Journal of Solid State Chemistry 242 (2016) 43–49

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

AgI alloying in SnTe boosts the thermoelectric performance via simultaneous valence band convergence and carrier concentration optimization

Ananya Banik, Kanishka Biswas*

New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P.O., Bangalore 560064, India

ARTICLE INFO

Article history:
Received 15 November 2015
Received in revised form
5 February 2016
Accepted 5 February 2016
Available online 6 February 2016

Keywords:
Thermoelectrics
Tin telluride
Seebeck coefficient
Band convergence
Carrier optimization

ABSTRACT

SnTe, a Pb-free analogue of PbTe, was earlier assumed to be a poor thermoelectric material due to excess *p*-type carrier concentration and large energy separation between light and heavy hole valence bands. Here, we report the enhancement of the thermoelectric performance of *p*-type SnTe by Ag and I co-doping. AgI (1–6 mol%) alloying in SnTe modulates its electronic structure by increasing the band gap of SnTe, which results in decrease in the energy separation between its light and heavy hole valence bands, thereby giving rise to valence band convergence. Additionally, iodine doping in the Te sublattice of SnTe decreases the excess *p*-type carrier concentration. Due to significant decrease in hole concentration and reduction of the energy separation between light and heavy hole valence bands, significant enhancement in Seebeck coefficient was achieved at the temperature range of 600–900 K for $Sn_{1-x}Ag_xTe_{1-x}I_x$ samples. A maximum thermoelectric figure of merit, *zT*, of ~1.05 was achieved at 860 K in high quality crystalline ingot of *p*-type $Sn_{0.95}Ag_{0.05}Te_{0.95}I_{0.05}$.

1. Introduction

Thermoelectric materials, capable of performing direct heat and electricity conversion, have received world-wide attention due to their potential role in the waste heat to electrical energy conversion [1–6]. The performance of these materials is represented by thermoelectric figure of merit, *zT*, which is the function of electrical conductivity (σ), Seebeck coefficient (S), total thermal conductivity ($\kappa_{total}=\kappa_{latt}$, lattice thermal conductivity,$+\kappa_{el}$, electronic thermal conductivity) and temperature (T) [1]. Materials systems that can be functioned around 400–900 K are mainly interesting because most of the waste heat generated in industry and automobile exhaust is within this range [7]. To date, the leading materials are lead chalcogenides [8–12], multiple filled $CoSb_3$ [13–15] and bismuth chalcogenide [16–18] etc.

The electrical conductivity, Seebeck coefficient and total thermal conductivity are interdependent via carrier concentration (n) [2]. Hence, significant enhancement in *zT* can be achieved via simultaneous optimization of n and minimization of κ_{latt}. Dopant can play an important role to tune the n of any material. Several advances in this field have been achieved in PbTe-based materials with the highest figure of merit, *zT* of 2.2 at 915 K [7,8]. *n*- and *p*-type PbTe, which is one of the popular thermoelectric material, has optimized n of $\sim10^{19}$ cm^{-3} [19]. Although PbTe based materials exhibit excellent thermoelectric efficiency, environmental concerns about Pb restricts its use in large scale application. Hence, researchers are in search for alternative material with similar efficiency.

Recently, an interest to study the thermoelectric properties of SnQ (Q=S, Se or Te) has emerged which are considered to be more environment friendly than PbTe with the goal to improve their performance to the same level as PbTe [20–30]. Among SnQ, only SnTe adopts the similar rock salt crystal structure and electronic band structure as PbTe, which makes SnTe a promising candidate for thermoelectrics [31–34]. Pristine SnTe, a *p*-type degenerate semiconductor, has rarely been considered as efficient thermoelectric material because of the following reasons: (i) the inability to control its very high *p*-type carrier concentration (10^{20}–10^{21} cm^{-3}) due to presence of intrinsic Sn vacancy and (ii) a large energy separation (ΔE_v ~0.35 eV) between the higher lying light hole valence band at the L point and the lower-lying heavy hole valence band at the Σ point, which limits hole transport to a single band, giving rise to a low Seebeck coefficient [33,35]. Recently, important studies have been performed to improve thermoelectric performance of SnTe [20–22, 24, 26–28, 36]. SnTe has been alloyed with other metal tellurides such as $AgSbTe_2$ and $AgBiTe_2$ in order to improve its thermoelectric performance via carrier concentration optimization and reduction of thermal conductivity

---

* Corresponding author.
E-mail address: kanishka@jncasr.ac.in (K. Biswas).

http://dx.doi.org/10.1016/j.jssc.2016.02.012
0022-4596/© 2016 Elsevier Inc. All rights reserved.

[23,37,38]. Significant enhancement in the Seebeck coefficient of SnTe has been achieved due to the formation of the resonant level in the valence band through In doping, which resulted in a *zT* of ~1.1 at 873 K [20]. Resonant level formation through In doping along with the increase in the contribution of heavy hole valence band through solid solution alloying significantly improved the Seebeck coefficient, which resulted in a promising *zT* in *p*-type 1.5 mol% In doped $SnTe_{0.85}Se_{0.15}$ sample [22]. The introduction of Cd, Mg, Hg or Mn in the Sn-site of SnTe is effective in achieving valence band convergence, giving rise to a notable enhancement of the Seebeck coefficient and thus the *zT* [21,24,26,28].

In order to obtain improved thermoelectric performance, it is necessary to decrease the excess hole concentration in SnTe to an optimized level, i.e., on the order of 10^{19} cm^{-3} [2]. For electronic fine tuning of the carrier concentration values and thereby controlling the electrical conductivity, bismuth or iodine was mostly applied as donor atoms in SnTe [39,40]. Iodine doping can effectively tune carrier concentration in the light hole valence band of SnTe [39]. However, due to presence of electron-hole bipolar effect above 600 K, iodine doping could not provide the expected efficiency in SnTe [39]. Alloying SnTe with AgI, which has larger band gap (E_g~1.2 eV) compared to that of SnTe (E_g ~0.18 eV), has the potential to optimize thermoelectric properties both via electronic structure modulation and carrier concentration optimization.

Here, we have investigated the effect of AgI alloying (0–6 mol%) on the thermoelectric properties of SnTe which has been synthesized by simple vacuum sealed tube melting reaction. Substitution of I^- for Te^{2-} in SnTe reduces carrier concentration to a value of $\sim 5.7 \times 10^{19}$ cm^{-3}. In addition, AgI alloying in SnTe increases the principle band gap, which was directly evidenced from the infrared diffuse reflectance spectroscopy. Thus, AgI alloying significantly tunes the electronic structure of SnTe and decreases energy difference between the light hole and heavy hole valence bands, leading to an enhanced Seebeck coefficient in the temperature range of 500–900 K. As a result, *p*-type $Sn_{0.95}Ag_{0.05}Te_{0.95}I_{0.05}$ sample exhibits a maximum *zT* of ~1.05 at ~860 K.

2. Experimental section

2.1. Reagents

Tin (Alfa Aesar 99.99+ %), tellurium (Alfa Aesar 99.999+ %), silver iodide powder (Alfa Aesar 99.999+ %), elemental silver ((Ag, 99.999%, metal basis) and tellurium iodide (TeI_4, 99.999%, metal basis) were used for synthesis without further purification.

2.2. Synthesis

High quality crystalline ingots (~7 g) of $Sn_{1-x}Ag_xTe_{1-x}I_x$ ($x=0-0.06$) were synthesized by mixing appropriate ratios of high-purity starting materials of Sn, AgI and Te in a quartz tube. $Sn_{1-x}Ag_xTe$ ($x=0.05$) was synthesized by mixing appropriate ratios of high-purity starting materials of Sn, Ag and Te in a quartz tube. For $SnTe_{1-x}I_x$ ($x=0.05$) preparation, Sn, Te and TeI_4 were used. The tubes were sealed under vacuum (10^{-5} Torr) and slowly heated to 450 °C over 12 h, then heated up to 900 °C in 5 h, soaked for 10 h, and cooled slowly to room temperature. In order to measure the thermoelectric properties, ingots were cut and polished by low speed diamond saw and mechanical polisher.

2.3. Powder X-ray diffraction

Powder X-ray diffraction for all of the samples were recorded using a Cu K_α ($\lambda=1.5406$ Å) radiation on a Bruker D8 diffractometer.

2.4. Band gap measurement

To estimate optical band gap, IR diffuse reflectance measurements have been performed with finely ground powder at room temperature using FT-IR Bruker IFS 66 V/S spectrometer in a frequency range of 4000–400 cm^{-1} with 2 cm^{-1} resolution and 50 scans. Absorption (α/Λ) data were calculated from reflectance data using Kubelka–Munk equations: $\alpha/\Lambda=(1-R)^2/(2R)$, where R is the reflectance, α and Λ are the absorption and scattering coefficients, respectively. The energy band gaps were derived from α/Λ vs E (eV) plots.

2.5. Hall measurement

Carrier concentrations were determined using Hall coefficient measurements at room temperature with a PPMS system. Four-contact Hall-bar geometry was used for the measurement. At 300 K, we have estimated the carrier concentration, n, from the formula: $n=1/eR_H$, where e is the electronic charge, R_H is hall coefficient.

2.6. Electrical transport

Electrical conductivities and Seebeck coefficients were measured simultaneously under He atmosphere from room temperature to 873 K on a ULVAC-RIKO ZEM-3 instrument system. The typical sample for measurement had parallelepiped shape with the dimensions of $\sim 2 \times 2 \times 8$ mm^3. Samples were spray-coated with boron nitride spray to minimize out gassing, except where needed for electrical contact with the thermocouples, heater, and voltage probes. The longer direction coincides with the direction in which the thermal conductivity has been measured. Heating and cooling cycles give repeatable electrical properties. The uncertainty of the Seebeck coefficient and electrical conductivity measurements is ~2%.

2.7. Thermal conductivity

The samples were coated with a thin layer of graphite to minimize errors from the emissivity of the material. Coins with ~8 mm diameter and ~2 mm thickness were used in all of the measurements. Thermal diffusivity, D, was directly measured in the range 300–873 K by using laser flash diffusivity method in a Netzsch LFA-457 (Fig. S1(a)). The thermal diffusivity data were analyzed using a Cowan model with pulse correction. Temperature dependent heat capacity, C_p, was derived using standard sample (pyroceram) in LFA457. Near room temperature C_p values of $Sn_{1-x}Ag_xTe_{1-x}I_x$ are in the range of 0.204–0.21 J $g^{-1}K^{-1}$ ((Fig. S1 (b)). The total thermal conductivity, κ_{total}, has been estimated using the formula, $\kappa_{total}=DC_p\rho$, where ρ is the density of the sample, measured using Archimedes method. The density of the pellets obtained was ~96% of the theoretical density. The uncertainty of the thermal conductivity is estimated to be within 5%.

3. Result and discussion

Crystalline ingots of $Sn_{1-x}Ag_xTe_{1-x}I_x$ ($x=0.01$, 0.02, 0.03, 0.05, 0.06) have been prepared by simple vacuum sealed tube reaction at 900 °C and characterized by PXRD. PXRD patterns in Fig. 1 (a) confirm formation of single phase within detection limit which could be indexed based on SnTe structure (Fm–3m). The lattice parameter (shown in Fig S2) increases with increasing AgI content up to 6 mol% (following Vegard's law type behavior, denoted by the dashed line), consistent with the larger radius of Ag^+ (1.29 Å) compared to that of Sn^{2+} (0.93 Å). The observed linear increase in