O U R N A L O F

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Thermoelectric properties of Sn_zCo₄Sb_{11.2}Te_{0.8} skutterudites

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 $Sn_zCo_4Sb_{11,2}Te_{0,8}$ skutterudites with various filling fractions ($0 \le z \le 0.4$) were synthesized by encapsulated induction melting, and their thermoelectric properties were examined from 300 K to 700 K. A single δ -phase was successfully obtained by subsequent heat treatment at 773 K for 5 days. Sn-filled/Te-doped $Sn_zCo_4Sb_{11,2}Te_{0,8}$ showed n-type conductivity at all temperatures examined, which suggests that Te atoms act as electron donors by substituting for Sb atoms. The thermal conductivity was reduced by filling and doping due to impurity-phonon scattering, and the dimensionless figure of merit (ZT) was improved. However, the ZT value decreased when the filling level was $z \ge 0.2$ due to an increase in electrical resistivity and thermal conductivity.

Key words: Thermoelectric, Skutterudite, Filling, Doping.

Introduction

The energy conversion efficiency of thermoelectric devices depends on the dimensionless figure of merit (ZT), which is defined as $ZT = \alpha^2 T \rho^{-1} \lambda^{-1}$, where α is the Seebeck coefficient, ρ is the electrical resistivity, λ is the thermal conductivity and T is the temperature in Kelvin. Thermoelectric materials for applications should have a thermal conductivity as low as a glass and an electrical conductivity as high as a crystal. This concept is known as the PGEC (phonon glass and electron crystal) approach [1]. CoSb₃-based skutterudites have attracted considerable interest in the thermoelectric field because they may satisfy the PGEC concept. CoSb₃ has two large voids (2a positions) in the skutterudite crystal structure, which supports void filling. Many researchers have attempted to fill the voids with rattlers [2, 3] and/or dope them with suitable impurities to reduce the thermal conductivity by introducing phonon scattering centers [4-7]. Void filling not only reduces the lattice thermal conductivity by reducing the phonon mean free path but also changes the electronic properties [8, 9].

The indirect pseudo gap for CoSb₃ according to a local density approximation (LDA) is 0.57 eV, whereas the corresponding direct band gap at Γ is 0.80 eV [10]. This band is due to hybridization of the transition metal, Co, and pnicogen element, Sb. This is evidence of a second band in CoSb₃ skutterudite. Nagamoto *et*

al. [11] synthesized $Co_4Sb_{11.52}Te_{0.48}$ by spark plasma sintering and reported that its thermoelectric properties obey the two band model. This is possible through the high electron concentration of 10^{20} cm⁻³ and the high Seebeck coefficient of -200 μ V/K. In this study, Sn-filled and Te-doped CoSb₃ skutterudites were prepared by encapsulated induction melting, and the effect of filling on the thermoelectric properties were examined.

Experimental Procedure

Sn-filled and Te-doped CoSb₃ skutterudites (Sn_zCo₄Sb_{11.2} $Te_{0.8}$: z = 0, 0.1, 0.2, 0.3 and 0.4) were synthesized by encapsulated induction melting. High purity Co (purity 99.95%), Sb (purity 99.999%), Sn (purity 99.99%) and Te (purity 99.99%) were placed into an evacuated quartz ampoule and melted with an RF electrical power of 7 kW and 40 kHz for 1 h. The ingots were annealed at 773 K for 5 days to allow sufficient time for Sn to fill the voids in the skutterudite structure as well as for dopant activation. The phase was analyzed by high resolution X-ray diffraction (HRXRD: Rigaku DMAX 2500VPC) 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 annealed ingot was cut to dimensions of $3 \times 3 \times 10 \text{ mm}^3$ for both the Seebeck coefficient and electrical resistivity measurements, and to a 10 mm (diameter) × 1 mm (thickness) disc-shaped piece for the thermal conductivity measurements. The Seebeck coefficient and electrical resistivity were measured by temperature differential and 4-point probe methods, respectively, using the Ulvac-Riko ZEM2-M8 equipment in a helium atmosphere. The thermal conductivity was determined by

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measuring the thermal diffusivity, specific heat and density using a laser flash Ulvac-Riko TC7000 system in a vacuum.

Results and Discussion

Fig. 1 shows the XRD patterns of Sn_zCo₄Sb_{11.2}Te_{0.8} skutterudites. The pattern confirmed these materials to be polycrystalline δ -phases according to the JCPDS file No. 19-0336 and were well matched to standard data. The Sn filler position was found to be located at the void site of (0, 0, 0), where the Co site is (0.25, 0.25, 0.25)0.25) and the Sb site is (0, 0.334, 0.157) [12, 13]. The filling fraction limit of the filled CoSb₃ skutterudite was reported by Shi et al. [14] based on the density function method keeping the thermodynamic stability of the filled skutterudite. If the filling fraction exceeds the limit, the unit cell expands and there is a likelihood of an unstably filled skutterudite, which causes the filler to interact with the host materials and form secondary phases. Fig. 1 shows that there are no secondary phases. This confirms that the Sn is located at the void sites, and $Sn_zCo_4Sb_{11.2}Te_{0.8}$ ($0 \le z \le 0.4$) skutterudite is thermodynamically stable.

Fig. 2 shows the Seebeck coefficient of $Sn_zCo_4Sb_{11,2}Te_{0.8}$ skutterudites as a function of temperature. All the specimens have a negative Seebeck coefficient (n-type conductivity) with the Seebeck coefficient decreasing with increasing temperature. The two band model [11] was found to be suitable for explaining the temperature dependence of the Seebeck coefficient. Singh and Pickett [10] reported details on the two band theory for CoSb₃ skutterudite who showed that there is another single band crossing the gap and touching at the conduction band at the minimum G point. This band is due to hybridization of the transition element Co and pnicogen element Sb. Filler Sn and dopant Te are partially responsible for the



Fig. 1. X-ray diffraction patterns of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ skutterudites prepared by encapsulated induction melting and post-annealed at 773 K for 5 days.



Fig. 2. The Seebeck coefficient of $Sn_zCo_4Sb_{11,2}Te_{0.8}$ as a function of temperature.

two band model. The Seebeck coefficient did not change significantly with increasing Sn content but its absolute value was reduced at high temperatures when z = 0.4. The decrease in the absolute Seebeck coefficient was attributed to the bipolar thermoelectric effect. The dopant Te donates electrons, whereas the filler Sn partially contributes to holes. In this situation, the net potential difference is reduced because both electrons and holes move to carry charge and heat simultaneously from the hot side to the cold side of a material. This is due to the opposite sign of the partial Seebeck coefficient and the bipolar conduction [15].

Fig. 3 shows the temperature dependence of the electrical resistivity of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ skutterudites. The electrical resistivity increased with increasing temperature, which confirms the highly degenerate nature of the material. Li *et al.* [7] reported that acoustic phonon scattering is dominant over ionized impurity scattering



Fig. 3. The electrical resistivity of $Sn_zCo_4Sb_{11,2}Te_{0.8}$ as a function of temperature.

0.12



Fig. 4. The thermal conductivity of $Sn_zCo_4Sb_{11,2}Te_{0.8}$ as a function of temperature.

with the substitution of Sb for Te. The electrical resistivity increased slightly with increasing Sn filling content due to the bipolar conductivity.

Fig. 4 shows the temperature dependence of the thermal conductivity of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ skutterudites. The intrinsic CoSb₃ has a much higher thermal conductivity, 0.11 W/cmK at 300 K, which decreases with increasing temperature to 0.074 W/cmK at 700 K [15]. The thermal conductivity was decreased significantly by Sn filling and Te doping. Co₄Sb_{11.2}Te_{0.8} and Sn_{0.1}Co₄Sb_{11.2}Te_{0.8} showed very low values of approximately 0.025-0.03 W/cmK at all temperatures examined. However, when $z \le 0.2$, the thermal conductivity was higher than that of Co₄Sb_{11.2}Te_{0.8} but lower than that of CoSb₃. It is clear that Sn fillers act as rattlers, which decrease the mean free path of phonons and the thermal conductivity. Moreover, doping with Te increases the level of impurity -phonon scattering.

Fig. 5 shows the variation in the dimensionless figure of merit (ZT) with temperature and Sn content in $Sn_zCo_4Sb_{112}Te_{0.8}$. ZT increased with increasing temperature, mainly due to the increase in Seebeck coefficient and low thermal conductivity. The ZT value of the $Sn_zCo_4Sb_{112}Te_{0.8}$ increased considerably compared with the intrinsic CoSb₃. The highest ZT value was observed in the $Sn_{0.1}Co_4Sb_{11.2}Te_{0.8}$ specimen due to Sn filling and Te doping.

Conclusions

 $Sn_zCo_4Sb_{11,2}Te_{0.8}$ skutterudites were prepared by encapsulated induction melting and subsequent isothermal annealing. XRD revealed all samples to be a single δ phase. The effects of Sn-filling and Te-doping on the thermoelectric properties were investigated. Te atoms acted as n-type dopants by substituting for Sb atoms. All specimens showed a negative Seebeck coefficient from 300 K and 700 K. The electrical resistivity increased with increasing Sn content, which is related to the two



Fig. 5. Variation in the ZT with temperature and Sn content in $Sn_zCo_4Sb_{11.2}Te_{0.8}$ oefficient of $Sn_zCo_4Sb_{11.2}Te_{0.8}$ as a function of temperature.

band model and bipolar thermoelectric effect. The thermal conductivity decreased by Sn filling and Te doping. However, it was found that Sn is not an effective filler atom in Te-doped $CoSb_3$ skutterudites, even though it is effective in intrinsic $CoSb_3$.

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