

Physical Properties of Semiconductors Used For Renewable Energies

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Abstract. In the last several decades many research are focused towards renewable energy sources among this sources there is the thermoelectricity which generated by thermoelectric materials. Thermoelectric materials is one of the most promising source of renewable energies. It's based on the conversation of waste energy to useful one. This work will focus on the enhancement of advanced thermoelectric materials CoSb₃ were prepared bay hot pressed and characterized by X-ray. Thermoelectric characterization was done through measurements of the electrical and thermal conductivities as well as the Seebeck coefficient between room temperature and 750K. All samples had p-type conductivity. The dimensionless thermoelectric figure of merit ZT increases with increasing temperature and reaches a maximum value of 0.15 at 750K.

Keywords: skutterudite, electrical conductivities, thermal conductivities, Seebeck coefficient, figure of merit ZT.

1. Introduction

Skutterudites are known as excellent thermoelectric (TE) materials because they can be produced easily and fast from cheap starting materials, they can be used in a wide temperature range and besides an excellent TE quality they also show stability and a good mechanical performance. The quality of every TE material is represented by the dimensionless figure of merit ZT. Among the filled skutterudites based on CoSb₃ high $ZT = \alpha^2 \sigma T / \lambda$, where α is the Seebeck coefficient, σ the electrical conductivity, and λ the thermal conductivity and T the absolute temperature.

The aim of the present work has therefore been to characterize the semi-conductor compound CoSb₃ filled with Sn Fe and prepared by hot-pressing between room temperature and 443 K. The characterization has been done via electrical and thermal measurements of the Seebeck coefficient. The results are discussed in terms of the optimal figure of merit of the material.

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2. Experimental procedure

Sample preparation—nearly single phase, polycrystalline samples of CoSb₃ doped with 1 at.% of Fe and 1 at.% of Sn were prepared. First, stoichiometric amounts of cobalt (99.998% pure), antimony shots (99.999% pure), iron powder (99.998%) and pewter shots (99.999%) were melted in sealed quartz ampoules. The melts were held at 1323 K for about 48 h for homogenization and quenched in water. Resulting ingots were ground in an agate mortar and analyzed by X-ray diffractometry (XRD). The powders were then sieved and only grains with a size of 100 μm or less were retained for further processing. The presynthesized powders were then hot-pressed into cylindrical samples. The hot pressing was conducted in graphite dies. The temperature and pressure of hot pressing were 943 K and 100 MPa. The samples (~12 mm in diameter and ~2 cm long) were crack-free and of good mechanical strength. XRD analyses were performed on a Siemens D-500 diffractometer using Cu K radiation with silicon as a standard. The chemical composition of the samples was analyzed by electron probe microanalysis (EPMA) that was performed using a CAMECA SX 50 electron superprobe. The standards used for composition analysis at the 1% level wavelength dispersive measurements were Co, Sb, Fe, and Sn. Samples about 1 mm thick and 12 mm in diameter were cut from the hot-pressed specimens (perpendicular to the hot pressing direction). They were then mechanically polished (0.25 μm) and ultrasonically cleaned in acetone.

Samples characterization

This was done through measurements of the electrical and thermal conductivities as well as the Seebeck coefficient between room temperature and 873 K. The electrical resistivity (ρ) was measured Using the Van der Pauw technique with a current of 100 mA using a special high temperature apparatus [5]. The Seebeck coefficient (α) of the samples was measured on the same samples as used for resistivity measurements using a high temperature light pulse technique [6]. The error of measurements of the Seebeck coefficient was estimated to be less than $\pm 1\%$. The thermal conductivity (λ) of the samples was calculated from the measured density, heat capacity and thermal diffusivity values. The thermal diffusivity was measured using a flash diffusivity technique [7]. The heat capacity (C) was measured on several samples using a PerkinElmer differential scanning calorimeter under argon atmosphere and using sapphire as the reference standard. The mass of samples was ~60 mg and a heating rate of 5 K min⁻¹ was employed. The overall error in the thermal conductivity value was at about $\pm 10\%$.

3. Results and discussion

We have measured the lattice parameter of Sb_{72.5}Co₂₅Sn_{2.5} hot-pressed samples by X-ray diffraction and it's equal to 9.0392 Å. The literature value of CoSb₃ is 9.036 Å [8]. The small augmentation in the lattice constant may indeed indicate that the atomic radius of Sb. However this could be due to only for the Sn substituting, it may be due to the uncertainty in the measurement of the lattice constant

The XRD profile of Sb_{72.5}Co₂₅Sn_{2.5} hot- pressed is showing in figure (1). No broadening or shift of Bragg peaks can be seen, thus revealing that the skutterudite phases are well crystallized and homogeneous

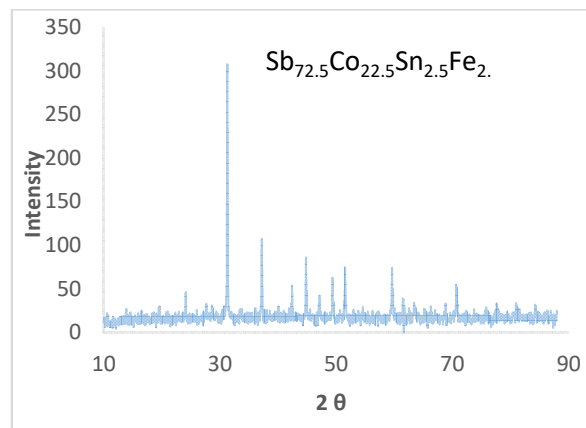


Fig 1 XRD profiles of p-type $\text{Sb}_{72.5}\text{Co}_{22.5}\text{Sn}_{2.5}\text{Fe}_{2.5}$

Back-scattered electron image of the hot pressed sample surface is shown in Fig. 2. The start composition of this sample is $\text{Co}_{23.87}\text{Sb}_{73.88}\text{Pd}_{1.125}\text{Se}_{1.125}$. Punctual analysis realized on the surface equal to $25 \mu\text{m}^2$ shows that the actual average composition (at. %) of the matrix is $\text{Sb} = 73.8625 \pm 0.2315$, $\text{Co} = 23.9125 \pm 0.1934$, $\text{Fe} = 1.0894 \pm 0.079$, $\text{Sn} = 0.9542 \pm 0.0965$, and of the dark points is $\text{Sb} = 97.5341 \pm 0.2065$,

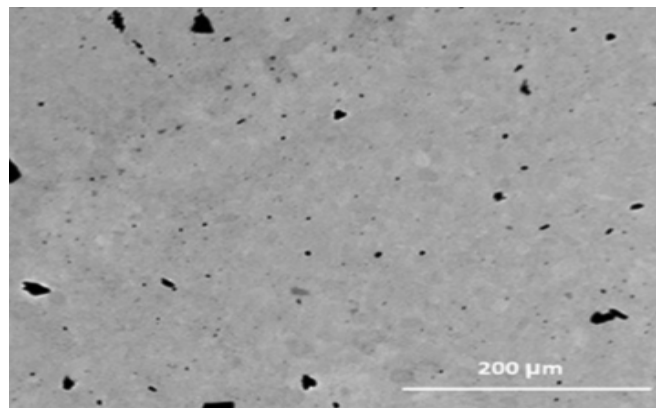


Fig 2: Back scattered image of the hot-pressed sample

From Figs (3) and (2), the electrical conductivity σ has decreased a dissimilar to that of α as a function of the temperature. The reason for the increase in the conductivity with the temperature is not the decrease in carrier concentration. It is an increase in the electron scattering rate due in part to the increased electron-phonon scattering at high temperature.

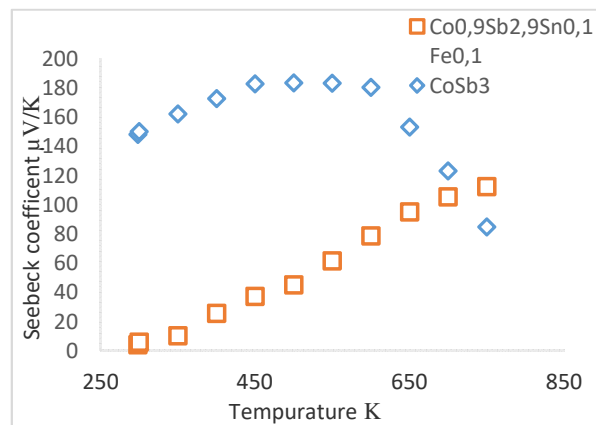


Fig.3 The values of Seebeck coefficient as function of the temperature for P-type $Sb_{72.5}Co_{22.5}Sn_{2.5}$

The result of thermal conductivity λ are presented in Fig (4). They vary between 3.8 and 3.31 W/mK. The thermal conductivity is the sum of an electron contribution (λ_e), a bipolar diffusion (λ_B) and a lattice thermal conductivity (λ_L).as the lattice thermal conductivity decreases with the increasing content of Sn. The thermal conductivity of p-type skutterdute ($Sb_{72.5}Co_{22.55}Sn_{2.5}Fe_{2.5}$) is lower than the thermal conductivity of $CoSb_3$. This reduction of lattice thermal conductivity (λ_L) can be attributed to that Sn and Fe would enter the compound substitutionally replacing Sb and Co respectively [1, 2].

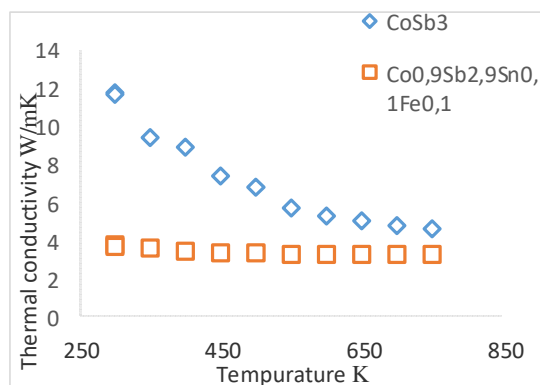


Fig. 4 Thermal conductivity as function of the temperature for P-type $Sb_{72.5}Co_{22.55}Sn_{2.5}Fe_{2.5}$

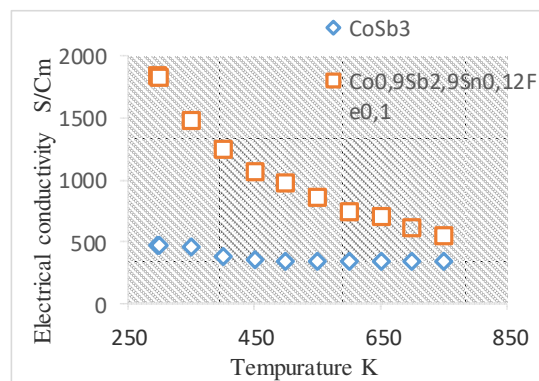


Fig.5 the electrical conductivity as function of the temperature for P-type $Sb_{72.5}Co_{22.55}Sn_{2.5}Fe_{2.5}$

From the three result obtained for the three transport properties, we calculated the dimensionless figure of merit ZT for our samples in the temperature range 300 -750 K. The CoSb₃ samples presents a maximum ZT value at 610 K close to 0.12. The maximum ZT value of $Sb_{72.5}Co_{22.55}Sn_{2.5}Fe_{2.5}$ samples is equal to 0,15 at 750 K. in the literature, the maximum ZT value is equal to 0.58 at 673 K for a P-type $In_{0.16}Co_4Sb_{11.95}Ge_{0.05}$ [4].Mi and al[3] have found ZT= 0.16 at 610 K for P-type $Fe_{0.375}Ni_{0.375}CO_{0.25}Sb_3$

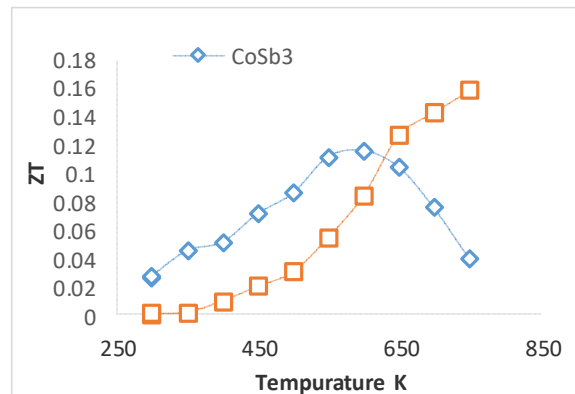


Fig.6 variation of the dimensional figure of merit ZT as function of the temperature for P-type $Sb_{72.5}Co_{22.55}Sn_{2.5}Fe_{2.5}$

Conclusion

Through this study we demonstrate that the CoSb₃ filed with Sn concentration in our samples not only enhance the power factor due to a better hole doping effect but also decrease the thermal conductivity. Positive sing of Seebeck coefficient confirm the dominate role of hole in the compound the figure of merit was enhanced only slightly this enhancement is primarily due to a reduction in thermal conductivity caused by a small portion of Sn and Fe filling into the voids.

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