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 ~47 $\mu Wcm^{-1}K^{-2}$ 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 co-efficient 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 thermo-electric 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 $Sn_{1.04-3x}Ca_{2x}In_xTe$ (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 $Sn_{1.04}Te$ 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 *Fm3m*. 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 (~6.32 Å) [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 $Sn_{1.04-3x}Ca_{2x}In_xTe$. The carrier concentration 'N_p' of SnTe reduces from 4.5×10^{20} cm^{-3} to 2.1×10^{20} cm^{-3} on self compensation of *Sn* vacancies as established in the previous report [14,21]. The carrier concentration decreases to 1.9×10^{20} cm^{-3} as the 'x' increases to 4 mol % in $Sn_{1.04-3x}Ca_{2x-}In_xTe$. 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 μVK^{-1} and 145 μVK^{-1} respectively. The co-doped sample shows room temperature Seebeck coefficient of 95 μVK^{-1} and a maximum value of 235 μVK^{-1} at 840 K (when x = 0.04 in $Sn_{1.04-3x}Ca_{2x}In_xTe$). 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 × 2 × 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 + δ point along M→Γ direction in the tetragonal supercell [14]. The electronic structure of SnTe which we obtained in our present calculation reveals a band gap of ~0.056 eV at Z point, slightly higher than the 0.049 eV reported by Banik et al. [26] The theoretically