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Thermoelectric Properties of Indium-Added Skutterudites $In_xCo_4Sb_{12}$

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The high-temperature thermoelectric properties of $In_xCo_4Sb_{12}$ ($0.05 \le x \le 0.40$) skutterudite compounds were investigated in this study. The phase states of the samples were identified by x-ray diffraction analysis and field-emission scanning electron microscopy at room temperature. InSb and $CoSb_2$ were found as secondary phases in samples with $x = 0.10$ to 0.40. The filling limit of In into the $CoSb_3$ cages of $In_xCo_4Sb_{12}$ was in the range $0.05 < x < 0.10$. The electrical resistivity, Seebeck coefficient, and thermal conductivity of the $In_xCo_4Sb_{12}$ samples were measured from room temperature to 773 K. The Seebeck coefficient of all samples was negative. Reduction of the thermal conductivity by In addition resulted in a high thermoelectric figure of merit (ZT) of 0.67 for $In_{0.35}Co_4Sb_{12}$ at 600 K.

Key words: Skutterudite, thermoelectric, Seebeck coefficient, electrical resistivity, thermal conductivity

INTRODUCTION

Thermoelectric (TE) materials can be used for energy conversion from heat into electrical power. The efficiency of the energy conversion of TE materials is determined by the dimensionless figure of merit, $ZT = S^2T/\rho/\kappa$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the electrical resistivity, and κ is the total thermal conductivity ($\kappa = \kappa_{lat} + \kappa_{el}$, where κ_{lat} and κ_{el} are the lattice and electronic contributions, respectively).[1–3] The ZT value directly reflects the efficiency of the energy conversion; therefore, the development of high-ZT materials is the main goal in this research area. According to the equation for ZT, large S, low ρ, and low κ are required to maximize ZT. These transport properties are interrelated with each other, so that optimization of these physical properties is required to maximize ZT.[2,3]

Skutterudite compounds are particularly promising candidates for advanced TE materials and have become a focus of lasting interest due to their highly tunable transport properties.[4] Skutterudite compounds have an MX_3 composition with the body-centered cubic structure, where M is a metal atom, such as Co, Rh, or Ir, and X represents a pnictogen atom, such as P, As, or Sb. There are two cages in each unit cell of the structure with sufficient size to accommodate metal atoms and form filled skutterudites. When a third atom is incorporated into the cage, the formula of the compounds becomes RM_4X_{12}, where R is the filling atom that is bonded weakly with the other atoms in the structure. Cage-filling atoms can act as electron donors, so that filling of the cage with various atoms can lead to an optimum electron concentration. These filled atoms also act as phonon scattering centers to significantly reduce κ_{lat}, which can result in improvement of the ZT for skutterudite compounds.[5–7]

$CoSb_3$ is a typical skutterudite that has a very high power factor (S^2/ρ), but a κ_{lat} that is too high. Our group has recently reported the TE properties of Tl- and Ga-filled $CoSb_3$.[8,9] The results indicate that, as the filling ratio of Tl and Ga into $CoSb_3$ is increased, κ_{lat} is significantly decreased, which

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