Thermoelectric Properties of Indium-Filled Skutterudites

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Structural, electrical, and thermal transport properties of $CoSb_3$ partially filled with indium are reported. Polycrystalline samples of $In_xCo_4Sb_{12}$ ($0 \le x \le 0.3$) were prepared by solid-state reaction under a gas mixture of 5% H_2 and 95% Ar. The solubility limit of the indium filling voids in $CoSb_3$ was found to be close to 0.22. Synchrotron X-ray diffraction refinement of the $x = 0.2$ sample showed that the indium is located in the classic rattler site and has a substantially larger thermal factor than those of Co and Sb. The electrical resistivity, Seebeck coefficients, and thermal conductivity of the $In_xCo_4Sb_{12}$ samples were measured in the temperature range of 300−600 K. All samples showed metal-like behavior, and the large negative Seebeck coefficients indicated *n*-type conduction. The thermal conductivity decreased with increasing temperature for all samples. A thermoelectric figure-of-merit (ZT) ≥ 1 (*n*-type) has been achieved when $x \ge 0.2$ in $In_xCo_4Sb_{12}$ at 575 K.

Introduction

Extensive research has been done on skutterudites since they were identified as promising thermoelectrics (TEs) at elevated temperatures about 10 years ago.[1,2] Skutterudites exhibit excellent transport properties, such as extremely high carrier mobilities that are desirable for good TE performance.[3,4] One remarkable feature of skutterudites is that their lattice thermal conductivity can be reduced dramatically by filling the oversized voids with the so-called "rattlers" (Figure 1).[5,6] The filler atoms are weakly bound to the cage and rattle about their equilibrium position as proved experimentally by their large atomic displacement parameters.[7,8] The "rattling" motion of the filler atoms effectively scatters heat-carrying phonons and markedly reduces the lattice contribution to the thermal conductivity.[6] Up to date, a large variety of atoms, including La, Ce, Pr, Nd, Sm, Eu, Yb, Ba, Sr, Ca, Ge, Sn, Pb, Tl, U, Th, and so forth, have been filled into the voids of the skutterudite structure. Both *n*- and *p*-type conduction has been obtained in the partially filled skutterudites. The best known *p*-type skutterudites are the $(La/Ce)_yCo_{4-x}Fe_xSb_{12}$ family of compounds which possess ZT values of ∼1.4 at 1000 K.[5,9] The best known *n*-type skutterudites are probably the $Ba_yCo_{4-x}Ni_xSb_{12}$ family of compounds with ZT values of 1.25 at 900 K.[10]

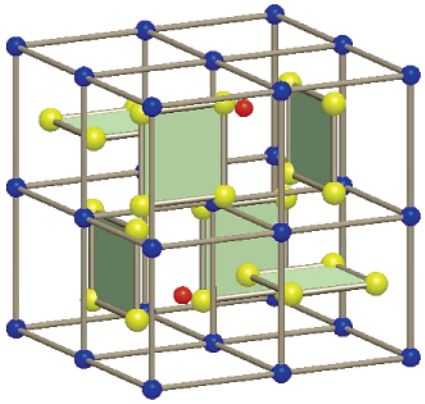

Figure 1. Crystal Structure of $CoSb_3$ showing the large voids with rattlers (red balls). The Co atoms (blue) form the cube, and the Sb_4 atom (yellow) square units are shown.

As most of the research focused on filling the cage of skutterudites with rare earth, alkali earth, or the IVA group elements, only limited work has been reported on other possible filler atoms such as Ag, Cd, and In.[11] Among them, indium containing $CoSb_3$ skutterudite showed large negative Seebeck coefficients. No electrical resistivity or thermal conductivity data were reported. Because indium is of small size (for In^{3+} with a coordination number of 8, its covalent radius is $r = 1.06$ Å), it is possible for indium to go onto the Co site (8c) as well as into the oversized cage site (2a). The smaller size would enable indium to rattle even more if it goes into the cage site. The large negative Seebeck coefficients also indicate possible good TE performance. So

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it would be of interest to evaluate the TE properties of indium containing $CoSb_3$ skutterudite in more detail.

Experimental Section

Polycrystalline samples of $In_xCo_4Sb_{12}$ ($0 \leq x \leq 0.3$) were prepared by solid-state reaction.[12] High purity powders of Co, Sb, and In were mixed thoroughly in a stoichiometric ratio and loaded into an alumina crucible. The powders were calcined at 610 °C for 12 h and then 675 °C for 36 h under a gas mixture of 5% H_2 and 95% Ar. The obtained powders were reground and pressed into 12.8 mm diameter/1−2 mm thick disks. The disks were sintered at 675 °C for 4 h under the same gas mixture and were used for measurements. The average particle size was less than 2 μm, and the densities of the pellets were about 75−80% of the theoretical density.

Powder X-ray diffraction data were collected using a Rigaku automated powder diffractometer, model Miniflex, using Cu Kα radiation. The lattice parameters of $In_xCo_4Sb_{12}$ were refined using the diffraction data over a 2θ range of 10−100°, with 2θ calibrated using tungsten as the internal standard. High-resolution synchrotron X-ray power diffraction data were collected for nominal composition $In_{0.2}Co_4Sb_{12}$. Synchrotron data were collected at beamline 5BMC of the DuPont−Northwestern−Dow Collaborative Access Team at the Advanced Photon Source, Argonne National Laboratory. The sample was ground in an agate mortar, placed in a 0.5 mm glass capillary, and spun at 1 rev/s. The diffracted beam was monitored with a scintillation detector equipped with a Ge ⟨220⟩ analyzer tuned to the incident wavelength of 0.350 26 Å. The chemical compositions of the samples were determined using the ICP (inductively coupled plasma) method.

The electrical resistivities were measured from 300 to 600 K by a standard four-probe technique in a vacuum. Silver paint was used to attach the copper leads to the pellets. The Seebeck coefficient was measured in the same temperature range in a vacuum using a commercial apparatus and constantan as a reference. The absolute uncertainty in both parameters is estimated to be below 5%.[13] The thermal conductivity was determined in Netzsch Laser Microflash with reference material of 1 mm or 2 mm gold-sputtered, graphite-coated Pyrex glass.[14]

Results and Discussion

Powder X-ray diffraction data show that all the $In_xCo_4Sb_{12}$ ($0 \leq x \leq 0.3$) samples crystallize in a cubic $Im\bar{3}$ structure. Figure 2 shows the X-ray diffraction patterns of $In_{0.1}Co_4Sb_{12}$ and $In_{0.3}Co_4Sb_{12}$. The solid-state reactions were carried out below the peritectic melting point of $CoSb_3$ (873 °C); the most common impurity phases of $CoSb_2$ or Sb are not observed in this study. The samples with indium content $x \leq 0.2$ are single phase materials, while the InSb impurity phase starts to appear for samples $In_{0.25}Co_4Sb_{12}$ and $In_{0.3}Co_4Sb_{12}$. This indicates that there is a limit to indium incorporation into the voids of the $CoSb_3$ structure.

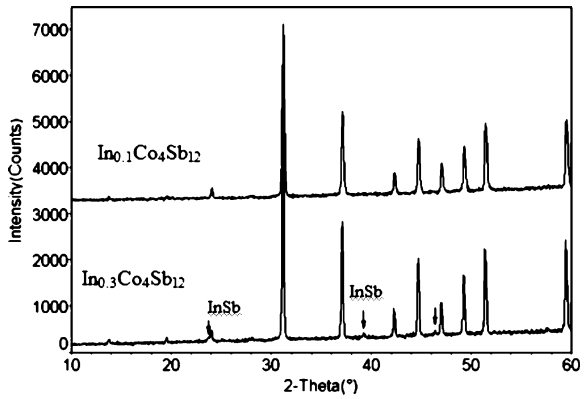

Figure 2. X-ray diffraction patterns of nominal composition $In_{0.1}Co_4Sb_{12}$ and $In_{0.3}Co_4Sb_{12}$. The arrows indicate the InSb impurity phase.

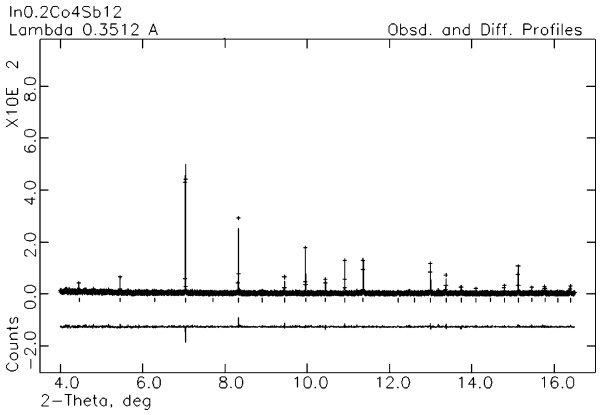

Figure 3. Synchrotron X-ray powder diffraction pattern for $In_{0.2}Co_4Sb_{12}$ at room temperature.

Table 1. Refined Atomic Coordinates and Thermal Parameters for the $In_{0.2}Co_4Sb_{12}$ Composition at Room Temperature[a]

atom	position	occu.	x	y	z	U_{iso} (Å^2 × 100)
Co	8c	1.0	0.25	0.25	0.25	0.35(22)
Sb	24g	1.0	0	0.335 57(31)	0.158 23(29)	0.54(10)
In	2a	0.2	0	0	0	3.6(19)

[a] The refined a lattice parameter is 9.052 94(6) Å. The refined R factors are wRp = 11% and Rp = 8% for 49 reflections fit over the 2θ range 8−23° at a wavelength of 0.3512 Å.

The crystallographic structure for $In_{0.2}Co_4Sb_{12}$ skutterudite was refined by full profile refinement of the synchrotron X-ray powder diffraction data collected at room temperature. Results are shown in Figure 3 and Table 1. Indium is found to be in the classic rattler site and has a much larger thermal factor than those of Co and Sb. No evidence for In substituting at the Co site has been found in the refinement. The thermal factor of indium is comparable to that of thallium in $Tl_{0.22}Co_4Sb_{12}$, which was reported to be 0.05 Å^2 with the thermal factors for Co and Sb both being 6×10^{-3} Å^2.[7]

The compositions obtained by wet chemical analysis (ICP,) and the room-temperature lattice constants of the $In_xCo_4Sb_{12}$ skutterudites are given in Table 2 and Figure 4. The lattice constant of the parent compound $CoSb_3$ ($x = 0$) synthesized under the same condition as the $In_xCo_4Sb_{12}$ samples is 9.0357 Å and agrees well with the reported value

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(13) Various kinds of known materials, such as high purity Co wire, Ni wire, Constantan wire, well-characterized *n*- and *p*-type Bi_2Te_3 pieces, and $YbAl_3$ single crystals, were used to determine the uncertainty of the electrical resistivity and Seebeck coefficient measurements.

(14) The laser flash method has been widely used to measure the thermal conductivity of TE materials. The uncertainties of the thermal diffusivity and specific heat measurement by Netzsch Laser Microflash are below 5 and 7%, respectively. The thermal conductivities of our skutterudite samples had been measured independently by the laser flash method in three different places: DuPont, Thermophysical Properties Research Laboratory, Inc., and Oak Ridge National Laboratory. The results showed repeatability of ±7%.

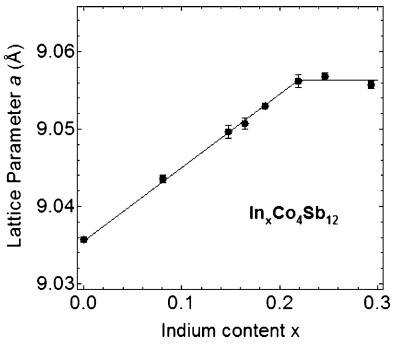

Figure 4. Relationship between the room-temperature lattice constant and the indium concentration in $In_xCo_4Sb_{12}$.

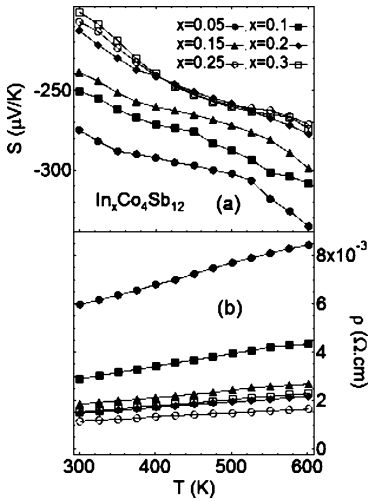

Figure 5. Temperature dependence of (a) the Seebeck coefficients and (b) the electrical resistivities of $In_xCo_4Sb_{12}$.

Table 2. Compositions Obtained by the ICP Tests (Normalizing to Full Sb Occupancy) and the Room-Temperature Lattice Constants of the $In_xCo_4Sb_{12}$ Skutterudites

nominal composition	ICP composition	lattice constant (Å)
Co_4Sb_{12}	$Co_{3.98}Sb_{12}$	9.0357(3)
$In_{0.05}Co_4Sb_{12}$	$In_{0.081}Co_{4.00}Sb_{12}$	9.0436(5)
$In_{0.1}Co_4Sb_{12}$	$In_{0.148}Co_{4.03}Sb_{12}$	9.0497(8)
$In_{0.15}Co_4Sb_{12}$	$In_{0.165}Co_{3.96}Sb_{12}$	9.0507(7)
$In_{0.2}Co_4Sb_{12}$	$In_{0.219}Co_{3.91}Sb_{12}$	9.0562(8)
	$In_{0.246}Co_{4.00}Sb_{12}$	
$In_{0.25}Co_4Sb_{12}$	($In_{0.246}Co_{4.00}Sb_{12}$ + 0.026InSb)	9.0568(5)

of 9.0345 Å for the $CoSb_3$ single crystal.[15] As indium is incorporated into the $CoSb_3$ structure, the unit cell expanded and reached a limit at around 9.056 Å when the indium content was higher than 0.22, indicating a solubility limit of indium in the structure. Because the X-ray diffraction pattern shows an InSb impurity in the sample with nominal composition of $In_{0.25}Co_4Sb_{12}$, this sample may be considered as composed of $In_{0.22}Co_{4.01}Sb_{12}$ and InSb in a 1:0.026 mole ratio.

The temperature dependence of the Seebeck coefficients and electrical resistivity of $In_xCo_4Sb_{12}$ are shown in Figure 5a,b, respectively. The as-synthesized binary $CoSb_3$ is *p*-type and showed a semiconducting behavior. The large negative Seebeck coefficients indicated that indium acts as an electron donor and that filling the voids with indium changes the conduction to *n*-type. The absolute values of the Seebeck coefficients increased with increasing temperature and decreased with increasing indium filling fraction up to $x = 0.2$. The temperature dependence of electrical resistivity is typical of heavily doped semiconductors. The electrical resistivity decreased with increasing indium filling fraction as more electrons are donated to the conduction band. The electrical resistivity of $In_{0.3}Co_4Sb_{12}$ is slightly higher than that of $In_{0.25}Co_4Sb_{12}$ and is probably due to the presence of more of the InSb impurity phase.

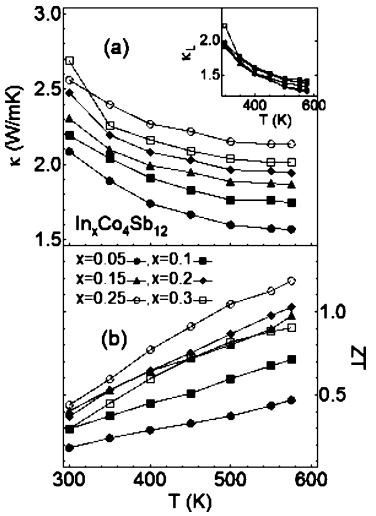

Figure 6. Temperature dependence of (a) the thermal conductivities and (b) ZT of $In_xCo_4Sb_{12}$. The inset of part a shows the temperature dependence of the lattice thermal conductivity of $In_xCo_4Sb_{12}$.

Figure 6a shows the measured thermal conductivities of $In_xCo_4Sb_{12}$ as a function of temperature. The thermal conductivity decreased with increasing temperature and increased with increasing indium filling fraction. When the experimental thermal conductivity, the electrical resistivity values, and the Wiedemann−Franz law, $\kappa_e = L_0T/\rho$ (where L_0 = Lorentz number = 2.44×10^{-8} V^2/K^2) are used, we estimated the lattice thermal conductivity of $In_xCo_4Sb_{12}$, which is shown in the inset of Figure 6a. The lattice thermal conductivities are similar at all indium filling levels, with a value about 2 W/(K·m) at 300 K. The increase in the total thermal conductivity of $In_xCo_4Sb_{12}$ with increasing indium filling fraction is mainly due to the electronic part.

The temperature dependence of the ZT of $In_xCo_4Sb_{12}$ is shown in Figure 6b. The ZT values increased with increasing temperature, and a promising ZT value of ~1.2 was obtained for the nominal composition $In_{0.25}Co_4Sb_{12}$ at 573 K. Low-temperature transport measurements, such as Hall measurement, may provide insight as to why indium filling helps to enhance ZT. To our knowledge, this is the highest ZT value reported for *n*-type $CoSb_3$-based skutterudites at 575 K and needs to be confirmed by measuring its efficiency in a TE power generation device. The TE properties of indium filled skutterudites might be further improved by substituting Ni, Pd, and/or Pt for Co, as these transition metals had been shown to have beneficial effects on *n*-type skutterudite based TEs.[16,17] The multifilling approach may also be promising

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because indium is of small size; a good match with another filler atom could scatter a broader spectrum of the phonon modes and further depress the lattice thermal conductivity. Such studies are in progress and will be reported soon.

Conclusion

Polycrystalline samples of $In_xCo_4Sb_{12}$ ($0 \leq x \leq 0.3$) were prepared, and their electrical resistivity, Seebeck coefficients, and thermal conductivity were measured from 300 to 600 K. All samples show *n*-type conduction indicating that indium was acting as an electron donor. A saturation limit of $x = 0.22$ was found for $In_xCo_4Sb_{12}$. A maximum ZT $\sim$ 1.2 was achieved in the composition $In_{0.25}Co_4Sb_{12}$ at 575 K. Further improvement may be achieved by substituting Ni, Pd, and/or Pt for Co and by the multifilling approach.

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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