Improvement of thermoelectric properties of Cu_3SbSe_4 compound by In doping

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ARTICLE INFO

ABSTRACT

In doped $Cu_3Sb_{1-x}In_xSe_4$ ($x = 0, 0.002, 0.003$ and 0.004) compounds have been fabricated via a combined process of melting-pulverization-hot pressing. Effect of In doping on their thermoelectric properties have been explored and it reveals that In occupies the site of Sb and plays a role of acceptor dopant. With the increase of In doping content, the electrical resistivity and Seebeck coefficient decrease, and the power factor is obviously improved at elevated temperature compared with un-doped Cu_3SbSe_4. Meanwhile, the thermal conductivity is also reduced due to the extra phonon scattering by point defects introduced by In doping. As a consequence, a maximum ZT value of 0.50 (at 648 K) is obtained for the doped sample ($x = 0.003$), which is about 47% higher than that of the un-doped Cu_3SbSe_4.

1. Introduction

The increasing global energy demands and dwindling fossil fuel reserves promote the R&D for alternative energy technologies [1,2]. Thermoelectric (TE) materials, which can convert waste heat into electrical energy, have been paid extensive attention in recent years. Generally, the efficiency of a TE device is determined by the figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. An ideal TE material should have both high power factor ($S^2\sigma$) and low thermal conductivity to ensure a large ZT. Therefore, it has always been a long term goal of researchers to develop high ZT materials.

Recently, ternary or quaternary copper-based chalcogenides, such as $CuInTe_2$ [3–6], $CuGaTe_2$ [7], $Cu_2ZnSnX_4(X = Se, S)$ [8–9], $Cu_2CdSnSe_4$ [10–11] and $Cu_3SbX_4(X = Se, S)$ [12–13], which are variations of the II-VI zinc blende semiconductors, have been stepping into view of thermoelectric researchers. Among them, Cu_3SbSe_4 shows more promising because of its good advantages of cheap constituent element, large carrier effective mass ($\sim 1.1 m_e$) and small band-gap (~ 0.29 eV) [14]. However, its intrinsic ZT value is still very poor due to the low carrier concentration and resulted poor electrical conductivity [15]. In this compound, the Cu—Se bonds network service as the hole conduction framework while Sb orbitals contribute less to the valence band maximum [13]. Therefore, the substitution of Sb sites with other atoms (such as Ge [12], Sn [14,15], Bi [16] and Al [17]) is a reasonable strategy to adjust the carrier concentration and electrical transport properties. Theoretically, if we can substitute the Sb sites with In atoms, more *p*-type carriers can be created in comparison to Ge, Sn, Bi elements and

hence the content of dopant can be reduced to reach the same optimal carrier concentration. What's more, smaller electronegativity and ionic radius difference between Sb make In easier to be doped into Sb site than Al atom [18]. Therefore, In is chosen and employed as the dopant to Cu_3SbSe_4 in this work, and In doped Cu_3SbSe_4 samples have been fabricated by a combined process of melting-pulverization-hot process. The doping can effectively increase the power factor at elevated temperature and decrease the thermal conductivity of Cu_3SbSe_4 simultaneously. As a result, a maximum ZT = 0.5 at 648 K was obtained in the In-doped sample, which was improved by 47% in compared with the undoped Cu_3SbSe_4.

2. Experimental

2.1. Preparation

$Cu_3Sb_{1-x}In_xSe_4$ (i.e. CSSx, $x = 0, 0.002, 0.003$ and 0.004) was synthesized by a conventional melting, pulverization and hot-pressing method. Stoichiometric mixtures of Cu (99.9%), Sb (99.99%), In (99.9%) and Se (99.99%) powders were sealed in evacuated silica tubes and then placed in a muffle furnace, which were slowly heated to 1173 K and kept for 12 h, then cooled to 773 K in the furnace and quenched to room temperature in water. The quenched ingots were subsequently milled by hand and then annealed at 573 K for 2 days to ensure homogeneity. After that, they were pulverized and then hot pressed at 673 K for 1 h under 120 MPa in a purified argon atmosphere.

2.2. Characterization and measurements

The phase structure and composition of the prepared samples were checked by X-ray diffraction (XRD) on a Philip X'Pert X-ray diffractometer equipped with Cu Kα X-ray diffractometer (PANalytical, Almelo,

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Netherlands). A simultaneous measurement of Seebeck coefficient and resistivity was performed on a commercial measurement system (Namicro-III, Wuhan Schwab Instruments, Wuhan, China) from room temperature to 648 K. The thermal conductivity (κ) was calculated as the product of the material density determined by the Archimedes' method, thermal diffusivity measured by a laser flash method (LFA 427, Netzsch Instruments, Selb, Germany) and specific heat derived by differential scanning calorimeter (Diamond DSC, PerkinElmer Instruments, Massachusetts, USA). Carrier concentration and mobility of the sample were measured with a Hall effect measurement system (HMS 5500, Ecopia, Anyang, South Korea) under constant magnetic fields of ± 0.5 T.

2.3. Computational details

Ab initio calculations have been carried out to determine to the real occupied position of In atom by using the Perdew–Burke–Ernzerhof (PBE) [19] generalized gradient approximation (GGA) and projector augmented wave (PAW) [20] pseudopotentials implemented in the Vienna ab initio simulation package (VASP) [21]. A supercell of $2 \times 2 \times 1$ tetragonal (64 atoms/unit cell) was chosen, a plane-wave cutoff energy of 400 eV and an energy conversion threshold of 1.0×10^{-5} eV per atom were used for calculations.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of the hot pressed CSS*x* samples. It can be seen that all the diffraction peaks match very well with the standard PDF card of Cu_3SbSe_4 (No. 01-085-0003) and no other peak is observed, indicating that all the In-doped samples are single phase with the same crystallographic structure. Due to the tiny amount of In-doping, no obvious peak shift can be observed for the doped samples (Fig. 1b) and their lattice constants also have no obvious change (Fig. S1). However, as shown in Fig. 2, the carrier concentrations (n_h) increases rapidly from 2.2×10^{18} cm^{-3} to 3.5×10^{19} cm^{-3} when the In doping content increases from 0 to 0.004. Apparently, In is an efficient hole dopant in Cu_3SbSe_4 compound, and each In atom can provide approximately 1.5 holes (Fig. 2). At the same time, the corresponding carrier mobility decreases after the In doping due to the extra ionized impurity scattering and enhanced carrier scattering [22,23].

Seemingly, there are three possible sites, i.e. Cu, Sb and Se sites in the lattice of Cu_3SbSe_4 for In to occupy. Due to the large difference in the electronegativity (0.77) and ionic radius (1.36 Å) between In and Se, it is difficult for In atom to occupy the Se site [18]. Therefore, Cu and Sb sites are more possible for In to enter. A formation energy calculation [24] was carried out to investigate the possible location of In atoms,
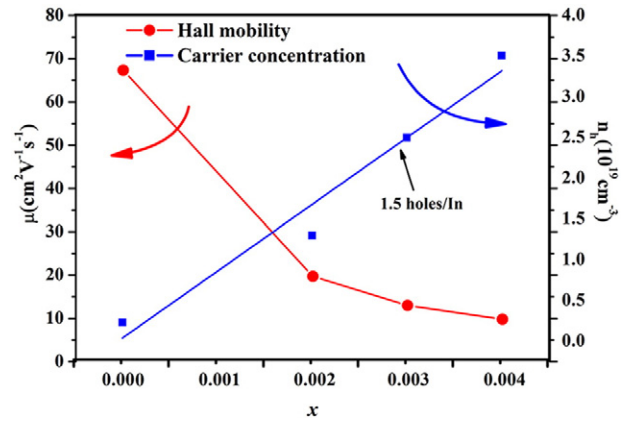

Fig. 2. Room temperature measured carrier mobility (μ) and carrier concentration (n_h) as a function of the In-doped content.

and it shows that the formation energies of In at Cu site (In$_{Cu}$) and Sb site (In$_{Sb}$) are -0.02 eV and -1.20 eV, respectively. That is to say, In substitution for Sb site in Cu_3SbSe_4 is more favorable thermodynamically. As shown in Fig. 3a, pure Cu_3SbSe_4 is an intrinsic semiconductor with three-fold degenerate valence band at Γ point, and In would act as an n-type dopant if it occupied the Cu site (In$_{Cu}$) and the Fermi level would lie in the conduction band as shown in both Fig. 3b and d. Obviously, this is inconsistent with the experiment results, which presents that the In doped Cu_3SbSe_4 is a p-type semiconductor, and one In atom contributes about 1.5 holes in Cu_3SbSe_4. While the calculation confirms that In plays a role as the p-type dopant when it enters the site of Sb (Fig. 3c and d). Based on the above theoretical calculation and experimental results, it can be concluded that In occupies the Sb site rather than Cu site and it dopes the compound into a p-type semiconductor.

Fig. 4 shows the thermoelectric properties of the hot pressed samples. As seen from Fig.4a, the electrical resistivity decreases with the increase of temperature, and it decreases with increasing the content of In dopant due to the more significant effect of hole concentration increase than the decrease of mobility (Fig. 2). The Seebeck coefficient of pure Cu_3SbSe_4 decreases with increasing temperature like a typical intrinsic semiconductor. However, the Seebeck coefficient of In-doped samples, increases with the increase of temperature until a vertex and then decreases with rising temperature, indicating a degenerate semiconductor behavior. The similar temperature-dependent behavior of ρ and S can also be found in other doped semiconductor [25]. In addition, the Seebeck coefficient decreases with increasing the amount of In doping
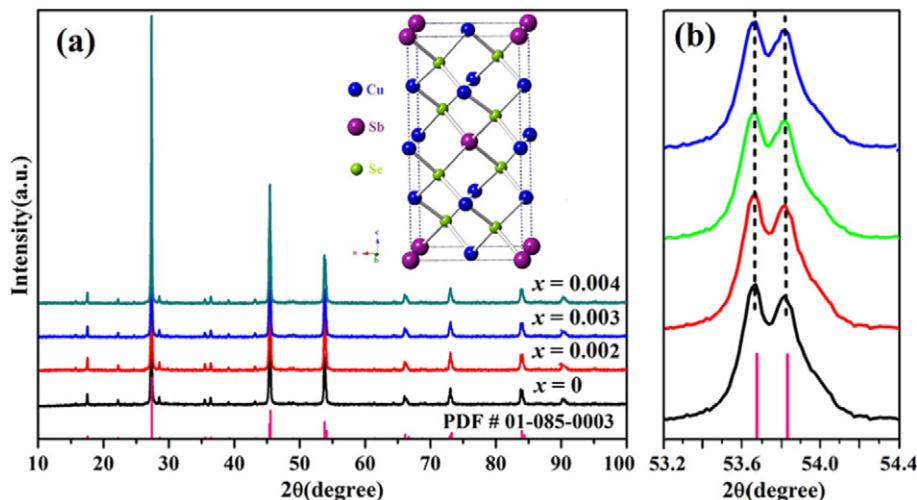

Fig. 1. (a) The observed XRD patterns of $Cu_3Sb_{1-x}In_xSe_4$ ($x = 0$, 0.002, 0.003 and 0.004) and (b) the magnified XRD patterns in 2θ range from 53.2^0–54.4^0.