient/electrical resistance measuring system. The total thermal conductivity, κ, was determined as a function of temperature from room temperature to 450 °C using the flash diffusivity method (LFA 457, Netzsch). The crystal structures of the samples were analyzed by x-ray powder diffraction (XRD; Rigaku DMAX 2100 powder diffractometer). The microstructure was analyzed by high resolution scanning electron microscopy (SEM; JEOL JSM-7400).

RESULTS AND DISCUSSION

SEM/XRD examination of the investigated Bi2Te3 doped PSTT0.5 alloys verified a uni-phase PbTe based matrix with lattice parameters, a, in agreement with the previously reported empirical a[A˚] = 6.4607 – 0.135x rule.19 The temperature dependence of the transport properties of the investigated alloys, Seebeck coefficient, z, electrical resistivity, ρ, thermal conductivity, κ, and the thermoelectric figure of merit, ZT, are shown in Figs. 2(a)–2(d), respectively. From this figure, it can be clearly seen that upon 0.1 mol. % Bi2Te3 doping of the investigated PSTT0.5 alloys with x values of 0.5 (curve 1 for each of the properties), 0.7 (curve 2) and 0.8 (curve 3), all of the compositions exhibit p-type conduction (positive z values). In addition, both z and ρ values decrease with increase in the Sn amount (x value), indicating the acceptor action of Sn, on increasing the hole concentration, in these alloys. Such an effect is expected from the increased contribution of the highly degenerated p-type SnTe compound. This acceptor action, on increasing the hole concentration upon increasing the x values, can be also noticed by the increased contribution of the charge carriers to the thermal conductivity, κ, values, shown in Fig. 3(a). The κ, values were calculated from Wiedemann-Franz relation, κ,q = Lρ−T, where ρ is the electrical resistivity (Fig. 2(b)), T is the absolute temperature, and L is the Lorenz number, defined in Eq. (1), in which k is the Boltzmann constant, r is the scattering parameter, equals to
−0.5 for PbTe based alloys, $e$ is the electron charge, $F_r$ is the Fermi integral, defined in Eq. (2), where $e$ is the kinetic energy of a charge carrier, $\eta$ is the reduced Fermi potential ($=E_F/kT$, where $E_F$ is the Fermi energy), and $f_0$ is the Fermi distribution function, defined in Eq. (3), in a procedure described previously.\(^\text{(20)}\)

\[
L = \left( \frac{k}{e} \right)^2 \left[ \frac{\left( r + \frac{7}{2} \right) \left( r + \frac{3}{2} \right) F_{r+2}(\eta)F_{r+2}(\eta) - \left( r + \frac{5}{2} \right)^2 F^2_{r+2}(\eta)}{\left( r + \frac{3}{2} \right)^2 F^2_{r+2}(\eta)} \right], \tag{1}
\]

\[
F_r = \int_0^\infty e f_0(\eta) de, \tag{2}
\]

\[
f_0(\eta) = \frac{1}{1 + \exp(e - \eta)}. \tag{3}
\]

In this procedure, the $\eta$ values of each of the investigated alloys were calculated from the measured $\alpha$ values (Fig. 2(a)) using the following equation:

\[
\alpha = \frac{k}{e} \left[ \frac{\left( \frac{5}{2} + r \right) F_{\frac{5}{2}+r}}{\left( \frac{3}{2} + r \right) F_{\frac{3}{2}+r}} - \eta \right]. \tag{4}
\]

Upon 0.01 (curve 4 in Figs. 2 and 3(a)), 0.1 (curve 1), 1 (curve 5), and 5 (curve 6) mol. % Bi\(_2\)Te\(_3\) doping of PSTT\(_{0.5}\), a clear donor compensating action of Bi\(_2\)Te\(_3\), reducing the net holes concentration of the $p$-type PSTT\(_{0.5}\) alloy, was

FIG. 2. Temperature dependence of (a) Seebeck coefficient, (b) electrical resistivity, (c) thermal conductivity and figure of merit (d) of 0.1 mol. % Bi\(_2\)Te\(_3\) doped PST\(_{0.5}\), with $x$ values of 0.5 (1), 0.7 (2), and 0.8 (3) as well as of 0.01 (4), 1 (5), and 5 (6) mol. % Bi\(_2\)Te\(_3\) doped PST\(_{0.5}\) alloys. The ZT values are compared to previously reported Pb\(_{0.99}\)Na\(_{0.01}\)Te and (Pb\(_{0.5}\)Sn\(_{0.5}\)Te)\(_{0.49}\)
Te\(_{0.50}\) compositions.\(^\text{(17)}\)

FIG. 3. (a) Temperature dependence of the electronic contribution to the thermal conductivity, $\kappa_e$, for the investigated alloys. The notations are in agreement with Fig. 2. (b) Ln electrical conductivity, $\ln(\sigma)$ vs. $T^{-1}$ values at the intrinsic range of the 1% Bi\(_2\)Te\(_3\) doped PSTT\(_{0.5}\) composition, indicating an energy gap, $E_g$, of $\sim$0.12 eV.
observed, indicated by the increased low temperature $x$ (Fig. 2(a)) and $\rho$ (Fig. 2(b)) values and the decreased $\kappa_e$ values (Fig. 3(a)) with an increase in the $\text{Bi}_2\text{Te}_3$ amount. Upon the maximal $\text{Bi}_2\text{Te}_3$ doping concentration applied, 5%, a full compensation of the holes was observed for obtaining $n$-type conduction, indicated by the negative Seebeck coefficient values (curve 6, Fig. 2(a)).

Besides the calculation of the $\kappa_e$ values, the measured $\rho$ values of the 1% $\text{Bi}_2\text{Te}_3$ doped PSTT$_{0.5}$ composition (curve 5, Fig. 2(b)), at the intrinsic range ($T > 325^\circ\text{C}$), in which a reduction trend is observed with increasing the temperature, were used for estimation of the energy gap as shown in Fig. 3(b). At this range, the electrical conductivity, $\sigma$, is known to obey the $\sigma = Ae^{-E_g/2kT}$ trend ($A$-constant, $E_g$-energy gap). Therefore, from the slope of the curve of this figure, an $E_g$ value of $\sim 0.12\text{eV}$ was obtained for the PSTT$_{0.5}$ composition, which agrees with the $E_g$ reduction trend, pointed out above, of $\text{PbTe}$ (0.360 eV) with increasing the Sn content, $x$, in the pseudo-binary $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys.

The lattice contribution of the thermal conductivity, $\kappa_l$, of the single-phased non-nano-structured investigated alloys were calculated by subtraction of the calculated $\kappa_e$ values (Fig. 3(a)) from the measured total thermal conductivity values (Fig. 2(c)), as shown in Fig. 4(a). From this figure, a significant $\kappa_l$ enhancement with the increase in the Sn content, $x$, from 0.5 (curves 1, 4–6) to 0.7 (curve 2) and 0.8 (curve 3) can be observed. In order to explain these results, the SnTe alloying effect of $\text{PbTe}$, in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, alloys on the $\kappa_l$ values, was calculated using a similar formulation applied recently for $\text{Ge}_{\text{Pb}}\text{Pb}_{1-x}\text{Te}^\text{alloys}$ as expressed by the following equation:

$$ \kappa_{l,\text{alloy}} = \frac{\text{arc tan}(u)}{\kappa_{l,\text{pure}}}, $$

$$ u^2 = \frac{\pi \cdot D \cdot \Omega}{2h \cdot \nu^2} \cdot \kappa_{l,\text{pure}} \cdot x (1-x) \left[ \frac{\Delta M}{M} \right]^2 + \left( \frac{\Delta a}{a} \right)^2, $$

(5)

where $\kappa_{l,\text{alloy}}$ represents the lattice thermal conductivity in $\text{A}_{\text{Bi}}\text{B}_{1-x}$ solid solution alloys, compared to the pure involved compounds, $\kappa_{l,\text{pure}}$, based on only umklapp and alloying/disordering point defects.

In this formulation, the elastic parameters, $\varepsilon$ and $\kappa_{l,\text{pure}}$, are expressed in Eqs. (6) and (7), respectively,

$$ \varepsilon = \frac{2}{9} \left[ \frac{(4 + 6.4\gamma)}{1 + r} \right] \left[ \frac{1 + r}{1 - r} \right], $$

(6)

$$ \kappa_{l,\text{pure}} = \frac{(6\pi^2)^{\frac{3}{2}}}{\Omega^3} \cdot \frac{M \cdot \nu^3}{T \cdot \Omega \cdot \gamma^2}, $$

(7)

where $\theta_D$—Debye temperature, $\nu$—average speed of sound, $T$—absolute temperature, $\Omega$—volume per atom, $\gamma$—Grüneisen parameter, quantifying the inharmonic interaction potentials of phonons in a material, and $r$—Poisson’s ratio. For isotropic-elastic media, such as the currently investigated polycrystalline materials, $r$ might be expressed according to Eq. (8), where $v_l$ and $v_t$ represent the longitudinal and transverse sound velocities, respectively,

$$ r = \frac{v_l^2 - 2v_r^2}{2(v_l^2 - v_t^2)}. $$

(8)

$M$ and $a$ are the average atomic weight and the lattice parameter of the pure compounds ($\Delta M$ and $\Delta a$ are the differences between the two components of the alloy), respectively, where $\Delta M/M$ and $\Delta a/a$ in the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ system can be described according to the following equation:

$$ \frac{\Delta M}{M} = \frac{M_{\text{PbTe}} - M_{\text{SnTe}}}{xM_{\text{PbTe}} + (1-x)M_{\text{SnTe}}}, $$

$$ \frac{\Delta a}{a} = \frac{a_{\text{PbTe}} - a_{\text{SnTe}}}{x a_{\text{PbTe}} + (1-x)a_{\text{SnTe}}}. $$

(9)

Substitution of the individual physical parameters for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, listed in Table I, into Eqs. (5)–(9), resulted in the solid curve shown in Fig. 4(b).

This figure reveals a good (within $\pm 10\%$) agreement between the low temperature experimental $\kappa_l$ points and the curve calculated by considering only umklapp and alloying/disordering effects. Furthermore, the increasing trend of $\kappa_l$ values from that of PSTT$_{0.5}$ toward those of the PSTT$_{0.7}$ and PSTT$_{0.8}$ alloys can be clearly explained by the reduced disordering effect while approaching toward the less disordered SnTe richer alloys.

The temperature dependence of the $ZT$ values of the various investigated $\text{Bi}_2\text{Te}_3$ doped PSTT$_x$ compositions, compared to previously reported $\text{Pb}_{0.99}\text{Na}_{0.01}\text{Te}$ and undoped PSTT$_{0.5}$ compositions, is shown in Fig. 2(d). It can be clearly seen in this figure that upon 0.1% $\text{Bi}_2\text{Te}_3$ doping of the PSTT$_{0.5,0.7,0.8}$ alloys (curves 1,2 and 3, respectively),
TABLE I. Useful SnTe and PbTe parameters for estimation of the lattice thermal conductivity values of Pb$_{1-x}$Sn$_x$Te alloys using Eqs. (5)–(9).

| Parameter                    | SnTe  | PbTe |
|------------------------------|-------|------|
| Atoms/unit cell, \(N\)       | 8     | 8    |
| Average atomic weight, \(M\) (g/mol) | 246.3 | 334.8 |
| Lattice parameter, \(a\) (Å)  | 6.320 (Ref. 23) | 6.454 (Ref. 27) |
| Volume per atom, \(\Omega = (a^2/\pi N) (\text{Å}^3)\)  | 31.55  | 33.6  |
| Debye temperature, \(\theta_D\) (K) | 165 (Ref. 24) | 130 (Ref. 28) |
| Grüneisen parameter, \(\gamma\) | 2.1 (Ref. 25) | 1.96 (Ref. 27) |
| Longitudinal sound velocity, \(v_l\) (m/s) | 3012 (Ref. 26) |        |
| Transverse sound velocity, \(v_t\) (m/s) | 1388 (Ref. 26) |        |
| Average speed of sound, \(v\) (m/s) | 1800 (Ref. 24) | 1770 (Ref. 27) |
| Poisson’s ratio, \(\nu\) | 0.36 ([Ref. 26], 0.27 (Ref. 28) Eq. (8)) |
| Lattice thermal conductivity, \(\kappa_l\) (W/m K) | 1.5 (Ref. 25) | 2.3 (Ref. 29) |

\(ZT_{\text{max}}\) is obtained at higher temperatures with the increase in the Sn amount. This is due to the more pronounced effect of the \(p\)-type degenerated SnTe compound, acting as an acceptor dopant,\(^1\) in the investigated PSTT\(_x\) alloys, initiating an intrinsic carrier contribution at higher temperatures. For the PSTT\(_{0.5}\) alloys, due to similar considerations, increasing the Bi$_2$Te$_3$ dopant amount from 0.01% to 0.1%, and 1% (curves 4, 1, and 5, respectively) resulted in an opposite effect of reducing the \(ZT_{\text{max}}\) temperatures, due to the donor nature of the Bi$_2$Te$_3$ on compensating the high inherent hole concentration of the undoped alloys. This doping effect resulted in higher ZTs compared to the previously reported undoped PSTT\(_{0.5}\) composition\(^1\) at temperatures lower than \(\sim 340, 280,\) and \(210^\circ\text{C}\) for the 0.01%, 0.1%, and 1% Bi$_2$Te$_3$ doped PSTT\(_{0.5}\) alloys and lower than \(\sim 300^\circ\text{C}\) for the 0.1% Bi$_2$Te$_3$ doped PSTT\(_{0.7}\) alloy, indicating a higher thermoelectric potential of the currently investigated alloys at lower temperatures compared to the previously reported undoped PSTT\(_{0.5}\) composition. It is interesting to note that even compared to the previously reported thermoelectrically efficient but less mechanically favorable Pb$_{0.99}$Na$_{0.01}$Te composition,\(^1\) the 0.1% and 1% Bi$_2$Te$_3$ doped PSTT\(_{0.5}\) alloys exhibit higher ZTs at temperatures lower than \(\sim 200\) and \(145^\circ\text{C}\), respectively. As pointed out in the introduction, related to Fig. 1, the investigated alloys exhibit even a higher thermoelectric potential upon practical applications under large temperature differences of 50–450\(^\circ\text{C}\) upon grading the Bi$_2$Te$_3$ doping level of PSTT\(_{0.5}\) (blue curve, Fig. 1) or the \(x\) values of 0.1% Bi$_2$Te$_3$ doped PSTT\(_x\) alloys (pink curve, Fig. 1). In this large temperature range, the average \(ZT\) upon grading the Bi$_2$Te$_3$ doping level of PSTT\(_{0.5}\) (blue curve, Fig. 1) equals to \(\sim 0.31\), while upon grading the \(x\) values (pink curve, Fig. 1), it equals to \(\sim 0.25\), which is almost identical to that of the previously reported undoped PSTT\(_{0.5}\) composition (red curve, Fig. 1)\(^1\) under the same temperatures range. Furthermore, additional segmenting of both of these grading combinations with the previously reported undoped PSTT\(_{0.5}\) composition, following the 1-2-3-10-11 and 5-6-9-11 routes in Fig. 1, is expected to exhibit average ZTs of \(\sim 0.37\) and \(\sim 0.34\), which are \(\sim 48\%\) and 36% higher, respectively, than the previously reported undoped PSTT\(_{0.5}\) composition. These values correspond to maximal thermo-electric efficiency values of 5.8% and 5.5%, which are 38% and 31%, respectively, higher than that of previously reported undoped composition. These absolute efficiency values are still relatively low for approaching the worldwide energetic demands. Yet, applying the currently proposed Bi$_2$Te$_3$ and/or SnTe grading approaches, for tuning the electronic properties of PSTT\(_x\) alloys, upon potentially nano-structuring of the alloys, while reducing the \(\kappa_l\) (below the values of Fig. 4(b)), is expected to increase the absolute ZT values, compared to any single homogeneous PSTT\(_x\) composition, dramatically.

**CONCLUSIONS**

In the current research, 0.01–5 mol.% Bi$_2$Te$_3$ doped (Pb$_{1-x}$Sn$_x$Te)$_{0.4955}$Te$_{0.5045}$ (PSTT\(_x\)) alloys with \(x\) values in the range of 0.5 < \(x\) < 0.8 were synthesized. In these alloys, maintaining the Bi$_2$Te$_3$ doping level while increasing the Sn content (\(x\) value) exhibited an acceptor action on increasing the total carrier concentration and the \(ZT_{\text{max}}\) temperature. Upon increasing the Bi$_2$Te$_3$ doping level of PSTT\(_{0.5}\), the opposite trend was observed due to a donor action of the Bi$_2$Te$_3$ dopant. In both of the cases, higher ZTs compared to those of the previously reported undoped PSTT\(_{0.5}\) alloy were obtained at temperatures lower than 210–340\(^\circ\text{C}\), depending of the exact Bi$_2$Te$_3$ doping and/or SnTe alloying level. Based on the individual ZTs, it was demonstrated that upon optimal grading of the Bi$_2$Te$_3$ doping concentration of PSTT\(_{0.5}\), a maximal thermoelectric efficiency enhancement of \(\sim 38\%\) compared to that of an undoped material is expected due to electronic optimization of the thermoelectric properties. Further efficiency enhancement is expected upon additional nano-structuring approaches that would reduce the lattice thermal conductivity of these compositions.

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