Effect of In and Cd co-doping on the thermoelectric properties of Sn$_{1-x}$Pb$_x$Te

Subhajit Roychowdhury$^1$ and Kanishka Biswas$^{1,2}$

$^1$ New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P O, Bangalore 560064, India
$^2$ School of Advanced Materials and International Centre of Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P O, Bangalore 560064, India

E-mail: kanishka@jnCASR.ac.in

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Abstract

Pristine tin telluride (SnTe) with a similar electronic structure to PbTe shows inferior thermoelectric performance owing to high p-type hole concentration ($10^{21}$ cm$^{-3}$), high lattice thermal conductivity, $\kappa_{latt}$ (~2.8 W mK$^{-1}$ at room temperature) and large energy gap between light and heavy hole valence bands. Interestingly, 30 mol% substitution of lead in SnTe decreases the excess hole carrier concentration and lattice thermal conductivity (~0.67 W m$^{-1}$K$^{-1}$ at 300 K) significantly. Here, we report the promising thermoelectric performance in Sn$_{0.70}$Pb$_{0.30}$Te by enhancing the Seebeck coefficient via the co-adjuvant effect of resonant level formation and valence band convergence. We obtain a Seebeck coefficient value of ~141 $\mu$V K$^{-1}$ at 300 K, which further increases to ~260 $\mu$V K$^{-1}$ at 708 K for Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.50% In sample. This is one of the highest $S$ values for SnTe based system, to the best of our knowledge. In and Cd have discrete but complementary roles to augment the Seebeck coefficient value of Sn$_{0.70}$Pb$_{0.30}$Te where In acts as a resonant dopant and Cd serves as valence band convergent, respectively, as demonstrated by the well-known Pisarenko plot of SnTe. Finally, we have achieved a maximum thermoelectric figure of merit, $zT$, of ~0.82 at 654 K for Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.25% In sample.

Introduction

Thermoelectric (TE) technology has attracted attention recently as they are able to convert waste heat directly into electricity. The efficiency of TE materials is dependent upon the delicate concert of adversely interdependent parameters and is quantified in term of a dimensionless figure of merit ($zT$), defined as

$$zT = \frac{S^2 \sigma}{\kappa_{el} + \kappa_{latt}} T$$

Where $S$ is Seebeck coefficient, $\sigma$ is electrical conductivity, $\kappa_{el}$ is electrical thermal conductivity, $\kappa_{latt}$ is lattice thermal conductivity and $T$ is absolute temperature [1–9]. These three mutually interdependent parameters such as $\sigma$, $S$ and $\kappa_{latt}$ provide hindrance in the pursuit of higher $zT$ in a single material [1, 2]. The last few decades have witnessed a significant enhancement of thermoelectric performance either by enhancing the Seebeck coefficient via manipulating the electronic band structure (band convergence or generation of the resonant level near Fermi level) [10–14] and/or reducing the thermal conductivity (lattice) by engineering phonon scattering sources [15–18].

PbTe is considered as an efficient thermoelectric material among IV–VI family for mid-temperature power generation applications [10, 13, 16]. However, pristine SnTe with a similar electronic structure to PbTe is not so popular as thermoelectric material because of its poor thermoelectric performance [5, 19]. This can be attributed to its high carrier concentration ($10^{21}$ cm$^{-3}$), resulting from intrinsic Sn vacancy and large energy separation between light and heavy hole valence bands (~0.3–0.4 eV) than that of PbTe (~0.18 eV) which inhibit the...
contribution of heavy hole valence band in the electrical transport and results low Seebeck coefficient [5, 16, 19–22]. Manipulation of electronic structure is an effective approach to improve the thermoelectric performance of SnTe by enhancing the Seebeck coefficient [5, 11, 12, 19, 23, 24]. Previously, Ren and coworkers revealed that indium (In) acts as a resonant dopant in SnTe and enhances the Seebeck coefficient significantly near room temperature [14]. Tan et al demonstrated that addition of Cd in SnTe decreases the energy gap between two valence bands and improves its Seebeck coefficient [23].

Moreover, pristine SnTe shows $k_{\text{lat}}$ of $\sim 2.8 \text{ W m}^{-1} \text{K}^{-1}$ which is notably higher compare to its theoretical limit of minimum lattice thermal conductivity ($k_{\text{min}} \sim 0.5 \text{ W m}^{-1} \text{K}^{-1}$) at 300 K [18]. However, several approaches have been endeavored to reduce the $k_{\text{lat}}$ of SnTe based alloys to enhance the thermoelectric performance such as entropy engineering via introduction of multi principle element alloying [25], addition of nanoprecipitates of CdSe/HgTe [23, 26], encapsulation of layered intergrowth compound in matrix [18]. Recently, we have effectively reduced the $k_{\text{lat}}$ to $\sim 0.67 \text{ W m}^{-1} \text{K}^{-1}$ in Sn$_{1-x}$Ge$_x$Te by introducing the ferroelectric instability concept in the system without degrading the electrical transport [27]. In our previous work, we have shown that substitution of 30 mol% of Pb in SnTe effectively reduced the excess hole carrier concentration of SnTe and lattice thermal conductivity to $\sim 0.67 \text{ W m}^{-1} \text{K}^{-1}$ at 300 K due to the enhanced solid solution point defect scattering [28]. Motivated by all these results, here, we thought to study the effect of co-substitution of In and Cd in Sn$_{0.70}$Pb$_{0.30}$Te sample, which may improve the S values over a broad temperature range through the co-adjuvant effect of the resonance level formation and valence band convergence. Herein, we demonstrate the promising thermoelectric performance of Sn$_{0.70}$Pb$_{0.30}$Te sample by enhancing its Seebeck coefficient via the co-adjuvant effect of formation of the resonance level by In doping and valence band convergence enables by Cd doping. Co-doping of In and Cd increases the Seebeck coefficient of Sn$_{0.70}$Pb$_{0.30}$Te sample significantly throughout the measured temperature range (300–710 K) compared to that of singly doped (In and Cd) Sn$_{0.70}$Pb$_{0.30}$Te samples. We have attained a Seebeck coefficient value of $\sim 141 \mu \text{V K}^{-1}$ at 300 K, which further increases to 260 $\mu \text{V K}^{-1}$ at 708 K for Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.50% In sample. As a result, a maximum $zT$ of $\sim 0.82$ at 654 K for Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.25% In sample which is higher compared to pristine SnTe and undoped Sn$_{0.70}$Pb$_{0.30}$Te samples.

Results and discussion

The balance between the resonant level and valence band convergence is necessary to optimize the thermoelectric performance of the Sn$_{0.70}$Pb$_{0.30}$Te system. Band convergence always requires relative high doping concentration to manipulate band dispersion in k-space [29]. In this work, we select Cd as the valence band convergent. The effect of band convergence will be stronger if the concentration of Cd is high [29]. Previous results confirm that the solubility of Cd is only 3 mol% in SnTe [23, 29]. Thus we fix the concentration of Cd is 3 mol% in the present work and then varies the concentration of resonant dopant, In. The resonant state is the deformation of the density of states (DOS) near Fermi level, and it reduces electrical conductivity significantly due to the reduction of carrier mobility at higher doping concentration [29]. Therefore, a lower concentration of resonant dopant and a higher concentration of band convergence dopant are always desired. Thus, the amount of In is varied from $x = 0$ to $x = 0.50$ mol%.

First, we have synthesized high quality crystalline ingots of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In ($x = 0$, $y = 0$; $x = 3$, $y = 0.05, 0.25, 0.50$) samples by vacuum sealed tube melting reaction (Details in methods, supporting information, SI). Powder x-ray diffraction (PXRD) patterns of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In ($x = 0$, $y = 0$; $x = 3$, $y = 0.05, 0.25, 0.50$) samples are presented in figures 1 and S1 available online at stacks.iop.org/MRX/6/104010/mmedia (zoomed version). The patterns confirm the formation of single-phase materials which crystallize in rock-salt structure (space group Fm-3m).

The temperature variations of electrical conductivity, $\sigma$, of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In ($x = 0$, $y = 0$; $x = 3$, $y = 0.05, 0.25, 0.50$) samples are shown in figure 2(a). The $\sigma$ values for all the samples decrease with increasing temperature, like a degenerate semiconductor. Substitution of 3 mol% Cd reduces the $\sigma$ from $\sim 4260$ S cm$^{-1}$ for Sn$_{0.70}$Pb$_{0.30}$Te to $\sim 2500$ S cm$^{-1}$ for Sn$_{0.67}$Cd$_{0.03}$Pb$_{0.30}$Te sample at 300 K (figures 2(a) and S2(a), SI). This confirms that the tendency of formation of Sn vacancy decreases with Cd substitution and reduces the hole carrier concentrations (table 1). Substitution of indium in Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd sample further decreases the electrical conductivity owing to the significant reduction in carrier mobility due to resonant scattering, resulting from In doping (see table 1). Typically, $\sigma$ of Sn$_{0.70}$Pb$_{0.30}$Te sample is to be $\sim 5471$ S cm$^{-1}$ at 300 K, which further decreases to $\sim 620$ S cm$^{-1}$ at $\sim 708$ K. At room temperature, Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.25% In sample exhibits a $\sigma$ value of $\sim 773$ S cm$^{-1}$ and reduces to $\sim 264$ S cm$^{-1}$ at 708 K.

To determine the carrier concentration of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In ($x = 0$, $y = 0$; $x = 3$, $y = 0.05, 0.25, 0.50$) samples, Hall measurements were carried out (table 1). At room temperature, Hall...
coefficients, $R_\text{HI}$ for all the samples are positive, indicating $p$-type conduction. Carrier concentration of undoped Sn$_{0.70}$Pb$_{0.30}$Te sample is $\approx 8 \times 10^{19}$ cm$^{-3}$. Substitution of 3 mol% Cd decreases the carrier concentration of Sn$_{0.70}$Pb$_{0.30}$Te sample due to the decreasing of Sn vacancies. The carrier concentration of Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and y% In samples decrease further with increasing In concentration (table 1). Notably, Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.50% In samples exhibit significantly low carrier mobility, resulting from resonant carrier scattering (table 1).

The temperature variations of Seebeck coefficient, $S$, of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In (x = 0, y = 0; x = 3, y = 0.05, 0.25, 0.50), controlled 3% Cd doped Sn$_{0.70}$Pb$_{0.30}$Te and 0.25% In doped Sn$_{0.70}$Pb$_{0.30}$Te samples are shown in figure 2(b) and S2(b), S1, respectively. Seebeck coefficient values for all the samples are positive which are consistent with our Hall coefficient data. Interestingly, for In and Cd co-doped Sn$_{0.70}$Pb$_{0.30}$Te samples exhibit higher Seebeck coefficient value throughout the measured temperature range (300–710 K) compared to that of controlled In or Cd single doped Sn$_{0.70}$Pb$_{0.30}$Te samples (figures S2(b), S1). Typically, the Seebeck coefficient value of Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.50% In sample is $\sim 140 \mu$ V K$^{-1}$ at 300 K and further increases to $\sim 260 \mu$ V K$^{-1}$ at 708 K (figures 2(b), S3, S1). Thus, the synergistic effect of In and Cd co-doping in Sn$_{0.70}$Pb$_{0.30}$Te is responsible for the observed notable augmentation in the Seebeck coefficient. At room temperature, highest Seebeck coefficient value is achieved in the present Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.50% In sample which is higher than that of state-of-art SnTe based materials, to the best of our awareness [11, 12, 23–29, 31, 32].

To gain further insight into the origin of high Seebeck coefficient, we have plotted $S$ values of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In (x = 0, y = 0; x = 3, y = 0.05, 0.25, 0.50) samples as a function of $p$ and compared with the renowned Pisarenko line of SnTe (figure 2(c)) at 300 K [14]. Controlled In doped sample exhibits higher $S$ value compared to theoretical Pisarenko line due to the formation of resonance level near the valence band of Sn$_{0.70}$Pb$_{0.30}$Te similar to previously reported In doped SnTe and In doped Sn$_{0.70}$Pb$_{0.30}$Te sample [14, 28]. Controlled Cd doped Sn$_{0.70}$Pb$_{0.30}$Te sample shows a slightly higher Seebeck value compared to Pisarenko line, which is attributed to the effective valence band convergence. Interestingly, Cd and In co-doped Sn$_{0.70}$Pb$_{0.30}$Te samples show remarkably higher Seebeck coefficient compared to that of singly doped (In and Cd) Sn$_{0.70}$Pb$_{0.30}$Te samples. This confirms that In and Cd have distinct but complementary role to enhance the Seebeck coefficient, where In forms resonant level near valence band and Cd enables valence band convergence synergistically.

The temperature variations of power factor, $S^2 \sigma$, of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In (x = 0, y = 0; x = 3, y = 0.05, 0.25, 0.50) samples are shown in figure 2(d). Typically, the Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.25% In sample exhibits an $S^2 \sigma$ value of $\sim 9.8 \mu$ W cm$^{-1}$ K$^{-2}$ at 300 K, which increases further to $\sim 15.9 \mu$ W cm$^{-1}$ K$^{-2}$ at 654 K. Co-substitution of In and Cd increases the Seebeck value in Sn$_{0.70}$Pb$_{0.30}$Te but no improvement in $S^2 \sigma$ value is observed owing to the significant decrease in electrical conductivity and mobility.

The temperature variations of total thermal conductivity, $\kappa_{\text{total}}$, of Sn$_{0.70}$Pb$_{0.30}$Te—x% Cd and y% In (x = 0, y = 0; x = 3, y = 0.05, 0.25, 0.50) samples are shown in figure 3(a). Co-substitution of In and Cd decreases the $\kappa_{\text{total}}$ value of Sn$_{0.70}$Pb$_{0.30}$Te sample. At 300 K, $\kappa_{\text{total}}$ value reduces from 4.62 W m$^{-1}$ K$^{-1}$ for Sn$_{0.70}$Pb$_{0.30}$Te to 1.54 W m$^{-1}$ K$^{-1}$ for Sn$_{0.70}$Pb$_{0.30}$Te—3% Cd and 0.25% In sample.

Figure 1. Powder XRD patterns of SnTe and Sn$_{0.70}$Pb$_{0.30}$Te—x % Cd and y% In (x = 0, y = 0; x = 3, y = 0.05, 0.25, 0.50) samples.
The noteworthy reduction in $\kappa_{\text{total}}$ can be ascribed to the decrease in electrical thermal conductivity ($\kappa_{\text{el}}$) (figure 3(b)). The $\kappa_{\text{el}}$ values for Sn$_{0.70}$Pb$_{0.30}$Te—$x\%$ Cd and $y\%$ In ($x = 0, y = 0; x = 3, y = 0.05, 0.25, 0.50$) samples are significantly lower compared to that of undoped Sn$_{0.70}$Pb$_{0.30}$Te, which is due to the considerably lower electrical conductivity for co-doped samples than that of undoped Sn$_{0.70}$Pb$_{0.30}$Te sample (figure 2(a)). The $\kappa_{\text{el}}$ values were calculated by using Wiedemann–Franz relation, $\kappa_{\text{el}} = L\sigma T$, where $\sigma$ is measured electrical conductivity and $L$ is calculated Lorenz number from reduced Fermi energy, which is acquired from the fitting of the temperature dependent $S$ value [11, 12]. Typically, Sn$_{0.70}$Pb$_{0.30}$Te—$3\%$ Cd and $0.25\%$ In sample exhibits $\kappa_{\text{el}}$ value of $\sim 0.43$ W m$^{-1}$K$^{-1}$ at 300 K and further reduces to $\sim 0.30$ W m$^{-1}$K$^{-1}$ at 708 K. The lattice thermal conductivity,
\(\kappa\)\text{\textsubscript{latt}} was estimated after subtraction of electronic contribution from total thermal conductivity.

\(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\)–3\% Cd and 0.25\% In sample shows \(\kappa\)\text{\textsubscript{latt}} value of 1.12 W m\(^{-1}\)K\(^{-1}\) at 300 K and decreases to 1.06 W m\(^{-1}\)K\(^{-1}\) at 708 K (figure S3, SI). Mention must be made that \(\kappa\)\text{\textsubscript{latt}} values for \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\)–y% In (y = 0.05, 0.25 and 0.50) samples do not follow any systematic trend with dopant concentration which is similar with previously reported Ag-In co-doped SnTe and In-Mg co-doped Sn\(_{0.70}\text{Pb}_{0.30}\text{Te}\) samples [11, 28].

The temperature variations of thermoelectric figure of merit, \(zT\), of \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\)–x% Cd and y% In (x = 0, y = 0; x = 3, y = 0.05, 0.25, 0.50) samples are shown in figure 4. \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\)–3\% Cd and 0.25\% In sample exhibits the highest \(zT\) of \(\sim 0.82\) at 654 K which is higher than undoped controlled \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\) sample (\(\sim 0.60\) at 708 K).

**Conclusions**

We have prepared crystalline ingots of In and Cd codoped \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\) samples via vacuum-sealed tube melting reaction. \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\) sample exhibits \(\kappa\)\text{\textsubscript{latt}} of \(\sim 0.67\) W m\(^{-1}\)K\(^{-1}\) at 300 which is close to the \(\kappa\)\text{\textsubscript{min}} of SnTe (\(\sim 0.50\) W m\(^{-1}\)K\(^{-1}\)) due to the enhanced solid solution point defect scattering. Co-substitution of In and Cd increases the Seebeck coefficient of \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\) sample significantly over a wide range of temperatures (300–710 K) compared to that of singly doped (In and Cd) \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\) samples due to the co-adjuvant effect of resonance level formation near Fermi level and effective valence band convergence. At room temperature, highest Seebeck coefficient value has been realized in the present \(\text{Sn}_{0.70}\text{Pb}_{0.30}\text{Te}\)–x% Cd and y% In sample (\(\sim 141\) \(\mu\)V K\(^{-1}\)) which is higher compared to that of state-of-the-art SnTe based materials. A maximum \(zT\) of...
~0.82 is observed for Sn0.70Pb0.30Te—3% Cd and 0.25% In sample at 654 K which is higher than that of pristine SnTe and controlled Sn0.70Pb0.30Te samples. Thermoelectric performance of Sn0.70Pb0.30Te sample can be further improved by engineering phonon scattering centers via nanostructuring or all-scale hierarchical architecture.

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ORCID iDs

Kanishka Biswas \(\text{https://orcid.org/0000-0001-9119-2455}\)

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