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Enhanced thermoelectric performance of p-type filled skutterudites via the coherency strain fields from spinodal decomposition

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ABSTRACT

Here we demonstrate that the coherency strain fields arising from spinodal decomposition can improve simultaneously the electronic density of states (DOS) near the Fermi level and the phonon-scattering rate in *p*-type filled skutterudites. Spinodal decomposition is appeared in the *p*-type filled skutterudite $La_{0.8}Ti_{0.1}Ga_{0.1}Fe_3CoSb_{12}$, which is produced by a combination of water-quenching, long-term annealing and hot-pressing approaches. Within each grain of the hot-pressed sample, there are La-poor and La-rich skutterudite phases. The size of each phase is then substantially reduced to about 200 nm by using rapid solidification of melting–spinning followed by hot-pressing method. Therefore, the coherency strain fields resulted from spinodal decomposition is significantly increased. High resolution transmission electron microscopy (HRTEM) reveals that most of these domains are in the state of tensile. Compared to the quenched sample, the Seebeck coefficient increases about 10% and the lattice thermal conductivity of the optimization sample is reduced about 30% at 700 K. Our theoretical analysis shows that grain boundary scattering has limited contribution to the reduction of lattice thermal conductivity in *p*-type filled skutterudites. The drastic reduction in the lattice thermal conductivity is mainly caused by phonon scattering through the coherency strain fields. As a result, a peak *ZT* of about 1.2 at 700 K is obtained in the spun sample. In addition, the spun sample displays good repeatable and stable characteristics.

1. Introduction

Thermoelectric (TE) materials have attracted much attention in these years, which can directly convert heat into electricity in a safe and clean way. The efficiency of TE materials is determined by the dimensionless figure of merit $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ the electrical conductivity, T the absolute temperature, and κ the thermal conductivity [1]. Generally, κ is sum of the electronic thermal conductivity κ_e and the lattice thermal conductivity κ_L.

Skutterudites are considered as one of the most promising middle temperature TE materials for power generation from the waste heat, such as car's exhaust, due to their excellent physical and mechanical property [2–7]. The crystal structure of skutterudites contains two large interstitial voids in a unit cell, where various atoms, such as rare earth elements and alkaline earth elements, can be filled to form filled skutterudites. It has been proved that the thermal conductivity of filled skutterudites can be reduced significantly by single, double and multiple filled [2,8–13]. Studies have shown that the filled atoms lead to a low κ_L by the excess phonons scattering or lower phonons group velocity, raising the *ZT* values above those of unfilled ones [14–19]. Recently, higher *ZT* value of 1.4 in double-filled and 1.7 in multiple-filled *n*-type skutterudites were reported [9,20–22]. However, the *ZT* values around 1.0 in *p*-type filled skutterudites are confirmed by experiment, much lower than *n*-type materials [23–26]. As known, both high thermoelectric performances of *n*-type and *p*-type materials are required in the thermoelectric module for industry applications. Therefore, searching for *p*-type skutterudites with *ZT* values comparable to those of *n*-type materials is very urgent.

Nanotechnologies, such as nanograins or nanoprecipates, have been utilized to further improve the performance of the thermoelectric materials. Nanograined TE materials, such as, half-Heusler alloys [27–29], BiSbTe alloys [30], MgAgSb alloys [31], GeSi alloys [32] possess improved thermoelectric performance due to the effective scattering of phonons by the large number of grain boundaries. Unfortunately, for highly-filled skutterudites with nanograins, the lattice thermal conductivity is insensitive to the grain size larger than hundreds of nanometers. For instance, even though the grain size is about 300–500 nm, κ_L

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of nanostructured p-type filled skutterudites with composition $CeFe_4Sb_{12}$ prepared by melt spinning is about $1.2\ W\ m^{-1}\ k^{-1}$ at room temperature [25], which is almost the same with the reported κ_L of $1.28\ W\ m^{-1}\ k^{-1}$ for the as-prepared sample using a traditional way [13]. Jie et al. [26] prepared nanostructured p-type skutterudites with different grain size by high energy ball milling. The results show that κ_L of $Ce_{0.45}Nd_{0.45}Fe_{3.5}Co_{0.5}Sb_{12}$ prepared in a traditional method is around $1.2\ W\ m^{-1}\ k^{-1}$, which is almost unchanged even though the grain size is reduced to lower than 100 nm.

On the other hand, nano precipitates with size of several tens nanometer improve ZT value of filled skutterudite by reducing κ_L, for example in $In_xCe_yCo_4Sb_{12}/InSb$ [17], $Yb_{0.26}Co_4Sb_{12}/y GaSb$ [33], $Yb_xCo_4Sb_{12}/Yb_2O_3$ [34], and $Yb_{0.6}Fe_2Co_2Sb_{12}/FeSb_2$ [35]. All the results indicate nano precipitates provide extra phonon scattering to reduce the thermal conductivity. However, nanoprecipitates also increase the charge carrier scattering, which has a detrimental effect on the power factor.

Recently, it has been proved that strain can intensify the phonon scattering and reduce thermal conductivity in many TE systems [36–38]. Rogl et al. improved the dislocation density in p-type and n-type skutterudites by using high-pressure torsion [36,37]. The strain resulted from dislocation enhanced the phonon scattering significantly and reduced the thermal conductivity. As a result, the ZT was enhanced. Biswas et al. prepared bulk p-type PbTe–SrTe with SrTe nanoprecipitates [38]. Their results show coherency strain fields resulted from nanoprecipitates provide an additional phonon scattering channel, further reducing κ_L. Meanwhile, experimental and theoretical works indicated that external stresses can improve the power factor of TE materials [39–44]. To our knowledge, the pure coherency strain without any precipitates has not been mentioned previously in any system to improve simultaneously the power factor and phonon scattering.

In this work, we report the pure coherency strain resulted from spinodal decomposition in p-type filled skutterudites $La_{0.8}Ti_{0.1}Ga_{0.1}Fe_3CoSb_{12}$. Large number of coherency strain fields was obtained by using a rapid solidification method to enhance the thermoelectric performance. The results indicate a state-of-the-art ZT value of about 1.2 originated from both the improvement of power factor and the reduced thermal conductivity in the spun sample via the advantageous coherency strain coming from spinodal decomposition. The influence of coherency strain on the microstructure and the thermoelectric properties has been discussed in detail.

Furthermore, the results convinced us that these spontaneous coherency strain fields can be applied to a variety of TE materials to enhance their ZT performance. The greatly shortened preparation period as well as the enhanced thermoelectric performance is suitable for commercial applications of this promising thermoelectric material.

2. Experimental

2.1. Sample preparation

La ingot (99.8%, Alfa Aesar), Sb balls (99.999%, Alfa Aesar), Ga ingot (99.999%, Alfa Aesar), Ti ingot (99.995%, Alfa Aesar), Fe ingot (99.99%, Alfa Aesar) and Co ingot (99.95%, Alfa Aesar) were prepared and weighted according to the chemical composition $La_{0.8}Ti_{0.1}Ga_{0.1}Fe_3CoSb_{12}$, and loaded into carbon crucible, and then were sealed in quartz tubes under vacuum ($<10^{-3}$Pa). After slowly heating to 1423 K and kept for 4 h, the quartz tube was quenched in water. The quenched ingot was annealed at 973 K for 100 h and then ground into fine powers in a glove box filled with high-purity Ar and sintered into bulk pellet with a diameter of 13.5 mm by hot-pressing at 923 K for 2 h under a pressure of 90 MPa and vacuum below 6.7×10^{-3} Pa. The obtained sample is called the quenched sample (QS). The annealed quenched sample was achieved by annealing the quenched sample at 973 K for another 100 h.

The spun sample was prepared by melting–spinning and hot-pressing method. The quenched ingots with chemical composition $La_{0.8}Ti_{0.1}Ga_{0.1}Fe_3CoSb_{12}$ were pulverized into small bulks with size about $5 \times 5 \times 5\ mm^3$ and placed in a quartz tube with a 0.5 mm diameter nozzle. To obtain ribbon, the small bulks were molten and injected under a pressure 0.05 MPa using high purity Ar onto a copper roller with a rotating speed of $50\ m\ s^{-1}$. The obtained ribbons were pulverized in a glove box filled with high-purity and then sintered into pellet with a diameter of 13.5 mm by hot-pressing at 923 K for 2 h under a pressure of 90 MPa and vacuum below 6.7×10^{-3} Pa. The obtained sample is named as the spun sample (SS). To confirm the stability of the spun sample, repeatability and annealing had been done. The spun sample is annealed at temperature of 973 °C for 100 h. The repeatability sample called as repeated SS sample and the annealed one called as annealed SS sample.

2.2. Sample characterization

The phase structure was analyzed by X-ray power diffraction (XRD) with a PANalyticalX'Pert Pro X-ray diffractometer using Cu Kα radiation and a low scanning velocity of 1° per minute. The morphologies and actual composition were analyzed using a Hitachi S4700 scanning electronic microscope (SEM) accompanied with the energy-dispersive X-ray spectroscopy (EDS). Hall coefficients at room temperature were measured in a Physical Property Measurement System (PPMS). The microstructure was investigated using a high resolution transmission electron microscope (HRTEM, TecnaiG2F30) and the TEM samples were prepared by conventional ion-sputtering method. Disks with diameter of 12.7 mm and 2 mm thick were used to measure the thermal diffusivity and volume density. The thermal conductivity (κ) could be calculated using the relationship $\kappa = D \times C_P \times d$, where D is thermal diffusivity, C_P is specific heat and d is density. The thermal diffusivity was measured on a laser flash apparatus (Netzsch LFA 457) with flowing argon gas protection. The C_P was measured by using DSC system (Netzsch DSC 404). The density was measured by an Archimedes method, and relative densities of all samples are higher than 96%. Bars with dimensions of $2 \times 2 \times 2\ mm^3$ were used to measure the power factor. The Seebeck coefficient and electrical conductivity were measured on a system (ULVAC ZEM-3).

3. Results and discussion

3.1. Spinodal decomposition for the skutterudite $La_{0.8}Ti_{0.1}Ga_{0.1}Fe_3CoSb_{12}$

Fig. 1a shows the XRD patterns of the quenched ingot and the quenched sample. The quenched ingot has a multiphase structure, including Sb, $FeSb_2$, La-containing and skutterudite phase. After annealing at 973 K for 100 h and hot-pressing, the structure of the quenched sample changes to single skutterudite phase without any second phases, which is consistent with the previous publication [25]. Fig. 1b shows the XRD patterns of the annealed ingot scanned at high angles (2θ = 68.5–70.5°) with a low scanning speed of 1° per minute. As shown, two obvious diffraction peaks appear around 70° and both of them can be indexed as (1 3 6) plane. These results point out there are two phases with skutterudite