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Thermoelectric performance of codoped (Bi, In)-GeTe and (Ag, In, Sb)-SnTe materials processed by Spark Plasma Sintering

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ABSTRACT

GeTe and SnTe based materials are emerging as viable alternatives for toxic PbTe based thermoelectric materials. Here, a systematic study of thermoelectric properties of Bi and In codoped GeTe, and Sb, In and Ag codoped SnTe alloys processed by Spark Plasma Sintering are presented. We report that codoping of Bi and In to GeTe, (i) enhances the thermoelectric performance by the synergistic effect of nanostructuring, suppression of carrier density and creation of resonant level, which enables to simultaneously enhance the thermopower and reduce the thermal transport, and (ii) promotes the $R3m \rightarrow Fm\text{-}3m$ structural transition. These cumulative effects help $Ge_{0.93}Bi_{0.05}In_{0.02}Te$ to maintain the peak figure of merit, $zT \sim 0.85$ over a wide spectrum of temperature from 550 to 773 K, making them a serious candidate for device fabrications. We also report that Sb and In codoping in SnTe enhances the thermoelectric performance, as $Sn_{0.845}Sb_{0.15}In_{0.005}Te$ exhibits an improved $zT \sim 0.8$ at 823 K, when compared to pristine SnTe.

1. Introduction

The thermoelectric (TE) material's efficiency is quantified by a dimensionless figure of merit, $zT = S^2\sigma T/\kappa$ where S, σ, T and κ are Seebeck coefficient, electrical conductivity, temperature and total thermal conductivity (sum of electronic and lattice parts, κ_e and κ_{latt}). Amongst the state-of-the-art TE materials, the extensively studied PbTe based materials are limited by their toxicity for any practical applications, despite their high zT [1]. Recently, GeTe and SnTe based materials have emerged as a clear alternative choice, as they have proven to exhibit higher performance (zT > 1), if optimally doped with suitable elements [2,3]. 6 mol% Bi doping in GeTe has shown to exhibit $zT \sim 1.3$ at 723 K [4], thanks to the collective phonon scattering from nanostructured precipitates and defects, which reduces their κ_{latt}. 2 mol% In doping in GeTe is also shown to exhibit $zT \sim 1.3$ at 650 K [4], thanks to the resonant levels induced by In which enhances the thermopower. With an objective to take advantage of these effects, if blended together, we tried codoping of Bi and In in GeTe, the results of which are presented in this work. Similarly, it has been shown that 15 mol% Sb doping in SnTe has improved the zT to ~1 at 800 K [6], thanks to the phonon scattering via layered intergrowth nanostructures; and the optimal presence of resonant dopant In in SnTe has helped

to achieve a peak $zT \sim 1.1$ at 873 K [5]; and Ag doping in SnTe has brought in valence band convergence [6]. The improvements achieved with these individual dopants in SnTe, and our foresight to bring in the combined benefits of synergistic band effects and nanostructuring, has inspired us to study the TE of SnTe codoped with Sb, In and Ag.

2. Materials and methods

The samples of $Ge_{1-x-y}Bi_xIn_yTe$ (x = 0.05, 0.07; y = 0.02) and $Sn_{1-x-y-z}Sb_xIn_yAg_zTe$ (x = 0.15; y = 0.0025, 0.005; z = 0, 0.0025, 0.005) were synthesized by vacuum sealed-tube melting process. The obtained ingots were crushed into powders and consolidated by Spark Plasma sintering (SPS) at 773 K for 5 mins under an axial pressure of 60 MPa. Other experimental details were discussed in detail in our previous works [7–9].

3. Results and discussion

The sharp reflections from XRD for GeTe and SnTe based systems indicate the crystalline nature of the phases. The main reflections in Fig. 1(a) can be indexed to rhombohedral ($R3m$) GeTe phase. The rhombohedral phase is further confirmed by the presence of double reflections [(0 2 4) and (2 2 0)] in the range of 2 θ values between 41° and 44°. Minor proportion of Ge-rich secondary phase is also present. In Fig. 1(b), the main reflections

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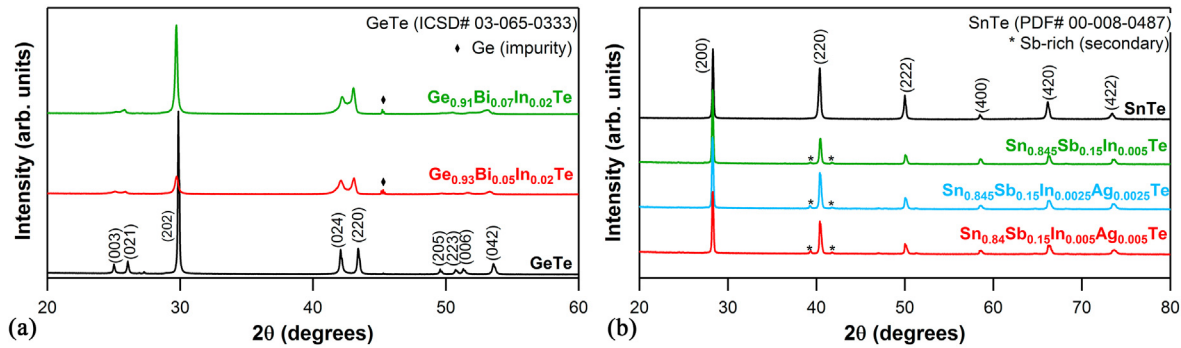*E-mail address:* bhuvanesh.srinivasan@univ-rennes1.fr (B. Srinivasan).

Fig. 1. XRD patterns for codoped (a) GeTe based and (b) SnTe based samples.

can be indexed to cubic ($Fm3m$) SnTe phase, and the secondary phase closely matches with the pattern of the layered intergrowth Sb-rich compound ($Sn_mSb_{2n}Te_{3n+m}$) [6].

Codoping of Bi and In to GeTe drastically decreases the electrical conductivity (Fig. 2a), due to the reduction in carrier density, as evident from the Hall measurement results (Table 1). As the Hall voltage is positive in all the samples, holes are the major charge carriers (p-type) in both GeTe and SnTe codoped systems. The reduction in hole concentration during codoping in GeTe, which can be attributed to the aliovalent donor dopant natures of Bi^{3+} and In^{3+} at the Ge^{2+} sub-lattices of GeTe, helps to significantly improve the Seebeck coefficient (Fig. 2b). This improvement in thermopower is anticipated, as In doping in GeTe is known to create resonant state near the Fermi-level (E_F) [4]. The power factor, PF = $\sigma^2 S$ is presented in Fig. 2(c). The total thermal conductivity (κ) is remarkably reduced by codoping of Bi and In to GeTe (Fig. 2d). This huge decrease in κ arises from the cumulative decrease of both lattice (κ_{latt}) and electronic (κ_e) contributions, as shown in the Supporting Info (SI, Fig. S1). Decreased carrier density is the key cause for suppression of κ_e, while nanostructuring can be the reason for suppression of lattice contribution, as both Bi doping in GeTe [2,7] and SPS processing are known to create nano-scale defect layers and precipitates, which are effective phonon scatterers. Bi and In codoping in GeTe has helped to concurrently improve the thermopower and suppress the thermal transport.

Codoping of Sb, In and Ag in SnTe has decreased σ (Fig. 2e) by suppressing the charge carrier mobility (due to impurity scattering caused by In doping [5,6]), and expectedly increased the Seebeck coefficient (Fig. 2f) due to resonant states created by In [5]. Just like codoped GeTe, κ has also been notably reduced in codoped SnTe (Fig. 2h) due to the cumulative decrease of both lattice and electronic contributions (SI, Fig. S2). The aggregate effect of nanostructuring, which is expected to arise from Sb doping to SnTe [6] and SPS processing, has strikingly decreased the thermal transport in codoped SnTe. Ag was codoped with an objective to bring in valence band convergence in SnTe [6], and as well as to compensate for the loss in σ by codoping of Sb and In in SnTe. But unfortunately, it was not the case, as addition of Ag to Sb and In codoped SnTe has not much beneficial impact on its transport properties. The resonance state, supposedly created by In in SnTe [5] has helped the In and Sb codoped sample ($Sn_{0.845}Sb_{0.15}In_{0.005}Te$) to exhibit a better thermopower from room temperature to 800 K and thereby an improved power factor over a wide spectrum of temperature (Fig. 2g).

Codoping of In and Bi to GeTe helps to maintain better zT (Fig. 3a) compared to pristine GeTe over a broad temperature domain, due to the simultaneous effects of improved thermopower and reduced thermal transport. Pristine GeTe exhibits peak zT only

after 673 K, whereas Bi and In codoped samples exhibit peak zT at temperatures as low as 550 K. The sample $Ge_{0.93}Bi_{0.05}In_{0.02}Te$ maintains a consistently high zT of 0.8 – 0.9 over a wide range of temperature (550–773 K). From a practical point of view, it is not the peak zT, but it is the average zT (zT_{ave}) value that determines the overall efficiency of a TE module. From 550 to 773 K, the maximum $zT_{ave} \sim 0.85$ is obtained for $Ge_{0.93}Bi_{0.05}In_{0.02}Te$ sample, which is much higher than pristine GeTe ($zT_{ave} \sim 0.6$) and is better than most of the Sb-free GeTe based materials [9]. The other key reason for such improved properties can be due to the fact that the codoping of Bi and In relaxes the rhombohedral structure of GeTe and pushes the system towards the cubic structure, as the atomic radii of Bi (1.43 Å) and In (1.56 Å) are larger comparing Ge (1.25 Å), evident from merging of the rhombohedral double reflections in range of 2 θ values between 41° and 44° (Fig. 1a). In other words, Bi and In codoping promotes the structural transition ($R3m \rightarrow Fm$-$3\ m$) faster in GeTe. This is proved by the DSC data (SI, Fig. S3), where the structural transition temperature conspicuously reduces from ~700 K for pristine GeTe [9] to ~580 K for $Ge_{0.93}Bi_{0.05}In_{0.02}Te$.

In the SnTe codoped system, $Sn_{0.845}Sb_{0.15}In_{0.005}Te$ exhibits a peak zT ~ 0.8 at 823 K, which is higher than undoped SnTe (zT ~ 0.55 at 823 K). Moreover, the cumulative effect of improved power factor over a broad spectrum of temperature and reduced thermal conductivity helps the Sb and In codoped SnTe to exhibit a higher zT_{ave} compared to pristine SnTe.

Though the TE properties for the codoped compositions when compared to their base materials are good, the doping elements which have distinctive roles and cause different band effects can at times heavily distort the density of states (DOS), if the codoping level is not balanced or optimized. Such heavy distortion of DOS can adversely affect σ (as in Fig. 2a and e). This explains the reason for the codoped compositions (double or triple doping) that is presented in this work for exhibiting a relatively lower zT when compared to the singly doped compositions.

4. Conclusion

Codoping of Bi and In to GeTe, expected to foster resonant state near Fermi-level (induced by In) and nanostructured precipitation (by Bi and SPS process), has helped to (i) suppress the carrier density, (ii) enhance the thermopower, (iii) reduce the thermal transport, and (iv) favored the rhombohedral to cubic structural transition, thus ultimately making them as potential candidates for mid-temperature device fabrications, as they maintain a constant high zT ~ 0.85 over a wide spectrum of temperature (550 – 773 K). Similarly, codoping of Sb and In to SnTe, expected to bring in In-induced resonance state and nanostructuring (by Sb and SPS