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Synthesis and Thermoelectric Properties of In and Pr Double-Filled Skutterudites $In_xPr_yCo_4Sb_{12}$

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Double-filled skutterudites $In_xPr_yCo_4Sb_{12}$, which are currently being investigated for potential applications as thermoelectric materials, have been successfully prepared by inductive melting and annealing. Our results showed that In and Pr double filling effectively improves both electrical conductivity and Seebeck coefficient compared with pristine or single-filled $CoSb_3$, giving rise to a respectable power factor. The largest power factor, 2.33 m Wm^{-1} K^{-2}, was achieved at 609 K for $In_{0.05}Pr_{0.05}Co_4Sb_{12}$; this value is approximately three times that for $In_xCo_4Sb_{12}$ ($x \leq 0.3$) skutterudites. These results imply that In and Pr double filling are better than In single filling for efficient improvement of the thermoelectric properties of $CoSb_3$ skutterudite.

Key words: Thermoelectric materials, skutterudites, thermoelectric properties, power factor

INTRODUCTION

Thermoelectricity has much potential for applications in cooling, heating, power generation, and waste heat recovery. The efficiency of advanced thermoelectric technology is determined by the materials dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where T, σ, S and κ are the absolute temperature, electrical conductivity, Seebeck coefficient, and thermal conductivity, respectively. $CoSb_3$-based skutterudites, which have typical phonon glass and electron crystal properties,[1,2] are believed to have strong potential for thermoelectric application.[3–6] However, their thermoelectric performance is still lower than those of many state-of-art thermoelectric materials, for example PbTe and Bi_2Te_3-based alloys. Two main methods have been proposed and widely used for optimizing the thermoelectric performance of skutterudites. One is to adjust the electrical transport properties, for example carrier concentration, carrier mobility, and carrier effective mass, by doping the crystal structure.[7] The other is to suppress lattice thermal conductivity by introducing extra phonon scattering.[8] Filling the voids of skutterudite crystal structures with other elements provides electrons for the host. The electrons in the shallow donor level can be easily excited, inducing a substantial increase in electron concentration.[9] Furthermore, the guest atoms "rattle" inside these oversized cages and disrupt phonon transport, which significantly reduces lattice thermal conductivity.[8] A large variety of rare earth elements, alkaline earth elements, and other filling atoms have been successfully used to fill the voids of $CoSb_3$-based skutterudites.[10–13] More interestingly, experimental results suggest that double filling of skutterudites results in better improvement of thermoelectric performance than single filling.[5,14–16] In addition, theory also suggests that dual-frequency resonant phonon scattering may induce a significant reduction in the lattice thermal conductivity of double-filled skutterudites.[17] To find the optimum combination of double-filling elements to further improve the thermoelectric properties of $CoSb_3$ skutterudites, we started from indium (In) single-filled skutterudites. Among the vast published work on filled skutterudites, indium (In) single-filled skutterudites have been reported to have excellent thermoelectric properties.[18] We have previously studied the thermoelectric properties of $In_xLu_yCo_4Sb_{12}$ and $In_xNd_yCo_4Sb_{12}$ double-filled skutterudites, and found that double filling of rare-earth elements

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with In was indeed more effective in improving thermoelectric properties than In single filling.[19–21] Pr as the second filling element aroused our interest, because filling the voids of skutterudites with the heavy rare earth element Pr results in much stronger resonant scattering than use of light metal elements, because of the large difference between resonant phonon frequencies for Pr and In. We were, therefore, curious to investigate whether the In and Pr double filling could improve the thermoelectric properties of pristine or In-single-filled skutterudites.

In this work, the effects of In and Pr double filling on the high-temperature thermoelectric properties of $CoSb_3$ skutterudites were investigated. We discovered that electrical conductivity and the Seebeck coefficient can be simultaneously enhanced by Pr and In double filling. The combined effects of In and Pr filling results in a respectable power factor. This study reveals that In and Pr double filling is indeed efficient in improving the thermoelectric properties of $CoSb_3$ skutterudite.

EXPERIMENTAL PROCEDURE

In (99.9999%, shot), Co (99.99%, ingot), Sb (99.9999%, ingot), and Pr (99.99%, ingot) were used as starting materials. Polycrystalline $In_xPr_yCo_4Sb_{12}$ samples were fabricated by inductive melting. The alloys obtained were placed in quartz tubes and the tubes were sealed under vacuum and transferred to a programmable furnace. Annealing was performed at 923 K for 144 h, to homogenize the sample; finally the furnace was cooled to room temperature.

The phase of all the samples was characterized by powder x-ray diffraction (XRD) with Cu Kα radiation. The chemical compositions of the samples were determined by use of an electron probe micro analyzer (EPMA). The high-temperature Seebeck coefficient and electrical conductivity were measured simultaneously by the standard four-probe method (Ulvac-riko: ZEM-3) in Ar atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $In_xPr_yCo_4Sb_{12}$ samples. From Fig. 1 it is apparent that all the main diffraction peaks correspond to the $CoSb_3$ phase. Small amounts of cubic InSb phase are detected by XRD in all the samples. Rietveld refinements were performed on the double-filled skutterudites. The results of these refinements are listed in Table I. The changes in lattice parameter imply that Pr and In enter the cages. EPMA compositions of all the samples are listed in Table I. EPMA revealed that all four constituent elements are present in each grain of the materials investigated. The composition determined by EPMA was used as the actual composition of the filled skutterudite phase.

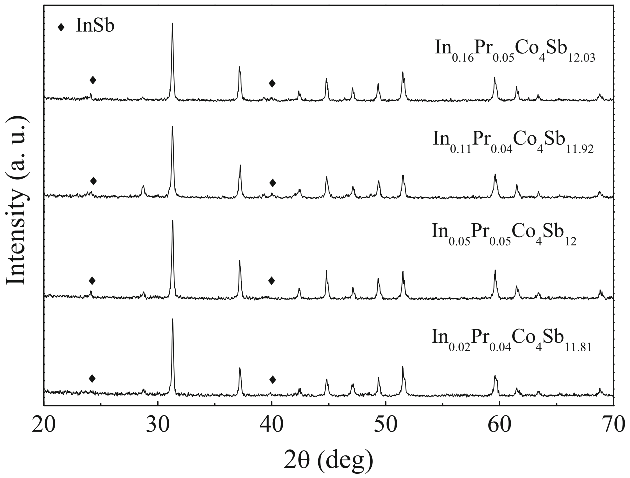

Fig. 1. XRD patterns of $In_xPr_yCo_4Sb_{12}$.

Figure 2 shows temperature dependence of the electrical conductivity (σ) for $In_xPr_yCo_4Sb_{12}$ samples. The gradual reduction in σ of $In_xPr_yCo_4Sb_{12}$ with increasing temperature indicates metallic like behavior, which is in good agreement with the results reported in Ref. 19. In and Pr double filling shifts donor levels toward the conduction band and induces overlapping of the donor levels with the conduction band, giving rise to the metal-like state of $In_xPr_yCo_4Sb_{12}$. It is found that $In_xPr_yCo_4Sb_{12}$ materials have higher σ than $In_xCo_4Sb_{12}$ materials.[13] Among the former series, $In_{0.11}Pr_{0.04}Co_4Sb_{11.92}$ has the largest σ in the temperature range investigated. This may be because of the InSb second phase which is detected by XRD. σ of $In_{0.11}Pr_{0.04}Co_4Sb_{11.92}$ is 11.4×10^4 S/m at room temperature and decreases to 9.1×10^4 S/m at 757 K. σ of $In_xPr_yCo_4Sb_{12}$ is a little lower than that of In and Ba double-filled skutterudites $In_xBa_yCo_4Sb_{12}$.[5] The reduction in σ can be attributed to increasing carrier scattering by heavy atom Pr filling.

The temperature dependence of the Seebeck coefficient (S) for $In_xPr_yCo_4Sb_{12}$ is shown in Fig. 3. The negative S of all samples indicates that electrons are the major carriers. The absolute values of S rise with increasing temperature and reach a maximum value at approximately 660 K. When the temperature enters the intrinsic range of these samples, absolute values of S decrease. The change of S reveals a transition from semimetallic to semiconducting. In the intrinsic range for the samples, electrons are excited by heat transfer from the valence band to the conduction band, giving rise to the same number of holes. The transport contributions of both electrons and holes should be taken into account. Then, S and σ can be expressed as:[22]

$$S = \frac{S_e\sigma_e + S_h\sigma_h}{\sigma_e + \sigma_h} \qquad (1)$$

$$\sigma = \sigma_e + \sigma_h = e(n_e\mu_e + n_n\mu_n) \qquad (2)$$

where e is the electron charge, n the carrier concentration, μ the carrier mobility, and subscript symbols "e" and "h" represent electrons and holes, respec-

Table I. Nominal composition, actual composition (determined by EPMA), and lattice parameter (*a*, Å) of the $In_xPr_yCo_4Sb_{12}$ skutterudites

	EPMA composition				
Nominal composition	**Co**	**Sb**	**In**	**Pr**	**a (Å)**
$In_{0.05}Pr_{0.05}Co_4Sb_{12}$	4.00	11.81	0.02	0.04	9.0351
$In_{0.15}Pr_{0.05}Co_4Sb_{12}$	4.00	12.00	0.05	0.05	9.0379
$In_{0.2}Pr_{0.05}Co_4Sb_{12}$	4.00	11.92	0.11	0.04	9.0366
$In_{0.25}Pr_{0.05}Co_4Sb_{12}$	4.00	12.03	0.16	0.05	9.0408

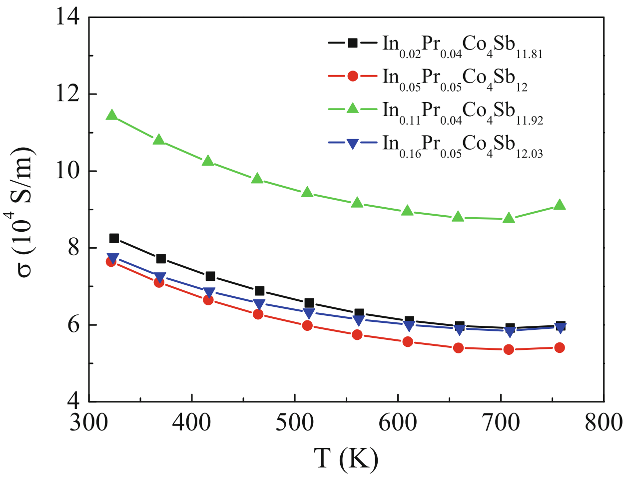

Fig. 2. Temperature dependence of the electrical conductivity (σ) of $In_xPr_yCo_4Sb_{12}$.

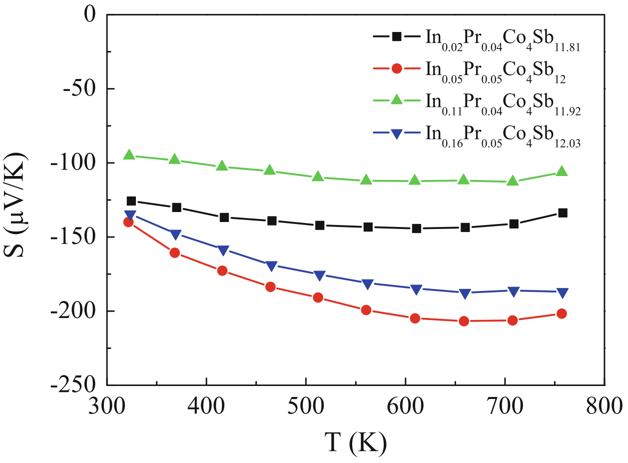

Fig. 3. Temperature dependence of the Seebeck coefficient (*S*) of $In_xPr_yCo_4Sb_{12}$.

tively. Because the contributions of electrons and holes to *S* are opposite, the negative effects of the holes induce the decrease in the absolute values of *S* above a specific temperature, in accordance with Eqs. 1 and 2. Among this series, $In_{0.05}Pr_{0.05}Co_4Sb_{12}$ has the largest absolute value of *S*. The InSb second phase that is dispersed at the boundaries are probably related to the enhanced *S* in $In_{0.05}Pr_{0.05}Co_4Sb_{12}$.

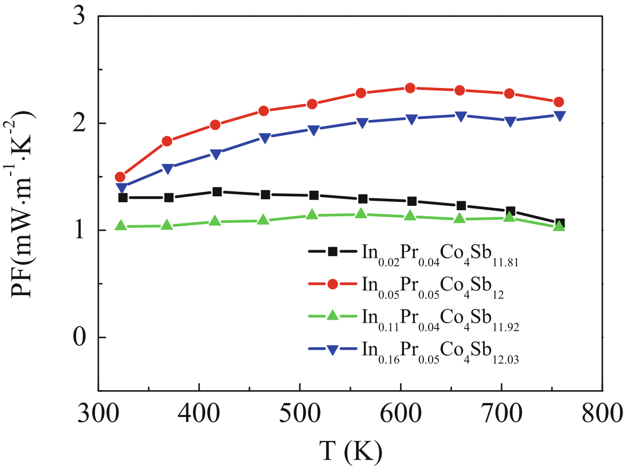

Fig. 4. The calculated power factor (PF) of $In_xPr_yCo_4Sb_{12}$.

The Seebeck coefficient of this material is enhanced to 207 μV/K at 660 K. As reported previously by us, the *S* value of 230 μV/K was achieved at 660 K for $In_{0.09}Nd_{0.03}Co_4Sb_{12.16}$ double-filled skutterudites.[19] The maximum value of 207 μV/K is lower than that of $In_{0.09}Nd_{0.03}Co_4Sb_{12.16}$. This may be explained in terms of the compromise between Seebeck coefficient (*S*) and electron concentration in these materials.[5]

The power factor (PF) calculated by use of the equation $PF = S^2\sigma$ is presented in Fig. 4. Although $In_{0.11}Pr_{0.04}Co_4Sb_{11.92}$ has a higher σ than the other samples, its PF value is quite low because of its low Seebeck coefficient. $In_{0.05}Pr_{0.05}Co_4Sb_{12}$ has the highest PF, because of its high Seebeck coefficient. The largest PF value, 2.33 m Wm^{-1} K^{-2}, is obtained at 609 K for $In_{0.05}Pr_{0.05}Co_4Sb_{12}$; this is approximately three times larger than that of $In_xCo_4Sb_{12}$ ($x \leq 0.3$) skutterudites.[23] This improvement in PF for $In_xPr_yCo_4Sb_{12}$ samples is ascribed to the enhanced electrical conductivity and absolute values of *S*. This work reveals that In and Pr double filling is indeed an efficient way of improving the thermoelectric properties of $CoSb_3$-based skutterudites.

CONCLUSIONS

Double-filled skutterudites $In_xPr_yCo_4Sb_{12}$ have been fabricated by inductive melting and annealing, and their high-temperature thermoelectric properties have been investigated. XRD analysis revealed that all the samples have a single-phase skutterudite structure. The combined effects of In and Pr filling improve both electrical conductivity and Seebeck coefficient, resulting in a respectable power factor. The largest PF value of 2.33 m $\mathrm{Wm^{-1}\,K^{-2}}$ (609 K) achieved for $\mathrm{In_{0.05}Pr_{0.05}Co_4Sb_{12}}$ is approximately three times that of $\mathrm{In_xCo_4Sb_{12}}$ ($x \le 0.3$) skutterudites. Further optimization of skutterudite materials may lead to applications in advanced thermoelectric energy conversion devices and systems.

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