

Enhanced thermoelectric performance of bulk tin telluride: Synergistic effect of calcium and indium co-doping

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ABSTRACT

SnTe based materials are considered recently as a lead-free replacement of the well-known PbTe based thermoelectric (TE) materials in addressing the energy crisis worldwide. Herein we report both experimental and theoretical study on the effect of co-doping of calcium and indium on electronic structure and TE properties of SnTe. We show that the resonant levels introduced by indium and band gap opening caused by calcium, valence band convergence induced by both calcium and indium, synergistically increases the Seebeck coefficient for a wide range of temperatures. The co-doped SnTe with a high ZT of ~ 1.65 at 840 K and record high power factor of $\sim 47 \mu\text{Wcm}^{-1}\text{K}^{-2}$ for SnTe based materials make it a promising material for TE applications.

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Introduction

Exhaustion of non-renewable fossil fuel resources caused due to its abuse has resulted in ever increasing energy crisis [1]. Materials for sustainable power generation is considered as a solution to this problem [2]. Thermoelectric materials which can directly and reversibly convert heat into electricity have attracted considerable attention in the scientific community as a pollution free technology [3,4]. The thermoelectric efficiency of a material is governed by its figure of merit ZT which is given by $ZT = \sigma S^2 T / \kappa$, where σ is electrical conductivity, S is Seebeck coefficient and κ is total thermal conductivity. Although at present all the materials are known have a nonzero thermoelectric effect, in most materials the ZT is too low to be useful [1]. Hence, there is a need to identify materials with higher efficiency than available at present [5–8]. Due to well-known interdependence of S , σ and κ , developing strategies to improve material's average ZT is complicated [3]. Due to environmental toxicity of lead, PbTe based materials are not advised for large scale usage, despite it being the best known TE material [9,10]. Hence there is need to develop thermoelectric materials containing non-toxic elements [11–16]. SnTe, being a homologue of PbTe has

similar crystal and electronic structure. Though safer than PbTe, SnTe suffers a drawback of low ZT due to high carrier concentration resulting out of inherent Sn vacancies, smaller band gap (~ 0.18 eV) and higher separation between the valence sub-bands (~ 0.3 eV) than PbTe [17,18]. In order to improve the ZT of SnTe, electronic structure has been engineered using dopants such as Bi, Ca, Cd, Hg, Ga, In, Mg, Mn, Sr and co-dopants such as Ag-In, Bi-In, Cd-In, Hg-In, Mg-In, Mn-In [14,19–36]. These work involve improving the power factor by achieving carrier concentration optimization, valence band convergence, introduction of resonance level or all of them together [14,19–36]. Further the thermal conductivity is reduced by employing various nanostructuring [1,21,22,24,27–30]. While doping of Bi causes modulation of carrier concentration and an increase in density of state effective mass, In introduces resonance states around Fermi level, enhancing the TE properties of SnTe [19,32]. Dopants like Ca, Cd, Hg, Ga, Mg, Mn, Sr are known to bring about opening of band gap of SnTe and cause convergence of valence sub-bands to increase the Seebeck coefficient which in turn enhances the power factors of SnTe. Since fabricating the device requires higher ZT throughout the temperature range, recently co-doping was employed to get beneficial effects of dopants active at lower (In due to introduction of resonance states) as well as higher temperature (elements like Ag, Cd, Hg, Mg, Mn due to their ability to modify the electronic structure of SnTe) [14,31,33–36]. In spite of these efforts, the maximum ZT achieved is in the range of 1.3–1.6 with most of the work involving harmful materials like Cd and Hg

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[15,21,22,33–35]. Recently, we reported enhancement of thermoelectric performance of bulk SnTe by co-doping Mg and In [14]. The synergistic action of the two dopants led to a ZT maximum of ~ 1.5 at 840 K. The study showed that the site occupied by the dopants play an important role in modification of its electronic structure. We know that for singly doped materials by far Ca doped SnTe holds the maximum ZT value of ~ 1.35 at 873 K [20]. It would be of interest to know if Ca also goes into zinc blende site like Mg and whether the site occupied by Ca in SnTe has any effect on its electronic structure [14,26]. Since in some of the co-doping cases such as Bi-In and Mg-In reported by Zhang et al. we see that the ZT maximum achieved is lower than the singly doped Bi and Mg in SnTe, we wanted to see how Ca and In would interact, whether the co-doping would decrease the ZT than singly doped Ca in SnTe or would it increase the ZT due to synergistic action as in the case of Cd-In co-doped SnTe reported by Tan et al. and Mg-In co-doped SnTe previously reported by us [14,19,26,32,33]. Hence, we thought it is worthwhile to investigate the effect of co-doping of Ca and In in SnTe both experimentally through synthesis using a combination of self propagating high temperature synthesis (SHS) and direct current sintering (DCS) and theoretically through simulations using first principles density functional theory (DFT) approach to see if we can achieve further improvement in ZT . We show that the resonant levels introduced by In and band gap opening caused by Ca, valence band convergence caused by both In and Ca, synergistically increases the Seebeck coefficient for a wide range of temperatures without involving toxic elements like Cd and Hg. We show through DFT simulations that unlike Mg, Ca prefers rock salt site in SnTe [14]. Thus, co-doping of Ca and In results in enhancement of figure of merit ZT due to complimentary role of Ca and In in modifying the electronic structure of SnTe producing a record high power factor and ZT in SnTe based materials. The synergism shown here is much higher than any co-doped SnTe based materials including the recently reported Mg-In co-doped SnTe [14].

Results and discussions

A series of samples $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$ ($x = 0$ to 0.04) was prepared by modified SHS and DCS process. The current strategies used to optimize the thermoelectric properties of SnTe largely depend on the solubility of the dopant in it [1,25]. Equilibrium phase diagram limits the solubility of the dopant in conventional solid solution alloying. Hence increasing the solubility is difficult. Since SHS is a non-equilibrium process higher solubility can be attained at room temperature [14,25]. SHS process is simple, quick and self-propagating due to the release of intense heat during the exothermic reaction. The combination of SHS-DCS process is cost effective and scalable for large scale production. Pristine SnTe is not considered as a good TE material due to large number of Sn vacancies. Self-compensation, addition of I or Bi have been proved to be a good way to reduce the carrier concentration in pristine SnTe [14,21,22]. Recently we reported an optimized concentration of $\text{Sn}_{1.04}\text{Te}$ and the same is implemented here [14]. We then co-dope it with Ca and In maintaining 2:1 ratio unlike in the case of Mg-In co-doped SnTe where the ratio of Mg:In was 1:1 [14]. 2:1 ratio was chosen to take advantage of higher solubility of Ca and to avoid rapid decrease in electrical conductivity caused due to increase in In dopant concentration as explained in later sections [20,21,24].

The powder X-ray diffraction pattern of the synthesized compound revealed in Fig. 1a could be indexed to cubic NaCl structure with space group $Fm\bar{3}m$. Impurity peaks were absent within the detection limits confirming the formation of single phase. We see that the calculated lattice parameter value 'a' gradually increases with increase in concentration of Ca and In during co-doping due to larger ionic radius of Ca^{2+} in comparison with Sn^{2+} [20]. In

substitution does not have much effect on the lattice parameter of SnTe as InTe and SnTe have approximately similar lattice parameter ($\sim 6.32 \text{ \AA}$) [14]. The linear increase in the lattice parameter with dopant concentration follows Vegard's law till 8 mol % of Ca (Fig. 1b).

Thermoelectric transport properties as a function of temperature were studied in the range 300 K–840 K. We observe that co-doping of Ca and In decreases the electrical conductivity values with increase in the concentration of the dopants and also with respect to increase in the temperature showing the degenerate nature of semiconducting materials (Fig. 2a) [22]. The values of electrical conductivity of the Ca-In co-doped samples are intermediate compared to the previously reported SnTe samples singly doped with Ca and In [20,24,25]. The room temperature electrical conductivity decreases from 6600 Scm^{-1} to 1970 Scm^{-1} as 'x' increases from 0 to 4 mol % in $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$. The carrier concentration ' N_p ' of SnTe reduces from $4.5 \times 10^{20} \text{ cm}^{-3}$ to $2.1 \times 10^{20} \text{ cm}^{-3}$ on self compensation of Sn vacancies as established in the previous report [14,21]. The carrier concentration decreases to $1.9 \times 10^{20} \text{ cm}^{-3}$ as the 'x' increases to 4 mol % in $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$. The details of carrier concentration and carrier mobility as a function of doping concentration are given in Fig. 2b. We observe that the carrier mobility ' μ ' decreases with increase in 'x' due to increase in scattering between the carriers, enhanced point defect scattering and increase in the effective mass of the carrier as explained in the later sections [20,33,37].

The Seebeck coefficient values show increasing trend with increase in temperature and dopant concentration (Fig. 3a). The positive value of Seebeck coefficient reveals that holes are the majority carriers leading to p-type conduction in the material [22]. The pristine and self compensated SnTe show a maximum value of Seebeck coefficient of $110 \mu\text{VK}^{-1}$ and $145 \mu\text{VK}^{-1}$ respectively. The co-doped sample shows room temperature Seebeck coefficient of $95 \mu\text{VK}^{-1}$ and a maximum value of $235 \mu\text{VK}^{-1}$ at 840 K (when $x = 0.04$ in $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$). To study the effect of co-dopants, we compared room temperature Seebeck coefficient versus N_p with the theoretical Pisarenko plot reported by Zhang et al. (Fig. 3b) [24]. The Pisarenko line is derived using two valence band model with light hole valence band having an effective mass of $0.168 m_e$ and heavy hole valence band having an effective mass of $1.92 m_e$ with the energy gap of 0.35 eV between the two sub-bands [24]. The Seebeck coefficient value for undoped SnTe falls exactly on top of the line indicating the validity of the theory. At room temperature the co-doped samples have significantly high Seebeck values than predicted by the Pisarenko line. The introduction of resonance levels by In increases the Seebeck coefficient values at lower temperatures by increasing the band effective mass m_b^* while, at higher temperatures the Seebeck value increases due to the decrease in the energy separation between the light hole and heavy hole valence sub-bands which is a consequence of Ca and In doping which is further studied making use of DFT calculations [1,14,24,25,31–36].

We carried out the simulations of pristine, Ca doped SnTe, In doped SnTe and Ca-In co-doped SnTe using a 32 atom supercell to achieve ~ 6.25 mol % doping concentration. SnTe with a primitive rock salt crystal structure is known to possess an electronic structure with principal band gap at L point and it also has a heavy hole valence band at Σ point. Since our calculations involve a $2 \times 2 \times 1$ supercell, the Brillouin zone folds accordingly and hence the states at L point in the primitive cell folds onto the Z point in the supercell while the states at Σ point corresponds to the states at $M + \delta$ point along $M \rightarrow \Gamma$ direction in the tetragonal supercell [14]. The electronic structure of SnTe which we obtained in our present calculation reveals a band gap of $\sim 0.056 \text{ eV}$ at Z point, slightly higher than the 0.049 eV reported by Banik et al. [26] The theoretically

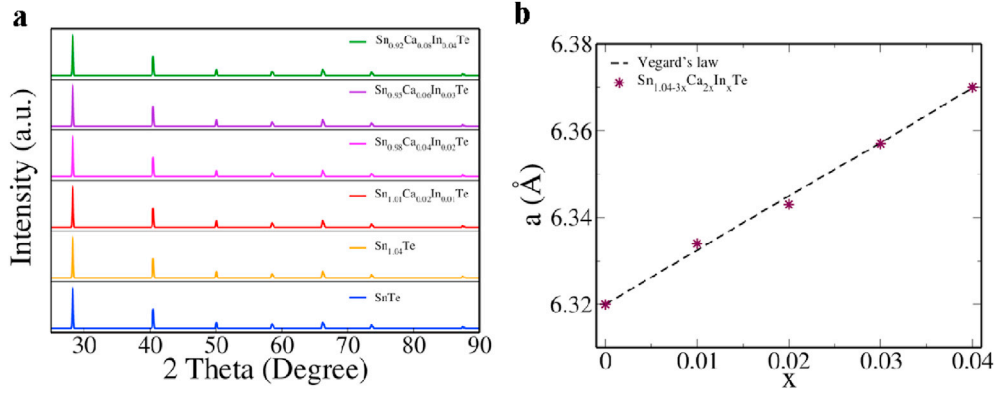


Fig. 1. a) pXRD pattern and b) Variation of lattice parameter 'a' with dopant concentration 'x' in Sn_{1.04-3x}Ca_{2x}In_xTe.

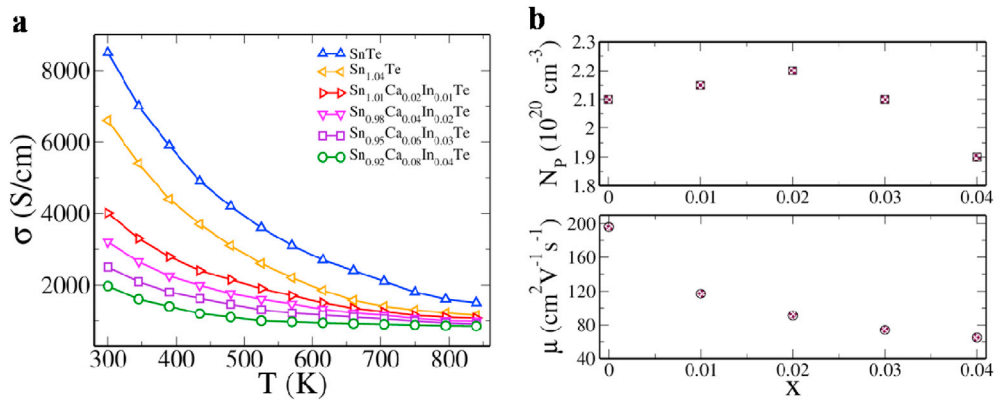


Fig. 2. Variation of a) electrical conductivity with temperature and b) Room temperature carrier concentration ' N_p ' (upper panel) and carrier mobility ' μ ' (lower panel) with dopant concentration 'x' in Sn_{1.04-3x}Ca_{2x}In_xTe.

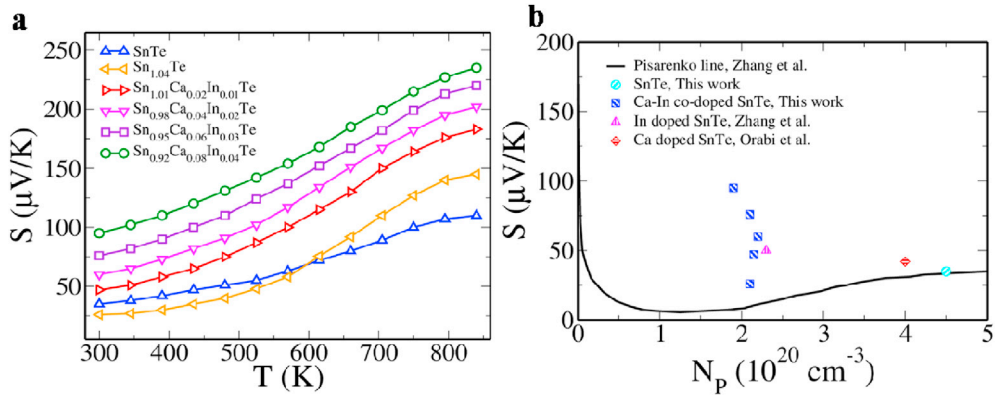


Fig. 3. a) Variation of Seebeck coefficient with temperature in Sn_{1.04-3x}Ca_{2x}In_xTe and b) Room temperature Seebeck coefficient versus carrier concentration of SnTe and Sn_{1.04-3x}Ca_{2x}In_xTe [x = 0 to 0.04]. Pisarenko plot is derived using two valence band model [24]. For comparison with previous reports the Seebeck values of optimized concentration of In and Ca singly doped SnTe has been marked with respect to their carrier concentration [20,24].

calculated value is lower than the experimental value due to the typical underestimation caused in DFT based calculations (Fig. 4a). The energy difference between the light and heavy hole valence sub-bands of SnTe is found to be -0.325 eV in our simulations.

When we dope Ca in SnTe by substituting Ca in the place of Sn in rock salt site the degeneracy of the bands is lost, the band gap increases to ~ 0.1 eV and the difference between the light and heavy hole valence bands decreases to ~ 0.2 eV (Fig. 3b). This is indicated by asymmetric increase in density of states (DOS) near the Fermi

level (Fig. S1). The convergence of light and heavy hole valence sub-bands at Z and M + δ point causes the number of equivalent degenerate valleys of band structure (N_v) to increase from 4 (contributed by the light hole bands) to 16, as heavy hole band adds a value of 12 to N_v [1]. In our previous report on Mg-In co-doped SnTe, we showed that the site occupied by the dopant affects its electronic structure [14]. In view of this, we performed calculations by introducing Ca in zinc blende site. In this case the electronic structure (Fig. S2a) reveals further loss of degeneracy of bands due

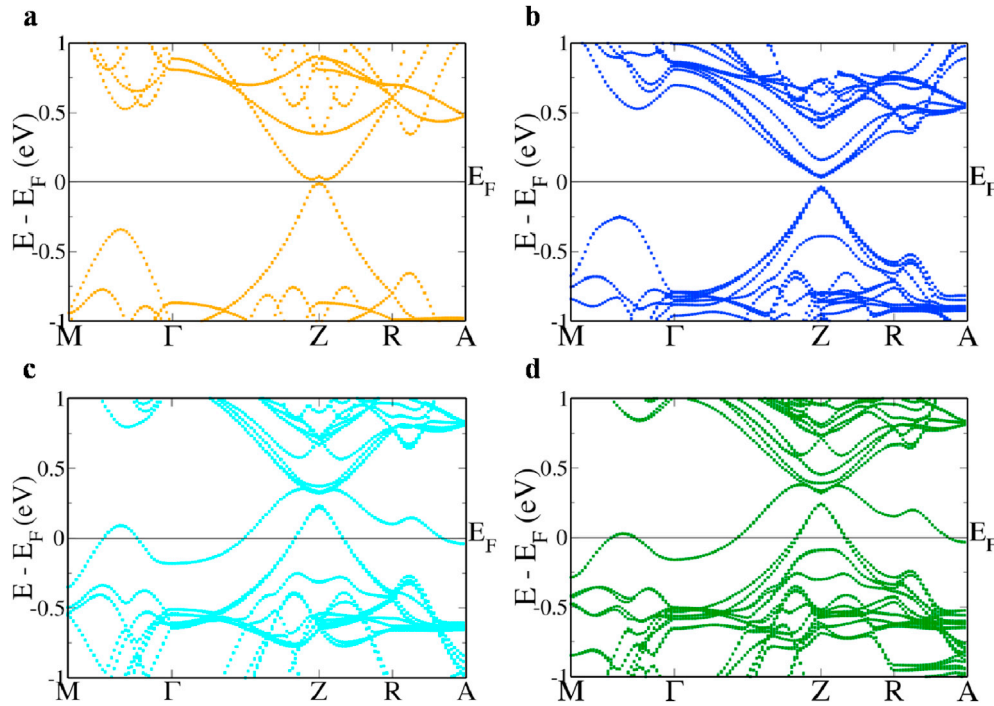


Fig. 4. Electronic structure of a) $\text{Sn}_{16}\text{Te}_{16}$, b) $\text{Sn}_{15}\text{CaTe}_{16}$, c) $\text{Sn}_{15}\text{InTe}_{16}$, d) $\text{Sn}_{14}\text{CaInTe}_{16}$.

to distortion of crystal symmetry. A direct band gap of ~ 0.098 eV is seen at Z point. In addition to this an indirect band gap of ~ 0.029 eV also appears. The W shape feature of the lower conduction bands which is common for dopants present in the zinc blende site is also seen, and is consistent with the earlier report [14]. The energy difference of ~ 0.3 eV between the valence sub-bands is higher than that in the case where Ca substitutes Sn in the rock salt site but is still lower than the one for pristine SnTe. The electronic structure of Ca-In co-doped SnTe where Ca is in the zinc blende site and In is in the rock salt site is given in Fig. S2b. Just like in the singly doped case here also we see loss of degeneracy of bands and presence of resonance level between the valence and conduction bands due to the introduction of In.

When we substituted In for Sn in the rock salt site, we see that the resonance level appears as a split off band at the top of valence band. The overlap of In 's' and Te 'p' orbitals in their antibonding state is believed to result in the formation of resonant states near the edge of the band gap [38]. Since, In orbitals are localized in narrow energy range of the valence band, the energy range where the contribution of In orbital is highest, that region appears as a hump due to increase in DOS. This feature is observed just after the Fermi level within the valence band (Fig. 4c) [14,31,33]. Higher the raise in energy of the split off band in the electronic structure sharper is the peak in DOS versus energy plot [14]. Apart from the heavy hole band at $M + \delta$ point, introduction of In raises the energy of heavy hole band at $R + \delta'$ point along $R \rightarrow A$ direction in the tetragonal supercell. The energy of which is slightly higher than that at $M + \delta$ point. Introduction of In results in the energy difference of ~ 0.235 eV and ~ 0.182 eV between the valence sub-bands at $M + \delta$ point and $R + \delta'$ point, respectively.

In the case of Ca-In co-doped SnTe, where both Ca and In is substituted for Sn in rock salt site we see that an additional split of band appears at Z point in the electronic structure which is a feature observed in the electronic structure of SnTe singly doped with Ca [20]. The effect of In is seen in the form of appearance of resonance level (Fig. 4d). Though the energy difference between

the valence sub-bands at $M + \delta$ point is ~ 0.295 eV, at $R + \delta'$ point it reduces to ~ 0.123 eV revealing the synergistic action of Ca-In co-doping in SnTe [14,31,33].

The resonance level and the valence band convergence both appear in DOS versus energy plot in the form of a well-defined peak near the Fermi level and the increase in the density of states near the top of the valence band, respectively (Fig. S1). Introduction of resonance levels by In and valence band convergence caused by In as well as Ca increases m_b^* and (N_v) . Since carrier effective mass m^* which is directly proportional to Seebeck coefficient, is also proportional to m_b^* and $(N_v)^{2/3}$, co-doping of Ca and In results in higher performance of the SnTe than doping of Ca and In alone [1,20,24]. Due to the synergistic action of resonance levels which acts at lower temperature and valence band convergence which is dominant at higher temperature Ca-In co-doped SnTe has Seebeck values higher than the individually doped samples reported in previous literature throughout the temperature range [20,24,25]. In addition to this, the increase in band gap caused due to the introduction of Ca decreases the bipolar conduction at higher temperatures. At higher temperatures the excitation of minority carriers across the band gap would have offset the effect of majority carriers causing detrimental effect on the Seebeck values which is averted in this case due to increase in the band gap.

One of the strategies to improve the ZT of a material is to increase the value of power factor which is the product of σ and S^2 [1,3]. It is observed that the maximum power factor value obtained in $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$ (when $x = 0.04$) is almost twice that of the self-compensated SnTe. The dependence of power factor on the temperature at different doping concentration is shown in Fig. 5a. The increase in the value of the Seebeck with the increase in the dopant concentration is responsible for the increase in the power factor. At low temperature In introduces resonance level causing peak increase in density of states which increases the Seebeck value substantially. At higher temperatures in addition to the convergence of valence sub-bands caused due to the temperature effect, Ca and In play important roles in contributing to this. This results in

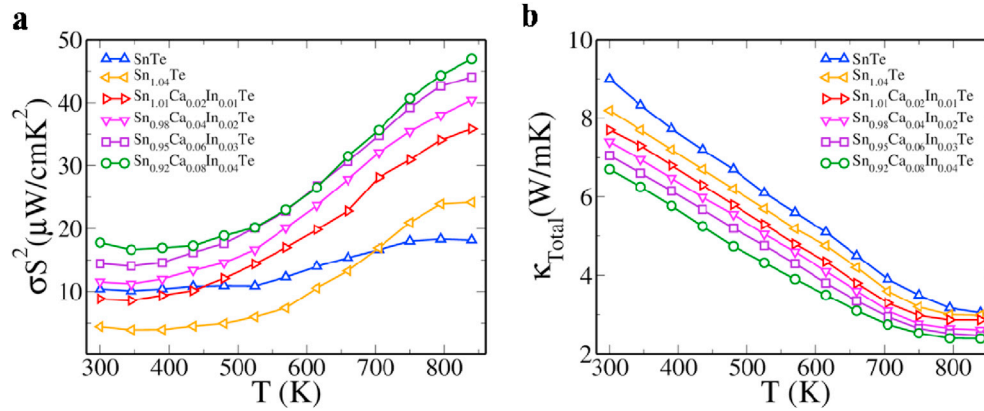


Fig. 5. Variation of a) power factor and b) total thermal conductivity with temperature in $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$.

the increase in the Seebeck coefficient throughout the studied temperature range which more than compensates for decrease in the electrical conductivity with increase in the doping fraction. We see that the power factor increases to $\sim 47 \mu\text{Wcm}^{-1}\text{K}^{-2}$ when $x = 0.04$ at 840 K. This is the highest reported power factor for SnTe based materials, even higher than $\sim 42 \mu\text{Wcm}^{-1}\text{K}^{-2}$ which we reported recently for *Mg-In* co-doped SnTe, which held the record by far [14]. Apart from these *Ag-In* co-doped SnTe and *Mg* doped SnTe have appreciable power factors of the order of $\sim 31.4 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and $\sim 30.3 \mu\text{Wcm}^{-1}\text{K}^{-2}$ [26,31]. Comparison of the power factors of SnTe based materials containing *Ca*, *In* or *In* as one of the dopants is given in Fig. 6b.

Fig. 5b shows the temperature dependence of the total thermal conductivity. The total thermal conductivity of the $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$ ($x = 0$ to 4) decreases with increase in value of 'x' as well as temperature. We see that *Ca-In* co-doped SnTe have thermal conductivity lesser than that of the pristine SnTe as well as self-compensated SnTe. The total thermal conductivity is the sum of lattice, electronic and bipolar thermal conductivities [1]. The electronic thermal conductivity (κ_{el}) is usually determined using Wiedemann-Franz law ($\kappa_{el} = L\sigma T$, where L is Lorenz number, σ is electrical conductivity and T is absolute temperature). Recent reports suggest that when multiple band co-exist at the Fermi level, the carriers move from one valley into another by means of a complex inter-valley scattering causing a large amount of heat transfer which cannot be determined accurately by value of L [14,31]. In the electronic structure of $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$ since we see convergence of the valence bands there is a possibility of intervalley

scattering and hence, we have not determined the electronic and lattice thermal conductivity. But it is safe to assume that the atomic point defects introduced due to elemental substitution decreases the total thermal conductivity with increase in doping concentration due to decrease in lattice component of the thermal conductivity. These point defects scatter the phonons causing additional thermal resistance [1].

Co-doping of *Ca* and *In* in self-compensated SnTe has an enormous effect on the ZT values, due to both increase in the power factor and decrease in the total thermal conductivity (Fig. 6a). The increase in ZT is much more than the previously reported cases of co-doping of *Ag-In* (~ 1 at 856 K), *Bi-In* (~ 0.62 at 873 K), *Cd-In* (~ 1.4 at 923 K, ~ 1.1 at 850 K), *Hg-In* (~ 0.9 at 850 K), *Mg-In* (~ 1.5 at 840 K, ~ 1 at 873 K) in SnTe; *Mg-In* (~ 1 at 710 K) in $\text{Sn}_{1-x}\text{Pb}_x\text{Te}$ where $x = 0.3$, *Mn-In* (~ 1.15 at 823 K), *Mn-Cu* (~ 1.6 at 927 K) or individually doped *Bi* (~ 1.1 at 873 K), *Ca* (~ 1.35 at 873 K), *Cd* (~ 1.3 at 873 K), *Ga* (~ 1 at 873 K), *Hg* (~ 1.35 at 910 K), *In* (~ 1.1 at 873 K, ~ 0.92 at 920 K), *Mg* (~ 1.2 at 856 K), *Mn* (~ 1.3 at 900 K, ~ 1.25 at 920 K), *Sr* (~ 1.2 at 823 K) in SnTe, some of which even employ nanostructuring. [14,15,19–36,39], Though the ZT reported in the current work is lesser than the recently reported *Mg* doped $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ (~ 2 at 840 K), our *Ca-In* co-doped SnTe has an advantage of being lead free material [40]. A comparison of maximum ZT of some of the SnTe based materials containing *Ca*, *In* or *In* as one of the dopants is given in Fig. 6b. The ZT values in the case of $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$ increased with increase in doping concentration (from $x = 0.00$ to $x = 0.04$) and a maximum ZT of ~ 1.65 at 840 K and a ZT_{avg} of ~ 0.87 considering 500 K and 840 K as cold and hot ends were obtained for $x = 0.04$ in

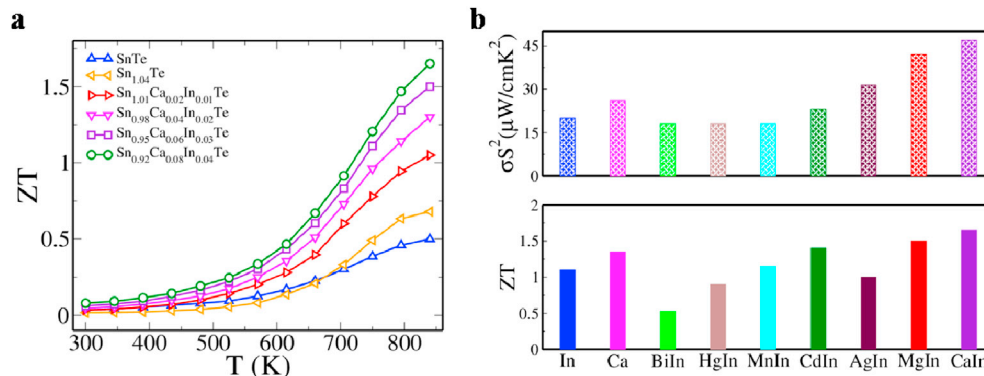


Fig. 6. a) Variation of ZT with temperature in $\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$ and b) Comparison of power factors (upper panel) and ZT values (lower panel) of SnTe materials doped with *In* [24], *Ca* [20], *Bi-In* [32], *Hg-In* [35], *Mn-In* [36], *Cd-In* [32], *Ag-In* [31], *Mg-In* [14], *Ca-In* (This work).

$\text{Sn}_{1.04-3x}\text{Ca}_{2x}\text{In}_x\text{Te}$ (Fig. 6a). A comparison of the ZT of Ca and In co-doped SnTe with different compositions is given in Fig. S3. As apparent from Fig. 6a and Fig. S3 in mid temperature regions we see that co-doping of Ca and In in appropriate ratio can bring about appreciable increase in the ZT due to the synergistic action of Ca and In higher than any other known co-dopants by far. The maximum ZT of ~ 1.65 suggests that this material has great promise for further study in the field of thermoelectrics as a non-toxic lead free alternative material [8,11–13].

Conclusions

We report a study on the enhanced thermoelectric performance of SnTe co-doped with Ca and In synthesized using a combination of SHS and DCS process. The samples are well characterized and studied for their transport properties experimentally. Theoretical approach through the first principles DFT electronic structure calculations is followed. We see that Ca increases the band gap, suppressing the bipolar thermal conduction at higher temperature. In , on the other hand introduces resonant levels increasing the Seebeck coefficient at lower temperatures. Valence band convergence caused due to both Ca and In enhances the Seebeck coefficient values throughout the temperature range more effectively at higher temperatures. The above-mentioned effects synergistically lead to a record high power factor of $\sim 47 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and high ZT over a wide range of temperature in the co-doped sample. The resulting high ZT of ~ 1.65 at 840 K and ZT_{avg} (in mid temperature region) of ~ 0.87 considering 500 K as cold and 840 K as hot end make SnTe doped with non-toxic elements a very suitable material for thermoelectric applications.

Conflicts of interest

There are no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.mtphys.2018.02.001>.

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