Rapid preparation of In$_x$Co$_4$Sb$_{12}$ with a record-breaking ZT = 1.5: the role of the In overfilling fraction limit and Sb overstoichiometry

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Samples of indium-filled In$_x$Co$_4$Sb$_{12}$ skutterudite were successfully synthesized by conventional induction melting without the use of evacuated quartz ampoules. Addition of In above the filling fraction limit ($x \approx 0.22$) and adjustment of Sb excess in the induction-melted In$_x$Co$_4$Sb$_{12}$ ingots allowed us to suppress formation of the unwanted CoSb$_2$ phase in the sintered samples and effectively control the amount of the InSb impurity phase which precipitated in nanometer-sized regions along the grain boundaries of the main skutterudite phase. Measurements of the Seebeck coefficient, electrical conductivity and thermal conductivity of the In$_x$Co$_4$Sb$_{12}$ samples with nominal In contents $x = 0.2$, 0.6, and 1.0 revealed a simultaneous increase in the electrical conductivity and decrease in the thermal conductivity. This results in the record value of the thermoelectric figure of merit $ZT = 1.5$ for single-filled skutterudites which was attained in the In$_2$Co$_4$Sb$_{12}$ sample at 725 K.

Introduction

Thermoelectric materials (TEs) have attracted much attention due to their environment-friendly applications in power generation and refrigeration. 1,2 Among TEs, skutterudite antimonides have been considered as one of the best materials for applications at intermediate temperatures. 3-5 The specific feature of skutterudites is the existence of interstitial voids in the body-centered cubic (bcc) crystal structure (space group Im3). Filling the voids by guest atoms allows one to greatly reduce the thermal conductivity of skutterudites which in turn significantly enhances the dimensionless thermoelectric figure of merit $ZT$ defined as $ZT = \sigma S^2T/k$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the absolute temperature, and $k$ is the total thermal conductivity. Since the guest atoms strongly reduce the thermal conductivity due to the “rattling effect” 6-7 and, at the same time, can also optimize the carrier concentration, filled skutterudites have been considered as a good example for the support of Slack’s “phonon glass–electron crystal” concept. 8

For undoped Co$_4$Sb$_{12}$, a ZT above unity has been reported for the case of filling by In (ZT$_{\text{max}} = 1.2$), 9-11 Yb (ZT$_{\text{max}} \sim 1.4$), 12-16 Ba (ZT$_{\text{max}} = 1.1$), 17 Na (ZT$_{\text{max}} = 1.25$), 18 and Li (under high-pressure sintering conditions, ZT$_{\text{max}} = 1.3$). 19 Double and triple filling of Co$_4$Sb$_{12}$-based skutterudites has been found to be a very effective approach toward reaching even a higher ZT in these materials due to introduction of several rattling modes into the host material 20 and optimization of the electrical transport properties by adjusting the filling fractions of the guest atoms. 21 Utilization of this approach has allowed one to increase the ZT up to 1.43 in double-filled 12,22-24 and up to 1.7 in triple-filled Co$_4$Sb$_{12}$-based skutterudites. 25-30 Moreover, it has been reported that the ZT approaches 2 in multi-filled skutterudites subjected to severe plastic deformation. 31-33

Due to an intricate picture of phase equilibria in filled antimony-based skutterudites, precipitate phases are usually presented alongside the main phase. For instance, InSb and CoSb$_2$ impurity phases as well as elemental antimony have been frequently observed in In$_x$Co$_4$Sb$_{12}$ skutterudites. 11,13,14,19,31-33 Judging by a number of reports, 36,40-42 the InSb impurity phase formed as in situ nanoinserts can considerably enhance the thermoelectric performance of the host phase due to simultaneous enhancement of its electrical transport properties and suppression of its thermal conductivity. It should be noted however that the concentration of InSb nanoinserts in In$_2$Co$_4$Sb$_{12}$ is limited because the formation of the InSb phase leads to a Sb deficiency which is accompanied by the appearance of the CoSb$_2$ phase.

Other critical issue in the large-scale production of filled Co$_4$Sb$_{12}$-based skutterudites is their preparation methods. Several rapid preparation methods, such as melt-spinning, 13,14 mechanical alloying 41 or microwave sintering, 44 have been proposed for the fabrication of antimony-based skutterudites. Traditional preparation methods consist of several steps, such as melting in a sealed quartz ampoule followed by a long-time annealing, grinding the ingot into powder and its consolidation by spark plasma sintering or hot pressing techniques. 35
Because of the high volatility of Sb, it is a common practice to use sealed quartz ampoules in the fabrication process of antimony-based skutterudites which is inconvenient for the large-scale production of these materials. Here we show that In0.1Co4Sb12 skutterudites can be prepared in large quantities by a conventional induction melting in ordinary Al2O3 crucibles. We also show that the concentration of InSb nanoinclusions in In0.1Co4Sb12 skutterudites can be effectively controlled by the adjustment of Sb excess and addition of In above the filling fraction limit which allowed us to reach the record-breaking value of the ZT in a single-filled In0.1Co4Sb12 skutterudite with a nominal In content x = 1.

**Experimental**

Ingots of In0.1Co4Sb12 skutterudites with nominal In contents x = 0.2, 0.6, and 1.0 were synthesized in a rapid mode by the conventional induction melting technique from elemental In (99.9%, chunks), Co (99.9%, flakes), and Sb (99.995%, chunks). Weighed in desired proportions In, Co, and Sb were melted in an Al2O3 crucible for 2 minutes and quenched in a cooper mold of a cylindrical form. After that, the ingots were annealed at 973 K for 5 hours to improve the chemical homogeneity. The annealed ingots were ground into fine powders by using a Fritsch planetary mill (Pulverisette 7 premium line) using zirconium oxide balls (ϕ 10 mm in diameter) for 5 hours at a revolving speed of 700 rpm. All work with the powders was performed under an Ar atmosphere in a glovebox. The powder was consolidated by using a spark plasma sintering (SPS) Labox 650 machine at 900 K under a pressure of 50 MPa for 10 minutes. The consolidated pellets were cut into a disc (ϕ 12 x 2 mm3) for thermal transport measurement and a slice (2 x 10 x 0.5 mm3) for electrical transport and Seebeck coefficient measurements.

Room-temperature X-ray diffraction (XRD) patterns were collected by using a SmartLab Rigaku diffractometer with CuKα radiation (λ = 1.54 Å) from 2θ = 10° to 2θ = 80° with a step of 0.01°. The structure of the samples was characterized by scanning electron microscopy (SEM, JEOI 6700) in backscattered electron signals. Transmission electron microscopy (TEM) investigations were done on a JEOL JEM1400 microscope operating at 120 kV. Transparent foils for the TEM studies were prepared by Ar ion milling at 5 keV energy at an angle of 3° and final fine milling at 2 keV, 2° glancing angle. The Seebeck coefficient S and electrical conductivity σ were measured independently at the NUST “MISIS” by a 4-probe method using a high-temperature transport measurement system (Cryotel, Co) with an accuracy of 8% for S(T) and 5% for σ(T) and at the Ioffe Institute using the standard DC 4-point configuration for the electrical conductivity measurements and the differential method for the Seebeck coefficient measurements. The thermal conductivity κ was calculated from the thermal diffusivity Dₜ, density ρ and specific heat Cₚ. The thermal diffusivity was measured independently at the NUST “MISIS” by a laser flash method (Netzsch LFA 447) and at ITMO University by using a Xenon flash apparatus Linseis XFA 500. The density of the samples was measured by the Archimedes method. The specific heat Cₚ measured by the differential scanning calorimetry method (Netzsch DSC 204 F1) was found to depend weakly on the temperature and does not exceed 0.22 J g⁻¹ K⁻¹.

**Results and discussion**

**Structural characterization**

The powder X-ray diffraction measurements revealed (Fig. 1) that all the In₀.xCo₄Sb₁₂ (x = 0.2, 0.6, 1.0) samples crystallize in a cubic structure (space group Im3). Analysis of the XRD data indicates that the crystal lattice parameter a slightly increases from a = 0.9041(3) nm to a = 0.9056(8) nm as the nominal In content increases from x = 0.2 to x = 1.0 which is in good agreement with the lattice parameter reported in ref. 38. Considering that the previous reports8-14 showed that the lattice parameter of In₀.xCo₄Sb₁₂ increases and saturates for the In content corresponding to the filling fraction limit, it can be suggested that the In filling fraction limit (~0.22) is reached neither in x = 0.2 nor in the x = 0.6 sample. The results of the EDX analysis confirmed this suggestion, e.g., the real chemical composition of the x = 0.6 sample was found to be In₀.1Co₄Sb₁₂. This implies that some of the In atoms in the x = 0.2 and x = 0.6 samples participated in the formation of the InSb phase or can be presented in the samples in the elemental form. Since no reflections corresponding to a foreign phase were observed in the corresponding X-ray diffraction patterns (Fig. 1), the amount of this phase should be below the XRD resolution limit. Also, taking into account the high vapor pressure of In, it is reasonable to consider that some indium was lost during the induction melting of the ingots.

The impurity InSb phase is clearly observed in the XRD patterns of the x = 0.6 and x = 1.0 samples (Fig. 1). According to the SEM characterization of this sample (Fig. 2), the InSb impurity phase is mainly distributed in nanometer-sized regions along the grain boundaries and in the main skutterudite phase. The real chemical composition of the main skutterudite phase in the x = 1.0 sample was determined to be In₀.15Co₄Sb₁₂₁, i.e., with the In content close to the filling fraction

![XRD patterns of In₀.xCo₄Sb₁₂ (from bottom to top: x = 0.2, 0.6, 1.0). The inset: a part of the XRD patterns showing a shift in the position of X-ray reflections.](image)
The fact that the frequently detected secondary phase of CoSb$_2$ in antimony-based skutterudites$^{34,35,37,38}$ is absent in our samples is presumably due to a rather large, $\sim 10$ wt%, excess of Sb which was added to the nominal composition before melting the ingots. We suggest that such a Sb excess is sufficient to compensate for Sb lost during the induction melting and to participate in the formation of the InSb phase thus preventing the formation of the unwanted CoSb$_2$ phase. The results of the SEM observations indicated that the samples are well consolidated. This is in accordance with the results of the density measurement which showed that the samples have a density of about 98% of the theoretical one.

Shown in Fig. 3 is an example of TEM images taken for the SPS-sintered samples. The average grain size is about 200 nm which is comparable with that reported for In-doped multilled skutterudites$^{32}$ with $ZT = 1.8$ and for SPS-compacted melt-spun ribbons of Yb$_{0.3}$Co$_{4}$Sb$_{12.3}$ with $ZT = 1.3$.13

**Thermoelectric properties**

The temperature dependencies of the Seebeck coefficient $S$ and electrical conductivity for the In$_x$Co$_4$Sb$_{12}$ ($x = 0.2$, 0.6, 1.0) samples are shown in Fig. 4. All samples have a negative Seebeck coefficient ranging from $-200$ to $-260$ $\mu$V K$^{-1}$, indicative of n-type semiconductors. The absolute value of the Seebeck coefficient decreases with increasing $x$ which is common for In-doped skutterudites.$^{34,35,37,39}$ The upturn in $S(T)$ seen near $\sim 580$ K is consistent with the data reported for a series of In$_y$Co$_4$Sb$_{12}$ samples by Li $et al.$$^{37}$ and Visnow $et al.$$^{39}$ and can be ascribed to the onset of bipolar conduction which involves thermal excitations of electrons over the band gap and resulting holes in the valence band. It is interesting to note that the behavior of $S(T)$ in our sample with $x = 0.2$ resembles that reported in ref. 35 and 37 for In$_y$Co$_4$Sb$_{12}$ with a low ($y = 0.05$) indium content. Recalling that the real In content in our samples is significantly smaller than the nominal one, the similarity of $S(T)$ seen in our $x = 0.2$ sample and
in the sample with \( y = 0.05 \) (ref. 35 and 37) can be linked to the dependence of the band gap width on the indium filling fraction.

The electrical conductivity measurements show (Fig. 5) that \( \sigma \) increases with increasing In content which suggests that some of the indium acts as an n-type dopant to increase the carrier concentration. As expected, the highest electrical conductivity is obtained for the sample with the largest nominal In content, \( x = 1.0 \). The decrease of \( \sigma \) with increasing temperature is indicative of heavily doped semiconductors and was previously reported for In-filled skutterudites.\(^{3,31,33}\) The upturn of the electrical conductivity which is clearly seen in the \( x = 0.2 \) sample at \( T \sim 600 \) K and in the other samples at a higher temperature indicates the onset of intrinsic semiconductor behavior. This is consistent with the literature data\(^{3,31,33}\) and our results of the Seebeck coefficient measurements (Fig. 4) which implies that the bipolar conduction is at play at temperatures above 600 K. Considering the absolute value of the electrical resistivity, our data for the \( x = 0.2 \) sample agree quite well with that reported by Sesselmann et al.\(^{35}\) for In\(_{0.25}\)Co\(_{0.75}\)Sb\(_{12}\) with a small In filling fraction \( (y = 0.05) \) (Fig. 5). As for the \( x = 0.6 \) and \( x = 1.0 \) samples, their electrical conductivity is generally lower than the value reported in the literature for In\(_{0.6}\)Co\(_{0.4}\)Sb\(_{12}\) samples with a large In filling fraction.\(^{3,31,33}\) This can be a consequence of the fine grain structure of our SPS sintered samples (Fig. 3) which enhances the charge carrier scattering.

The temperature dependencies of the total thermal conductivity \( \kappa \) and lattice thermal conductivity \( \kappa_L \) of In\(_{x}\)Co\(_{1-x}\)Sb\(_{12}\) \((x = 0.2, 0.6, 1.0)\) are shown in Fig. 6. For the calculation of \( \kappa_\text{L} \), we used the Wiedemann–Franz law assuming that the Lorentz number \( L_0 = 2.45 \times 10^{-8} \text{V}^{-2} \text{K}^{-2} \).\(^{38}\) The thermal conductivity decreases with increasing temperature. In the \( x = 0.2 \) and \( x = 0.6 \) samples \( \kappa \) exhibits an upturn at \( T > 600 \) K which can be explained in the framework of the bipolar conduction scenario caused by the enhancement of the electronic thermal conductivity. Decrease of the thermal conductivity with increasing In nominal content is clearly seen (Fig. 6) which unambiguously shows that the indium filling fraction progressively increases from sample to sample. Generally, the thermal conductivity of all our samples is lower than the reported values of \( \kappa \) in samples with a large In filling fraction\(^{34,35,37,39}\) and is comparable with the thermal conductivity observed in multi-filled skutterudites.\(^{3,31,33}\) We believe that the suppression of the thermal conductivity in our samples is conditioned by several factors. First, the small grain size (Fig. 3) gives a sizable contribution to phonon scattering processes. Second, the InSb impurity phase whose presence is anticipated in the \( x = 0.2 \) and \( x = 0.6 \) samples and clearly seen in the \( x = 1.0 \) samples (Fig. 1) acts as effective formation of the desired InSb nanoinclusions and suppresses appearance of the unwanted CoSb\(_2\) impurity phase.

The temperature dependencies of the dimensionless thermoelectric figure of merit \( ZT \) for the studied In\(_{x}\)Co\(_{1-x}\)Sb\(_{12}\) samples are shown in Fig. 7. Due to the significant reduction of the thermal conductivity, a considerable enhancement of the \( ZT \) is observed for the \( x = 0.6 \) and \( x = 1.0 \) samples. The \( ZT \) markedly increases with increasing nominal In content and the maximum \( ZT \) value of 1.5 was obtained for the In\(_{0.1}\)Co\(_{0.9}\)Sb\(_{12}\) sample at 725 K.

**Conclusions**

In conclusion, we have found that Sb overstoichiometry plays a crucial role in the suppression of the unwanted CoSb\(_2\) secondary phase. On the other hand, Sb excess combined with the addition of In above the filling limit favors the formation of...
InSb nanoscaled precipitates which strongly affect the thermoelectric properties of the samples. Adjustment of the content of the InSb phase allows one to enhance significantly the $ZT$ of the system. For the In$_2$Co$_2$Sb$_2$$_2$ sample with the nominal indium content $x = 1.0$, the $ZT$ reaches 1.5 at 725 K which is the record value for single-filled skutterudite compounds. Moreover, the proposed method of sample preparation without the use of evacuated quartz ampoules is very convenient for the large-scale production of skutterudites with a high thermoelectric performance.

Acknowledgements

The authors gratefully acknowledge the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST "MISIS".

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