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Effect of Pb doped on thermal stability and electrical transport properties of single crystalline β-Zn_4Sb_3

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ABSTRACT

In this study, we report the effect of Pb doping on both thermal stability and electrical transport properties of the single crystalline β-Zn_4Sb_3 , prepared based on the initial stoichiometric ratios of $Zn_{4-x}Sb_3Pb_xSn_3$ (x = 0, 0.2, 0.4, 0.6 and 0.8). All samples possess a metallic luster surface and hardly defects and pores. The TG-DSC results show that the Pb doping samples exhibit an excellent thermal stability. Electrical transport properties of the samples were optimized by Pb doping. Among all samples exhibit p-type conduction with carrier concentrations varying from 4.88 × 10^{19} to 14.29 × 10^{19} cm^{-3}, as carrier mobility changes from 31.1 to 66.4 $cm^2\ V^{-1}\ s^{-1}$ at room temperature. With the increase of Pb initial content, Seebeck coefficient increases and electrical conductivity decreases. The sample with Pb initial content x = 0.6 exhibits an excellent electrical properties, and obtains maximum power factor of 1.69 × 10^{-3} $W\ m^{-1}\ K^{-2}$ at 390 K.

1. Introduction

Owing to the Seebeck effect and Peltier effect, thermoelectric (TE) materials have become a promising functional material in the field of energy conversion and power generation [1–3]. The efficiency of TE materials are characterized by the dimensionless thermoelectric figure of merit (*ZT*) defined as $ZT = \alpha^2\sigma T/\kappa$, where α, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. In the past decades, various approaches to enhance *ZT* have been reported by increasing electrical conductivity, Seebeck coefficient, and reducing the thermal conductivity simultaneously [4,5]. However, it is not easy to improve *ZT* due to interrelated relation in these parameters.

Attributing to the extraordinarily low thermal conductivity which being likened to “phonon glass-electron crystal” TE property [6], the p-type β-Zn_4Sb_3 TE material obtained a high *ZT* value in the medium temperature area (473–673 K) [7,8]. The high TE performance of β-Zn_4Sb_3 mainly originates from relatively low thermal conductivity for the complex and disordered crystal structure, which the lattice thermal conductivity at room temperature is about 0.65 $Wm^{-1}\ K^{-1}$ [9]. However, the reported poor stability and weak mechanical property of polycrystalline β-Zn_4Sb_3 due to many micro-cracks or phase decomposition limit the practical applications [10,11].

Experimental results and theoretical calculations show that heavier metal doping in β-Zn_4Sb_3 can improve its thermal stability because of the hampering of Zn migration and freezing the liquid Zn in local disordered structure [12–14]. Meanwhile, theoretical calculation [15] reveals that the electrical properties of β-Zn_4Sb_3 are very sensitive to minute amounts of metal doping, which offers a method to optimize the TE properties. In fact, the optimization of TE properties for β-Zn_4Sb_3 is often focus on doping or solution by regulating the electronic structures and adjusting the carrier concentration [16,17], such as In, Pb, Sn, Cd, Bi, Mg etc. For example, Shai et al. [18] recently demonstrated the realization of a high TE figure of merit in Sn-substituted β-Zn_4Sb_3; The slight Pb-doping polycrystalline β-Zn_4Sb_3 [19] can enhance TE performance and thermal stability prepared by a method of the melting-quenching and spark plasma sintering. The result reported by Nyle´n et al. [20] shows that Pb-doping significantly suppresses the low temperature phase transition and improves thermal stability. Our former experimental results revealed that β-Zn_4Sb_3 single crystals obtained by Sn-flux method possess superior performance [25], and the phase decomposition is suppressed [21]. However, Pb-substitution in single crystal β-Zn_4Sb_3 has been rarely reported so far. In order to explore the effects of Pb doping on the structure and properties of β-Zn_4Sb_3 single crystals, in this paper , a series of Pb doped β-Zn_4Sb_3 are prepared by using Sn-flux method and we try to extract useful

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information to understand the effect of Pb doping on both thermal stability and electrical transport properties for β-Zn_4Sb_3.

2. Experimental

Pb doped single crystalline β-Zn_4Sb_3 samples were prepared by using Sn-flux method. The high-purity elements of Zn (grains, 5 N), Sb (grains, 5 N), Pb (ingots, 5 N) and Sn (grains, 5 N) were weighed and mixed according to an stoichiometric ratios of Zn:Sb:Pb:Sn = 4-x:3:x:3 (x = 0, 0.2, 0.4, 0.6 and 0.8, respectively) as raw materials. The mixture was sealed in an evacuated quartz tube, and then was heated slowly to 853 K for 2 h, after 12 h, it gradually cooled within 40 h to 573 K at cooling rate of 10 K/min before tube was removed from the furnace, the crystal samples were separated from the molten Sn solvent by centrifuging.

Phase constitutions of samples are analyzed with X-ray diffraction (XRD, Ultima IV) using Cu Kα radiation (λ = 1□5403 Å). Elemental compositions in single crystal samples were determined by wave-length dispersive electron-probe microanalysis (EPMA, JXA-8230). The scanning electron micrograph of the samples were examined by field emission scanning electron microscopy (FESEM, SUPRA 55VP) equipped with electron energy dispersive X-ray spectroscopy (EDS, Oxford). Thermal stability was determined by the thermogravimetric-differential scanning calorimetry (TG-DSC, STA 449F3 Jupiter) in an open alumina crucibles with a heating rate of 10 K/min over temperature ranging from 300 K to 900 K, and high-purity nitrogen was used as purge gas. Hall coefficient R_H of all the samples at room temperature was measured using a HL5500 Hall System (Nanometrics) with a magnetic field of 0.55 T. Measurements of Seebeck coefficient α and electrical conductivity σ were performed from 300 K to 660 K in a vacuum. The electrical conductivity σ of the samples were measured using a standard four-point probe method with a direct current (DC), and the DC current was maintained at 20 mA. The Seebeck coefficients were obtained by a comparative method with the temperature difference within 2 K. And the Konstantan (Ni: 40%) acted as a reference sample. Carrier density n and carrier mobility μ_H at room temperature were calculated from the Hall coefficient and electrical conductivity σ via the relation $n = \frac{1}{eR_H}$ and $\mu_H = \sigma \times R_H$, respectively, where e is the electron charge.

3. Results and discussion

3.1. Structure, compositions and lattice parameters

Single crystal samples prepared by Sn-flux method with shiny metallic luster surface were obtained, and the sizes are approximately 5 mm. As an example, Fig. 1(a) shows an image of single crystal sample with x = 0.2 and is stable in the air and water. Fig. 1(b) displays the scanning electron micrograph (SEM) of the sample polished using a suspension of 50 nm Al_2O_3 particles under high vacuum condition at an operating voltage of 20 kV. Fig. 1(c) shows the EDS results(c) of the sample with x = 0. As observed in the SEM image in the Fig. 1(b), small amount of an impurity phase Sn is detected in the specimens coming from Sn flux. At the same time, microscopic cracks or defects are invisible at 10k time magnification which indicates the crystals should have good mechanical properties [22].

For phase identification, the technique of XRD was employed. Fig. 2(a) displays the powder XRD spectra of the samples. All the characteristic peaks are well indexed by β-Zn_4Sb_3 phase with the space group $R\bar{3}c$. However, for the samples with x = 0.6, 0.8, additional peaks were observed virtually 23.5°, 27° and 33.5° in 2θ, being attributed to ZnSb phase due to the Zn content.

Table 1 displays the actual compositions and lattice parameters for among all samples. Based on the EPMA analyses, a small amount of Sn is observed in the chemical compositions, and attributed to Sn phase

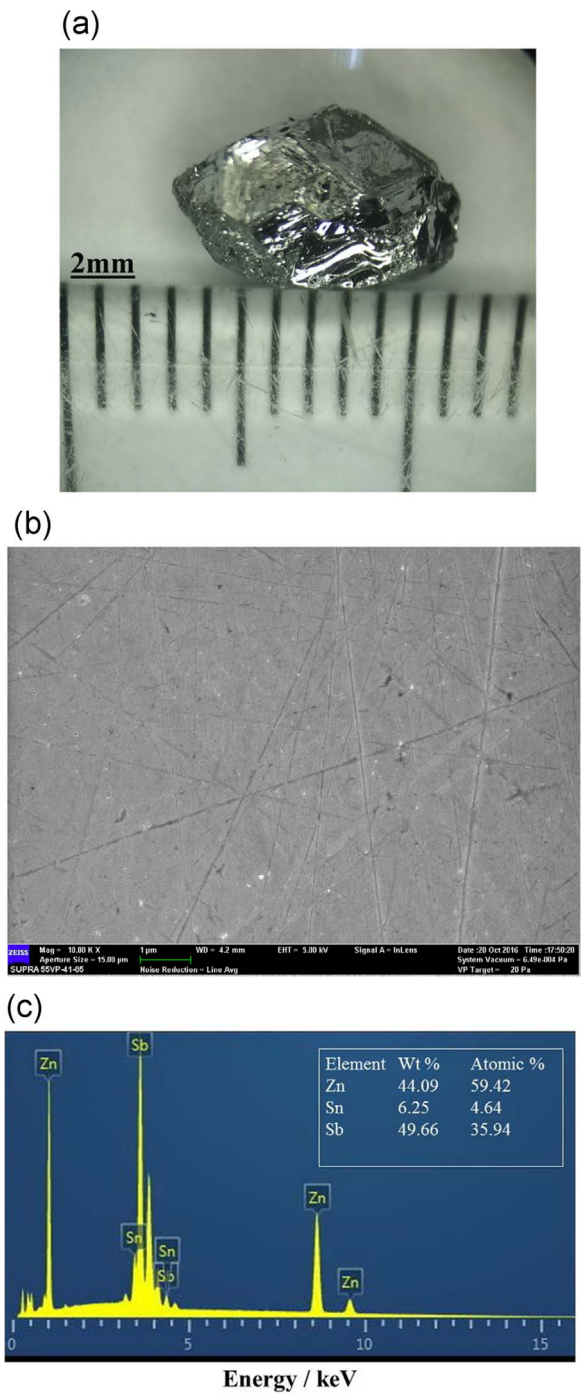

Fig. 1. The picture (a) and scanning electron micrograph (SEM) (b) of the single crystal sample with Pb content x = 0.2 and EDS results(c) of the sample with x = 0.

existing in the boundary of the crystal as an impurity. The Sn element is easily incorporated in the lattice of β-Zn_4Sb_3 resulting from the using of Sn flux. And we can conclude that these samples are roughly consistent with the ratio of (ZnSnPb): Sb = 3.8:3, which is lower than the previous reports [18,23]. EDS analysis (Fig. 1(c)) reveals that the sample with x = 0 consists of Zn, Sb and Sn, and quantitative EDS results indicate that the atomic ratio of Zn, Sb and Sn agree with the EPMA results. As we can see, both Pb and Sn prefer to substitute for Zn, and only a small amount of Pb is incorporated which indicates a small solid solubility of Pb in the compound. This phenomenon agrees with the result reported by Wang et al. [19].

The lattice parameters with Pb initial content for all the samples are shown in Table 1. It can be seen that the lattice parameters (a, b, c)