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Synthesis and electronic transport properties of $In_zCo_4Sb_{12-y}Te_y$ skutterudites

Jae-Yong Jung and Il-Ho Kim*

Department of Materials Science and Engineering/RIC-ReSEM, Chungju National University, 72 Daehangno, Chungju, Chungbuk 380-702, Korea

$In_zCo_4Sb_{12-y}Te_y$ skutterudites were prepared by encapsulated induction melting, and their electronic transport properties were investigated. Single phase d-$CoSb_3$ was obtained successfully by encapsulated induction melting and subsequent heat treatment at 823 K for 5 days. The Te atoms acted as electron donors by substituting for Sb atoms. The Hall coefficient and the Seebeck coefficient showed negative values, which confirmed the $In_zCo_4Sb_{12-y}Te_y$ skutterudites are n-type semiconductors. The electronic transport properties were affected greatly by Te doping rather than by In filling. The carrier concentration ranged from 7×10^{19} to 4×10^{20} cm^{-3}, and carrier mobility was 2 to 22 cm^2/Vs. The Seebeck coefficient was increased and the electrical resistivity was decreased by Te doping and In filling. The thermal conductivity was reduced considerably by doping and filling due to phonon scattering, which is responsible for the decrease in lattice thermal conductivity.

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

Introduction

The requirements for good thermoelectric materials are as follows: a large unit cell, a complex crystal structure, heavy constituent atom masses, highly covalent atomic bonds, a large effective mass, large carrier mobility, a very narrow band gap and low differences in electronegativity between the constituent atoms. Since $CoSb_3$-based skutterudites can satisfy all these conditions and the PGEC (phonon glass and electron crystal) concept [1], there have been many studies on thermoelectric skutterudites [2-4]. Thermoelectric skutterudites are expected to be the most promising thermoelectric materials for intermediate temperature applications. $CoSb_3$-based skutterudites 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 in the search for good thermoelectric materials. The most exciting part of the skutterudites are their two large voids (2a positions) that favor the PGEC. 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 known as the rattling effect.

Filled skutterudite has the general form, RT_4X_{12}, where R is the filler (rattler) atom, T is the transition metal atom and X is the pnicogen atom. Many studies have attempted to fill the voids with rattlers [5, 6] and/or to dope them with suitable impurities to reduce the thermal conductivity by introducing phonon scattering centers [7-11]. He *et al.* [5] examined the structural, electrical and thermal transport properties of $CoSb_3$, which was partially filled with indium and prepared by a solid-state reaction. They reported the solubility limit of In filling the voids in $CoSb_3$ to be approximately 0.22, and that the thermoelectric properties could be enhanced considerably by In filling. Wojciechowski *et al.* [9] investigated the structural and electronic transport properties of Se- and Te-doped $CoSb_3$ prepared by hot pressing. They concluded that in view of structural stability and doping effect, Te is more effective in $CoSb_3$ than Se.

In this study, In-filled and Te-doped $CoSb_3$ skutterudites ($In_zCo_4Sb_{12-y}Te_y$) were prepared by encapsulated induction melting, and their filling and doping effects on the electronic transport properties were examined. The basic criterion for selecting In as a filler was that its covalent radius (1.44 Å) is smaller than the void radius (1.892 Å). The reason for selecting Te as a dopant is that it can substitute for Sb and generate excess electrons.

Experimental Procedure

$In_zCo_4Sb_{12-y}Te_y$ ($z = 0.05$, 0.25 and $y = 0.1$, 0.8) was prepared by encapsulated induction melting (EIM), which is widely used to synthesize homogeneous materials. Elemental In (purity 99.99%), Co (purity 99.95%), Sb (purity 99.999%) and Te (purity 99.99%) were mixed and melted in an encapsulated quartz ampoule with an RF electrical power of 7 kW and 40 kHz for 1 h with mechanical vibration. The ingot was annealed at 823 K for 5 days to homogenize the sample and allow sufficient time for In to fill the voids in the skutterudite structure as well as for dopant activation. A 10 mm (diameter) × 30 mm (length) ingot was cut to rectangular-shaped

*Corresponding author:
Tel : +82-43-841-5387
Fax: +82-43-841-5380
E-mail: ihkim@cjnu.ac.kr

pieces, $3 \times 3 \times 10\ mm^3$ in size, for both the Seebeck coefficient and electrical resistivity measurements. A 10 mm (diameter) × 1 mm (thickness) disc-shaped piece was prepared for both the thermal conductivity and Hall effect measurements.

The phase was analyzed by high resolution X-ray diffraction (HRXRD: Rigaku DMAX2500VPC) using Cu K_α radiation (40 kV, 200 mA) with a step size of 0.004 and a scan speed of 1 degree/minute. The Seebeck coefficient (α), electrical resistivity (ρ) and thermal conductivity (λ) were measured from 300 K to 700 K, and the dimensionless thermoelectric figure of merit ($ZT = \alpha^2 T\rho^{-1}\lambda^{-1}$) was evaluated, where T is the temperature in Kelvin. The Seebeck coefficient and electrical resistivity were measured using temperature differential and 4-point probe methods in a helium atmosphere on a Ulvac-Riko ZEM2-M8. The thermal conductivity ($\lambda = dCD$) was evaluated from the thermal diffusivity (D), specific heat (C) and density (d) measurements using a laser flash Ulvac-Riko TC7000 system in a vacuum. The Hall effect (Keithley 7065) measurement were carried out in a constant magnetic field (1T) and electric current (50 mA) at 300 K. The Hall coefficient (R_H), carrier mobility (μ_H) and carrier concentration (n) were examined. The thermal conductivity ($\lambda = \lambda_L + \lambda_E$) was separated from the lattice thermal conductivity (λ_L) and electronic thermal conductivity (λ_E) according to the Wiedemann-Franz law ($\lambda_E = LT\rho^{-1}$), where the Lorenz number was assumed to be constant ($L = 2.45 \times 10^{-8}\ V^2/K^2$) for the evaluation [12].

Results and Discussion

Fig. 1 shows a scanning electron microscope image of the microstructure of $In_{0.05}Co_4Sb_{11.2}Te_{0.8}$. The specimen had a single d-phase with a typical dendritic structure. Fig. 2 shows HRXRD patterns of the In-filled and Te-doped $In_zCo_4Sb_{12-y}Te_y$. A single d-phase was identified in all specimens. This confirms that subsequent heat-treatment at 823 K for 5 days is enough for the phase transformation

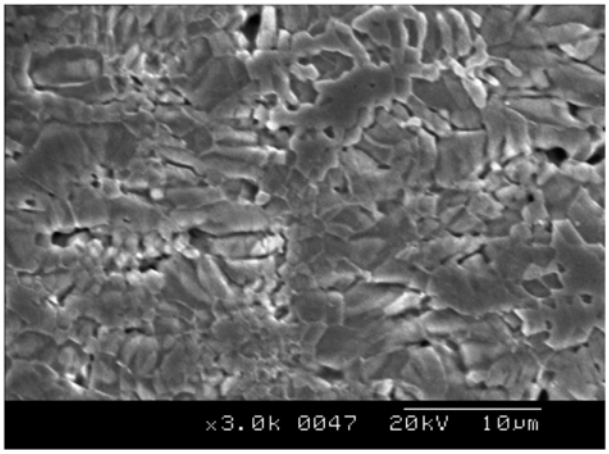

Fig. 1. Scanning electron microscope image of $In_{0.05}Co_4Sb_{11.2}Te_{0.8}$ prepared by EIM and post-annealed at 823 K for 5 days.

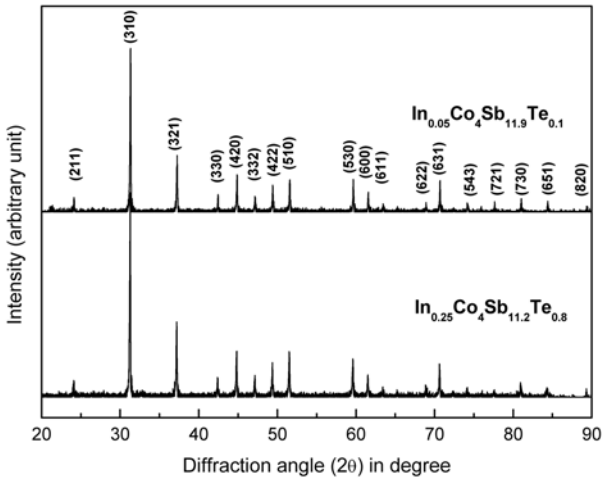

Fig. 2. X-ray diffraction patterns of $In_zCo_4Sb_{12-y}Te_y$ skutterudites prepared by EIM and post-annealed at 823 K for 5 days.

and void filling of In as well as for Sb-Te substitution. The filling fraction limit of the filled $CoSb_3$ skutterudite is described based on the density function method with the thermodynamic stability of the filled skutterudite maintained. If the filling fraction exceeds the limit then the unit cell expands, which might form an unstable filled skutterudite. This can cause the filler to interact with the host materials and form secondary phases. These secondary phases are more thermodynamically stable than filled skutterudite. In this study, no secondary phases were found. This means that the In atoms are located at the void sites, the $In_zCo_4Sb_{12-y}Te_y$ skutterudites are thermodynamically stable up to $z = 0.25$ and the Te atoms successfully substitute for Sb atoms.

Fig. 3 shows the electronic transport properties of $In_zCo_4Sb_{12-y}Te_y$ at 300K. The Hall effect measurements confirmed that all the samples showed a negative Hall coefficient (n-type conductivity). In fillers can affect the electronic structure of $CoSb_3$ and generate excess charge carriers (electrons) [5]. However, the carrier concentration and mobility showed little dependency on the In filler content. Since the Te dopants act as electron donors in the $In_zCo_4Sb_{12-y}Te_y$, the carrier concentration showed relatively high values, ranging from high-10^{19} to mid-$10^{20}\ cm^{-3}$. Therefore, the materials are in a highly degenerate state and are expected to show a temperature dependent electrical resistivity similar to metallic behavior. The carrier mobility was decreased by Te doping, which indicates that the electron mean free path was reduced by ionized impurity scattering.

Fig. 4 shows the thermoelectric properties of $In_zCo_4Sb_{12-y}Te_y$ at 300 K. The Seebeck coefficient increased and the electrical resistivity decreased with increasing In filling and Te doping. The thermal conductivity was reduced remarkably by In filling and Te doping. The lattice thermal conductivity reduction is mainly responsible for the total decrease in thermal conductivity. The thermal conductivity consists of the lattice thermal conductivity (λ_L) and electronic thermal conductivity (λ_E). These can be separated by the Wiedemann-Franz law. The Lorenz

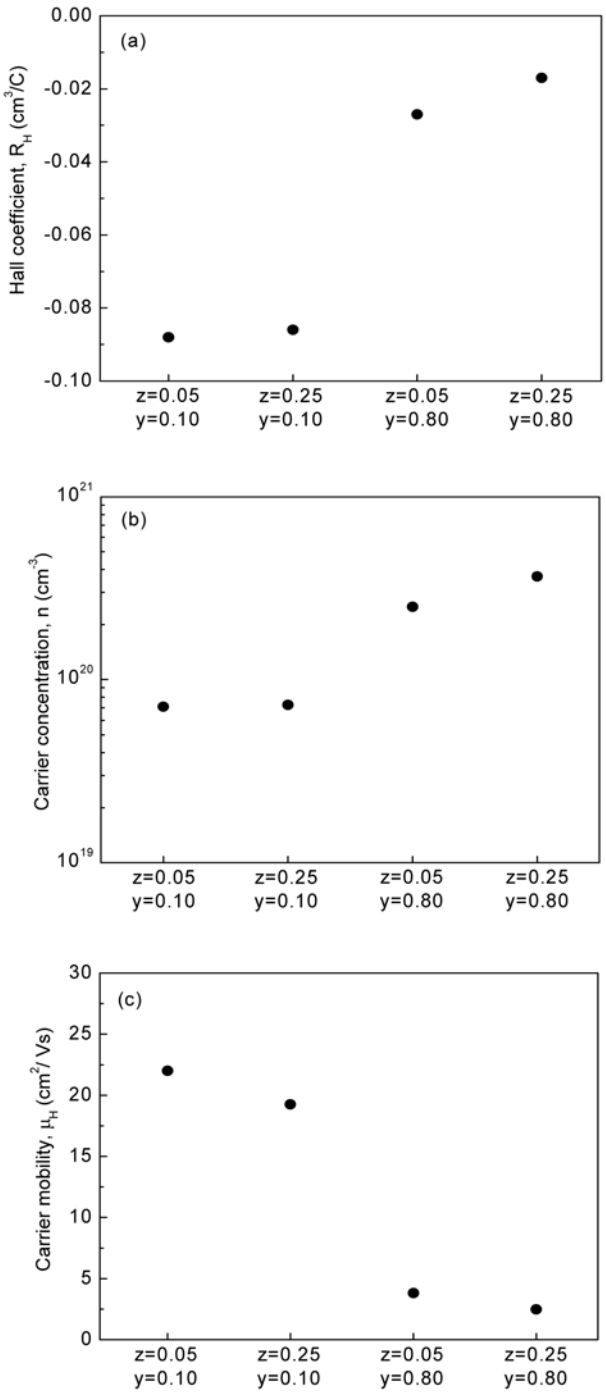

Fig. 3. Electronic transport properties of $In_zCo_4Sb_{12-y}Te_y$ content at 300 K; (a) Hall coefficient, (b) carrier concentration and (c) carrier mobility.

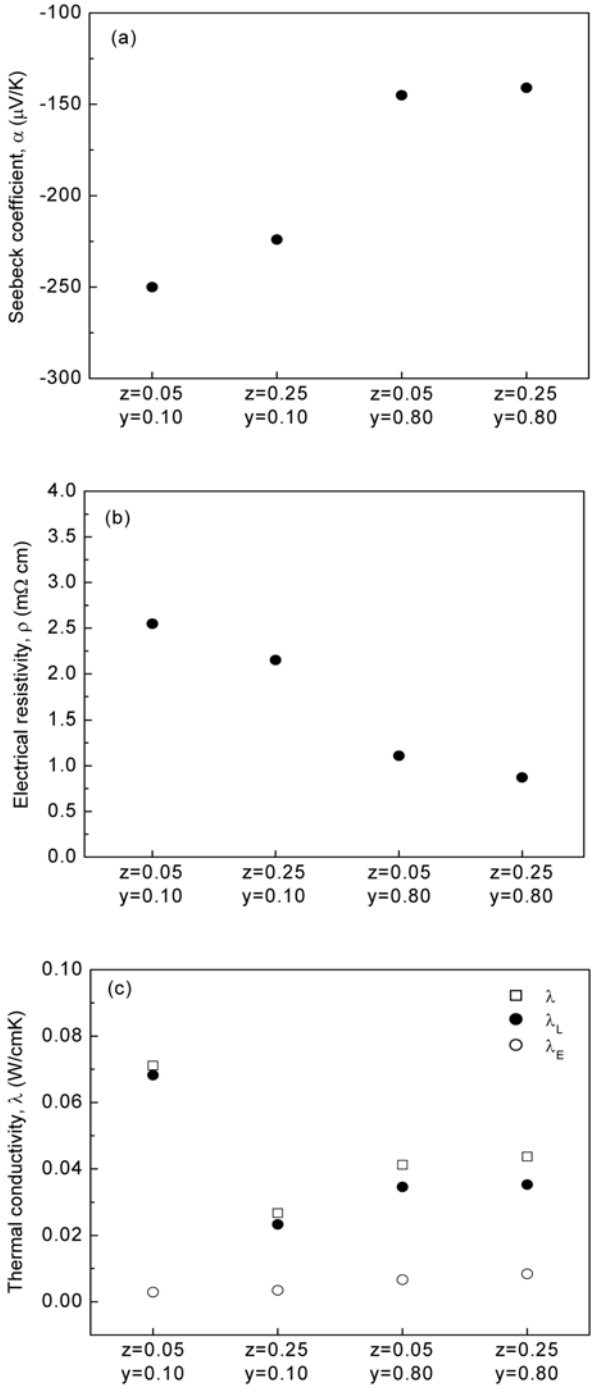

Fig. 4. Thermoelectric properties of $In_zCo_4Sb_{12-y}Te_y$ at 300 K; (a) Seebeck coefficient, (b) electrical resistivity and (c) thermal conductivity.

number is defined as $L\ \lambda_E \rho T^{-1}$ and was assumed to be a constant ($L = 2.45 \times 10^{-8}\ V^2/K^2$) for the calculation [12]. The lattice thermal conductivity was found to be dominant in $In_zCo_4Sb_{12-y}Te_y$ skutterudites.

Fig. 5 shows the temperature dependence of the thermal conductivity of $In_{0.05}Co_4Sb_{11.2}Te_{0.8}$. The lattice contribution to the total thermal conductivity was dominant over the electronic contribution at all temperatures examined. The thermal conductivity is proportional to the phonon mean free path because phonon scattering decreases 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 will absorb heat (lattice vibration). If the voids are

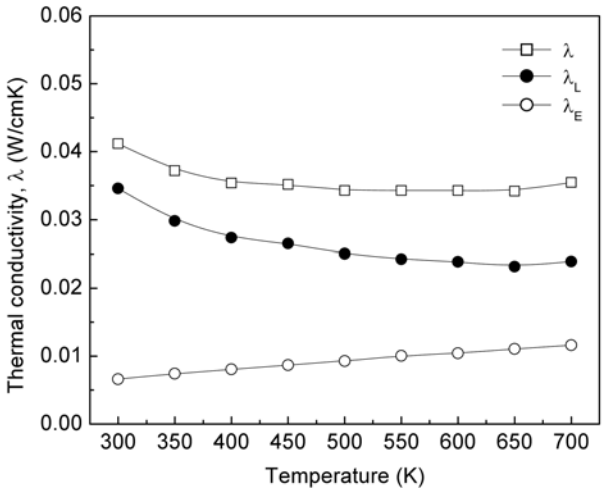

Fig. 5. Temperature dependence of the thermal conductivity of $In_{0.05}Co_4Sb_{11.2}Te_{0.8}$.

fully filled, there would less chance of filler rattling inside the voids and less effect on the frequency or mean free path of the outside phonon.

Dopants contribute to electronic thermal conduction as well as phonon scattering centers, which decreases the lattice thermal conductivity. The atomic size and charge state (valence) of a dopant, and doping (substitution) limit need to be considered in order to have thermodynamically stable skutterudites. The thermal conductivity of the intrinsic $CoSb_3$ is approximately 0.15 W/cmK at room temperature [4]. However, in this study, the $In_{0.05}Co_4Sb_{11.2}Te_{0.8}$ specimen was 0.04 W/cmK, which means that the thermal conductivity can also be reduced by doping. Substituting Sb with Te should not significantly alter the lattice component of thermal conductivity due to the similar atomic masses of Te and Sb. On the other hand, an increase in carrier concentration should result in an increase in the electronic contribution of thermal conductivity. However, calculations based on the Wiedemann-Franz law showed the electronic contribution in the total thermal conductivity to be relatively low, as shown in Fig. 4 (c) and Fig. 5.

Conclusions

In-filled and Te-doped $In_zCo_4Sb_{12-y}Te_y$ skutterudites were prepared by encapsulated induction melting and their electronic transport properties were examined. A single d-phase was identified for all specimens. No secondary phases were found. This means that the In atoms are located at the void sites. $In_zCo_4Sb_{12-y}Te_y$ skutterudites are thermodynamically stable up to $z = 0.25$ and the Te atoms successfully substitute for Sb atoms. $In_zCo_4Sb_{12-y}Te_y$ skutterudites showed a negative Hall coefficient, which means n-type conduction. The carrier concentration and mobility showed little dependency on the In filler content. However, Te dopants acted as electron donors in the $In_zCo_4Sb_{12-y}Te_y$ and the carrier concentration showed relatively high values, ranging from the high-10^{19} to mid-10^{20} cm^{-3}. The Seebeck coefficient increased and the electrical resistivity decreased with increasing In filling and Te doping. The thermal conductivity was reduced remarkably by In filling and Te doping, and the lattice thermal conductivity reduction was mainly responsible for the total decrease in thermal conductivity. The lattice contribution had a larger effect on the total thermal conductivity than the electronic contribution at all temperatures examined.

Acknowledgments

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