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High pressure synthesis and thermoelectric properties of micro/nano structures $CoSb_3$

L. Deng[a,*], Jing Ni[b], J.M. Qin[a], X.P. Jia[c,*]

[a] Department of Material Science and Engineering, Changchun University of Science and Technology, Changchun 130022, PR China
[b] FAW-Volkswagen Automotive Company Ltd, Changchun 130011, PR China
[c] National Lab of Superhard Materials, Jinlin University, Changchun 130012, PR China

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ABSTRACT

Nano-particle and defect have been proved to be effective in depressing the lattice thermal conductivity and improving the performance of thermoelectric materials. In this work, $In_{0.5}Sn_xCo_4Sb_{12}$ were prepared using a high pressure and high temperature (HPHT) method, In and Sn was assumed that In plays the role of a filler and occupies the Sb-icosahedron voids. Doping of In and Sn results in the defects, nanostructuring, and mesoscale structuring were all combined into a single skutterudite matrix. The thermoelectric properties were measured in the temperature range of 321–710 K. As expected, with the synthetic pressures increased , the thermal conductivity of samples improved significantly. The minimum value of $In_{0.5}Sn_{0.4}Co_4Sb_{12}$ synthesized at 3.8 GPa is 1.79 $Wm^{-1} K^{-1}$ and the highest Seebeck coefficient of sample $In_{0.5}Sn_{0.2}Co_4Sb_{12}$ synthesized at 2.8 GPa reached 222 $\mu V K^{-1}$ finally.

1. Introduction

Thermoelectric materials are still of great scientific interest due to their many excellent properties [1–5]. These materials display an exceedingly rich spectrum of physical behavior, including semiconducting behavior, superconductivity, heavy fermion-like characteristics, and low thermal conductivities, all of the above are direct results of the nature of the structure and bonding in these materials. The coefficient of performance of a thermoelectric cooler and the conversion efficiency of a thermoelectric generator depend on the dimensionless figure of merit (ZT), which is defined as $ZT=\alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the temperature in Kelvin [6–10].

$CoSb_3$, as one of the most studied high thermoelectric properties materials systems, retain the high ZT values, which has ever been obtained in bulk TE materials. $CoSb_3$-based material is a semiconductor with a small band gap, high carrier mobility, and modest thermopower. However, the high thermal conductivity of $CoSb_3$ seriously hinders its application in thermoelectric applications. So, much of effort on skutterudite $CoSb_3$ compounds has focused on the lattice thermal conductivity reducing [11–13]. Tan reported that most of the heat could be transferred by short and medium wavelength phonons, and the phonons could be scattered by point defects and second-phase nano-particles effectively. But, many long-wavelength phonons remaining also contributed to the lattice thermal conductivity [14]. So, all types of phonons can be effectively scattered only when point defects, nanostructuring, and mesoscale structuring are all combined into a single thermoelectric material. So far, many synthetic methods have been used to synthesize various functional inorganic nanostructures [15–24]. HPHT method has been used to synthesize skutterudite compounds successfully and has obtained desired results. Compared with other methods, the HPHT method not only shortens the synthesis time to half an hour, but also reduces the synthesis temperature to 873 K. The key of this technique is the synthetic pressure, which can press the atoms into the voids of the skutterudites.

So far, various nanocomposite materials with improved thermoelectric performance have been reported and the most of the previous work has been put on the investigation of synthesis processes to realize the homogeneous distribution of nano particles in the thermoelectric material matrix [25–27]. Due to In and Sn has two possibilities of filling and doping, and the remaining elements can be dispersed in the form of matrix materials, we choose the two concentrations of the preparation for contrast. Because the limitations of that alkali group elements are easily oxidized, In and Sn double filled $CoSb_3$ samples were prepared by high pressure synthesis first. The thermal conductivity of samples prepared by HPHT method were decreased obviously compare with that of the samples synthesized by other method. The aim was to reduce the thermal conductivity achieved by using point

* Corresponding authors.
E-mail address: dengyue520619@126.com (L. Deng).

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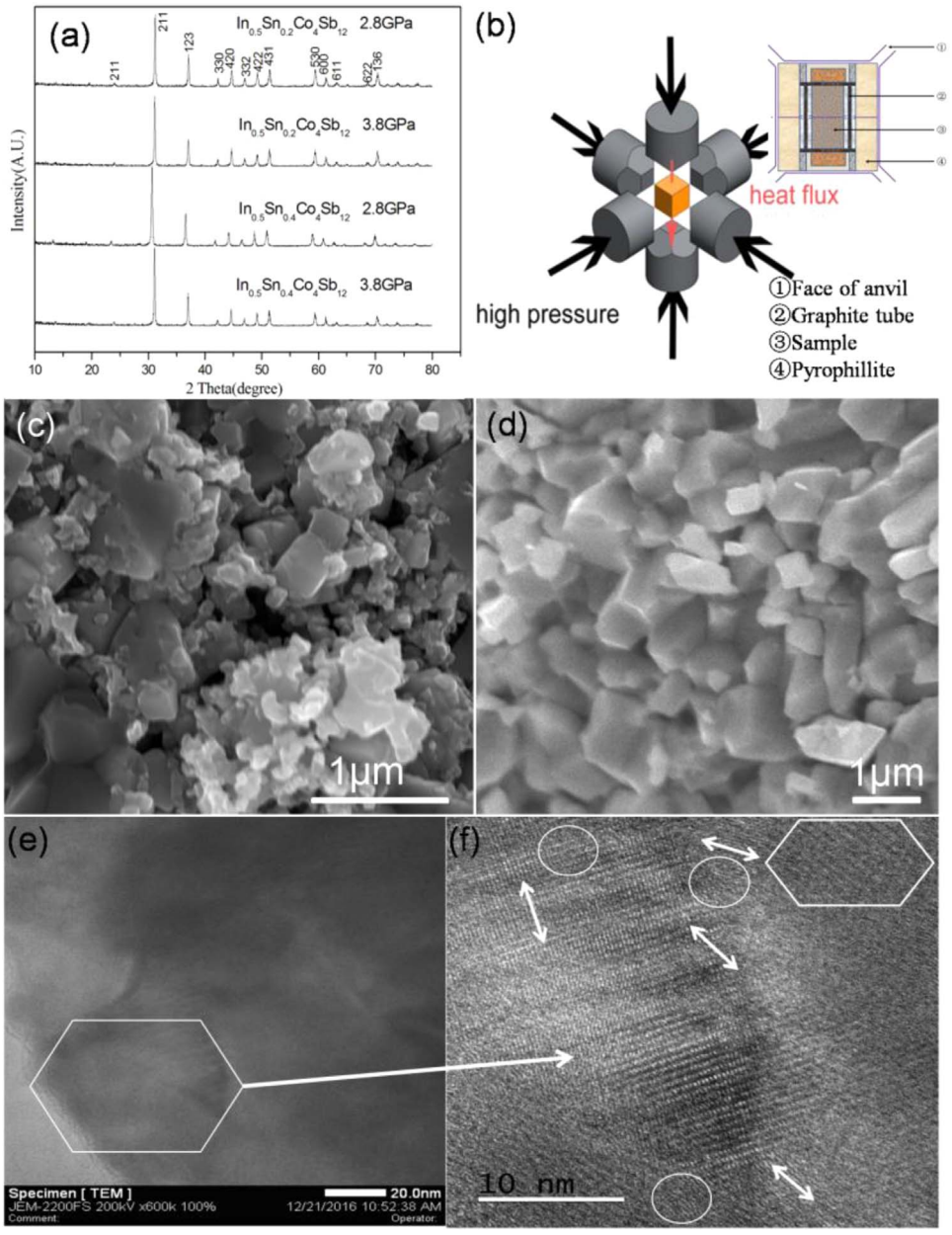

Fig. 1. (a) the XRD image, (b) the sample assembly for HPHT, SEM micrographs of (c) $In_{0.5}Sn_{0.4}Co_4Sb_{12}$ prepared at 3.8 GPa, (d) $In_{0.4}Co_4Sb_{12}$(Ref. [15]), (e) TEM image and (f) HRTEM image of $In_{0.5}Sn_{0.4}Co_4Sb_{12}$ prepared at 3.8 GPa.

defects, nanostructuring, and mesoscale structuring, which generated by both high pressure and doping with In and Sn.

2. Experimental procedure

The nominal chemical ratio $In_{0.5}Sn_xCo_4Sb_{12}$ samples were prepared with In, Sn, Sb and Co (99.9% in purity) powders as sources. The source of materials was purchased from Aladdin. Shanghai of China. The mixtures were grinded by agate mortar under the protection of argon, which were compressed into a thick 3 cm and diameter of 10 cm cylindrical sample by pressure. After that, the samples were prepared by a cubic anvil high pressure apparatus (SPD 6×1200 made in China) at about 900 K. The phase structures were characterized by X-ray diffraction (XRD) measurements with Cu-K_α radiation (D/MAX-RA). The morphology of the fractured surface and the investigation of microstructures were observed by field emission scanning electron microscopy (JEOL JSM-6700F) and high-resolution transmission electron microscopy (JEOL JEM-2200FS). The Seebeck coefficient (S) and electrical conductivity (ρ) were measured simultaneously by a ZEM-3 commercial equipment (Ulvac-Riko) in the temperature range of 321–710 K. The thermal diffusivity was measured on a laser flash thermal constants measuring with the commercial system (Netzsch LFA 427) apparatus in the temperature range of 321–710 K.

3. Results and discussion

Typical XRD patterns of $In_{0.5}Sn_xCo_4Sb_{12}$ samples are shown in Fig. 1a. The XRD patterns of $In_{0.5}Sn_xCo_4Sb_{12}$ samples prepared under different synthetic pressures are nearly the same. It can be known that the major phases of $In_{0.5}Sn_xCo_4Sb_{12}$ prepared by HPHT are all matched to that of the single phase of $CoSb_3$ at normal pressure. We find that a slight shift in the XRD peaks of the samples prepared by different pressures, which is mainly due to the decreased spacing of the crystal planes produced at higher pressures. The cavity structure