Vol 16 No 11, November 2007
1009-1963/2007/16(11)/3549-04
Chinese Physics
© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Fast preparation and thermal transport property of TiCoSb-based half-Heusler compounds*

Xie Wen-Jie(谢文杰), Tang Xin-Feng(唐新峰)†, and Zhang Qing-Jie(张清杰)

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070*, China*

(Received 4 January 2007; revised manuscript received 13 April 2007)

TiCoSb-based half-Heusler compounds with the substitution of Zr for Ti have been prepared quickly by combining high-energy ball milling method with spark plasma sintering technique, and their thermal transport properties have been investigated. With the increase of the concentration of Zr, the thermal conductivity of $Ti_{1-x}Zr_xCoSb$ compounds decreases significantly. Compared with the thermal conductivity of TiCoSb compound, that of $Ti_{0.5}Zr_{0.5}CoSb$ decreases by 107% at 1000 K.

Keywords: thermoelectric, half-Heusler compounds, thermal conductivity
PACC: 8120, 7215, 6590

1. Introduction

Recently, with the continuing deterioration of energy crisis, the pro-environmental new energy materials — thermoelectric materials which can achieve energy transformation between thermal power and electrical energy without any additional driving devices, attract considerable attention.[1−9] The thermoelectric performance of a material is related to the dimensionless parameter (ZT) which is given by $ZT = \alpha^2\sigma T/\kappa$, where α, σ, κ and T are Seebeck coefficient, electrical conductivity, thermal conductivity and absolutely temperature, respectively. Therefore, the state-of-the-art thermoelectric materials should possess high Seebeck coefficient, high electrical conductivity and low thermal conductivity.

TiCoSb-based half-Heusler compounds have a cubic MgAgAs-type structure,[10] which has the space group $F\bar{4}3$ m. The band gap of TiCoSb compounds is about 0.95 eV calculated by Tobola *et al*,[11] which leads to a large Seebeck coefficient of the material. Xia *et al* [12] reported that the Seebeck coefficient of $TiCoSb_{1+x}$ can be increased significantly by adjusting the value of x. When x changes from 0 to 0.5, the Seebeck coefficient of $TiCoSb_{1+x}$ rises from -265 to $-500\,\mu$V/K. Besides, the electric transport properties of the TiCoSb-based half-Heusler compounds are closely related to their 18 valence electron counts (VEC), and they can be controlled by doping with other metallic element.[12−15] However, the thermal conductivity of TiCoSb compound is about $16 - 18$ W/mK at room temperature,[16] which is far higher than that of some ideal thermoelectric materials such as Bi_2Te_3 and its alloys. Therefore, it is most important for TiCoSb compounds to decrease their high thermal conductivity. Zhou *et al* [17] reported the effect of partial substitution of Co by Rh and Ti by Zr on the thermal conductivity in the TiCoSb half-Heusler system. Combining experimental results and theoretical calculation, they predicted that the lattice thermal conductivity of $Ti_{0.5}Zr_{0.5}Co_{0.5}Rh_{0.5}Sb$ may be 0.3–0.5 W/m K between 300 and 900 K.

However, up to now, it has not yet been reported how the substitution of Zr on Ti site affects the thermal conductivity of the TiCoSb-based half-Heusler compounds. Furthermore, the traditional methods to obtain TiCoSb-based half-Heusler compounds are solid reaction[13,14] and arc melting method,[16,18] which need a long time annealing reaction in order to obtain single phase compound with good structure. These methods not only consume lots of time and large amount of energy, but also need fur-

*Project supported by the State Key Development Program for Basic Research of China (Grant No 2007CB607501), the Major International Cooperation Program of the National Natural Science Foundation of China (Grant No 50310353) and the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (Grant No 705035).
†E-mail: tangxf@whut.edu.cn

ther sintering to have bulk materials. Therefore, in this paper, bulk TiCoSb-based half-Heusler materials are prepared quickly by combining high-energy ball milling method with spark plasma sintering (SPS). The effect of the substitution of Zr on Ti site on the thermal transport property is investigated.

2. Experiments

$Ti_{1-x}Zr_xCoSb$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) samples were prepared by combining high-energy ball milling method with SPS. Starting materials were highly pure powders of titanium (99.99%), zirconium (99%), cobalt (99.99%) and antimony (99.99%). The starting powders were mixed adequately by high-energy milling equipment (Pulveristte 4) under the protection of Ar atmosphere. In order to cool pot and mix homogeneously, a predetermined amount of alcohol was added during ball milling. And then the mixed powders were dried in a vacuum drying oven at 348 K for 12 h. Finally the dry mixed powders were sintered by SPS technique at 1273 K for 25 min to obtain the $Ti_{1-x}Zr_xCoSb$ bulk materials.

Phase structures of the bulk materials were determined by x-ray diffraction (XRD, Rigaku D/Max-2550P diffractometer) using Cu Kα radiation (λ = 0.15406 nm). The chemical composition and element distribution in $Ti_{1-x}Zr_xCoSb$ compounds were obtained by electron probe microanalysis (EPMA, JXA-8800R); and the morphology of bulk material sintered by SPS was analysed by field emitted scanning electron microscopy (FESEM, Sirion 200 FESEM). As for thermal conductivity (κ), it was calculated from the measured thermal diffusivity (D), specific heat (C_p), and density (d) using the relationship $\kappa = D \times C_p \times d$; D and C_p were measured by a laser flash method (Shinkuriko: TC–7000) in a vacuum.

3. Results and discussion

3.1. Structure characterization

Figure 1 shows the XRD patterns of the bulk materials of $Ti_{1-x}Zr_xCoSb$ compounds with different substitution concentrations (x). As shown in Fig.1, all bulk materials have a single MgAgAs-type lattice structure. The diffraction peak positions move to the small-angle side, which indicates that the lattice parameter of $Ti_{1-x}Zr_xCoSb$ compounds rises with the increase of x, because the atomic radius of Zr (0.160 nm) is bigger than that of Ti (0.145 nm).

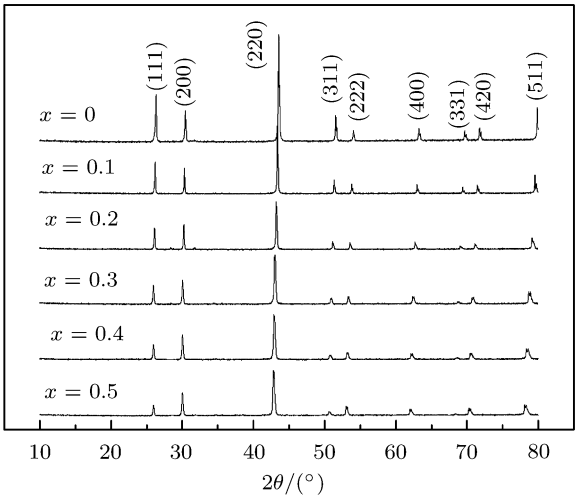


Fig.1. XRD patterns of $Ti_{1-x}Zr_xCoSb$ bulk materials prepared by SPS.

3.2. Composition analysis and microstructure

The nominal composition and EPMA-analyzed composition of $Ti_{1-x}Zr_xCoSb$ are summarized in Table 1, from which we see the EPMA-analyzed compositions of Ti_{1-x} Zr_xCoSb are close to the nominal compositions of the compounds, and the small deviation is due to the loss caused by the milling process.

Table 1. The nominal composition and EPMA analysis composition of $Ti_{1-x}Zr_xCoSb$ compounds.

x	nominal composition	EPMA analyzed composition
0	TiCoSb	$Ti_{1.17}Co_{1.03}Sb$
0.1	$Ti_{0.9}Zr_{0.1}CoSb$	$Ti_{0.89}Zr_{0.11}Co_{1.10}Sb$
0.2	$Ti_{0.8}Zr_{0.2}CoSb$	$Ti_{0.76}Zr_{0.23}Co_{1.10}Sb$
0.3	$Ti_{0.7}Zr_{0.3}CoSb$	$Ti_{0.69}Zr_{0.37}Co_{1.14}Sb$
0.4	$Ti_{0.6}Zr_{0.4}CoSb$	$Ti_{0.57}Zr_{0.49}Co_{1.19}Sb$
0.5	$Ti_{0.5}Zr_{0.5}CoSb$	$Ti_{0.47}Zr_{0.62}Co_{1.21}Sb$

Figure 2 presents the element distribution of $Ti_{0.5}Zr_{0.5}CoSb$ compound. As shown in Fig.2, there is no obvious segregation of any element, and all elements distribute homogeneously in the matrix. It also indicates that the single phase half-Heusler materials can be synthesized by SPS technique. The microstructure of the bulk $Ti_{0.5}Zr_{0.5}CoSb$ material is shown in Fig.3. The size of grains are about $1-5\,\mu$m.

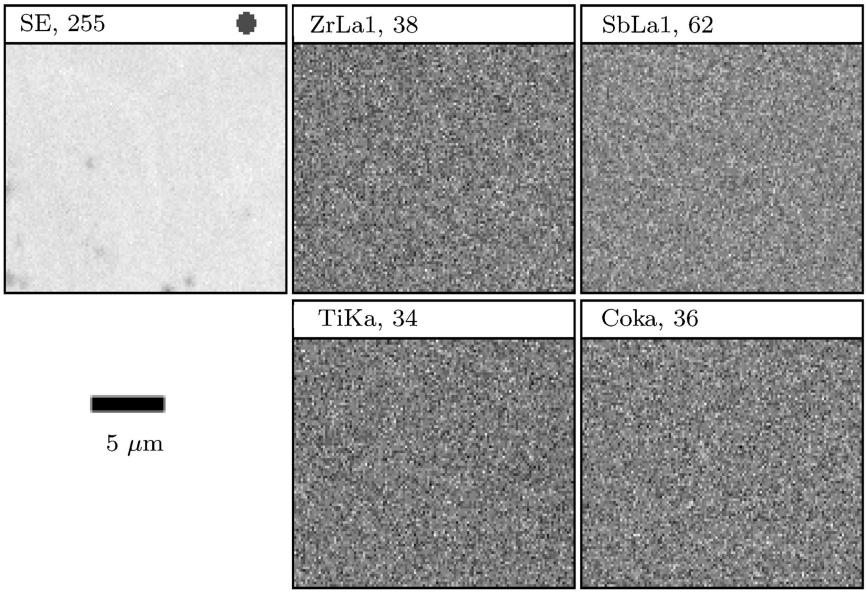


Fig.2. Element distribution of the $Ti_{0.5}Zr_{0.5}CoSb$ compound.

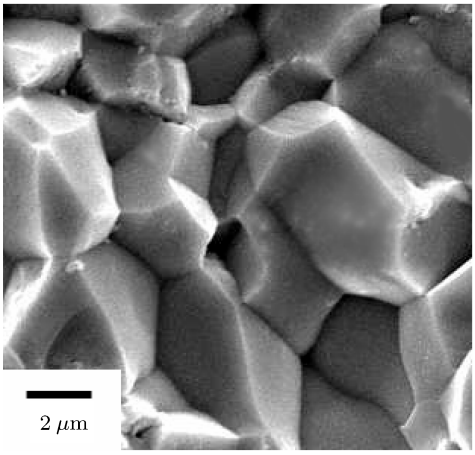


Fig.3. Microstructure of the $Ti_{0.5}Zr_{0.5}CoSb$ compound.

3.3. Thermal transport property

Effects of substitution concentration (x) and temperature (T) on the thermal conductivity (κ) of compounds $Ti_{1-x}Zr_xCoSb$ are shown in Fig.4, from which we see that the thermal conductivity decreases with the increase of the substitution concentration at the same temperature. According to theoretical calculation and experimental results,[19−22] the thermal conductivity will be decreased significantly in the MNiSn and MCoSb (M = Ti, Zr, Hf) systems because of isoelectronic alloying of Ti, Zr and Hf on the M site. In this study, the substitution of Zr on Ti site induces lattice distortion and defect owing to the differences of masses, radii, and stiffness constants between the Ti and Zr atoms. Therefore, the phonon scattering effect increases due to mass fluctuation and strain field fluctuation in the lattice. In the $Ti_{1-x}Zr_xCoSb$ system, phonon mass fluctuation scattering and phonon strain field fluctuation scattering will be enhanced gradually with the increase of x. As a result, the thermal conductivity of the $Ti_{0.5}Zr_{0.5}CoSb$ compound is about 3.46 W/mK at 1000 K. Compared with the unsubstituted TiCoSb compound (7.17W/mK at 1000K), it decreases by 107% at the same temperature (see the inset in Fig.4).

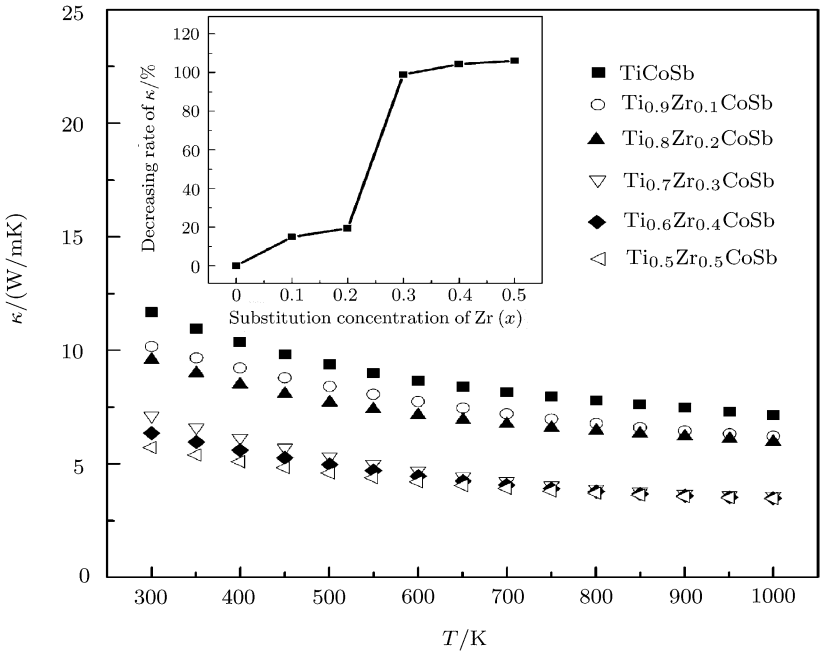


Fig.4. Effects of substitution concentration (x) and temperature (T) on the thermal conductivity (κ) of the $Ti_{1-x}Zr_xCoSb$ compounds (the inset shows the thermal conductivity's decreasing rate of substituted samples as compared with unsubstituted TiCoSb compound at 1000 K).

4. Conclusions

TiCoSb-based half-Heusler compounds with the substitution of Zr on Ti site have been prepared by combining high-energy ball milling method combined with SPS technique. The results show that single-phase $Ti_{1-x}Zr_xCoSb$ compounds can be synthesized under our processing conditions. With the increase of the substitution concentration of Zr on Ti site, the thermal conductivity of $Ti_{1-x}Zr_xCoSb$ compounds decreases significantly. Compared with the thermal conductivity of TiCoSb compound, that of $Ti_{0.5}Zr_{0.5}CoSb$ decreases by 107% at 1000K. According to our results, the ZT value of TiCoSb-based half-Heusler compounds will be enhanced.

References

[1] Tritt T M 1999 *Science* **283** 804

[2] Venkatasubramanian R, Siivola E, Colpitts V and O'Quinn B 2001 *Nature* (London) **413** 597

[3] Sales B C 2002 *Science* **295** 1248

[4] Jiang J, Xu G J, Cui P and Chen L D 2006 *Acta Phys. Sin.* **55** 4849 (in Chinese)

[5] Yang L, Wu J S and Zhang L T 2004 *Chin. Phys.* **13** 516

[6] Liu T X, Tang X F, Li H, Song C, Yang X L and Zhang Q J 2006 *Acta Phys. Sin.* **55** 4837 (in Chinese)

[7] Liu H Q, Tang X F, Wang K, Song C and Zhang Q J 2006 *Acta Phys. Sin.* **55** 2003 (in Chinese)

[8] Zhang W Q, Shi X, Mei Z G, Xu Y, Chen L D, Yang J and Meisner G P 2006 *Appl. Phys. Lett.* **89** 112105

[9] Wang H, Li J F, Nan C W, Zhou M, Liu W S, Zhang B P and Kita T 2006 *Appl. Phys. Lett.* **88** 092104.

[10] Jeitschko W 1970 *Metall. Trans.* A **1** 3159

[11] Tobola J, Pierre J, Kaprayk S, Skolozdra R V and Kouacou M A 1998 *J. Phys.: Condens. Matter* **10** 1013

[12] Xia Y, Ponnambalam V, Bhattacharya S, Pope A L, Poon S J and Tritt T M 2001 *J. Phys.: Condens. Matter* **13** 77

[13] Zhou M, Feng C D, Chen L D and Huang X Y 2005 *J. Alloys Compd.* **391** 194

[14] Kawaharada Y, Kurosaki K, Muta H, Uno M and Yamanaka S 2004 *J. Alloys Compd.* **384** 308

[15] Sekimoto T, Kurosaki K, Muta H, Uno M and Yamanaka S 2006 *J. Alloys Compd.* **407** 326

[16] Sekimoto T, Kurosaki K, Muta H and Yamanaka S 2005 *J. Alloys Compd.* **394** 122

[17] Zhou M, Chen L D, Zhang W Q and Feng C D 2005 *J. Appl. Phys.* **98** 013708

[18] Kurosaki K, Maekawa T, Muta H and Yamanaka S 2005 *J. Alloys Compd.* **397** 296

[19] Shen Q, Chen L D, Goto T, Hirai T, Yang J, Meisner G P and Uher C 2001 *Appl. Phys. Lett.* **79** 4165

[20] Sakurada S and Shutoh N 2005 *Appl. Phys. Lett.* **86** 082105

[21] Shutoh N and Sakurada S 2005 *J. Alloys Compd.* **389** 204

[22] Yang J, Meisner G P and Chen L D 2004 *Appl. Phys. Lett.* **85** 1140