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Enhanced thermoelectric performance of β-Zn_4Sb_3 based composites incorporated with large proportion of nanophase Cu_3SbSe_4

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ABSTRACT

Thermoelectric properties of β-Zn_4Sb_3 based composites, Cu_3SbSe_4/β-Zn_4Sb_3, incorporated with large volume fraction, f (10–20 vol.%), of p-type nanophase Cu_3SbSe_4 have been investigated. The results indicate that as Cu_3SbSe_4 with a relatively lager thermopower, S, and a greater carrier mobility, μ, is incorporated into β-Zn_4Sb_3, the S of the composite system increases greatly, and at $T > 500$ K thermoelectric power factor (PF) becomes larger than that of the β-Zn_4Sb_3 matrix due to increased mobility of the composites. Especially, for the composite system with 15 vol.% of Cu_3SbSe_4, an increase of ~30% in the PF and a reduction of ~40% in the total thermal conductivity are achieved at 648 K, which allow the thermoelectric figure of merit (ZT) to reach 1.23 (at 648 K), a value that is 1.6 times larger than that (0.75) of matrix, β-Zn_4Sb_3 in the present study. Our results suggest that incorporation of secondary phase with larger S and greater μ in large proportion in a host material could be an easy, direct and effective way to elevate the thermoelectric performance of the host.

1. Introduction

During the last decade, substantial efforts have been made to search high performance thermoelectric materials due to the demand for cooling electric devices and power generation from waste heat [1–4]. Thermoelectric materials can convert energies between heat and electricity, but the challenge is to design efficient, environmentally-friendly and sustainable materials systems. The conversion efficiency of a thermoelectric material is characterized by the figure of merit, ZT, defined as: $ZT = (S^2/\rho\kappa)T$, where S, ρ, κ are the Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively [5–8]. To date, a great amount of research work that deals with intermediate temperature regime (500–700 K) thermoelectric materials for power generation usually focuses on Pb or/and Te-based materials such as PbTe [9], $AgPb_mSbTe_{m+2}$ [10], $AgPb_mSn_nSbTe_{2+m+n}$ [11], $NaPbmSbTe_{2+m}$ [12]. However, Pb is not environmentally-friendly, and Te is, not only rare in the Earth's crust, but also increasingly used in a number of other applications, such as steel metallurgy and solar cells. Hence, explorations of Pb and Te-free high-performance thermoelectric materials are vital to their wide applications, among which β-Zn_4Sb_3 is one of the attractive materials [13–15]. However, the thermal conductivity of β-Zn_4Sb_3 is around 1 W m^{-1} K^{-1} [16–18], close to the estimated minimum value for the thermal conductivity in solids[19,20], which suggests that there is not much room to elevate its ZT by lowering the thermal conductivity, and further improvement of its thermoelectric performance mainly relies on improvement of its thermoelectric power factor ($PF = S^2/\rho$).

There are several ways to improve ZT through elevating PF. One approach is to enhance S through introducing resonance distortion of electronic density of states (DOS) by doping, as in PbTe doped with Tl [21]. Unfortunately, this approach lacks universality, due to the difficulties in the match of the band structure of the hosts with doping elements, as demonstrated in PbTe doped with Cd [9]. The other possible method is to enhance S by an energy filtering effect through introduction of interface potential barriers (wells) [22]. Theoretical investigations show that interface potentials in the nanocomposites with semiconducting [23] or metallic [24] nanoinclusions can cause enhanced S through an energy filtering effect. However, experiments indicate [25,26] that due to large decrease in carrier mobility PF was not increased or even declined steeply though S enhanced through energy filtering effect. Hence, it is a great challenge to find an easy and a more generic approach to elevating PF to gain enhancement of ZT of a material.

In the present work complete Pb and Te-free β-Zn_4Sb_3-based composites incorporated with large volume fraction, f(10–20 vol.%), of p-type nanophase Cu_3SbSe_4 were synthesized. Cu_3SbSe_4 is a p-type semiconductor with large thermopower and large carrier mobility [27], while β-Zn_4Sb_3 has low lattice thermal conductivity and relatively small thermopower. One could expect that incorporation of large proportion of Cu_3SbSe_4 into β-Zn_4Sb_3 will enhance thermoelectric performance of the composite system by combining respective advantages. As expected, our results show

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that incorporation of nanophase Cu_3SbSe_4 into β-Zn_4Sb_3 with a large amount of results in an increase of ~30% in PF and a reduction of ~40% in thermal conductivity κ at 648 K, which leads to a largest ZT, 1.23, obtained at 648 K in the composite system with $f = 15$ vol.%.

2. Experimental procedures

2.1. Materials preparation

Pure β-Zn_4Sb_3 was prepared from elemental Zn (99.9999%, powder) and Sb (99.999%, powder) in stoichiometric proportions. Slight excess of Zn was taken to balance the loss of Zn during the experimental processing. The elements were then sealed into evacuated quartz tubes under vacuum (10^{-3} Pa). The tubes were heated to 1023 K for 12 h. Then they were quenched in cool water. An agate mortar was used to grind the β-Zn_4Sb_3 ingots obtained into powders. Nanophase Cu_3SbSe_4 inclusions were prepared by sovothermal synthesis from constituent elements CuCl (99%, powder), $SbCl_3$ (99%, powder) and Se (99%, powder), which were put into a 800 ml glass breaker containing 300 ml ethylenediamine to react. The solution was stirred by a magnetic rotor at 400 K for 2 h. The collected powder was filtered, washed and dried in a vacuum oven. The nanometer-sized Cu_3SbSe_4 and β-Zn_4Sb_3 powders were mixed for 4 h in accordance with the volume ratios of 10:90, 15:85 and 20:80 in a planetary mill. Then the disk-shaped bulk nanocomposite samples were obtained by hot-pressing the blended powders under a pressure of 600 MPa in vacuum at 550 K for 1 h.

2.2. Microstructure characterization and property measurements

X-ray diffraction (Philips-X PERT PRO) with Cu Kα radiation was used to check the phase constitutions. Moreover, microstructure investigations were also carried out with the help of high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2010) operating at a 200 kV accelerating voltage. The HRTEM samples were prepared as follows: small square-shape pieces with approximate sizes of 5 mm × 5 mm × 2 mm were first cut from the ingot by a wire saw (South Bay Technology Inc.). The samples were then hand-polished with sand paper to about 80–100 μm in thickness. Circular-shape specimens of 3 mm in diameter were cut by a Gatan model 601 ultrasonic disc cutter; and then they were thinned by a Gatan model 656 precession dimple grinder and low-angle ion milled (2–4°) to electron transparency by a Gatan model 691 precession ion-polishing system. Hall coefficients were measured by using a physical property measurement system (PPMS, Quantum Design). The electrical resistivity and Seebeck coefficient were measured simultaneously by the standard four-probe method (ULVAC-RIKO: ZEM-3) in Helium atmosphere from 300 K to 650 K by using bar-shaped specimens cut from the disk-shaped samples by an electrical-spark cutting machine. The thermal diffusivity α was measured with a NETZSCH LFA-457 instrument in the temperature range of 300 K to 700 K, where the cylinder disks (~2 mm in thickness) coated with graphite were utilized. The thermal conductivity κ was calculated according to $\kappa = DCp\alpha$, where Cp is the specific thermal capacity obtained by using differential scanning calorimetry (DSC, perkin-Elmer) and D is the sample density measured by Archimedes method.

3. Results

3.1. Microstructure characterization

Phase constitutions of Cu_3SbSe_4, β-Zn_4Sb_3 and $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 ($f = 10$, 15, and 20 vol.%) nanocomposite samples were analyzed with XRD, as shown in Fig. 1. It can be seen from curve (a) in Fig. 1 that all the diffraction peaks can be perfectly indexed to tetragonal structure Cu_3SbSe_4 (standard JCPDS number: 00-025-0263; space group I-42 m) with lattice constants $a = 5.63$ Å and $c = 11.23$ Å; while all the diffraction peaks of curve (b) in Fig. 1 can be accurately indexed to rhombohedral structure β-Zn_4Sb_3 (standard JCPDS number: 89-1969; space group R-3c) with lattice constants $a = 12.233$ Å, $b = 12.233$ Å and $c = 12.428$ Å, which demonstrate that pure Cu_3SbSe_4 and pure β-Zn_4Sb_3 samples have been obtained in the study. Moreover, in patterns from (c) to (e) other than reflection peaks from β-Zn_4Sb_3, there is an additional small peak at $2\theta \sim 27.5°$ (it becomes increasingly evident with the increase of Cu_3SbSe_4 content) that corresponds to (112) peak of Cu_3SbSe_4, indicating that there are two phases in $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 ($f = 10$, 15 and 20 vol.%) composite samples: β-Zn_4Sb_3 and Cu_3SbSe_4, no obvious impurity phase being detected.

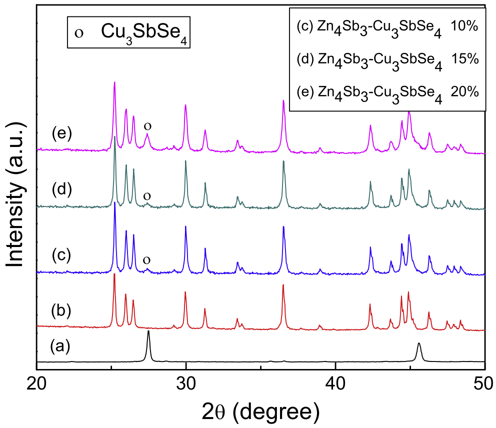

Fig. 1. XRD patterns of (a) Cu_3SbSe_4 and (b) β-Zn_4Sb_3 and (c–e) $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 ($f = 10$, 15 and 20 vol.%, respectively).

Fig. 2(a) shows the HRTEM bright-field image of $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 with $f = 15$ vol.%. One can see that its microstructure is composed of coarse-grained (most grain sizes are larger than ~200 nm) smooth areas and granular regime, which correspond to β-Zn_4Sb_3 matrix and incorporated Cu_3SbSe_4 phase, respectively. Fig. 2(b) is a lattice image of the rectangle area in (a), which shows clearly that other than β-Zn_4Sb_3 phase (upper part of the image) the incorporated Cu_3SbSe_4 phase possesses nanostructures (lower part of the image) with grain sizes ranging from ~5 nm to over 10 nm. The lattice constants obtained from lattice image of both β-Zn_4Sb_3 matrix and Cu_3SbSe_4 (as shown in Fig. 2(b)) phase indicate that nanophase Cu_3SbSe_4 are successfully incorporated in p-type semiconducting β-Zn_4Sb_3 matrix, forming $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 bulk nanocomposites, in agreement with the result obtained from XRD analysis.

3.2. Thermoelectric transport properties

The electrical resistivity, ρ, of β-Zn_4Sb_3, Cu_3SbSe_4 and $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 ($f = 10$, 15 and 20 vol.%) is shown in Fig. 3 as a function of temperature. It can be seen that ρ for β-Zn_4Sb_3 increases with increasing T, showing typical degenerate behavior. In contrast, ρ for Cu_3SbSe_4 initially increases with increasing temperature to around 400 K; then it decreases steeply with further increase in temperature, exhibiting non-degenerate behavior. Especially, ρ of Cu_3SbSe_4 is over 10 times larger than that of β-Zn_4Sb_3. Moreover, one finds that ρ of the nanocomposite samples increase with the increasing content of Cu_3SbSe_4. For instance, at 300 K ρ increases from 5×10^{-5} Ω m to 15×10^{-5} Ω m and then to 18×10^{-5} Ω m as f increases from 10, 15 to 20 vol.%, respectively. Then ρ of the nanocomposite samples decreases slowly with temperature, which indicates that the bulk materials exhibit partial degenerate semiconducting behavior in the whole temperature range investigated. In addition, as the content of nanophase Cu_3SbSe_4 increases, the slope of the resistivity of nanocomposites $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 ($f = 10$, 15 and 20 vol.%) increases.

Fig. 4 shows the variations of Seebeck coefficient, S, for all the samples. Positive values of S over the whole temperature range (Fig. 4(a)) indicate that the major charge carriers are holes. One can see that S for β-Zn_4Sb_3 increases with increasing temperature, showing degenerate behavior, while S for Cu_3SbSe_4 decreases basically with increasing temperature, showing non-degenerate behavior. The values of S for composites $f(Cu_3SbSe_4)$/β-Zn_4Sb_3 ($f = 15$ and 20 vol.%) are in-between that of Cu_3SbSe_4 and β-Zn_4Sb_3 in the temperature range of ~300 K to ~650 K.