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Letter

Beneficial effect of high pressure and double-atom-doped skutterudite compounds $Co_4Sb_{11.5-x}Te_{0.5}Sn_x$ by HPHT

Hairui Sun [a,*], Xiaopeng Jia [a], Le Deng [b], Cheng Wang [c], Pin Lv [a], Xin Guo [a], Bing Sun [a], Yuewen Zhang [a], Binwu Liu [a], Hongan Ma [a,*]

[a] National Key Lab of Superhard Materials, Jilin University, Changchun 130012, China
[b] Department of Material Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China
[c] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, China

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ABSTRACT

Double-atom-doped polycrystalline skutterudite compounds $Co_4Sb_{11.5-x}Te_{0.5}Sn_x$ ($x = 0.1$, 0.2 and 0.3) has been prepared successfully by high pressure and high-temperature (HPHT) method. The method can dope Te and Sb atoms in skutterudite crystal structure to substitute Sb-atom simultaneously. The thermoelectric properties including Seebeck coefficient, electrical resistivity and thermal conductivity were studied at room temperature. The experimental data were as we would expect: with the synthesis pressure rise, a larger absolute Seebeck coefficient was maintained, which was likely due to the large effective mass arising from the doped atoms. Moreover, the lattice thermal conductivity of $Co_4Sb_{11.5-x}Te_{0.5}Sn_x$ was observed to decrease monotonously with the pressure increasing at room temperature, which was attributed to the high densities of grain boundaries and point defects in the Sb cages. Comparing with other methods, HPHT could shorten the synthesis time from several days to half an hour. Results indicated that the method of HPHT combined with double-atom-doping could optimize electrical and thermal transports in a relatively independent way, and the excellent properties gained at high pressure can be partially maintained to ambient pressure.

1. Introduction

In an effort to improve the performance of solid-state power generation devices utilizing the thermoelectric effect, compounds with the skutterudite crystal structure have drawn great interest. Skutterudite-based materials have attracted great attention for their potential thermoelectric application in power generation at intermediate temperatures [1,2]. $CoSb_3$-based skutterudites, which have typical phonon glass and electron crystal properties, are believed to have strong potential for thermoelectric application [3–5]. The effectiveness of a material for thermoelectric application can be quantified by the dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where α, σ, κ, T are the Seebeck coefficient, electrical conductivity, thermal conductivity and the temperature in Kelvin, respectively [6]. Therefore, to maximize ZT of a material, large α and σ as well as low κ are required. Nevertheless, $CoSb_3$-based skutterudite cannot be used in thermoelectric applications because of its high thermal conductivity. So, much of effort on pure $CoSb_3$ compounds has focused on reducing the lattice thermal conductivity. One of the effective methods to reduce thermal conductivity is doping with atoms, which can substantially impede the lattice phonon propagation, and thus lower the thermal conductivity [7–10].

It has been reported that the ZT value could be improved extraordinarily by high pressure. But the biggest disappointment is that the perfect performance under high pressure returns back to the origin state when the pressure is unloaded. HPHT method has been proved an effective and potential processing route to prepare thermoelectric materials, which can improve thermoelectric properties obviously and maintain the excellent properties to ambient pressure [11–13]. The method of HPHT can also tune thermoelectric properties rapidly and cleanly. In addition, the synthesis eriod of time is shortened greatly [14].

In this work, we have successfully synthesized $Co_4Sb_{11.5-x}Te_{0.5}Sn_x$ ($x = 0.1$, 0.2 and 0.3) solid solution by HPHT. The goal in this research is obtaining compounds with the lowest possible thermal conductivity. As might be expected, the good results of Te, Sn doping in Co_4Sb_{12} were obtained. The thermoelectric properties were studied far intensively such as Seebeck coefficient, electrical resistivity, power factor, and thermal conductivity.

* Corresponding author. Fax: +86 431 85168858.
E-mail addresses: hairuisun1216@163.com (H. Sun), maha@jlu.edu.cn (H. Ma).

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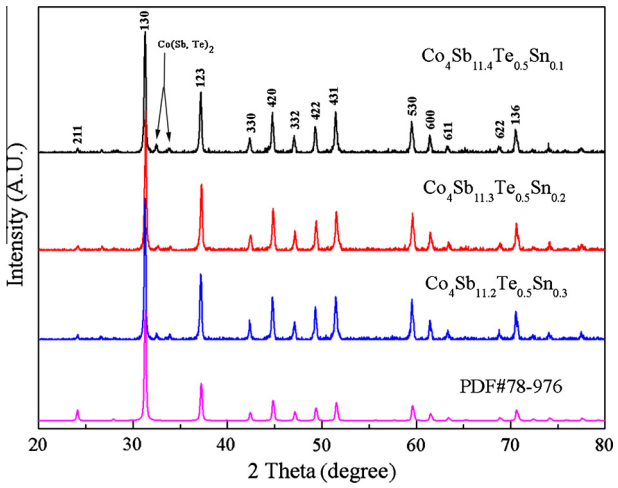

Fig. 1. XRD patterns of $Co_4Sb_{11.5-x}Te_{0.5}Sn_x$ synthesized at 0.5–3 GPa.

2. Experimental procedure

The $Co_4Sb_{11.5-x}Te_{0.5}Sn_x$ (x = 0.1, 0.2 and 0.3) samples were prepared with cobalt, antimony, tellurium and tin (99.99% in purity) powders as sources, which were weighed according to the stoichiometry. After being uniformly mixed with an agate mortar in a glove box under the nitrogen gas atmosphere, the mixtures were shaped a cylinder with about 3–4 mm thick and 10.5 mm in diameter by press, and then the pole shaped samples were assembled for HPHT synthesis. The samples were prepared in a China-type large volume cubic high-pressure apparatus (CHPA) (SPD-6 × 1200) with a sample chamber of 23 mm on an edge at 1000 K and 0.5–3GPa, and the synthesis time was selected as half an hour. X-ray diffraction (XRD) measurements with Cu Kα (λ = 1.5418 Å) radiation were examined by an X-ray diffractometer (D/MAX-RA). The Seebeck coefficient (α) was calculated by: $\alpha = \triangle V/\triangle T$, among them, ΔT for the difference in temperature on both ends of the semiconductor, $\triangle V$ is at the ends of the temperature difference electromotive force. In this experiment, α was tested by a home-made instrument according to the distortion formula: $\alpha = -V_1^*(\alpha_{NiAl} - \alpha_{NiCr})/(V_1 - V_2) + \alpha_{NiAl}$, where α_{NiAl} and α_{NiCr} are the α of type K-(chromel–alumel)-thermocouple (as the known values); V_1 and V_2 are monitored by computer using the VI-Logger program provided by NI-company. The error in α measurement did not exceed 5% at room temperature. The electrical resistivity was measured by typical DC four-probe configuration. The thermal diffusivity (λ) was measured based on the laser flash technique (Netzsch LFA-427), and the specific heat (Cp) measurement by DSC conversion was obtained using a Linseis STA PT-1750 equipment with the sapphire revision. We got the relative den-

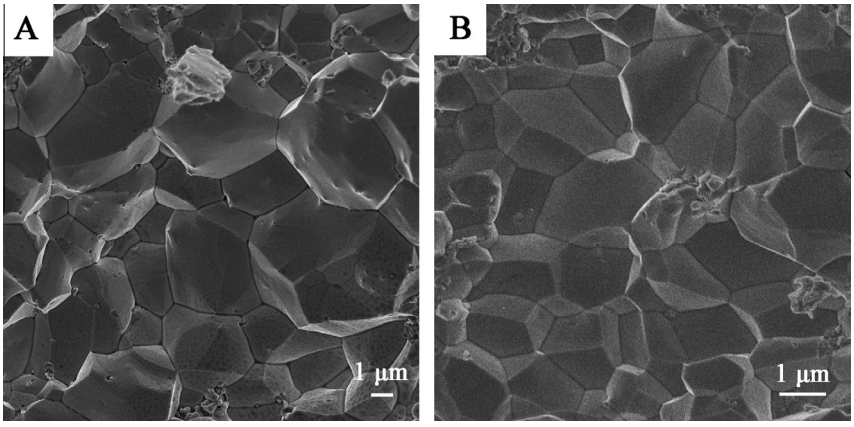

Fig. 2. (A) and (B) SEM micrographs of $Co_4Sb_{11.5-x}Te_{0.5}Sn_x$ at 0.5 GPa and 3 GPa.

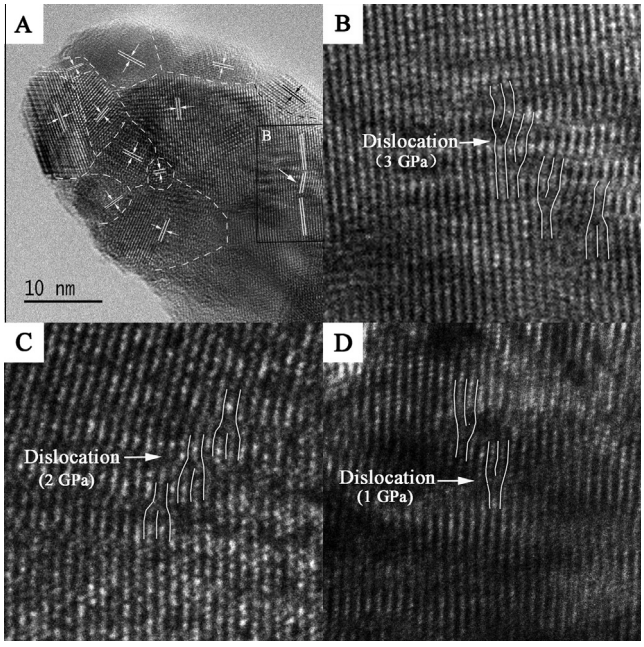

Fig. 3. (A) HR-TEM image of $Co_4Sb_{11.2}Te_{0.5}Sn_{0.3}$ prepared at 3 GPa by HPHT. (B)High-magnification image from region B in image (A) includes several clear dislocations. (C) and (D) HR-TEM images of $Co_4Sb_{11.2}Te_{0.5}Sn_{0.3}$ prepared at 2 GPa and 1 GPa by HPHT.