The thermoelectric properties of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ synthesized at different pressure

L B. Wang^a, Jing Ni^b, X P. Jia^c, J M. Qin^a, X. Guo^a, L. Deng^{a*}

^aDepartment of Material Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China

^bFAW-Volkswagen Automotive Company Ltd, Changchun 130011, P. R. China

^cNational Lab of Superhard Materials, Jinlin University, Changchun 130012, China

Abstract: A series of skutterudite compounds $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ ($x=0.05, 0.1, 0.15$) have been prepared successfully by high pressure and high temperature (HPHT) method and then characterized with X-ray diffraction and electron microprobe analysis. The thermoelectric properties including Seebeck coefficient α , electrical resistivity ρ and thermal conductivity κ were measured at room temperature. As expected, with the synthetic pressure increased, the Seebeck coefficient and thermal conductivity of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ both improved significantly. Moreover, the lattice thermal conductivity decreased distinctly with pressure increasing, which was mainly due to the abundant grain boundaries, which could enhance the phonon scattering effectively at grain boundaries. The test results suggest that the HPHT technique is a superior method to optimize thermoelectric properties of thermoelectric materials.

Keywords: Thermoelectric properties; Skutterudite; HPHT; Thermal conductivity

1. Introduction

On account of the ability of convert directly and reversibly between thermal and electrical energy, the thermoelectric technology has captured much attention in the fields of practical power generation, cooling, and waste heat recovery systems. Thermoelectric devices have numerous advantages, such as being silent, good reliability and scalability, environmental friendly, no moving components and long operating times[1-3]. The performance of thermoelectric materials is determined by the dimensionless thermoelectric (figure of merit) $ZT=\alpha^2\sigma T/\kappa$, where α , σ , T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity ($\kappa=\kappa_L+\kappa_c$, where κ_L is the lattice thermal conductivity, and κ_c is the carrier thermal conductivity), respectively [4]. An excellent thermoelectric material should possess a high power factor ($\alpha^2\sigma$) and low thermal conductivity. However, it is extremely arduous to increase $\alpha^2\sigma$ and reduce κ simultaneously, as a result of the complex interaction among α , σ and κ .

* To whom correspondence should be addressed. Fax, 86-431-85583016, Email: dengyue520619@126.com.

Among many thermoelectric materials, CoSb₃-based skutterudite thermoelectric materials being intensely pursued in hopes of developing efficient thermoelectric materials because of their reasonable band gaps and high carrier motilities[5-7]. Nevertheless, the high thermal conductivity of bare CoSb₃ is a serious impediment to its application[8], which should not be ignored. Binary CoSb₃ skutterudites crystallize in a body-centered cubic structure and have two interstitial voids at the 2a positions in the unit cell[9]. By filling in the intrinsic nanocages with foreign atoms and doping it with suitable impurities, the skutterudites compounds would like a glass with low thermal conductivity and a crystal with high electrical conductivity[10], which make them excellent thermoelectric materials according to the phonon glass-electron crystal (PG-EC) concept proposed by Slack et al[11]. The filling and doping atoms can introduce the phonon scattering centers, and consequently reduce the lattice thermal conductivity[12].

HPHT method has been proved to be an effective and potential processing approach to prepare thermoelectric materials[13-14]. The benefits of HPHT are obviously, such as the tune rapidly, simplify procedures and retain the high pressure properties of ambient pressure. In addition, comparing with other traditional processes, HPHT method can effectively shorten the synthetic time. In our previous work, although the Co₄Sb_{12-x}Te_x samples synthesized by HPHT exhibited high Power Factors, the reduction of the thermal conductivity is very limited. In this work, Ba_xIn_{0.2-x}Co₄Sb_{11.5}Te_{0.5} (x=0.05, 0.1, 0.15) was successfully synthesized by HPHT. The lattice thermal conductivity was observed to decrease distinctly with pressure increasing, and the minimum value of thermal conductivity is significantly lower than the previous work. Moreover, the microstructure and the relationships between thermoelectric properties and synthetic pressure of Co₄Sb_{11.5}Te_{0.5}Ba_xIn_{0.2-x} have been studied carefully.

2. Experimental procedure

The Ba_xIn_{0.2-x}Co₄Sb_{11.5}Te_{0.5} (x=0.05, 0.1, 0.15) samples were prepared with Co, Sb, (99.5% in purity), Te(99.9%), BaN₆(99%), and In(99.9%) powders as raw materials. These powders were weighed according to the stoichiometry of Ba_xIn_{0.2-x}Co₄Sb_{11.5}Te_{0.5} (x=0.05, 0.1, 0.15), and then mixed in an agate mortar in a glove box under the protection of the nitrogen gas atmosphere. The pulverous mixtures were shaped to a cylinder with about 3-4 mm thick and 10 mm in diameter by cold compression. The pole shaped samples were protected by molybdenum foil against other elements and then inside an appropriate graphite heating chamber, and were assembled for HPHT synthesis. The assembled samples were carried out in a China-type large volume cubic high-pressure apparatus

(SPD-6×1200) with a sample chamber of 22 mm on an edge at 900 K and 1-3GPa, and the synthesis time was selected as half an hour. The synthesis temperature was measured with a K-type thermocouple placed near the sample and the heating power was adjusted through heating source controlled by a EC-7 control unit.

X-ray diffraction (XRD) measurements with Cu-K α ($\lambda=1.5418$ Å) radiation were performed on an X-ray diffractometer (Ultima IV), which to check lattice constant and phase purity. The morphology and microstructure of synthetic samples were performed on field emission scanning electron microscope (SEM, JEOL JSM-6700F). The Seebeck coefficient was measured by a homemade ZEM-3 apparatus with the advantage of the size or shape of the sample not being demanded strictly, at room temperature. The electrical resistivity was measured by typical DC four-probe configuration and the relative error was estimated to be less than 7%. The thermal conductivity κ was calculated by $\kappa=\lambda dC_p$. The thermal diffusivity λ was measured based on the laser flash technique (Netzsch LFA-427), and the specific heat C_p was measured by DSC conversion with simultaneous thermal analysis (Linseis STA PT-1750) with the sapphire revision. The relative densities (d) were calculated with the Archimedes method.

3. Results and discussion

The XRD patterns of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ ($x=0.05, 0.1, 0.15$) under synthetic pressure 2.5GPa are shown in Fig. 1. It can be seen that all of the diffraction peak positions and (hkl) values match very well with the standard diffraction data of pure CoSb_3 , which indicates that the different stoichiometric ratios of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_x\text{In}_{0.2-x}$ have been successfully synthesized by HPHT method. Besides, compared with the other traditional method, the processing time using the HPHT method was reduced from several days to half an hour.

Fig.1. XRD patterns of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ synthesized by HPHT at 2.5 GPa

Fig. 2 (A) and (B) are the SEM micrographs for the fractured surfaces of $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ synthesized at 1GPa and 3GPa, respectively. From Fig. 2 (B) we can see that the mean grain size of $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ synthesized under 3GPa is about 1~2 μm . As can be noticed, the $\text{Ba}_{0.1}\text{In}_{0.1}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ sample synthesized under 3GPa possesses a smaller crystal grain size and more abundant grain boundaries than the sample synthesized under 1GPa, which may be beneficial to decrease its thermal conductivity. The result infers that the HPHT method may restrain the growth of particles, introduce abundant grain boundaries, and homogenize the particle size. The fine grain size and abundant grain boundaries of samples could reduce lattice thermal conductivity as the result of strengthen the phonon scattering[15]. Furthermore, it could be seen that the surface of the grain is decorated with nano-sized particles (Fig. 2 C). The internal boundary is considered as independent phase boundary. In order to further find out the difference between the two phases, the chemical composition of different regions (separated by internal boundary) has been measured. For areas 1 and 2, the content of Sb and In are less than that of area 3(Fig. 2 D).

Fig.2. (A) and (B) SEM micrographs of $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ under 1 GPa and 3 GPa, respectively, (C) high magnification and (D) EDS results of the selected areas of sample $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ synthesized at 3 GPa

Fig. 3 (A) demonstrates the relationship between the absolute value of the Seebeck coefficient for $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ and the synthetic pressure at room temperature. The absolute values of Seebeck coefficient decrease almost linearly with the synthetic pressure rise. The tendency indicates that the HPHT is an excellent method to improve Seebeck coefficient. The maximum absolute value of Seebeck coefficient is $253.2 \mu\text{VK}^{-1}$ for $\text{Ba}_{0.1}\text{In}_{0.1}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ at 3 GPa. The enhancement of Seebeck may be due to the compositional difference and the impacts of high pressure. In addition, all samples have negative Seebeck coefficient values, indicating that the majority carriers are electrons and all the samples are n-type in the whole synthetic pressure range.

The dependence of electrical resistivity of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ samples on synthetic pressure is presented in Fig. 3 (B). The electrical resistivity increases with the increasing synthetic pressure in the range of 1-3 GPa. The result can be attributed to the high pressure could decrease the carrier concentration and enhance the mobility of carriers. In addition, more abundant grain boundaries might exhibit a negative effect on the electrical conductivity. We can also note that all the samples possess low electrical resistivity, and the minimum value ($1.65 \text{ m}\Omega\text{cm}$) for $\text{Ba}_{0.1}\text{In}_{0.1}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ is obtained under 1 GPa.

Fig.3. Relationship between (A) absolute Seebeck coefficient and (B) electrical resistivity of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_x\text{In}_{0.2-x}$ and synthetic pressure measured at room temperature.

Fig. 4 displays the power factor (PF) values of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ synthesized at different pressure, which were calculated by absolute Seebeck coefficient (α) and the electrical resistivity (ρ) according to the formula: $\text{PF} = \alpha^2/\rho$. As we see, the PF values decreased slightly when the synthetic pressure rise, which may be attributed to the influence of the improved electrical resistivity. The maximum PF value reached $11.03 \mu\text{Wcm}^{-1}\text{K}^{-2}$ for $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ under 1 GPa.

Fig.4. Relationship between Power Factor (PF) of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ and synthetic pressure measured at room temperature.

Fig. 5(A) exhibits the relationship between the thermal conductivities of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ with different synthetic pressure. It can be noted that the thermal conductivities of all the samples exhibit a remarkable decrease with the synthesis pressure rise. The figure shows that all the compounds possess quite small values of thermal conductivity, and the minimum value of thermal conductivity of $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ synthesized under 3 GPa is $1.73 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature, which is much

lower than previous report [16].

As is well known, the thermal conductivity κ includes carrier thermal conductivity κ_c and lattice thermal conductivity κ_L . The carrier thermal conductivity κ_c was calculated by the Wiedemann-Franz equation $\kappa_c = LT/\rho$, where L , T , and ρ are Lorenz number, absolute temperature and electrical resistivity, respectively. From the formula, the carrier thermal conductivity exhibits an opposite tendency compared with the increasing electrical resistivity at room temperature caused by the higher synthetic pressure. The lattice thermal conductivity at room temperature of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ under different synthetic pressures is shown in Fig. 5(B). Dramatically, the synthetic pressure dependence of the thermal conductivity is quite similar to that of the lattice thermal conductivity as the consequence of the low value of the carrier thermal conductivity. The reducing of the thermal conductivity with the increased pressure mainly due to the abundant grain boundaries caused by high synthetic pressure, which could enhance the phonon scattering effectively at grain boundaries. In addition, the lattices disorder is a momentous factor to enhance the phonon scattering, and then reduce lattice thermal conductivity, which should not be ignored [17]. Unquestionably, the results indicated that the HPHT method is an effective approach to restrain the thermal conductivity distinctly.

Fig.5. Relationship between (A) thermal conductivity and lattice (B) thermal conductivity of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ and synthetic pressure measured at room temperature.

Fig. 6 shows the synthetic pressure dependence of the thermoelectric figure of merit, Z , of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ at room temperature. As expected, all the samples possess high Z values, which mainly related to the excellent electrical properties and the low thermal conductivity for $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ compounds. The maximum Z value for $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ under 1GPa is $4.01 \times 10^{-4}\text{K}^{-1}$ at room temperature.

Fig.6. Relationship between figure of merit, Z , of $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ and synthetic pressure measured at room temperature.

4. Conclusion

To summarize, a series of skutterudite compounds $\text{Ba}_x\text{In}_{0.2-x}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ ($x=0.05, 0.1, 0.15$) have been successfully synthesized by HPHT. As we expected, the Seebeck coefficient and electrical resistivity both increased with an increase of the synthesis pressure. Moreover, all the compounds possess quite small values of thermal conductivity, and the thermal conductivity decreased greatly with the synthesis pressure increasing, which indicated that the HPHT method is an effective approach to restrain the thermal conductivity distinctly. The minimum value of thermal conductivity for $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ under 3GPa is $1.73 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. The figure of merit, Z , of $\text{Ba}_{0.05}\text{In}_{0.15}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$ under 1GPa shows the maximum value of $4.01 \times 10^{-4} \text{ K}^{-1}$ at room temperature. As a consequence, the results indicated that the HPHT method could optimize the thermoelectric properties of CoSb_3 system significantly.

Acknowledgments

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References

- [1] L.E. Bell, Science. 321 (2008) 1457-1461.
- [2] Y. Z. Pei, A.D. LaLonde, N.A. Heinz, X.Y. Shi, S. Iwanaga, H. Wang, Adv. Mater. 23 (2011) 5674-5678.

- [3] L. D. Zhao, G. J. Tan, S. Q. Hao, J. Q. He, Y. L. Pei, H. Chi, *Science*. 351 (2016) 141.
- [4] X. H. Li, Q. Zhang, Y. L. Kang, C. Chen, L. Zhang, D. L. Yu, *J. Alloys Comp.* 677 (2016) 61-65
- [5] R.J. Mehta, Y. L. Zhang, C. Karthik, B. Singh, R.W. Siegel, T.B. Tasciuc, *Nat. Mater.* 11 (2012) 233-240.
- [6] H. L. Gao, T. J. Zhu, X. X. Liu, L. X. Chen, X. B. Zhao, *J. Mater. Chem.* 21 (2011) 5933-5937.
- [7] M.S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, *Adv. Mater.* 19 (2009) 1043-1053.
- [8] B. Feng, J. Xie, G. S. Cao, T. J. Zhu, X. B. Zhao, *J. Mater. Chem. A.* 1 (2013) 13111-13119.
- [9] J. Eilertsen, M.A. Subramanian, J.J. Kruzic, *J. Alloys Comp.* 552 (2013) 492-498.
- [10] T. Liang, X. L. Su, Y. G. Yan, G. Zheng, Q. Zhang, H. Chi, *J. Mater. Chem. A.* 2 (2014) 17914-17918.
- [11] G.A. Slack, V.G. Tsoukala, *J. Appl. Phys.* 76 (1994) 1665-1671.
- [12] K.T. Wojciechowski, J. Toboła, J. Leszczyn'ski, *J. Alloys Comp.* 361 (1) (2003) 19-27.
- [13] S.V. Ovsyannikov, V.V. Shchennikov, G.V. Vorontsov, A.Y. Manakov, A.Y. Likhacheva, V.A. Kulbachinskii, *J. Appl. Phys.* 104 (2008) 053713.
- [14] T. C. Su, X. P. Jia, H. A. Ma, J. G. Guo, Y. P. Jiang, *J. Alloys Comp.* 468 (2009) 410-413.
- [15] C. Mortensen, M. Beekman, D.C. Johnson, *Sci. Adv. Mater.* 3 (2011) 639-645.
- [16] H. R. Sun, X. P. Jia, L. Deng, P. Lv, X. Guo, Y. W. Zhang, *J. Mater. Chem. A.* 3 (2015) 4637-4641.
- [17] X. Yan, W. S. Liu, H. Wang, S. Chen, J. Shiomi, K. Esfarjani, *Energy Environ. Sci.* 5 (2012) 7543-7548.

Illustration of figures:

Fig. 1 XRD patterns of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_x\text{In}_{0.2-x}$ synthesized by HPHT under 2.5 GPa.

Fig.2 (A) and (B) SEM micrographs of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_{0.05}\text{In}_{0.15}$ under 1 GPa and 3 GPa, respectively, (C) high magnification and (D) EDS results of the selected areas of sample $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_{0.05}\text{In}_{0.15}$ synthesized at 3 GPa

Fig.3 Relationship between (A) absolute Seebeck coefficient and (B) electrical resistivity of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_x\text{In}_{0.2-x}$ and synthetic pressure measured at room temperature.

Fig. 4 Relationship between Power Factor of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_x\text{In}_{0.2-x}$ and synthetic pressure measured at room temperature.

Fig. 5 Relationship between (A) thermal conductivity and (B) lattice thermal conductivity of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_x\text{In}_{0.2-x}$ and synthetic pressure measured at room temperature.

Fig. 6 Relationship between figure of merit, Z, of $\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}\text{Ba}_x\text{In}_{0.2-x}$ and synthetic pressure measured at room temperature.