Journal of Alloys and Compounds 509 (2011) 2392–2394

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Thermoelectric properties of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ prepared by HPHT

Le Deng, Hongan Ma, Taichao Su, Yiping Jiang, Shizhao Zheng, Xiaopeng Jia*

National Lab of Superhard Materials, Jinlin University, Changchun 130012, China

ARTICLE INFO

Article history:
Received 16 July 2010
Received in revised form 26 October 2010
Accepted 3 November 2010
Available online 12 November 2010

Keywords:
Skutterudite
Thermoelectric properties
HPHT
$CoSb_3$

ABSTRACT

$Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ has been prepared successfully by high pressure and high-temperature (HPHT) method. The samples were characterized by X-ray diffraction, electron microprobe analysis, and thermoelectric properties measurements. The power factor and the figure of merit, *ZT*, of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ all increased with the increasing temperature. Comparing with the sample of unfilled $Co_4Sb_{11.5}Te_{0.5}$, a higher *ZT* value of 0.702 was obtained at the temperature of 706 K, which was related to the higher power factor of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$. The results indicated that Ti-filled $CoSb_3$ prepared by HPHT is an effective method to enhance the thermoelectric properties of $CoSb_3$.

1. Introduction

The skutterudite compounds, which have been identified as one of the most important promising materials for the applications of thermoelectricity in the intermediate temperature range [1,2], have been extensively studied worldwide over the past several years. The properties of thermoelectric (TE) materials are characterized by the dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where S, σ, κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature respectively. To increase *ZT*, improving the power factor without deteriorating the thermal conductivity is necessary, and as a result, many researchers have been stimulated to the investigations of materials exploration and optimization [3,4].

Among different types of skutterudites, $CoSb_3$ based materials not only exhibit large electrical conductivity and Seebeck coefficient, but also have less expensive compound elements than other types of skutterudite materials. However, as an efficient thermoelectric material, the thermal conductivity of $CoSb_3$ is still high. To make the thermal conductivity lower, the works of fabricating doped $CoSb_3$ [5] and filled $CoSb_3$ [6] have been attempted.

HPHT method has been proved an effective and potential processing route to prepare TE materials with improved thermoelectric properties [7–11]. According to the results of Hirotsugu Takizawa [6], high pressure could help to improve the filling fraction of $CoSb_3$. In our previous work, the properties of Te doped skutterudites have been studied [12]. The previous research shows that $Co_4Sb_{12-x}Te_x$ compounds prepared at high pressure have higher power factor. To further optimize thermoelectric performance of these materials, two approaches are often used. One is to adjust the electrical 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, a series of Ti-filled and Te-doped skutterudites compounds $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ has been synthesized by HPHT at 3.0 GPa using both of the two approaches. As a result, the lattice thermal conductivity of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ decreased slightly, and the power factor increased obviously, which indicated that the series of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ should be an attractive material for thermoelectric applications.

2. Experimental procedure

The $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ and $Co_4Sb_{11.5}Te_{0.5}$ samples were prepared with the element of 3N tellurium, cobalt, titanium and antimony. As sources which were weighed according to the stoichiometric rate, and then mixed in an agate mortar. The mixtures were shaped by press and the pole shaped 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, and the synthetic pressure at 3.0 GPa, temperature was around 900 K. The synthesis time was selected as 24 min in this work. The samples were about 3 mm thick and 10 mm in diameter. The temperature was estimated by the relationship of input heater power and temperature, which was measured by the platinum–rhodium thermocouples.

X-ray diffraction (XRD) measurements with Cu·Kα radiation were performed on an X-ray diffractometer(D/MAX-RA). The microstructure analysis was carried out on a HITACIS-4800 scanning electron microscope (SEM). The Seebeck coefficient and electrical conductivity were measured simultaneously by a ZEM-3 apparatus. The thermal conductivity κ was calculated by $\kappa = \alpha C_p \rho$, the thermal diffusivity and specific heat of the samples, were measured on a TC-7000 (ULVAC-RIKO Inc., Japan) Laser Flash Thermal Constants Measuring Apparatus.

* Corresponding author. Fax: +86 431 85168858.
E-mail address: jiaxp@jlu.edu.cn (X. Jia).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.11.027

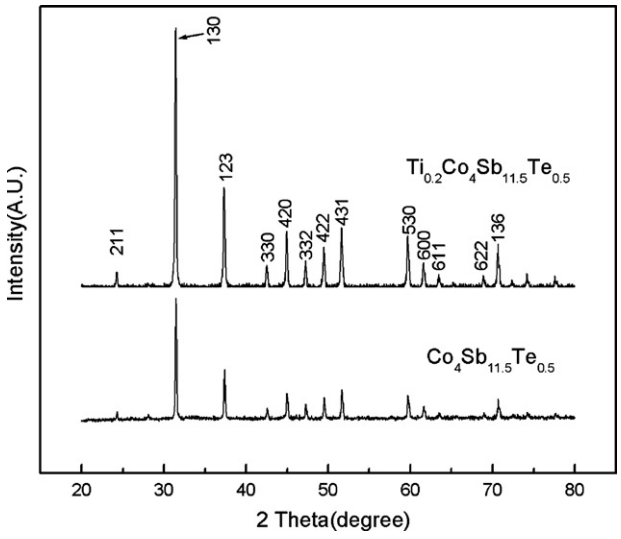

Fig. 1. XRD patterns of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ and $Co_4Sb_{11.5}Te_{0.5}$.

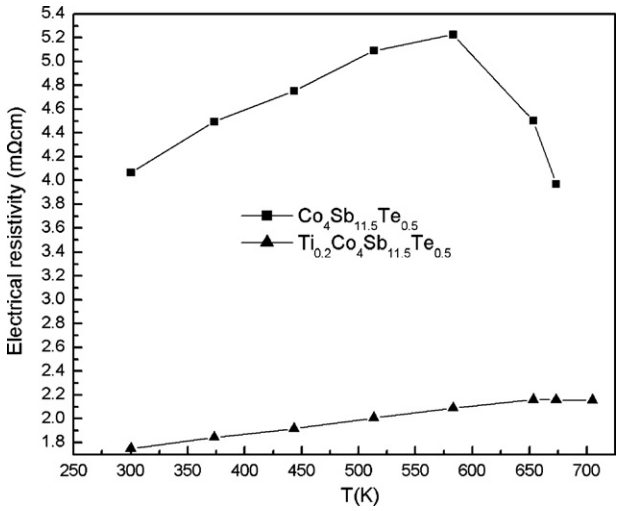

Fig. 3. Temperature dependence of electrical resistivity for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ and $Co_4Sb_{11.5}Te_{0.5}$.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the samples of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ and $Co_4Sb_{11.5}Te_{0.5}$ which were prepared at 3.0 GPa. It can be seen that the XRD spectra of $Co_4Sb_{11.5}Te_{0.5}$ and $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ are near single phase $CoSb_3$. The XRD patterns of HPHT shows sharper diffraction peaks than the solvothermal synthesized powder, indicating that the grain grew up in the HPHT process [13].

Fig. 2 gives the SEM microphotograph of the section plane inner for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ sample. From the pattern, we can see that the mean grain size is about 1 μm and abundant of grain boundaries was found, which was helpful to decrease their thermal conductivity. The microstructure of sample agrees with the advantages of high pressure synthesis, which corresponds to the results of pressure-quenching reported by Li et al. [14].

Fig. 3 shows the temperature dependence of the electrical resistivity for $Co_4Sb_{11.5}Te_{0.5}$ and $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$. The electrical resistivity of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ increases linearly with increasing temperature from 300 K to 706 K. It is noted that the electrical resistivity of $Co_4Sb_{11.5}Te_{0.5}$ is much higher than that of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$. We can also note that, the two compounds all possess a minimum value of electrical resistivity at about 300 K,

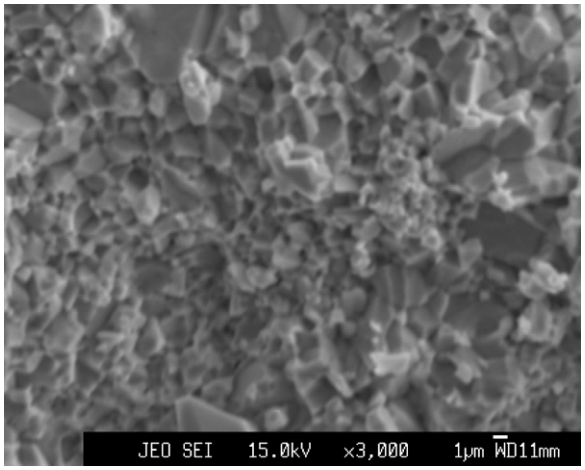

Fig. 2. SEM micrograph of the fractured surface for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ (b).

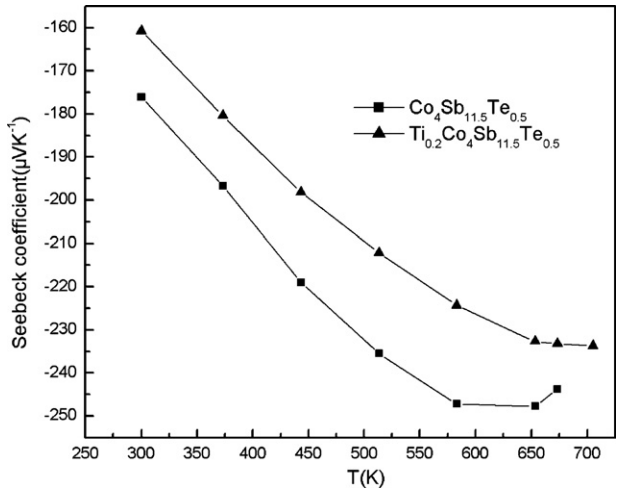

Fig. 4. Relationship between the Seebeck coefficients and temperature for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ and $Co_4Sb_{11.5}Te_{0.5}$.

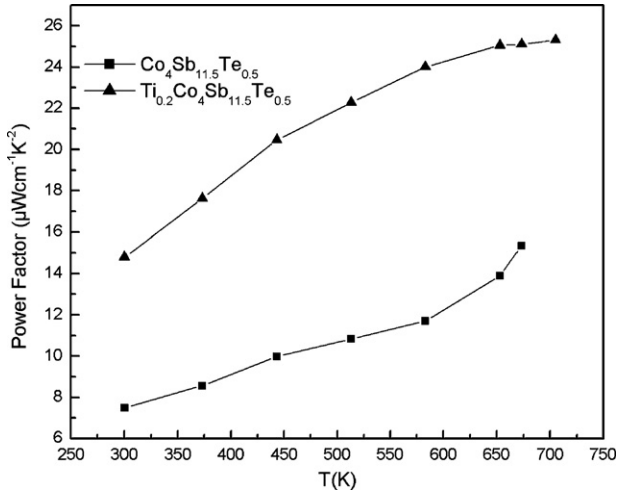

Fig. 5. Temperature dependence of power factors for $Co_4Sb_{11.5}Te_{0.5}$ and $CoSb_3$.

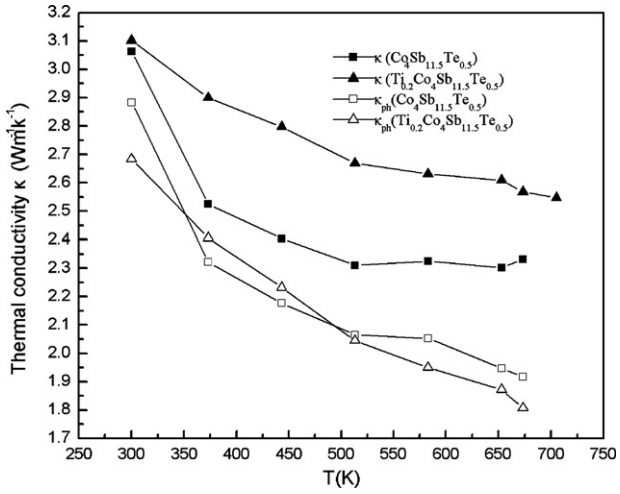

Fig. 6. Temperature dependence of thermal conductivity for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ and $Co_4Sb_{11.5}Te_{0.5}$.

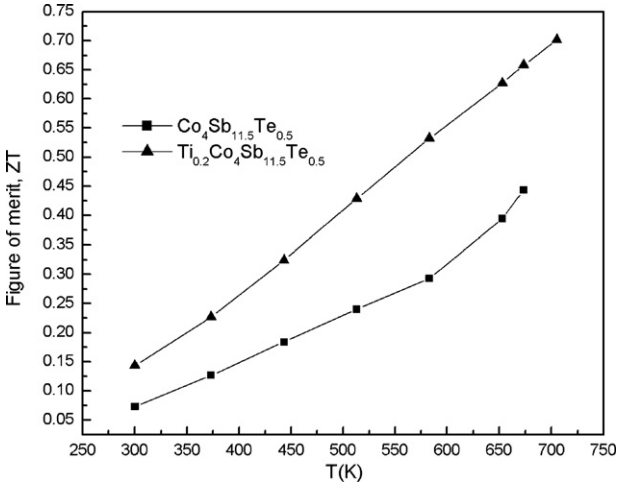

Fig. 7. Temperature dependence of figure of merit, *ZT*, for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ and $Co_4Sb_{11.5}Te_{0.5}$.

and the minimum value (1.75×10^{-3} cm Ω) of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ was obtained.

Fig. 4 shows that the Seebeck coefficient for $Co_4Sb_{11.5}Te_{0.5}$ and $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ as a function of temperature. The sign of the Seebeck coefficient of the sample is negative which indicates n type semiconductor. The Seebeck coefficient of $Co_4Sb_{11.5}Te_{0.5}$ gradually increases with increasing temperature and shows a maximum value at about 706 K. The absolute value of the Seebeck coefficient for the sample of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ is generally smaller than that for $Co_4Sb_{11.5}Te_{0.5}$, and its maximum absolute value attains to about 233.71 μV K^{-1}. It is noted that the Seebeck coefficient of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ compound is a little lower than that of $Co_4Sb_{11.5}Te_{0.5}$ prepared at the same pressure.

The power factor of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ was calculated from the measured Seebeck coefficient and electrical resistivity as shown in Fig. 5. The power factor of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ increases linearly with increasing temperature from 300 K to 706 K. It is noted that the power factor of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ is much higher than that of $Co_4Sb_{11.5}Te_{0.5}$, and the maximum value of 25.3 μW cm^{-1} K^{-2} was obtained at 706 K. It is related to the small electrical resistivity for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ compound.

The thermal conductivity for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ measured from 300 K to 706 K is shown in Fig. 6. The thermal conductivity of the sample decreases with an increase of temperature. The minimum value of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ synthesized at 3.0 GPa was 2.53 W m^{-1} K^{-1}, which is a little higher than that of the without filling sample of $Co_4Sb_{11.5}Te_{0.5}$ (2.301 W m^{-1} K^{-1}) which was prepared at 3.0 GPa too. As well known, the thermal conductivity contains two parts, one is the carrier thermal conductivity κ_e and the other is phonon thermal conductivity κ_{ph}. The carrier thermal conductivity can be expressed by the Wiedemann–Franz's law $\kappa_e = L\sigma T$. Fig. 6 shows that κ_{ph} of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ gives primary contribution to κ_{total}. It is noted that the κ_{ph} of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ is lower than that of $Co_4Sb_{11.5}Te_{0.5}$ in the range of 500–675 K.

Finally, the *ZT* values were discussed and shown in Fig. 7. The temperature dependence of the *ZT* values is quite similar for the two samples: increasing with increasing temperature. The maximum value of $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ (0.702) was obtained at 706 K, which is higher than that of $Co_4Sb_{11.5}Te_{0.5}$ (0.443). It is related to the high power factor and the low phonon thermal conductivity for $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ compound.

4. Conclusion

The single phase skutterudite compound $Ti_{0.2}Co_4Sb_{11.5}Te_{0.5}$ was successfully synthesized by HPHT method. A maximum *ZT* value of 0.702 was obtained for a n-type sample at a temperature of 706 K. We found that filling Ti in Te-doped skutterudite and higher synthesized pressure could enhance the power factor and reduce the phonon thermal conductivity.

Acknowledgment

This work was financially supported by the National Science Foundation of China (50731006, 51071074 and 50801030).

References

[1] B.C. Sales, D. Mandrus, R.K. Williams, Science 272 (1996) 1325–1328.
[2] G.S. Nolas, J.L. Cohn, G.A. Slack, Phys. Rev. B 58 (1998) 164.
[3] X. Zhang, Q.M. Lu, J.X. Zhang, Q. Wei, D.M. Liu, Y.Q. Liu, J. Alloys Compd. 457 (2007) 368–371.
[4] G. Homm, P.J. Homm, J. Teubert, W. Heimbrodt, Appl. Phys. Lett. 93 (2008) 042107.
[5] Q.Y. He, S.J. Hu, X.G. Tang, Y.C. Lan, J. Yang, X.W. Wang, Z.F. Ren, Q. Hao, G. Chen, Appl. Phys. Lett. 93 (2008) 042108.
[6] H. Takizawa, Rev. High Press. Sci. Technol. 16 (2006) 322–328.
[7] Y.P. Jiang, X.P. Jia, F.R. Yu, L. Deng, S.Z. Zheng, Y.J. Tian, H.A. Ma, J. Rare Earths 28 (2010) 407–410.
[8] T.C. Su, X.P. Jia, H.A. Ma, J.G. Guo, Y.P. Jiang, N. Dong, L. Deng, X.B. Zhao, T.J. Zhu, C. Wei, J. Alloys Compd. 468 (2009) 410–413.
[9] N. Dong, X.P. Jia, T.C. Su, F.R. Yu, Y.J. Tian, Y.P. Jiang, L. Deng, H.A. Ma, J. Alloys Compd. 480 (2009) 882–884.
[10] H.A. Ma, T.C. Su, P.W. Zhu, J.G. Guo, X.P. Jia, J. Alloys Compd. 454 (2008) 415–418.
[11] J.G. Guo, X. Jia, T.C. Su, N. Dong, H.A. Ma, J. Alloys Compd. 458 (2008) 428–431.
[12] L. Deng, H.A. Ma, T.C. Su, et al., Mater. Lett. 63 (2009) 2139–2141.
[13] J.L. Mi, T.J. Zhu, X.B. Zhao, J. Ma, J. Appl. Phys. 101 (2007) 054314.
[14] D.J. Li, B.J. Ding, B. Yao, Z.Q. Hu, J. Mater. 4 (1996) 912.