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HPHT synthesis and thermoelectric properties of $CoSb_3$ and $Fe_{0.6}Co_{3.4}Sb_{12}$ skutterudites

N. Dong [a], X. Jia [a], T.C. Su [a], F.R. Yu [b], Y.J. Tian [b], Y.P. Jiang [a], L. Deng [a], H.A. Ma [a,*]

[a] State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
[b] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

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ABSTRACT

P-type skutterudite compounds $CoSb_3$ and $Fe_{0.6}Co_{3.4}Sb_{12}$ with bcc crystal structure were prepared by high pressure and high temperature method. The electrical resistivities, Seebeck coefficients and thermal conductivities of the samples were measured in the temperature range of 300–680 K. The temperature-dependent thermoelectric transport properties, including electrical resistivity, Seebeck coefficient and thermal conductivity were investigated in detail. The results indicate that with temperature increasing the electrical resistivity increases, the Seebeck coefficient first increases and then decreases after about 580 K. The thermal conductivity decreases with increasing temperature. Compared with those of the same samples prepared at ambient pressure, the electrical transport properties of the samples prepared by HPHT method are improved greatly. The room temperature power factor of $Fe_{0.6}Co_{3.4}Sb_{12}$ is nearly four times higher than that of the same sample prepared at ambient pressure. The dimensionless thermoelectric figure of merit, *ZT*, reaches the maximal values of 0.17 and 0.09 for $CoSb_3$ and $Fe_{0.6}Co_{3.4}Sb_{12}$ respectively at 550 K.

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1. Introduction

Novel thermoelectric (TE) materials with super transport properties continue to be of interest scientifically and have received much attention now [1–7]. The performance of a TE material is generally characterized by the dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where α, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity, respectively. The electrical properties are determined by the power factor, which defined as $\alpha^2\sigma$. Skutterudite compounds exhibit a wide range of electrical and thermal transport phenomena by the phonon-glass and electron-crystal (PGEC) approach [7], they have high thermo-power and high charge-carrier mobility, so they become fascinating family of materials continuously [8–10]. $CoSb_3$ and its related skutterudite compounds are expected to be the most promising TE materials. However, undoped pure $CoSb_3$ cannot be used in thermoelectric applications because of its high thermal conductivity. Most previous studies have proved that doping and/or filling [1,7] can reduce thermal conductivity and improve effectively thermoelectric properties. For example, Fe and Ni substituting for Co [4,5], and Te substituting for Sb [11] have been found to be active dopants. Peng [4] and Zhang [5] have reported that there is a maximal *ZT* value for $Fe_{0.6}Co_{3.4}Sb_{12}$ among substituting Fe-doped $CoSb_3$ compounds.

Many techniques [4,5,12,13] have been used to synthesize skutterudite compounds, however, most methods have their limitations. For example, the melting and annealing method need a long time to obtain the skutterudite structure; impurities can be easily brought in sample by mechanical alloying technology for its long annealing process and ball milling. Compared with other methods, HPHT method has many advantages, including the ability to tune rapidly and cleanly, typically without introducing disorder and phase separation, or other complicating factors. In our previous reports [14–16], this technology has been used to synthesize other compounds successfully and obtained perfect results. In this work, the skutterudite compounds $CoSb_3$ and $Fe_{0.6}Co_{3.4}Sb_3$ were successfully synthesized by HPHT method, and the temperature-dependent thermoelectric properties were investigated in detail.

2. Experimental procedure

Co powder (99.9%), Sb powder (99.9%) and Fe powder (99.9%) were used as starting materials. These powders were weighed according to the stoichiometry of $CoSb_3$ and $Fe_{0.6}Co_{3.4}Sb_{12}$, and then mixed in an agate mortar. The mixtures were shaped to a cylinder with about 3 mm thick and 10 mm in diameter by press. The cylinder samples were assembled for HPHT synthesis. The samples were prepared in a cubic anvil high pressure apparatus (SPD 6 × 1200) with a sample chamber of 23 mm on an edge at 900 K and 1.5 GPa. The pressure was estimated by the oil press load, which was calibrated by the pressure induced phase transitions of bismuth, thallium and barium. The temperature was estimated by the relationship of input heater power and temperature, which was measured by the Chromel–Alumel thermocouples.

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* Corresponding author. Tel.: +86 431 85168858; fax: +86 431 85168858.
E-mail address: maha@jlu.edu.cn (H.A. Ma).

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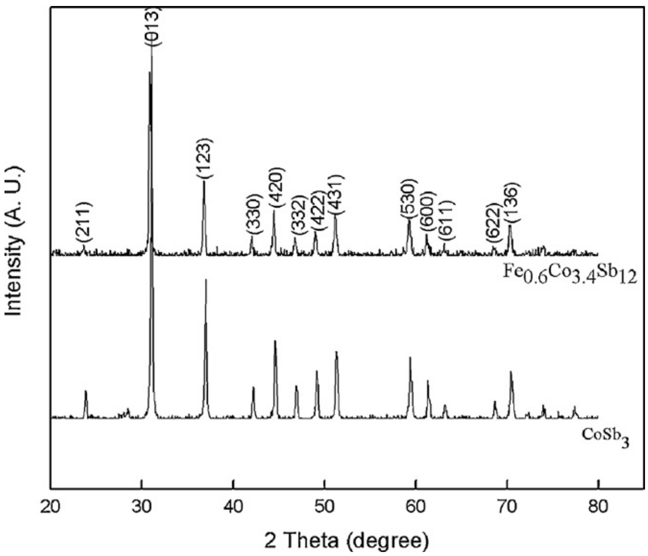

Fig. 1. XRD patterns of $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$.

X-ray diffraction (XRD) measurements with Cu-Kα radiation were performed on an X-ray diffractometer (D/MAX-RA). Scanning electron microscopy (SEM) (JXA-8200) was used to observe the fractured surface. The Seebeck coefficient and electrical conductivity were measured simultaneously by a ZEM-3 apparatus. The thermal conductivity κ was measured on a TC-7000 (ULVAC-RIKO Inc., Japan) Laser Flash Thermal Constants Measuring Apparatus. All the thermoelectric properties were measured in the temperature range from room temperature to 680 K.

3. Results and discussion

Fig. 1 shows the XRD patterns for the sample of $CoSb_3$ and $Fe_{0.6}Co_{3.4}Sb_{12}$ prepared at 1.5 GPa and 900 K. From Fig. 1, we can see that the XRD patterns of both the samples match very well with the standard diffraction data of $CoSb_3$ skutterudite structure, which is a typical body-central-cubic structure with a space group of Im-3.

Fig. 2(a) and (b) are the SEM micrographs for the fractured surfaces of $CoSb_3$ and $Fe_{0.6}Co_{3.4}Sb_{12}$ respectively. From the SEM micrographs in Fig. 2, we can see that the samples prepared at high pressure are very condensed, and the crystal grain size is in the order of micro meter. In addition, $Fe_{0.6}Co_{3.4}Sb_{12}$ sample has smaller crystal grain size and more abundant grain boundary than those of $CoSb_3$ sample, which may be helpful to decrease its thermal conductivity.

The relationship between the electrical resistivity (ρ) and temperature is shown in Fig. 3. It is obvious that the electrical resistivities of both the samples increase with an increase of temperature, and the electrical resistivity of $Fe_{0.6}Co_{3.4}Sb_{12}$ in the whole temperature range is larger than that of $CoSb_3$. The room temperature electrical resistivity of $Fe_{0.6}Co_{3.4}Sb_{12}$ is about $1.6 \times 10^{-3}\ \Omega$ cm, which is much lower than that of the same sample prepared at ambient pressure (about $2.5 \times 10^{-3}\ \Omega$ cm) [17].

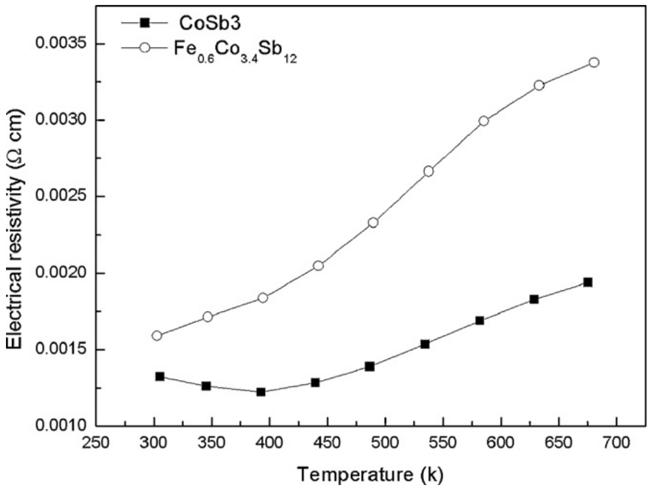

Fig. 3. Temperature dependence of electrical resistivity for $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$.

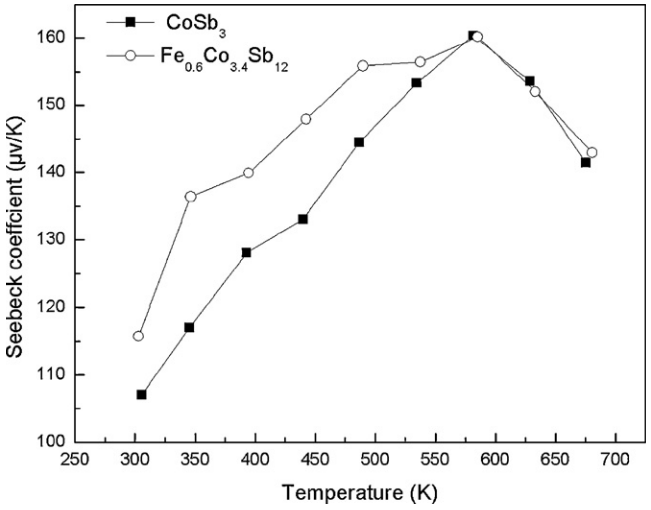

Fig. 4. Temperature dependence of Seebeck coefficient for $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$.

The dependence of Seebeck coefficient for the synthesized samples on temperature is presented in Fig. 4. As can be seen from Fig. 4, the Seebeck coefficients of both the samples are positive which imply that they are p-type semiconductors. With increasing temperature, the Seebeck coefficient firstly increases and then decreases after about 580 K, which is consistent with the result of Zeming [17]. In addition, the Seebeck coefficient of $Fe_{0.6}Co_{3.4}Sb_{12}$ is

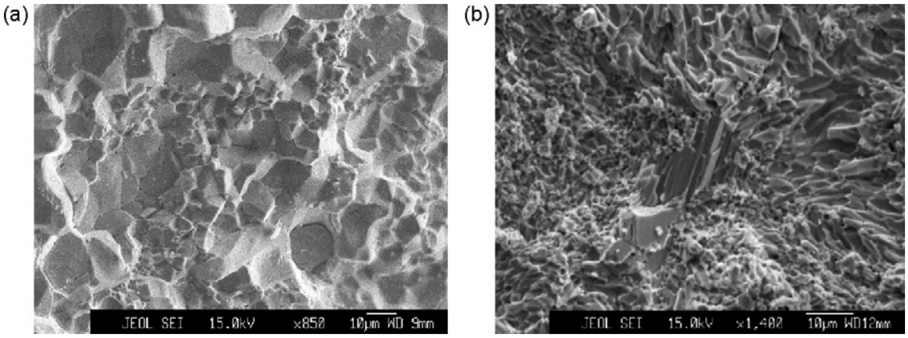

Fig. 2. SEM micrographs of the fractured surface for $CoSb_3$ (a) and $Fe_{0.6}Co_{3.4}Sb_{12}$ (b).

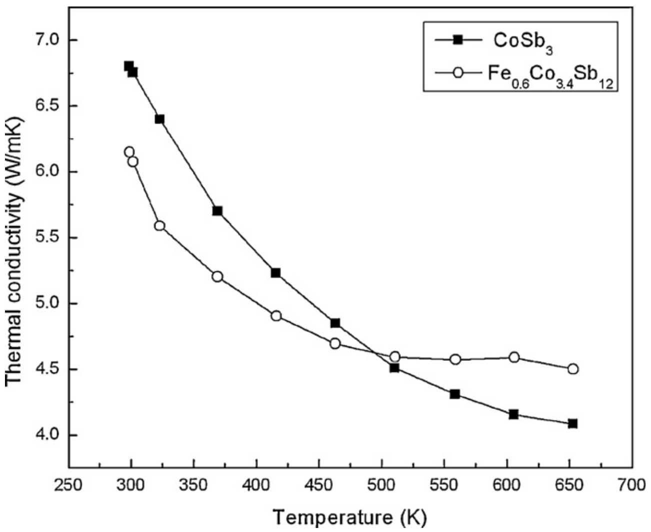

Fig. 5. Temperature dependence of thermal conductivity for $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$.

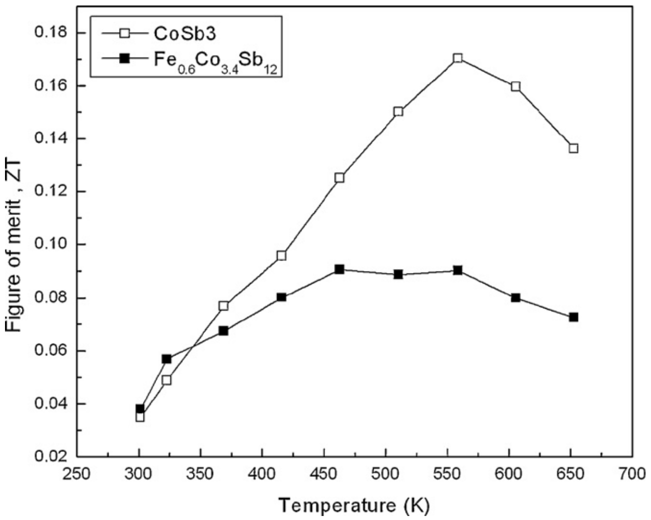

Fig. 6. Temperature dependence of figure of merit, *ZT*, for $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$.

higher than that of $CoSb_3$, which is possibly due to the decreasing carrier concentration by Fe substituting for Co. Especially, the maximal Seebeck coefficient 148.77 μV/K was obtained for $Fe_{0.6}Co_{3.4}Sb_{12}$ at about 550 K, which is higher than the result of Soon-Chul Ur (~80 μV/K) [18].

The room temperature power factor of $Fe_{0.6}Co_{3.4}Sb_{12}$ calculated by the room temperature Seebeck coefficient and electrical resistivity is about 9.84 μW/(cm K^2), which is nearly four times higher than that of the same sample prepared at ambient pressure (2.56 μW/(cm K^2))[18].

The above results agree with the advantages of high-pressure synthesis. The electrical transport properties can be improved significantly at high pressure and the excellent properties gained at high pressure can be partially kept to ambient pressure.

The thermal conductivity (κ) is plotted versus temperature in Fig. 5. The thermal conductivities of both the samples decrease with an increase of temperature, which can be contributed to the intensified phonon scattering as the temperature increasing. The room temperature thermal conductivity of $Fe_{0.6}Co_{3.4}Sb_{12}$ (6.15 W/mK) is lower than that of $CoSb_3$ (6.8 W/mK), however, the high temperature (>500 K) thermal conductivity of $Fe_{0.6}Co_{3.4}Sb_{12}$ is higher than that of $CoSb_3$, which indicates that the thermal conductivity cannot be effectively reduced only by Fe substituting doping. In order to reduce thermal conductivity and obtain high figure of merit (*ZT*), further research on filled skutterudite compounds by high-pressure technique should be performed in our next work.

The figure of merit (*ZT*) is calculated by the measured data of α, σ and κ. Fig. 6 shows the temperature dependence of the figure of merit (*ZT*) for $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$. The *ZT* values for both the samples firstly increase and then decrease with increasing temperature. At about 550 K, $Fe_{0.6}Co_{3.4}Sb_{12}$ sample obtains the maximal *ZT* value (0.09), which is larger than the result of Kim (about 0.05) [19], however, unfortunately smaller than that of undoped $CoSb_3$ (0.17). It is related to the large electrical resistivity for $Fe_{0.6}Co_{3.4}Sb_{12}$ compound.

4. Conclusions

P-type single phase skutterudite compounds $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$ were successfully synthesized by HPHT method at 1.5 GPa and 900 K. In the temperature range from room temperature to 680 K, with temperature increasing the electrical resistivity increases and Seebeck coefficient firstly increases then decreases, however, the thermal conductivity decreases for both the samples. Compared with ambient pressure methods, high pressure method can effectively enhance the electrical transport properties of Fe substituting doped $CoSb_3$, but unfortunately the thermal conductivity is not improved only by Fe substituting doping. The maximum *ZT* value is 0.09 and 0.17 for $Fe_{0.6}Co_{3.4}Sb_{12}$ and $CoSb_3$ respectively at 550 K.

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