Thermoelectric Properties of Pure and In-added $CoSb_3$ Skutterudite Materials

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Abstract
$CoSb_3$ and In-added material with the nominal composition $In_{0.5}CoSb_3$ were synthesized by induction melting, quenching and annealing. The δ-phase of $CoSb_3$ and impurity phases (γ-$CoSb_2$ and $InSb$) were verified by XRD in the In-added samples. TE properties were measured from room temperature up to 700 K. The Seebeck coefficient of $CoSb_3$ is negative at room temperature. At 430 K, it changes its sign and remains p-type at higher temperature. Negative Seebeck values were observed for the three-phase composite of $In_{0.5}CoSb_3$. The temperature dependence of the electrical conductivity shows the semiconductor nature of the samples. The thermal conductivity of $CoSb_3$ decreases with increase in temperature. The lower part of the quenched ingot shows a lower thermal conductivity than the upper part. With In added, the trend of the temperature variation remains the same but the lower section of the ingot shows higher thermal conductivity than the upper, in parallel to a higher In content. The effect of excess addition of the dopant and/or filler element In and of the impurity phases on the figure of merit *ZT* is discussed.

1. Introduction

The importance of clean energy is becoming more urgent and varieties of renewable energies such as wind, solar, geothermal energy etc. have been studied. Thermoelectric energy is a promising source of renewable energy. Still the efficiency of thermoelectric converter modules has to be improved to match the requirements of the market and to compete with the established green energy sources. This is why the search for new TE materials as well as the optimization of existing ones is important. Skutterudite materials have shown very promising TE properties during the last few years, but still have to be improved. Here we study the influence of Indium addition to $CoSb_3$ on the material structure, phase constitution, and TE properties. Binary $CoSb_3$ skutterudites have cubic crystal structure (space group $Im\bar{3}$) with two voids (2*a* positions) at the dodecahedral cage of Sb atoms in the unit cell [1]. It was found that $CoSb_3$ is a semiconductor and its band gap is estimated to be around 0.5 eV at room temperature [2]. $CoSb_3$ is a promising thermoelectric phase but has a low figure of merit due to its high thermal conductivity. Filling the large voids in the skutterudite crystal structure may lead to effective reduction of thermal conduction, thus approximating the phonon glass / electron crystal (PGEC) concept [3]. Many researchers have tried to fill the voids with rattlers [4-6] and/or to dope with suitable impurities to reduce the thermal conductivity by introducing phonon scattering centres [7-8]. The basic criterion for selecting Indium as a filler ("rattler") is that the ionic radius of In (0.8 Å) is considerably smaller than the void radius (1.892 Å). Here we have examined the TE properties with an In concentration of 0.5 according to complete filling of all voids ($In_{0.5}CoSb_3$ = $In_2Co_4Sb_{12}$) although literature results suggest that the filling limit is by far lower [5]. Hence, secondary phases are formed.

From a practical point of view, sometimes it might be difficult to prepare the material phase-pure when it is fabricated on a larger scale. Therefore we have grown the material with high Indium concentration, so that the Indium is only partly incorporated in the skutterudite phase, and the remaining part forms secondary phases. The effect of the impurity phases is reported here.

2. Experimental

CoSb$_3$ and In-filled CoSb$_3$ skutterudites were synthesized by vacuum induction melting. High purity elemental materials of Co (4N), Sb (5N), and In (4N) were sealed in an evacuated quartz ampoule, melted in an RF field for one hour, and passively cooled down. Afterwards the ampoules were heated in a vertical furnace up to 1323 K for 2 hours and quenched in water. The ingots were annealed at 823 K for 144 h for phase homogenization, similarly as previously reported [6]. The annealed ingots were cut to discs of 10 mm $\varnothing$ and 1 mm in thickness (see Fig. 1) for the measurement of Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ). Phase structures were analyzed by X-ray diffractometry (Rigaku DMAX 2500 VPC) using Cu K$_\alpha$ radiation (λ = 1.5406 Å; 40 kV, 200 mA) with a step size of 0.02 deg and a scan rate of 1 deg/min. Morphology was observed using SEM. Seebeck coefficient and electrical conductivity were measured by the temperature differenttial and 4-point probe methods with an accuracy of $\pm$ 5%.
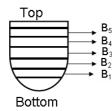

Fig. 1. Schematic of the ingot and sample names

The thermal conductivity ($\kappa = Dc_p\rho$) was evaluated from the thermal diffusivity (D) measured by the laser flash method (LFA 427, Netzsch), specific heat (c_p) by DSC (Netzsch DSC-404), and the sample density (ρ) with an accuracy of $\pm$8%. The TE properties were measured in the range from 300 K to 700 K, and the TE figure of merit was evaluated.

3. Results and Discussion

Figure 2 shows the XRD patterns of the annealed CoSb$_3$ and In$_{0.5}$CoSb$_3$. The samples B1, B3, B5-CoSb$_3$ are polycrystalline and single δ-phase, which was identified with the

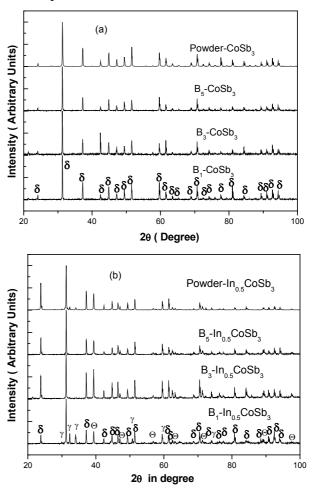JCPDS file No. 19-0336 and well matched with reported data [5, 9].

Fig.2. XRD patterns of pure and In-added CoSb$_3$

Table.1 EDX compositions of the Co-Sb phase(s) of non-doped and In-added CoSb$_3$, at.%

Sample	CoSb$_3$		In$_{0.5}$CoSb$_3$		
	Co	Sb	Co	Sb	In
B1	21.93	78.07	23.89	73.84	2.277
B3	23.37	76.83	23.16	75.40	1.435
B5	22.74	77.26	23.04	75.43	1.522

The XRD patterns of B1, B3, B5 In$_{0.5}$CoSb$_3$ show a polycrystalline mixture containing the δ-phase of CoSb$_3$ and impurity phases (γ-CoSb$_2$ and Θ-InSb). The samples from the bottom part B1, middle part B3 and top part of the ingot B5 have different phase constitution. The bottom part of the ingot contains more InSb as compared to the middle and top part. The high fraction of In was, as expected, resulting in formation of secondary phases. Fig. 3 shows the SEM image of B1-In$_{0.5}$CoSb$_3$ (annealed) which confirms the

presence of δ-$CoSb_3$, γ-$CoSb_2$ and Θ-InSb phase. Energy dispersive X-ray spectroscopy (EDX) results provided compositional data of the Co–Sb phase of all the samples (see Table 1). Notably, the In content is different in different samples, and is higher where also the InSb phase fraction is higher. On the other hand, it could be expected that after long annealing the thermodynamic equilibrium has been reached. Thus, the solubility limit of In in the $CoSb_3$ phase should have been reached in all samples where a separate InSb phase appears [10]. Furthermore, in all of these samples, the In content seems to be higher than the limit of 1.37 at.% known from [5]. Thus we conclude that the larger phase areas in the micrograph (Fig. 3) represent a phase mixture of $CoSb_3$ and $CoSb_2$, where the solubility of In in $CoSb_2$ is higher than in $CoSb_3$. The quenching of the ingot results in a segregation of In in the ingot. Higher In fraction will lead to higher InSb and simultaneously to higher $CoSb_2$ fraction. In the equilibrium, In is incorporated up to its solubility limits both into $CoSb_3$ and $CoSb_2$, respectively, and the latter appears fine distributed in the Skutterudite phase.
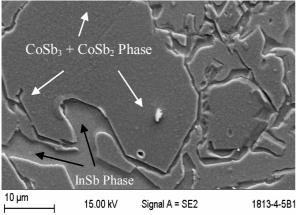
Fig. 3. SEM image of annealed B1-$In_{0.5}CoSb_3$

Figure 4 shows the temperature dependence of the electrical conductivity of the samples B1, B3, B5 of $CoSb_3$ and $In_{0.5}CoSb_3$, resp. B1-$CoSb_3$ has lower electrical conductivity as compared to B3 and B5-$CoSb_3$, simultaneously to a lower Co:Sb ratio (see Tab. 1). The temperature curves are nearly identical except a constant factor. B3 and B5-$CoSb_3$ have nearly equal conductivity. The electrical conductivity of all samples increases with temperature (much stronger for $CoSb_3$ than for $In_{0.5}CoSb_3$) showing semiconducting behaviour.
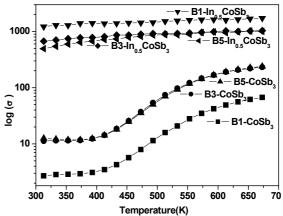
Fig. 4. The temperature dependence of the electrical conductivity (σ) of $CoSb_3$ and $In_{0.5}CoSb_3$

There is a rise in electrical conductivity for the $CoSb_3$ samples onsetting at about 420 K which is probably due to the activation of holes [11]. Among the $In_{0.5}CoSb_3$ samples, B3 and B5 have somewhat lower conductivity than B1. A content of In higher by about 50% (Tab. 1) has led to an increase of the electrical conductivity by about 10%.
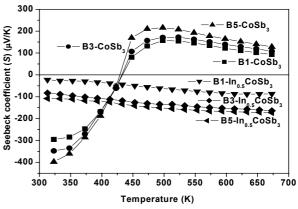
Fig. 5. The temperature dependence of the Seebeck coefficient (S) of $CoSb_3$ and $In_{0.5}CoSb_3$

Fig. 5 shows the Seebeck curves over temperature of all the samples. All $CoSb_3$ samples are n-type at 300 K and change to p-type nearly at the same temperature of 430 K. B5 and B3 have a higher amount of Seebeck coefficient than B1, both in the p-type and n-type region. Like for the electrical conductivity, the deviation between the samples may be described by a constant factor. Details of the p/n transition are discussed

elsewhere [4]. The increase in electrical conductivity over temperature and the sign change of the Seebeck coefficient imply that high temperature conduction in $CoSb_3$ is carried out mainly by mobile holes. Near 430 K the hole contribution becomes larger than the electron conductivity.

B5 and B3 $In_{0.5}CoSb_3$ have a higher Seebeck coefficient than B1, simultaneously to a lower electrical conductivity. The amount of the Seebeck coefficient increases with temperature and remains negative over the investigated temperature range. This confirms the n-type nature of the In-added $CoSb_3$ which is the thermoelectrically best of the involved phases. The addition of In contributes to the electron concentration whereas no direct evidence on the lattice position where In is incorporated can be given. In the light of previous discussion on the microstructure, saturation of the $CoSb_3$ phase with In can be expected. Accordingly, equal TE properties of this phase are assumed in all samples of the In-added material. Thus the effect of the secondary phases is mainly to significantly reduce the Seebeck coefficient but increase the conductivity, as would be caused by a metallic phase. From pure $CoSb_2$, both low electrical conductivity and Seebeck are known [12]. However, we have concluded on a significant content of In solved in $CoSb_2$ which may increase its conductivity [13]. From the morphology, InSb as occurring in elongated domains surrounding the thermoelectrically active phase is more probable to effectively short-circuit the thermo-power of the composite, rather than $CoSb_2$ which is fine distributed in small seemingly compact-shaped domains.

Fig. 6 shows the thermal conductivity of the $CoSb_3$ and $In_{0.5}CoSb_3$ samples, respectively. B1-$CoSb_3$ has a lower thermal conductivity compared to B3 and B5. In the light of the lowered Co:Sb ratio, it could be suggested that Sb precipitations would reduce the thermal conductivity. All temperature curves show the typical shape of lattice thermal conductivity, decreasing with temperature. The bottom part of $In_{0.5}CoSb_3$ has a significantly higher thermal conductivity

compared to the other samples because of the high content of InSb phase. The thermal conductivity of InSb is much higher than $CoSb_3$ [11]. By chance, the thermal conductivity of B3, B5-$In_{0.5}CoSb_3$ is close to that of B3, B5-$CoSb_3$. However, due to the presence of the InSb phase in the composite, the In-added $CoSb_3$ phase will have a lower thermal conductivity than the effective value. Thus we have indirect evidence on the reducing effect of In addition on κ.

Figure 7 shows the temperature dependence of the dimension-less figure of merit of $CoSb_3$ and $In_{0.5}CoSb_3$. $CoSb_3$ shows a low figure of merit of $ZT_{max} = 0.08$ at 673 K whereas $In_{0.5}CoSb_3$ reaches 0.53 at 673 K.
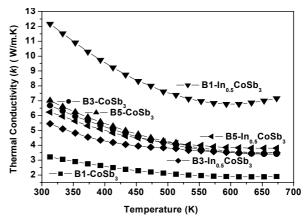

Fig. 6. Temperature dependence of the thermal conductivity (k) of $CoSb_3$ and $In_{0.5}CoSb_3$

In the case of $In_{0.5}CoSb_3$ the excess of indium contributes to the electron density and causes increase of the electrical conductivity as well as lowers the Seebeck coefficient.
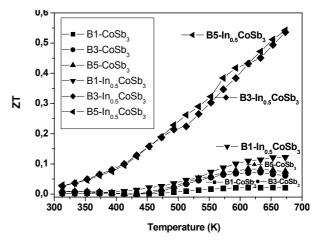

Fig. 7. Temperature dependence of ZT of $CoSb_3$ and $In_{0.5}CoSb_3$

The γ-CoSb$_2$ and Θ-InSb have a lower Seebeck coefficient compared to the δ-CoSb$_3$ phase. Due to the large fraction of secondary phases, the net Seebeck coefficient is reduced [12]. Pure CoSb$_3$ samples have a lower thermal conductivity as compared to B1-In$_{0.5}$CoSb$_3$. The bottom part of the CoSb$_3$ ingot contains more Sb than other parts. The secondary phases and high indium content have affected the thermal conductivity of In$_{0.5}$CoSb$_3$ in a controversy manner. The thermal conductivity is mainly representing the lattice contribution.

Since other studies report to have achieved void filling by the same preparation route as was applied here, we assume to have reached the filling limit by In although no direct evidence by structural analysis was obtained. Despite of a quite high contents of secondary phases, quite moderate to good values of the figure of merit ($ZT = 0.53$) were achieved in the middle and top part of In$_{0.5}$CoSb$_3$. Hence the main practical outcome of this study is that slightly exceeding the solubility limit of In by the added amount would probably not critically reduce the achievable performance.

4. Conclusions

CoSb$_3$ and In-added CoSb$_3$ were prepared by vacuum induction melting. Structural characterization by XRD revealed that CoSb$_3$ is occurring in the δ phase. Material with In added (nominal composition of In$_{0.5}$CoSb$_3$) contains a lot of secondary phases (γ-CoSb$_2$ and Θ-InSb). The SEM results indicated the presence of clearly separated phase domains of Co-Sb and Θ-especially with the Co–Sb phase mainly consisting of CoSb$_3$ and fine-distributed CoSb$_2$ where both phases contain dissolved In up to the solubility limit. Undoped CoSb$_3$ shows n-type conductivity at 300 K and a sign change at 430 K where the material becomes p-type up to high temperature whereas In-doped CoSb$_3$ is n-type. Electrical conductivity and thermal conductivity increase with increasing In content. ZT was considerably enhanced by the In addition. The maximum achieved value of ZT is 0.53 indicating that moderate content of secondary phases induced by In excess will not worsen TE performance too much.

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