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The Enhanced Thermoelectric Properties of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ Prepared by the High-Pressure and High-Temperature Method

Abstract: Polycrystalline skutterudite $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ with a bcc crystal structure was prepared by the High-Pressure and High-Temperature (HPHT) method. The study explored a chemical method for introducing Ba atoms into the voids of $CoSb_3$ to optimize the thermoelectric figure of merit ZT in the system of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. The samples were characterized by X-ray diffraction, electron microprobe analysis, and thermoelectric properties measurement. The electrical resistivity, Seebeck coefficients and thermal conductivities of the samples were measured in the temperature range of 300–743 K. The power factor and the figure of merit, *ZT*, of the samples all increased with the increasing temperature. A dimensionless thermoelectric figure of merit of 0.87 at 743 K was achieved for n-type $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ at last. The results indicated Ba-filled $CoSb_3$ prepared by HPHT method is an effective method to greatly enhance the thermoelectric properties of skutterudite compounds.

Keywords: skutterudite, high-pressure and high-temperature method, thermoelectric properties, $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$

PACS® (2010). 72.15.JF, 81.05.Cy, 81.05.Dz, 81.05.Za, 84.60.Rb

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1 Introduction

It has been well known that advanced thermoelectric materials (TE) can be used both as refrigerator that utilize electricity for cooling and power generators that convert heat into electricity [1, 2, 3]. Moreover, thermoelectric devices have many advantages, such as lightweight, small and without any moving parts or bulk fluids. The world's demand for energy is causing a dramatic escalation of social and political unrest. One way to improve the sustainability of our electricity base is through the scavenging of waste heat with thermoelectric generators [4, 5, 6]. The performance of thermoelectric materials is generally evaluated in terms of the dimensionless figure of merit *ZT* defined as $ZT = s^2\sigma T/\kappa$, where s is the Seebeck coefficient, σ is electrical conductivity, *T* is the absolute temperature and κ is the total thermal conductivity with its lattice and electronic contributions. The electrical properties are determined by the power factor defined as $s^2\sigma$ or s^2/ρ, where ρ is the electrical resistivity. It is believed that the *ZT* value of 3 to 4 is necessary for practical thermoelectric generators. Thus, the current research on thermoelectric materials is focused on finding thermoelectric materials with large value of *ZT*.

The Co_4Sb_{12} compounds have attracted much attention since it was found [7]. It exhibits a wide range of electrical and thermal transport phenomena by the phonon-glass and electron-crystal (PGEC) approach which was proposed by slack. The Co_4Sb_{12} and its related skutterudite compounds are a continuously fascinating family of materials because they have high charge-carrier mobility, large Seebeck coefficient and high electrical conductivity, however, pure Co_4Sb_{12} have a bad thermoelectric performance. One of the main obstacles to further improving their thermoelectric performance is reducing their relatively high thermal conductivity [8]. A variety of strategies have been employed to decrease its thermal conductivity simultaneously not deteriorate the power factor (s^2/ρ), for instance, doping by partial Co-site or Sb-site substitution, filling structure voids, and multisite substitution [9, 10, 11]. For example, Chen and his group decreased the thermal conductivity of skutterudite by multiple-filled atoms [12]. He and his group decreased thermal conductivity of TE materials by introducing pores [13]. Binary skutterudite has a cubic linked octahedral produces a void at the center of (Tx-6)-cluster and the cubic lattice. This void is large enough to accommodate large atoms such as rare earth or alkaline earth ions to obtain filled skutterudite or stuffed skutterudite. When atoms are placed into the interstitial voids or cages of skutterudite

materials, the lattice thermal conductivity can be substantially reduced compared with that of unfilled skutterudite. Tang and his group successfully decreased thermal conductivity by filling and substituting atoms [14, 15]. Those approaches have been shown to result in an enhanced thermoelectric property [16, 17]. However, there was little information so far focusing on the effect of Ba as filled atom for Co_4Sb_{12}-based skutterudite compounds by HPHT method. Herein, we investigate the effect of Ba atom on thermal transport properties of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ skutterudite. We confirm that this approach can further decrease the thermal conductivity of the TE materials and improve the thermoelectric properties.

Many techniques have been used to synthesize Co_4Sb_{12}-based skutterudite compounds. However, most methods have their limitations. Compared with other methods, the HPHT method has many advantages such as typically restraining the disorder and phase separation, the ability to tune rapidly and cleanly and other complicating factor [18]. It is well known that the HPHT method is the most direct method to obtain the high pressure phase materials, such as the diamond and h-BN. In our previous reports, this technology have been used to synthesize other compounds successfully and obtained some results [19, 20]. To further optimize thermoelectric performance of materials, two approaches are often used. One is to adjust the electric properties by doping on the crystal structure; the other is to further depress the lattice thermal conductivity via introducing extra phonon scattering. In this paper, the skutterudite $Ba_xCo_4Sb_{11.7}Te_{0.3}$ ($x = 0,\ 0.4$) were successfully prepared by HPHT method at 1.5 GPa using both the two approaches. As a result, the lattice thermal conductivity of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ is depressed largely, and the power factor increase obviously, which indicate that the series of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ should be an attractive material for thermoelectric applications.

2 Experimental method

Cobalt powder (99.9%), antimony powder (99.9%), high purity tellurium powder (99.999) and barium azide powder (99.5%) were used as starting material. These powders were weighed according to the stoichiometric rate of $Ba_xCo_4Sb_{11.7}Te_{0.3}$($x = 0,\ 0.4$) and then mixed in an agate mortar under an argon atmosphere. 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 (spd6*1200) with a sample chamber of 23 mm on an edge at 900 K and 1.5 GPa for 30 min. The samples were under vacuum during synthetic process. The pressure was estimated by the oil press load, which was calibrated by the pressure induced phase transitions of bismuth, thallium and barium metals. The temperature was estimated by the relationship of input heater power and temperature, which was measured by chromel-alumel thermocouples. The collected samples were polished on the surface and cleaned by alcohol for thermoelectric measurements.

X-ray powder diffraction (XRD) measurements with Cu K_α radiation were performed on an x-ray diffractometer (D/MAX-RA). The fractured fresh surface was observed by scanning electron microscope (SEM) (JEOL 6340f). The Thermal conductivity κ of the samples was measured on a TC-7000 (ULVAC-R1KO Inc., Japan) laser flash thermal constant measuring apparatus. The Seebeck coefficient and electrical conductivity were measured simultaneously by a ZEM-3 apparatus. All the thermoelectric properties were measured in the temperature range from 300 K to 743 K.

3 Results and discussion

The XRD spectra of $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ prepared by HPHT method at 1.5 GPa and 900 K are shown in Fig. 1. All peaks visible in the Co_4Sb_{12} diffractogram can be indexed to the skutterudite crystal structure, which are a typical body-central-cubic structure with a space group of Im-3. In addition, compared with the traditional method, the processing time of the HPHT method has been reduced from a few days to half an hour.

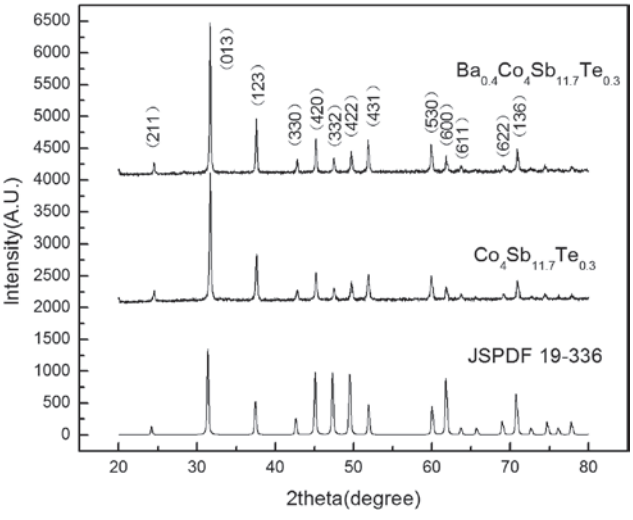

Fig. 1: The XRD patterns of $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ prepared by HPHT method.

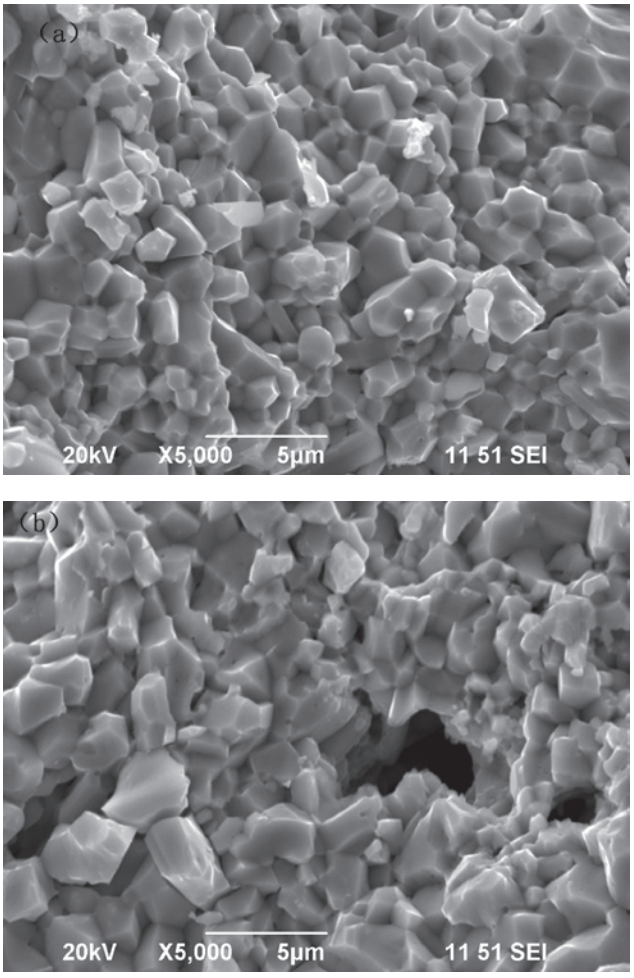

Fig. 2: The SEM micrographs of the fractured fresh surface for (a) $Co_4Sb_{11.7}Te_{0.3}$ and (b) $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ prepared by HPHT method.

Figure 2 is the SEM plot for the fractured fresh surface of $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. Figure 2(a) and (b) stand for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ respectively. As seen in Fig. 2, the samples prepared at high pressure have smaller crystal grain sizes and abundant grain boundaries, which was helpful to decrease their thermal conductivity. The microstructure of the samples agrees with the advantages of the HPHT methods. Those advantages include introducing abundant grain boundaries, restraining disorder, etc. SEM investigation indicated that there are pores with diameter ranging from 1 to 5 um in the $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ sample as expected, which are barium and nitrogen decomposed by BaN_6 when it was under high pressure and high temperature.

Fig. 3(a) shows the temperature dependence of the absolute Seebeck coefficient for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. All samples have negative Seebeck coefficients, indicating that the dominating carries are electrons. The absolute Seebeck coefficient of $Co_4Sb_{11.7}Te_{0.3}$

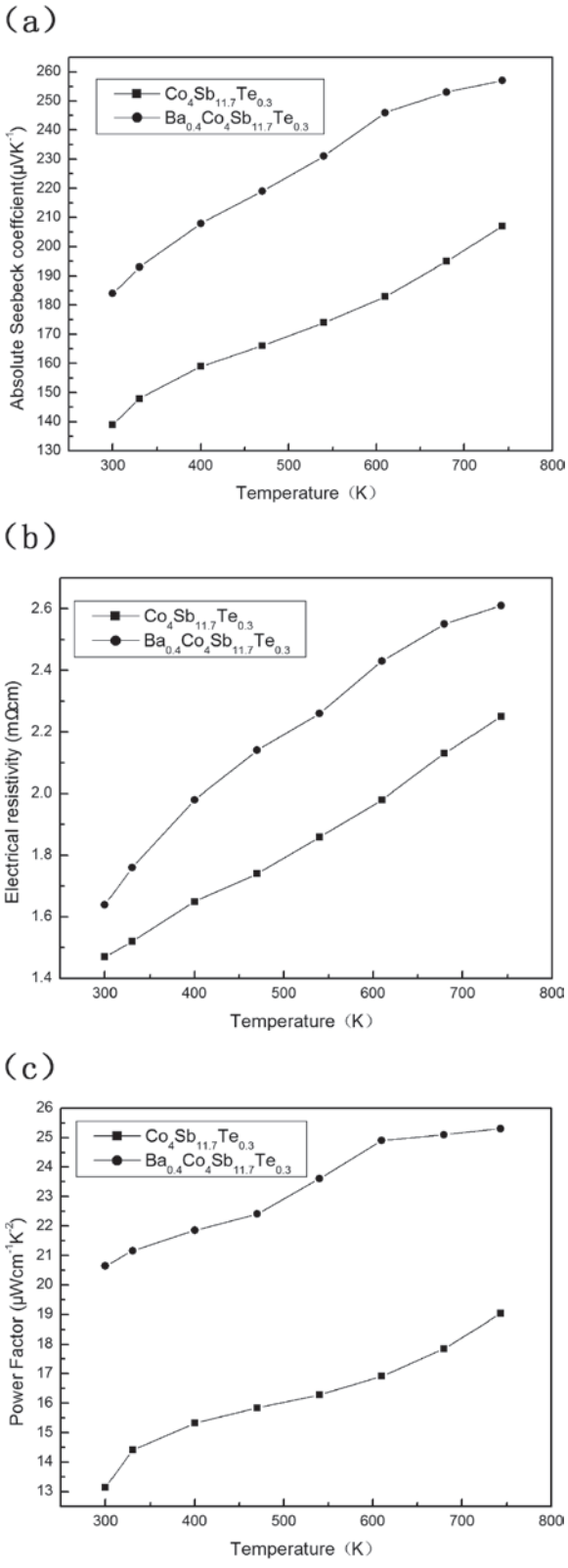

Fig. 3: (a) Temperature dependence of Seebeck coefficient for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. (b) Temperature dependence of electrical resistivity for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. (c) Temperature dependence of power factor for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$.

and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ gradually increases with increasing temperature. The absolute value of the Seebeck coefficient for the sample of $Co_4Sb_{11.7}Te_{0.3}$ is generally smaller than that for $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$, and its maximum absolute value attains to about 2.57×10^{-4} V · K^{-1} at 743 K. Fig. 3(b) shows the temperature dependence of the electrical resistivity for $Ba_xCo_4Sb_{11.7}Te_{0.3}$. The electrical resistivity for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ increases linearly with increasing temperature from 300 K to 743 K. It is noted that the electrical resistivity of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ is little higher than that of $Co_4Sb_{11.7}Te_{0.3}$. We can also note that the two compounds all possess a minimum value of electrical resistivity at about 300 K and the minimum value of 1.47×10^{-5} Ω · m was obtained at 300 K, which is much lower. According to the previous studies, Ba and Te atoms serve as electron donors in $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. Each Te atom can provide 0.3–0.33 effective electrons to contribute to the electrical conduction. It is realized that pores in $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ can markedly increase the Seebeck coefficients, significantly reduce the electrical conductivity. Power factor (PF) was calculated from the measured Seebeck coefficient and electrical resistivity as shown in Fig. 3(c). The power factors of $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ increase with increasing temperature from 300 K to 743 K. It is noted that the power factor of $Co_4Sb_{11.7}Te_{0.3}$ is much higher than that of $Co_4Sb_{11.7}Te_{0.3}$ and the maximum value of 25.31×10^{-4} W · m^{-1} · K^{-2} was obtained at 743 K.

The thermal conductivity (κ) of $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ measured from 300 K to 743 K is shown in Fig. 4. The temperature dependences of the total thermal conductivity and lattice thermal conductivity for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ are shown in Fig. 4. The total thermal conductivity of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ is much lower than that of $Co_4Sb_{11.7}Te_{0.3}$ in the range of 300 K to 743 K. The minimum value of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ is 2.057 W · m^{-1} · K^{-1} attained at 743 K. The value is much lower than that of the unfilled sample prepared by HPHT method.

As is well known, the thermal conductivity contains two parts, one is the carrier thermal conductivity κ_e and the other is phonon conductivity κ_{ph}. The carrier thermal conductivity can be expressed by the Wiedemann-Franz's law $\kappa_e = L \cdot \sigma \cdot T$. Fig. 4 shows that κ_{ph} of $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ gives primary contribution to κ_{total}. It is noted that the κ_{ph} of $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ is lower than that of $Co_4Sb_{11.7}Te_{0.3}$ in the range of 300 K to 743 K. The "rattling" motion of the filled ions scatters heat-carrying phonons effectively and markedly reduces the lattice contribution. It is concluded that filling is an effective way to reduce the thermal conductivity.

Finally, Fig. 5 shows the temperature dependence of the figure of merit (ZT) for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. The figure of merit ($ZT$) for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ increases linearly with the increase of temperature in the measured temperature range. The maximum value 0.87 was obtained at 743 K for $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$. It is related to the high power factor and the lower phonon thermal conductivity for $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ compound.

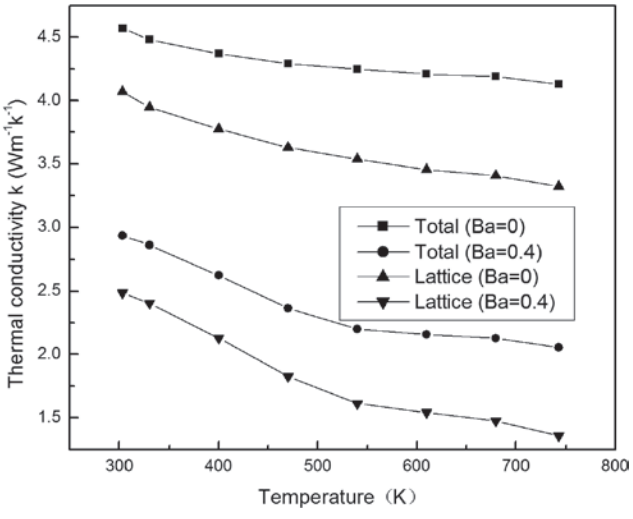

Fig. 4: Temperature dependence of total thermal conductivity κ and lattice thermal conductivity, for $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$.

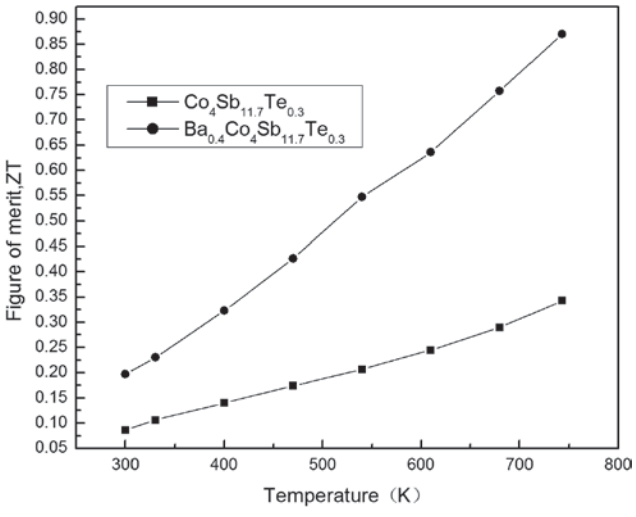

Fig. 5: Temperature dependence of figure of merit (ZT) of $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$.

4 Conclusions

The single phase skutterudite $Co_4Sb_{11.7}Te_{0.3}$ and $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ were successfully prepared at HPHT method. The samples show a typical behavior of n-type semiconductor. We found that filling Ba atoms in Te-doped skutterudite ($Co_4Sb_{11.7}Te_{0.3}$) reduced the thermal conductivity value for $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ notably. The minimum value 2.057 $W \cdot m^{-1} \cdot K^{-1}$ was obtained at 743 K. The maximum *ZT* value of 0.87 was obtained for $Ba_{0.4}Co_4Sb_{11.7}Te_{0.3}$ at temperature of 743 K, which is much higher than that of $Co_4Sb_{11.7}Te_{0.3}$ (0.34) and also higher than the result of G.S. Nolas (0.7) [21]. In summary, we conclude that The Ba atoms-filled in skutterudite can markedly increase the Seebeck coefficients, significantly reduce the thermal conductivity, almost do not change the electrical conductivity, and consequently greatly improve the *ZT*.

Acknowledgments: This work was financially supported by the National Science Foundation of China (50801030, 51171070).

Received: February 21, 2013. Accepted: April 13, 2013.

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