Thermoelectric properties of rare earth-doped n -type $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ nanocomposites

FANG WU^{1,2}, HONGZHANG SONG¹, JIANFENG JIA¹ and XING HU^{1,*}

¹School of Physical Engineering, Zhengzhou University, Zhengzhou 450052, China

²Department of Physics, Henan Institute of Education, Zhengzhou 450053, China

MS received 6 March 2013; revised 23 May 2013

Abstract. n -Type $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ ($\text{R} = \text{Ce}, \text{Y}$ and Sm) nanopowders were synthesized by hydrothermal method and the thermoelectric properties of the bulk samples made by hot-pressing these nanopowders were investigated. The Ce, Y and Sm doping have significant effects on the morphologies of the synthesized nanopowders. The thermoelectric property results show that Ce, Y and Sm doping not only help to decrease the electrical resistivity, but also help to reduce the thermal conductivity. Among rare earth elements-doped samples, it seems that the $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ bulk has a suitable microstructure, which scatters phonons effectively but does not scatter electronic carriers as much. As a result, the ZT values of $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ can reach 1.21 at 413 K, which is higher than those of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ ingots made by zone-melting method.

Keywords. Thermoelectric materials; elements doping; hydrothermal method; thermoelectric properties.

1. Introduction

Thermoelectric (TE) devices have attracted extensive interest for several decades because of their unique features, such as quiet operation without moving parts, low environmental impact and high reliability in applications of solid-state electronic cooling and power generation. The efficiency of TE devices is strongly associated with the dimensionless figure of merit (ZT) of TE materials, defined as $ZT = (S^2\sigma/\kappa)T$, where S , σ , κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively (DiSalvo 1999; Sootsman *et al* 2009; Lan *et al* 2010; Li *et al* 2010; Zhang *et al* 2010). Materials with a high electrical conductivity (corresponding to low joule heating), a large Seebeck coefficient (corresponding to large potential difference) and a low thermal conductivity (corresponding to a large temperature difference) are therefore required in order to realize a high effective performance. However, since these transport characteristics are correlated with each other, obtaining a material with a high ZT value is not an easy job (Snyder and Toberer 2008; Lan *et al* 2010). In recent years, employing band engineering (usually through elements doping) and nanostructure engineering (reduce the size of the sample or grains in a bulk to nanoscale) to enhance the ZT value of thermoelectric materials have come in focus (Dresselhaus *et al* 2007; Snyder and Toberer 2008; Zhang *et al* 2010).

Bi_2Te_3 and its related alloys, including p -type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ and n -type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, still remain the best thermoelectric materials operated at room temperature. Compared with the p -type Bi_2Te_3 -based materials, which already show significant progress in recent years (Poudel *et al* 2008; Xie *et al* 2010), the n -type Bi_2Te_3 -based materials have not shown significant improvement and their ZT values still remain about one for several decades. Since both type of materials are required in fabricating TE devices, it is also important to optimize the thermoelectric performances of n -type Bi_2Te_3 -based materials. Recently, Yan *et al* (2010) successfully enhanced the ZT value of n -type $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ to 1.04 by increasing the electrical conductivity through reorientation of the a - b planes of small crystals by employing a multiple-step hot-pressing method with ball-milled nanopowders. Wang *et al* (2011) employed the melt spinning method combined with a subsequent spark plasma sintering technique to fabricate nanostructured n -type $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ samples which can show a maximum ZT of 1.05 at 420 K. Liu *et al* (2011) found that a ZT value of 1.06 at 418 K could be achieved in n -type nanocrystalline $\text{Cu}_{0.01}\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ samples made by ball-milling and hot-pressing, followed by re-pressing texturing. It was reported that the special electronic structures of some rare earth metals can lead to an unusually intermediate valence state in a rare earth intermetallic compound, which may result in a high TE power factor $S^2\sigma$ (Tritt *et al* 2006; Lan *et al* 2010). In the present work, we report the synthesis of n -type rare earth elements-doped $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ ($\text{R} = \text{Ce}, \text{Y}$ and Sm) nanopowders using hydrothermal method and investigate the

*Author for correspondence (xhu@zzu.edu.cn)

thermoelectric properties of the bulk samples made by these nanopowders. We find that Ce, Y and Sm doping has significant effects on the morphologies of the synthesized nanopowders and the resulted bulk samples. As a combination of the band engineering and nanostructure engineering, the ZT values of $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ can reach 1.21 at 413 K, which is higher than that of the $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ ingots made by the traditional zone-melting method.

2. Experimental

Analytical grade of chemicals $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (or $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 5 N pure Se and Te powders were used as the precursors for the synthesis of rare earth elements doping $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$. The precursors with the nominal compositions of $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ ($\text{R} = \text{Ce}, \text{Y}$ and Sm) were put into a teflon-lined autoclave filled with about 400 mL distilled water. About 3.5 g NaBH_4 was added as the reductant, 8 g NaOH as the pH-value controller and 2 g ethylenediamine-tetraacetic disodium salt (EDTA) as the organic complexing reagent. The autoclave was then sealed and maintained at 423 K for 24 h. During the reaction, the solution was stirred by a stainless steel stirrer with a rotational speed of about 360 rpm. After the system was cooled down to room temperature, the dark grey powders in the autoclave were filtered, washed with distilled water, ethanol and acetone several times to remove the residual precursors and by-products. Then, the powders were dried in vacuum at 373 K for 6 h. Finally, the resultant powders were hot-pressed into pellets of diameter of 15 or 12.5 mm at 673 K for 30 min under pressure of 60 MPa in vacuum.

The phases of the obtained $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ powders were identified by X-ray diffraction (XRD) using an X'Pert Pro diffractometer (PANalytical, The Netherlands). The morphologies of the powders were observed by field-emission scanning electron microscopy (FESEM) on a JSM-6700F microscope (JEM; JEOL, Tokyo, Japan). The density of samples was measured using the Archimedes method. The electrical resistivity and Seebeck coefficients were measured at several temperature points using an LSR-3/800 Seebeck coefficient/electric resistance measuring system (LINSEIS, Germany) under He atmosphere. The thermal conductivity was measured by a thermal diffusivity system (FLASHLINETM 3000, ANTER Corporation, USA) using Pyroceram (provided by ANTER) as the reference sample at several temperature points. Repeated measurements on the samples made by the same procedure showed that the variations were within a few percent, so the data are reproducible.

3. Results and discussion

Figure 1 shows the XRD patterns of the obtained nanopowders. All the reflection peaks of the powders can

Figure 1. XRD patterns of the synthesized powders (a) $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$; (b) $\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$; (c) $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ and (d) $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$.

be indexed to the rhombohedral Bi_2Te_3 , and no remarkable impure phases such as tellurium, bismuth, selenium, cerium (or yttrium and samarium) or their other compounds were observed. It is believed that Se, Ce (or Y and Sm) have entered the lattice of Bi_2Te_3 . The lattice constants of the samples were calculated by rietveld refinement and are shown in table 1. It can be seen that the lattice parameters, $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ are all slightly higher than $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$. The little changes of crystal constant can be attributed to the small differences between the atomic radii of cerium (1.85 Å), yttrium (1.80 Å), samarium (1.85 Å) and bismuth (1.60 Å).

Figure 2 shows the morphologies of the synthesized nanopowders observed by SEM. It can be seen that when doping with rare earth elements, the morphologies of the nanopowders change greatly. As shown in figure 2(a), the powders are nanosheet agglomerates, and the average size is about 100 nm. When doping with Ce, the sample shows nanorod shape and the width of the nanorod is about 100 nm, as shown in figure 2(b). Figure 2(c) shows that $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ powders are shaped like flowers and the comprised petal is a nanosheet <100 nm. Meanwhile, $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ powders are round plates with thickness <100 nm, as shown in figure 2(d).

Bi_2Te_3 has a layered hexagonal structure with Te and Bi atom layers arranged in the order of $-\text{Te}(1)-\text{Bi}-\text{Te}(2)-\text{Bi}-\text{Te}(1)-$ along the c -axis. Between two $-\text{Te}(1)-$ layers, there are van der Waals bonds, while all others are covalent bonds. As the energy required to break a covalent bond is much higher than that required to break a van der Waals bond, Bi_2Te_3 crystal grows much faster along a - and b -axes than along c -axis. Thus, flake morphology is easily formed in a natural growth process (Zhao and Wang 2010). Since in our experiments the EDTA was used as surfactant, as reported in Deng *et al* (2003), this

Table 1. Lattice parameters of the synthesized powders.

Sample	$\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$	$\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$	$\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$	$\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$
a (Å)	4.375 (± 6)	4.378 (± 5)	4.376 (± 4)	4.377 (± 5)
c (Å)	30.43 (± 3)	30.47 (± 3)	30.465 (± 4)	30.442 (± 2)

Figure 2. SEM images of the nanopowders (a) $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$; (b) $\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$; (c) $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ and (d) $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$.

surfactant would facilitate the growth of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ nanosheets along the surface of its agglomerates and help the structure-directing growth of the $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ nanosheets. It is not very clearly known at present why rare earth elements doping can change the morphologies significantly. The possible reason may be that replacing Bi by rare earth elements can change the bonds strength and affect the growth rate along a -, b - and c -axes.

Figure 3 shows the microstructures of the hot-pressed bulk samples, which indicate that the samples are compacting. The measured densities are 7.77, 7.75, 7.69 and 7.68 g/cm³ for samples $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$, $\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$, $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ and $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$, respectively, which are very close to the theoretical density of Bi_2Te_3 (7.78 g/cm³). Although, due to the crystal growth, the morphologies of the hot-pressed bulks are changed greatly from the morphologies of the corresponding nanopowders, difference in the bulks using different nanopowders can

still be observed. As shown in figure 3, the grain sizes of the $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ and $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ bulk are much larger than the other two. Moreover, for these two bulks, there are some tiny grains among the larger ones, which show an obvious non-uniformity. While the grain sizes of the $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ and $\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ bulks are relatively small and the distribution of the grain sizes show good uniformity, as shown in figures 3(a) and (b).

Figure 4 shows the electrical resistivity of the bulk samples measured from room temperature to 473 K. As shown in figure 4, the electrical resistivity of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ bulk is much larger than the others and it shows negative temperature dependence indicating a normal semiconductor behaviour. While the electrical resistivity of the rare earth elements-doped samples show remarkable difference from the undoped sample. First, their electrical resistivities are much smaller than the undoped sample. Second, their electrical resistivities show positive

Figure 3. SEM images of the hot-pressed samples (a) $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$; (b) $\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$; (c) $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ and (d) $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$.

Figure 4. Electrical resistivity of hot-pressed samples.

temperature dependence, indicating degenerated semiconductor behaviours. Among rare earth elements-doped samples, the electrical resistivity of $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ is smallest. It indicates that the rare earth elements doping can decrease the electrical resistivity effectively. Based on the equation $\rho = 1/\mu ne$, the electrical resistivity ρ is

inversely proportional to the carrier mobility, μ and carrier concentration, n , the variations of n and μ will co-affect the electrical resistivity. Rare earth element doping can decrease the carrier mobility due to intensifying alloying scattering, thus, resulting in higher electrical resistivity (Snyder and Toberer 2008; Sharp *et al* 2001). Therefore, lower electrical resistivities of the rare earth elements-doped samples should be caused by the higher electron concentrations due to rare earth elements doping. Moreover, the different morphologies of synthesized powders may also be a possible reason leading to different electrical resistivities (Zhao *et al* 2010).

Figure 5 shows the temperature dependencies of Seebeck coefficients. All samples with and without rare earth elements doping exhibit as n -type semiconductors, since they all have negative Seebeck coefficients in the measured temperature range. The Seebeck coefficients of the $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ bulk (absolute value) decrease with increasing temperature, from $-204 \mu\text{V/K}$ at room temperature (298 K) drop to $-134 \mu\text{V/K}$ at 473 K. While for the rare earth elements-doped samples, the Seebeck coefficients show non-monotonic variation and change smoothly from room temperature to 473 K. It can be seen that the rare earth elements doping causes a shift of the Seebeck coefficient peak, from 298 to 413 K (or 473 and 433 K), for

$\text{Bi}_2\text{Se}_0.3\text{Te}_{2.7}$ and $\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ (or $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ and $\text{Sm}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$), respectively. This is a typical behaviour in thermoelectric materials since the increased external major carriers suppress the generation of minor carriers and, hence, increase in the onset temperature of bipolar effect (Liu *et al* 2012). Opposite to the electrical conductivity, rare earth elements doping decreases the Seebeck coefficients at lower temperature. This is due to the co-relationship between Seebeck coefficients and electrical conductivity. Higher electrical conductivity usually results in a lower Seebeck coefficient. However, as shown in figure 5, the Seebeck coefficients of the doped samples are higher than the undoped ones at higher temperature. The reason may be that Ce substituting for Bi in the alloys introduces a number of defects, which can largely intensify the alloy scattering and lead to a larger scattering parameter γ . The larger γ can increase the Seebeck coefficients (He *et al* 2012). With increasing

temperature, the scattering due to rare earth elements doping may be more effective, so the Seebeck coefficients of the doped samples will exceed the undoped sample at an elevated temperature.

Figure 6 shows the thermal conductivities of the samples with temperature. The thermal conductivities of the $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ samples are all lower than that of the $\text{Bi}_2\text{Se}_0.3\text{Te}_{2.7}$ in the measured temperature range. The reason may be that rare earth elements substituting for Bi in the $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ alloys introduced a number of point defects that lead to effective phonon scattering and reduce thermal conductivity. Among rare earth elements-doped samples, the thermal conductivity of $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ is the smallest. Combining the results of the thermal conductivity and electrical resistivity, it seems that the $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ bulk has a suitable microstructure, which scatters phonons effectively but does not scatter carriers as much (Xie *et al* 2010). The possible reasons are as follows: as mentioned earlier, there are some tiny grains among the larger ones in the $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ bulk, which shows obvious non-uniformity. The charge carriers likely ‘select’ a path—the low resistivity channel connected by the large grains—whereas the phonons do not choose their path. Lower thermal conductivity values can be obtained by grain boundary scattering due to the presence of tiny grains. So the system of channels via coarse grains included finer particles would have low electrical resistivity and thermal conductivity (Li *et al* 2010).

The dimensionless figure of merit, ZT , calculated by using the measured values of S , σ and κ are shown in figure 7. The ZT values of the $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ samples are all higher than that of the $\text{Bi}_2\text{Se}_0.3\text{Te}_{2.7}$ sample in the measured temperature range. The ZT values of the $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ sample are much higher than that of the others and are larger than 0.6 in a wide temperature range

Figure 5. Seebeck coefficients of hot-pressed samples.

Figure 6. Thermal conductivities of hot-pressed samples.

Figure 7. ZT values of hot-pressed bulk samples.

from 373 to 473 K. And the peak value reaches 1.21 at 413 K, which is not only much higher than other reported rare earth elements doping Bi_2Te_3 -based alloys (Ji *et al* 2005; Zhang *et al* 2007), but also higher than zone-melting ingots and other reported *n*-type Bi_2Te_3 -based alloys (Yan *et al* 2010; Liu *et al* 2011; Wang *et al* 2011).

4. Conclusions

n-Type $\text{R}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ (R = Ce, Y and Sm) nanopowders were synthesized by hydrothermal method and the thermoelectric properties of the bulk samples made by hot-pressing these nanopowders were investigated. The Ce, Y and Sm doping has significant effects on the morphologies of the synthesized nanopowders. The possible reason may be that replacing Bi by rare earth elements can change the bonds strength and affect the growth rate along the *a*-, *b*- and *c*-axes. The Ce, Y and Sm doping not only help to decrease the electrical resistivity, but also help to reduce the thermal conductivity. Among rare earth elements-doped samples, it seems that the $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ bulk has a suitable microstructure, which scatters phonons effectively, but does not scatter carriers as much. As a result, the *ZT* values of $\text{Y}_{0.2}\text{Bi}_{1.8}\text{Se}_{0.3}\text{Te}_{2.7}$ can reach 1.21 at 413 K, which is not only much higher than other reported rare earth elements doping Bi_2Te_3 -based alloys (Ji *et al* 2005; Zhang *et al* 2007), but also higher than zone-melting ingots and other reported *n*-type Bi_2Te_3 -based alloys (Yan *et al* 2010; Liu *et al* 2011; Wang *et al* 2011). The combination of element doping and nanostructure should be a focus for further development of novel thermoelectric materials.

References

- Deng Y, Nan C W, Wei G D, Guo L and Lin Y H 2003 *Chem. Phys. Lett.* **374** 410
- DiSalvo F J 1999 *Science* **285** 703
- Dresselhaus M S, Chen G, Tang M Y, Yang R G, Lee H, Wang D Z, Ren Z F, Fleurial J P and Gogna P 2007 *Adv. Mater.* **19** 1043
- He M, Ge J, Lin Z Q, Feng X H, Wang X W, Lu H B, Yang Y L and Qiu F 2012 *Energy Environ. Sci.* **5** 8351
- Ji X H, Zhao X B, Zhang H, Lu B H and Ni H L 2005 *J. Alloys Compd.* **387** 282
- Lan Y C, Minnich A J, Chen G and Ren Z F 2010 *Adv. Funct. Mater.* **20** 357
- Li J F, Liu W S, Zhao L D and Zhou M 2010 *NPG Asia Mater.* **2** 152
- Liu W S, Zhang QY, Lan Y C, Chen S, Yan X, Zhang Q, Wang H, Wang D Z, Chen G and Ren Z F 2011 *Adv. Energy Mater.* **1** 577
- Liu W S, Yan X, Chen G and Ren Z F 2012 *Nano Energy* **1** 42
- Poudel B *et al* 2008 *Science* **320** 634
- Sharp J W, Poon S J and Goldsmid H J 2001 *Phys. Status Solidi (A)* **187** 507
- Snyder G J and Toberer E S 2008 *Nat. Mater.* **7** 105
- Sootsman J R, Chung D Y and Kanatzidis M G 2009 *Angew. Chem. Int. Ed.* **48** 8616
- Tritt T M and Subramanian M A 2006 *Mrs Bull.* **31** 188
- Wang S, Xie W, Li H and Tang X 2011 *Intermetallics* **19** 1024
- Xie W J, He J, Kang H J, Tang X F, Zhu S, Laver M, Wang S Y, Copley J R D, Brown C M, Zhang Q J and Tritt T M 2010 *Nano. Lett.* **10** 3283
- Yan X, Poudel B, Ma Y, Liu W S, Joshi G, Wang H, Lan Y C, Wang D Z, Chen G and Ren Z F 2010 *Nano. Lett.* **10** 3373
- Zhang Y H, Zhu T J, Tu J P and Zhao X B 2007 *Mater. Chem. Phys.* **103** 484
- Zhang G Q, Yu Q X, Wang W and Li X G 2010 *Adv. Mater.* **22** 1959
- Zhao Q and Wang Y G 2010 *J. Alloys Compd.* **497** 57