

Synthesis and electronic transport properties of $\text{CoSb}_{3-y}\text{Te}_y$ skutterudites

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$\text{CoSb}_{3-y}\text{Te}_y$ skutterudites were prepared by encapsulated induction melting, and their thermoelectric and electronic transport properties were investigated. Single δ -phase was successfully obtained by the subsequent annealing at 773 K for 24 h. The Seebeck coefficient and the Hall coefficient confirmed that all the Te-doped CoSb_3 showed n-type conduction. Te atoms successfully acted as electron donors by substituting Sb atoms. The carrier concentration increased to an order of 10^{21} cm^{-3} by Te doping, whereas the carrier mobility decreased as the doping content increased. The Seebeck coefficient and the electrical resistivity decreased with an increase in the Te content. The thermal conductivity was considerably reduced by doping due to electron-phonon scattering and the lattice contribution was dominant over the electronic contribution.

Key words: Thermoelectric, Skutterudite, Doping.

Introduction

Recently, many studies on thermoelectric skutterudites have been reported [1-3] since they satisfy the basic requirements for a high thermoelectric figure of merit, such as a large unit cell, a complex crystal structure, heavy constituent atom masses, highly covalent atomic bonds, a large effective mass, a large carrier mobility, a very narrow band gap, and low electronegativity differences between the constituent atoms [4]. CoSb_3 -based skutterudites are expected to be one of the most promising thermoelectric materials, which can be semiconducting phases by doping and optimizing carrier concentration. Undoped intrinsic CoSb_3 shows p-type conduction at room temperature but some reports have shown that binary CoSb_3 is n-type depending on carrier concentration and stoichiometry, which might originate from residual impurities, phase changes, and being slightly off-stoichiometry [3, 5]. CoSb_3 -based skutterudites are of great interest due to their excellent electrical transport properties and large Seebeck coefficient, and they have the possibility to meet the PGEC (phonon-glass and electron-crystal) concept [6]. Unfortunately, the thermal conductivity of the binary CoSb_3 is too large for thermoelectric applications.

It was found that structural modification of these materials, such as doping with heavy atoms or making a solid solution of skutterudites, greatly improves their thermoelectric properties [7]. The substitution of Co or Sb by dopants can influence the electronic structure and

electrical properties, in particular a substantial change of the carrier masses. Furthermore, it can be expected that doping can affect the lattice thermal conductivity due to enhanced phonon scattering by impurities [8]. It is of great importance to know the relationship between the electronic properties and thermoelectric properties for the selection and optimization of thermoelectric materials. However there have been few systematic studies concerning the doping effects on the thermoelectric properties of CoSb_3 . Although several researchers reported the thermoelectric properties of n-type CoSb_3 doped with different impurities [9, 10], the impurity dependence of the transport and thermoelectric properties is still an important subject to be examined. It is expected that tellurium atoms can act as electron donors (n-type dopants) for CoSb_3 by substituting for antimony atoms. In this study, encapsulated induction melting was employed to prepare Te-doped CoSb_3 skutterudites and their doping effects on the thermoelectric and electronic transport properties were investigated.

Experimental Procedure

Te-doped CoSb_3 skutterudites ($\text{CoSb}_{3-y}\text{Te}_y$; $y = 0.003$ to 0.2) were prepared by encapsulated induction melting (EIM) which is widely used to synthesize homogeneous materials. Elemental 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. Subsequent isothermal annealing was carried out at 773 K for 24 h in a vacuum for homogenization and dopant activation. Phase transformations were analyzed by a high resolution X-ray diffractometer (HRXRD, Rigaku DMAX2500VPC) using $\text{Cu K}\alpha$ radiation (40 kV, 200 mA). Hall effect measurements (Keithley 7065)

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were carried out in a constant magnetic field (1 T) and electric current (50 mA) at 300 K. Hall coefficient (R_H), carrier mobility (μ_H) and carrier concentration (n) were examined. The Seebeck coefficient (α), electrical resistivity (ρ) and thermal conductivity (λ) were measured from 300 K to 700 K.

An ingot with the dimensions of 10 mm (diameter) $\times$ 30 mm (length) was cut to a rectangular-shaped piece with the dimensions of $3 \times 3 \times 10 \text{ mm}^3$ for both Seebeck coefficient and electrical resistivity measurements, and cut to a disc-shaped piece with the dimensions of 10 mm (diameter) $\times$ 1 mm (thickness) for both thermal conductivity and Hall measurements. The Seebeck coefficient and the electrical resistivity were measured by the temperature differential and 4-point probe methods in a helium atmosphere by an Ulvac-Riko ZEM2-M8 equipment. The thermal conductivity ($\lambda = dCD$) was evaluated from the measurements of the thermal diffusivity (D), the specific heat (C) and the density (d) by a laser flash Ulvac-Riko TC7000 system in vacuum.

Results and Discussion

Figure 1 shows the phase analysis result for $\text{CoSb}_{2.8}\text{Te}_{0.2}$

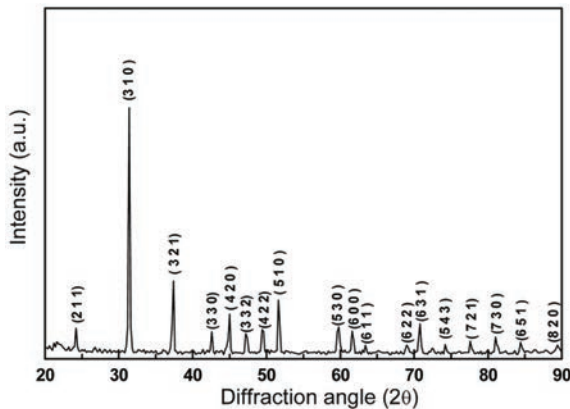


Fig. 1. XRD pattern of $\text{CoSb}_{2.8}\text{Te}_{0.2}$ prepared by encapsulated induction melting and subsequent annealing at 773 K for 24 h.

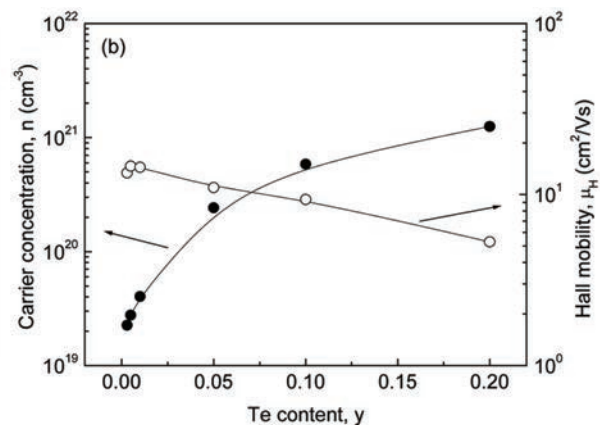
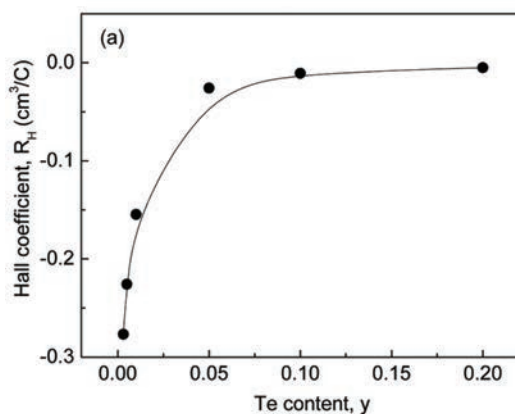


Fig. 2. Variation of electronic transport properties of $\text{CoSb}_{3-y}\text{Te}_y$ with Te doping content at 300 K; (a) Hall coefficient and (b) carrier concentration and mobility.

of the Te-doped CoSb_3 specimens. Single δ -phase was identified in all the specimens and no other secondary phases were detected. This confirms that subsequent annealing at 773 K for 24 h is adequate and sufficient for tellurium atoms to substitute antimony atoms.

Figure 2 indicates the electronic transport properties of $\text{CoSb}_{3-y}\text{Te}_y$ at 300 K. The Hall effect measurements confirmed that all the Te-doped samples showed a negative Hall coefficient, which means n-type conduction. The carrier concentration rapidly increased as the doping content increased. It was found that the Te dopant can affect the electronic structure of CoSb_3 and generate excess charge carriers (electrons). However, the carrier mobility decreased with an increase in the doping content, which indicates that the electron mean free path was reduced by the ionized impurity scattering.

Figure 3 shows the thermoelectric property variation of Te-doped CoSb_3 with carrier concentration at 300 K. The Seebeck coefficient of Te-doped CoSb_3 showed a negative value and it is in good agreement with the Hall coefficient data as shown in Figure 2(a), which means that the major charge carriers of Te-doped CoSb_3 are electrons. The Seebeck coefficient was changed to less negative values as the carrier concentration increased. That is, the absolute Seebeck coefficient decreased with an increase in the electron concentration. The electrical resistivity greatly decreased and saturated to the order of $10^{-3} \Omega\text{cm}$ because the increase in carrier concentration overcame the decrease in carrier mobility. The thermal conductivity decreased with an increase in the carrier concentration, which means that dopants can act as phonon scattering centers. The thermal conductivity ($\lambda = \lambda_L + \lambda_E$) was separated to the lattice thermal conductivity (λ_L) and the electronic thermal conductivity (λ_E) by the Wiedemann-Franz law ($\lambda_E = L T \rho^{-1}$), where the Lorenz number is assumed to be a constant ($L = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$) for evaluation. It was found that the lattice thermal conductivity was dominant in the Te-doped CoSb_3 skutterudites.

Figure 4 represents the thermoelectric properties of $\text{CoSb}_{2.8}\text{Te}_{0.2}$ specimens as an optimized Te-doped CoSb_3 .

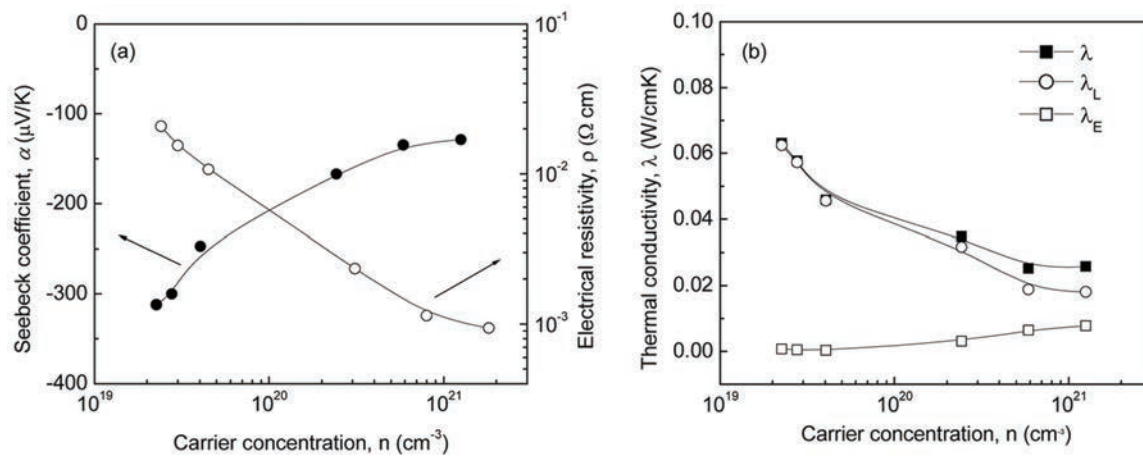


Fig. 3. Variation of thermoelectric properties of Te-doped CoSb_3 with carrier concentration at 300 K; (a) Seebeck coefficient and electrical resistivity and (b) thermal conductivity.

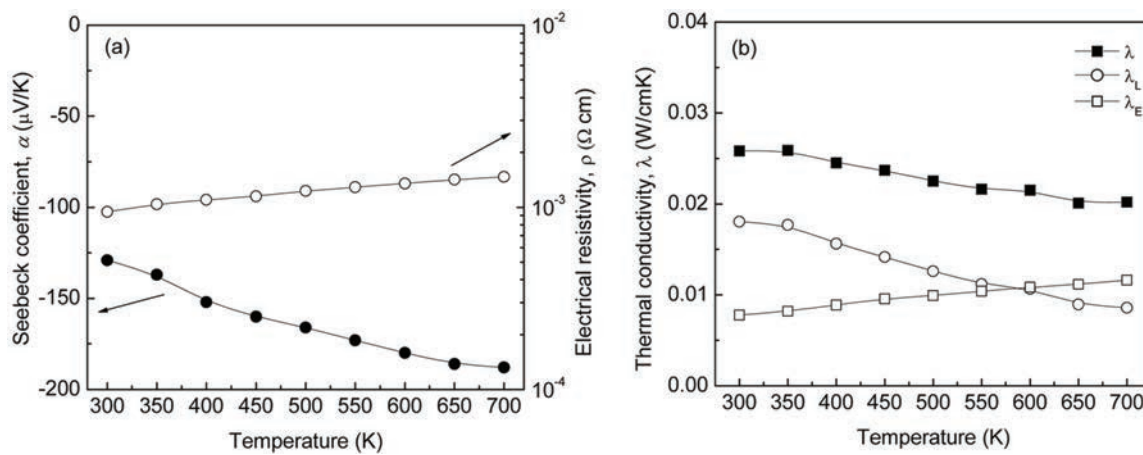


Fig. 4. Temperature dependence of thermoelectric properties of $\text{CoSb}_{2.8}\text{Te}_{0.2}$; (a) Seebeck coefficient and electrical resistivity and (b) thermal conductivity.

Te-doped CoSb_3 showed the n-type conduction at all the temperatures examined. Therefore, Te atoms acted as electron donors by substituting for Sb atoms as expected. The Seebeck coefficient increased more negatively as the temperature increased and it showed $-188 \mu\text{V/K}$ at 700 K. The temperature dependence of the electrical resistivity of intrinsic CoSb_3 has been studied and reported elsewhere [11], and it has been proved to be a non-degenerate semiconductor. The electrical resistivity of undoped CoSb_3 showed a very high value of $10^{-1} \Omega\text{cm}$ at room temperature, but it considerably decreased with an increase in temperature. In this study, it was drastically reduced to the order of $10^{-3} \Omega\text{cm}$ by Te doping, which indicates that the Te atoms were well activated and acted as electron donors. The electrical resistivity of Te-doped CoSb_3 was almost independent of temperature. This is consistent with the result reported by Wojciechowski et al. [8] that Te-doped CoSb_3 skutterudites are degenerate semiconductors and that the electrical resistivity is nearly independent of temperature due to the scattering of charge carriers.

The thermal conductivity is proportional to the phonon

mean free path since a phonon scattering increase gives rise to a decrease in the phonon mean free path. The dopants contribute to the electronic thermal conduction as well as the phonon scattering centers, which decrease the lattice thermal conductivity. The thermal conductivity of intrinsic CoSb_3 was known as about 0.1 W/cmK at room temperature [11], but in this study, the $\text{CoSb}_{2.8}\text{Te}_{0.2}$ specimen showed 0.025 W/cmK , which means that the thermal conductivity can be reduced by doping as well. Substituting Sb with Te should not significantly change the lattice component of thermal conductivity because the atomic masses of Te and Sb are very close. On the other hand, the increase of carrier concentration should result in an increase of the electronic contribution of thermal conductivity. However, calculations based on the Wiedemann-Franz law have shown the electronic contribution in the total thermal conductivity is relatively low as shown in Fig 3(b) and Fig 4(b). Caillat et al. [1] investigated the effects of Te doping on the transport properties of CoSb_3 . They noticed a significant decrease in the lattice thermal conductivity with an increase of the carrier concentration and concluded that this behavior

is mainly the result of electron-phonon scattering.

Conclusions

Encapsulated induction melting was employed to prepare Te-doped CoSb_3 skutterudites and their thermoelectric and electronic transport properties were investigated. Single δ -phase was successfully obtained by encapsulated induction melting and subsequent annealing at 773 K for 24 h. The Hall and Seebeck coefficients confirmed that all the Te-doped CoSb_3 showed n-type conduction. The carrier concentration rapidly increased with an increase in the doping content. However, the carrier mobility decreased with an increase in the doping content since the electron mean free path was reduced by scattering due to the ionized impurity. The Seebeck coefficient was changed to less negative values as the carrier concentration increased. The electrical resistivity greatly decreased because the increase in carrier concentration overcame the decrease in carrier mobility. The thermal conductivity decreased with an increase in the carrier concentration because Te dopants acted as phonon scattering centers. Calculations based on the Wiedemann-Franz law have shown that the lattice contribution in the total thermal conductivity is predominant. It was found that a Te atom is a very effective n-type dopant for CoSb_3 .

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