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Synthesis and electronic transport properties of Sn-filled/Te-doped $CoSb_3$

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Sn-filled/Te-doped $CoSb_3$ skutterudites ($Sn_zCo_4Sb_{11.2}Te_{0.8}$) were prepared by encapsulated induction melting, and their electronic transport properties were investigated. A single δ-phase was obtained successfully by a subsequent isothermal heat treatment at 773 K for 5 days. The Seebeck coefficient and Hall coefficient confirmed that all the samples exhibited n-type conductivity. Te atoms acted as electron donors by substituting for Sb atoms. The temperature dependence of the electrical resistivity suggested that $Sn_zCo_4Sb_{11.2}Te_{0.8}$ is a highly degenerate semiconducting material. The lattice contribution was found to be dominant over the thermal conductivity of $Sn_zCo_4Sb_{11.2}Te_{0.8}$.

Key words: Skutterudite, Thermoelectric, Void filling, Doping, Transport property.

Introduction

Since $CoSb_3$-based skutterudites can satisfy the PGEC (phonon glass and electron crystal) concept [1], there have been many studies on thermoelectric skutterudites [2-4]. $CoSb_3$-based skutterudites are expected to be the most promising thermoelectric materials for intermediate temperature applications. They have attracted considerable interest on account of their excellent electrical transport properties and large Seebeck coefficient. Unfortunately, the thermal conductivity of binary $CoSb_3$ is too large for thermoelectric applications. The PGEC concept has given a new direction to the search for good thermoelectric materials. The most exciting part of skutterudites is the two large voids (2a positions) that favor the PGEC concept. The phonon mean free path, which is related directly to the thermal conductivity, can be reduced by the incorporation of filler atoms into the voids, which is called the rattling effect.

Filled skutterudite has the general form, RT_4X_{12}, where R is the filler atom, the so-called the rattler (La, Ce, Ca, Ba, etc.), T is the transition metal atom (Co, Rh, Ir) and X is the pnicogen atom (P, As, Sb). The R, T and X atoms occupy the 2a positions (0, 0, 0), 8c positions (¼, ¼, ¼) and 24 g positions (0, y, z), respectively [5, 6]. Many attempts have been made to fill the voids with rattlers [7, 8] and/or dope with suitable impurities to reduce the thermal conductivity by introducing phonon scattering centers [9-13]. In this study, an attempt was made to fill the voids with tin atoms and substitute (dope) antimony with tellurium. The basic criteria for selecting Sn as a filler are as follows: its covalent radius (1.41 Å) is smaller than the void radius (1.892 Å); and it has mixed valence of 4^+ and 2^+. In this study, Sn-filled/Te-doped $CoSb_3$ skutterudites ($Sn_zCo_4Sb_{11.2}Te_{0.8}$) were prepared by encapsulated induction melting, and their filling effect on the electronic transport properties was investigated.

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Experimental Procedure

$Sn_zCo_4Sb_{11.2}Te_{0.8}$ ($0 \le z \le 0.4$) skutterudites were prepared by encapsulated induction melting, which is widely used to synthesize homogeneous materials. Elemental Co (purity 99.95%), Sb (purity 99.999%), Sn (purity 99.99%) and Te (purity 99.99%) were mixed and melted in an encapsulated quartz ampoule with an RF electrical power of 7 kW at 40 kHz for 1 h with mechanical vibration. Subsequent isothermal heat treatment was carried out at 773 K for 5 days for phase homogenization and dopant activation. The ingot with dimensions of 10 mm (diameter) ×30 mm (length) was cut to a rectangular-shaped piece, 3 × 3 × 10 mm^3 in size, for both the Seebeck coefficient and electrical resistivity measurements. Samples were also cut to 10 mm (diameter) × 1 mm (thickness) disc-shaped pieces for the thermal conductivity and Hall measurements.

The phase transformations were analyzed by high resolution X-ray diffraction(HRXRD, Rigaku DMAX2500VPC) using Cu K_α radiation (40 kV/200 mA). The Hall effect measurements (Keithley 7065) were carried out in a constant magnetic field (1 T) and electric current (50 mA) at 300 K. The Hall coefficient, carrier mobility and carrier concentration were examined. The Seebeck coefficient, electrical resistivity and thermal conductivity were measured from 300 K to 700 K. The Seebeck coefficient and electrical resistivity was measured using temperature differential and 4-point probe methods in a helium atmosphere on a Ulvac-Riko ZEM2-M8. The thermal conductivity was evaluated by measuring the thermal diffusivity, specific

heat and density by the laser flash Ulvac-Riko TC7000 equipment in a vacuum. The thermal conductivity was separated into the lattice thermal conductivity and electronic thermal conductivity according to the Wiedemann-Franz law, where the Lorenz number is assumed to be constant ($L = 2.45 \times 10^{-8}\ V^2/K^2$) for evaluation [14].

Results and Discussion

Fig. 1 shows a scanning electron microscope (SEM) image of the microstructure of the Sn-filled/Te-doped $CoSb_3$ ($Sn_{0.1}Co_4Sb_{11.2}Te_{0.8}$). The specimen has a single δ-phase with a typical dendritic structure. Fig. 2 shows the phase analysis results for the unfilled and Sn-filled $Co_4Sb_{11.2}Te_{0.8}$. A single δ-phase was identified with no other secondary phases. This confirms that subsequent heat-treatment at 773 K for 5 days is enough for the phase transformation and void filling. The filling fraction limit of the filled $CoSb_3$ skutterudite is described based on the density function method but with the thermodynamic stability of the filled skutterudite being maintained. If the filling fraction exceeds the limit then the unit cell expands to form an unstable filled skutterudite, which causes the filler to interact with the host materials and form secondary phases. These secondary phases are more thermodynamically stable than the filled skutterudite. In this study, no secondary phases were found. This means that the Sn atoms were located at the void sites. Moreover, the $Sn_zCo_4Sb_{11.2}Te_{0.8}$ skutterudites were thermodynamically stable up to $z = 0.4$ and Te atoms successfully substitute for the Sb atoms.

Fig. 3 presents the electronic transport properties of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ at 300 K. The Hall effect measurements confirmed that all the samples had a negative Hall coefficient, which means n-type conductivity. The Sn fillers can affect the electronic structure of $CoSb_3$ and generate excess charge carriers (holes) [4]. However, the carrier concentration and mobility were not dependent on the Sn filler content. Since the Te dopants act as electron donors in $Sn_zCo_4Sb_{11.2}Te_{0.8}$, bipolar conduction can occur due to the

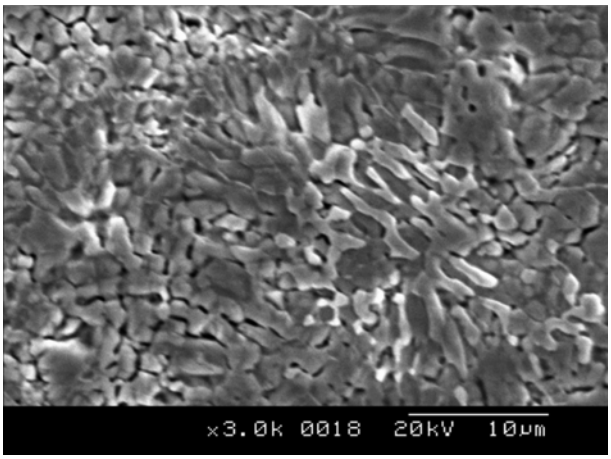

Fig. 1. Scanning electron microscope image of $Sn_{0.1}Co_4Sb_{11.2}Te_{0.8}$ skutterudite prepared by encapsulated induction melting and post-annealing at 773 K for 5 days.

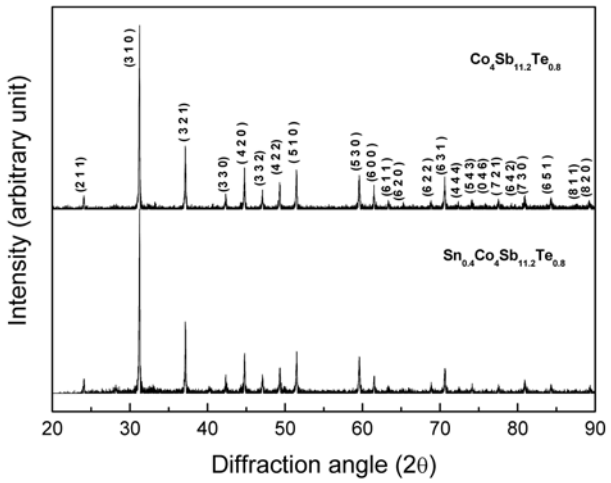

Fig. 2. X-ray diffraction patterns of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ skutterudites prepared by encapsulated induction melting and post-annealing at 773 K for 5 days.

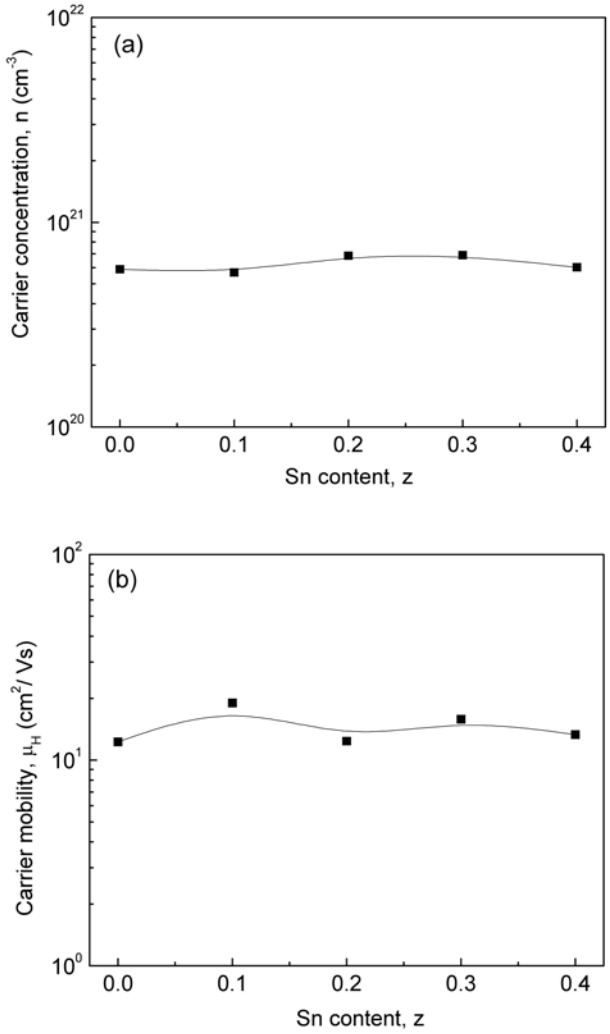

Fig. 3. Variation of the electronic transport properties of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ with Sn filling content at 300 K: (a) carrier concentration and (b) carrier mobility.

Sn fillers. The carrier concentrations of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ showed relatively high values in the mid-10^{20} cm^{-3}. Therefore, these materials are in a highly degenerate state and are expected to show a temperature dependent electrical resistivity similar to metallic behavior.

Fig. 4 shows the thermoelectric properties of a $Sn_{0.1}Co_4Sb_{11.2}Te_{0.8}$ specimen as an optimized Sn-filled/Te-doped $CoSb_3$. The Seebeck coefficient decreased with increasing temperature and the n-type conductivity remained up to 700 K. However, the electrical resistivity was independent of temperature. The temperature dependence of the electrical resistivity of the filled $CoSb_3$ skutterudites has been examined by many researchers [9, 15], and they have been proven to be almost degenerate semiconductors. This is due to the decrease in the Fermi level and the increase in the carrier concentrations by adding filler atoms.

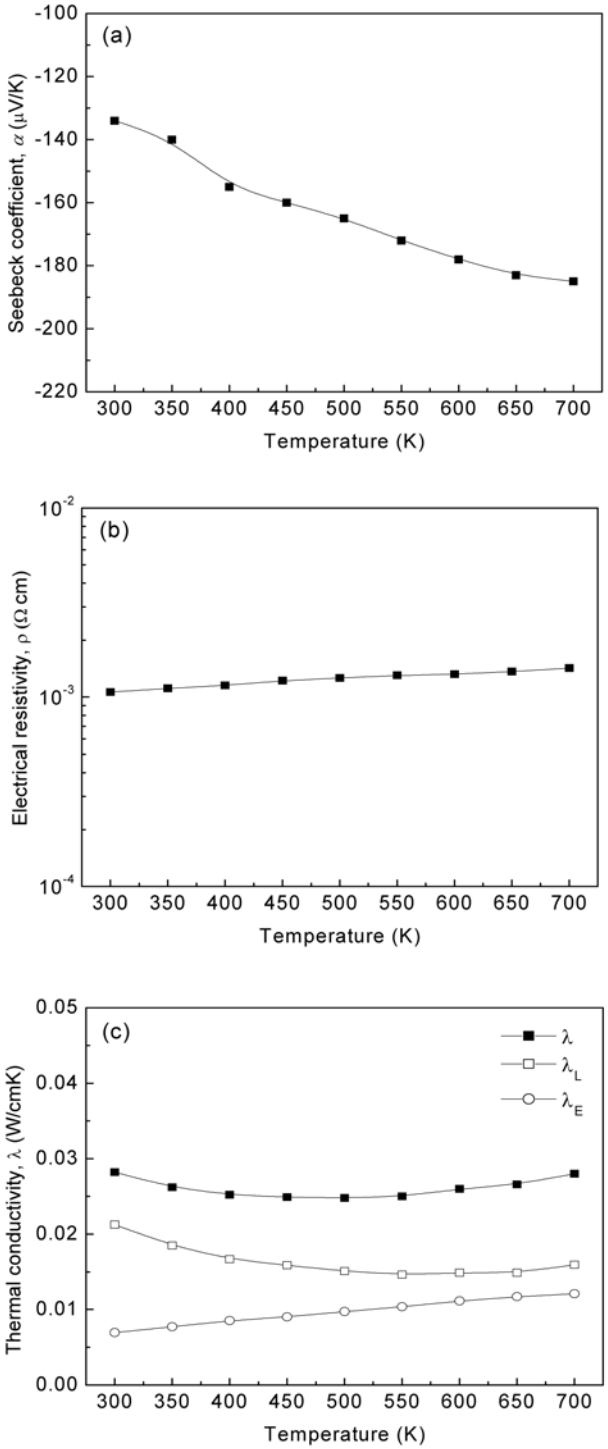

Fig. 4. Temperature dependence of thermoelectric properties of $Sn_{0.1}Co_4Sb_{11.2}Te_{0.8}$: (a) Seebeck coefficient, (b) electrical resistivity and (c) thermal conductivity.

The thermal conductivity consists of the lattice thermal conductivity (λ_L) and electronic thermal conductivity (λ_E), and can be separated by the Wiedemann-Franz law. The Lorenz number is defined as $L \equiv \lambda_E \rho T^{-1}$, and it is assumed to be constant ($L = 2.45 \times 10^{-8}$ V^2/K^2) for the calculation [14]. It was reported that the lattice thermal conductivity was dominant in $Sn_zCo_4Sb_{11.2}Te_{0.8}$ skutterudites. The thermal conductivity is proportional to the phonon mean free path because phonon scattering gives rise to a decrease in the phonon mean free path. Reducing the lattice contribution of the thermal conductivity has been achieved by filling the voids with different atoms. The filler atomic size, charge state, electronegativity and filling fraction limit need to be considered in order to have a thermodynamically stable compound. If the filler is completely inside the void and can rattle well, the rattling of the filler atoms inside the voids can absorb heat (lattice vibrations). If the voids are fully filled, there would be less chance of the filler rattling inside the voids, which would have less of an effect on the frequency or mean free path of the outside phonon.

Conclusions

$Sn_zCo_4Sb_{11.2}Te_{0.8}$ skutterudites were synthesized successfully by the encapsulated induction melting and subsequent annealing at 773 K for 5 days. A single δ-phase was identified in all specimens with no other secondary phases. The Seebeck coefficient and Hall coefficient confirmed that all the samples showed n-type conductivity. The temperature dependence of the electrical resistivity suggested that $Sn_zCo_4Sb_{11.2}Te_{0.8}$ is a highly degenerate semiconducting material. The thermal conductivity could be reduced by filling and doping, and the lattice contribution was dominant.

Acknowledgments

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