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Optimization of Thermoelectric Properties of $CoSb_3$ by Donor Doping

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Abstract

Cobalt triantimonide $CoSb_3$ is a narrow-band semiconductor with very promising chemical and transport properties which make it a potential candidate for high-temperature thermoelectric applications. The work presents the results of theoretical investigations concerning optimization of concentration of donor carrier *n* in order to receive maximum value of thermoelectric figure of merit *ZT*.

Keywords: Thermoelectric material, Semiconductor, Electrical properties, $CoSb_3$

OPTYMALIZACJA WŁAŚCIWOŚCI TERMOELEKTRYCZNYCH $CoSb_3$ POPRZEZ DOMIESZKOWANIE DONOROWE

Trójantymonek kobaltu $CoSb_3$ jest półprzewodnikiem o wąskim paśmie wzbronionym i bardzo obiecujących właściwościach chemicznych i transportowych, które czynią go potencjalnym kandydatem w przypadku wysokotemperaturowych zastosowań termoelektrycznych. Praca przedstawia wyniki badań teoretycznych dotyczących optymalizacji stężenia nośnika donorowego *n* w celu otrzymania maksymalnej wartości współczynnika dobroci termoelektrycznej *ZT*.

Słowa kluczowe: materiał termoelektryczny, półprzewodnik, właściwości elektryczne, $CoSb_3$

1. Introduction

$CoSb_3$ is a member of a large family of compounds with the skutterudite structure, which has been recently identified as a potential new material for thermoelectric applications. Skutterudites, especially of *n*-type conductivity, are subjects of interest due to their excellent electrical transport properties and large Seebeck coefficient α. Unfortunately, thermal conductivity of the binary skutterudites is too large for thermoelectric applications. It was found that structural modification of these compounds, *i.e.* doping them with heavy atoms or making mixed crystals of skutterudites greatly improves their thermoelectric properties [1-7].

Binary skutterudite compounds AB_3, (where A = VIIIB group metals and B = P, As, or Sb) crystallize in a body centered structure (Im3 space group) consisting of a simple cubic array of A atoms at the (8g) crystallographic site of the unit cell. Each one of those atoms is surrounded by octahedra of B atoms (24g). The unit cell contains 2 large structural vacancies (in site 2a) which can be "filled" by heavy rare-earth atoms as Ce [2, 6, 7], La [4], or Yb [1] (Fig. 1). Such filled skutterudites exhibit lower thermal conductivity due to enhanced phonon scattering. While void filling can produce a strong reduction in the thermal conductivity λ, the substituting antimony with metals or semimetals as Sn, Se, Te, can influence the electronic structure and increase carrier concentration and electric conductivity of the material. Furthermore, it is suggested that an increase in carrier concentration can be very effective in reducing the lattice thermal conductivity due to enhanced phonon-electron scattering.

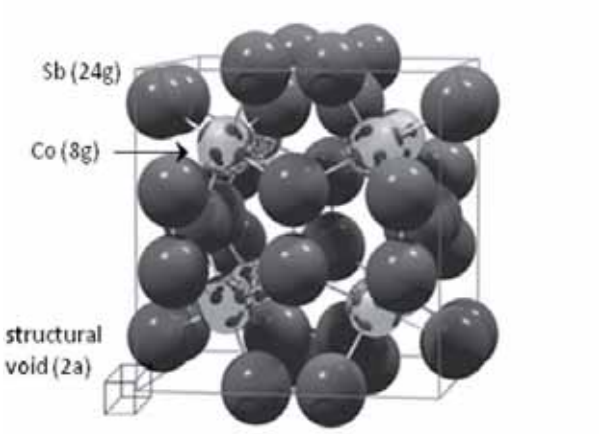

Fig. 1. The unit cell of the $CoSb_3$ skutterudite structure (s.g. Im3).

It was shown in previous theoretical and experimental works that donor doping (*e.g.*, by substitution of Sb by Te or Se; Co by Ni, Pt, Pd or filling the void in position 2a, *e.g.*, by lanthanides or alkaline elements) leads to the increase of efficiency in energy conversion [5-6].

1.1. Donor doping of $CoSb_3$

The thermoelectric efficiency of materials is usually assessed by their dimensionless thermoelectric figure of merit *ZT*:

$$ZT = \alpha^2\sigma\lambda^{-1}T, \quad (1)$$

where *T* is temperature, α – Seebeck coefficient, λ – thermal conductivity, σ – electrical conductivity of a material. The Bi_2Te_3 and Sb_2Te_3 alloys with maximum value of $ZT_{max} = 1$ at temperature of about 500 K were considered to be the best TE materials for quite a long time and still are commonly used for the production of thermoelectric elements and devices for thermoelectric cooling and power generation [8].

Pure, undoped single crystals of $CoSb_3$ exhibit the maximum *ZT* value of about 0.2 at 700 K. Relatively low *ZT* values are the consequence of too low electrical conductivity σ resulting from non-optimal concentration of current carries *n* in this material. An increase in carrier concentration usually leads to the increase of both electrical σ and thermal conductivity λ and simultaneous decrease in thermopower values α.

For particular carriers concentration n_{opt} the term $\alpha^2\sigma\lambda^{-1}$ in Eq. 1 reaches maximum (see Fig. 2 for illustration).

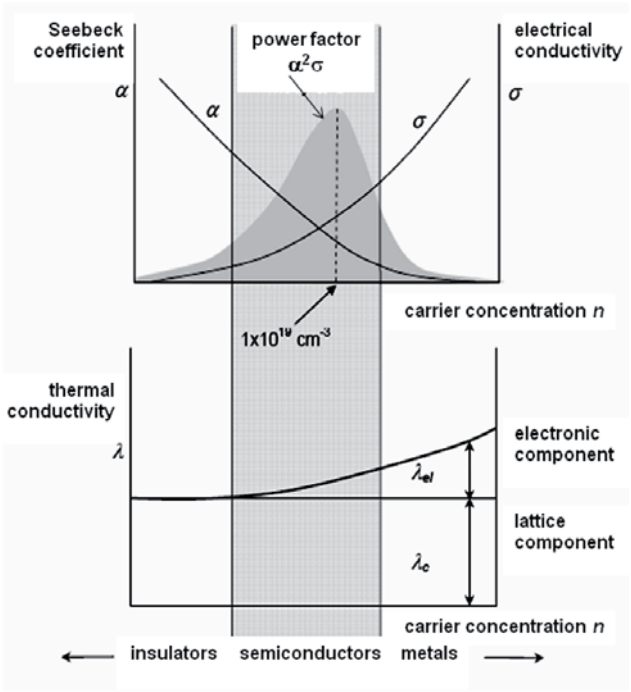

Fig. 2. The schematic diagram showing the dependence of basic thermoelectric parameters vs. carrier concentration.

The aim of present work was to determine the optimal concentration of donor carrier in order to gain the maximum value of thermoelectric figure of merit ZT and comparison of obtained theoretical results with previously received experimental data for Te and Se doped $CoSb_3$.

2. Experimental

The materials were prepared by direct reaction of the elements: cobalt, antimony, selenium, and tellurium. The detailed preparation is described in previous papers [6-7]. Microscopic observations on polished and fractured surfaces of the samples revealed that the resulting polycrystalline materials, in range solubility of donor elements of Te and Se were single-phased, and had a uniform microstructure. The samples contained well-formed grains with sizes ranging from 2 to 10 μm. The measured densities were found to be of about 98.0-99.8 % of the theoretical density of $CoSb_3$.

The measurements of the thermal conductivity λ, electrical conductivity σ and Seebeck coefficient α were carried out over temperatures ranging from 76 to 540 K at steady–state conditions in a heat radiation-shielded vacuum probe. The Hall coefficient was measured using low frequency (7 Hz) AC sample current in a constant magnetic field of 0.705 T at room temperature. The carrier concentration was calculated from the Hall coefficient, assuming a Hall scattering factor equal to 1.0.

Results of Seebeck and Hall coefficient measurements show that all the samples, including undoped $CoSb_3$, exhibit the *n*–type behaviour. Electrical conductivity results confirm that materials are narrow band-gap semiconductors. Table 1 contains selected results of measurements.

Table 1. Physical properties of Te- doped $CoSb_3$ at 300 K.

T=300 K			
n [cm^{-1}]	α [μVK^{-1}]	σ [$S \cdot m^{-1}$]	λ [$Wm^{-1}K^{-1}$]
$2.5 \cdot 10^{18}$	-442	3356	9.0
$7.3 \cdot 10^{18}$	-380	7825	8.6
$2.2 \cdot 10^{19}$	-349	28577	9.3
$9.1 \cdot 10^{19}$	-255	57014	8.2
$2.5 \cdot 10^{20}$	-220	108516	5.1
$4.5 \cdot 10^{20}$	-176	111097	4.9

3. Optimization of carrier concentration

Obtained experimental data enable calculating a dimensionless thermoelectric figure of merit *ZT* for materials as well as effective masses of current curriers. Using Eq. 1 the *ZT* parameter can be determined for each sample. Figure 3 presents the selected results for two temperatures.

The electron effective mass m^* can be estimated using the Seebeck coefficient and Hall carrier concentration data assuming a single parabolic band model with acoustic phonon scattering as a predominant carrier scattering mechanism.

In this model, the Seebeck coefficient α can be expressed as follows:

$$\alpha = -\frac{k_B}{e}\left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta\right). \quad (2)$$

The carrier concentration *n* is

$$n = 4\pi\left(\frac{2m^* k_B T}{h^2}\right)^{3/2} F_{1/2}(\eta), \quad (3)$$

where k_B is the Boltzmann's constant, η – reduced Fermi energy, F_x – the Fermi integral of order *x*, m^* – the effective mass, and *T* – the absolute temperature.

The results of calculations are shown in Fig. 3. The carrier concentration n_d (of about 10^{20} cm^{-3}) for which reduced Fermi energy $\eta = 0$ has also been marked. It can be noted that the effective mass values m^* of electrons, for concentra-

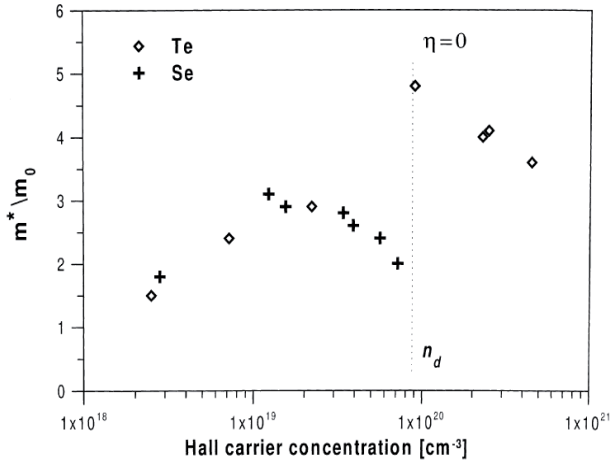

Fig. 3. The electron effective mass as a function of the Hall carrier concentration at RT. The dashed line shows calculated carrier concentration n_d for which calculated reduced Fermi energy η equals 0 [7].

tions lower than n_d, are between 1.5 and 3 m_0, whereas for electron concentrations greater than n_d their mass values jump up to 5 m_0. Moreover, this sudden increase is related to the change in the nature of the mass *vs.* carrier concentration dependency.

Above results remain in close agreement with results of our computations of electronic band structure [7]. It was found that for charge transport in $CoSb_3$ there are responsible carriers originating from at least two conduction bands located close to the Fermi level η. Conduction bands near the *H* point are much more flat than the valence bands at the Γ point. Thus, electrons are expected to possess considerably heavier effective masses (m^*) than holes. By fitting calculated dispersion curves to parabolic band we have obtained the electron masses as large as 3-4 m_0 (along H-Γ) and 0.9-1.4 m_0 (along H-N). These values are in close agreement to experimental values.

Contributions of these carries in charge transport depend on of position of reduced Fermi level. Therefore the effective masses dependence on Fermi level position can be approximated by two empirical equations describing both sets of experimental data:

$$m^* = m_0 \cdot (4.60 + 0.95\eta) \qquad (\eta > 0) \tag{4}$$

and

$$m^* = m_0 \cdot (4.38 - 0.45\eta) \qquad (\eta \le 0) \tag{5}$$

Next, above dependences of effective masses can be used for calculations of dependence of other transport parameters on Fermi energy.

Optimal transport parameters (*e.g.,* α, σ, *L*) as well as carrier concentration n_{opt} can be estimated using a methodology developed by Chasmar and Stratton [9]. According to their approach, *ZT* parameter for a general case of both degenerated and non-degenerated semiconductors can be expressed in the form:

$$ZT = \left(\frac{ea}{k_B}\right)^2 \left[\frac{\sigma_0}{\sigma\beta} + \left(\frac{e}{k_B}\right)^2 L\right]^{-1}, \tag{6}$$

where: σ_0 and β are defined as follows:

$$\sigma_0 = 2e\mu\left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2}, \tag{7}$$

and

$$\beta = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_0 T}{\lambda_{latt.}} = 5{,}745 \cdot 10^{-6} \frac{\mu}{\lambda_{latt}} \left(\frac{m^*}{m_0}\right)^{3/2} T^{5/2}. \tag{8}$$

Transport parameters can be expressed as functions of reduced Fermi energy η, Eqs. 2-5, and electrical conductivity σ:

$$\sigma = \sigma_0 \frac{F_r(\eta)}{\Gamma(r + 3/2)}, \tag{9}$$

where Γ is the Euler's gamma function.

Given the above dependences and experimental values λ_{latt} and m^*, *ZT* parameter can be estimated as a function of reduced Fermi level η for the given temperature. For the determination of Fermi level η_{exp} corresponding to experimental *ZT* values Seebeck coefficient data (Eq. 2) were used. Alike in previous calculations, scattering factor $r = -1/2$ was assumed which is the appropriate value for either acoustic-mode lattice scattering or alloy scattering.

Fig. 3 shows the results of computations and experimental *ZT* for selected samples with different values of carrier concentration. The theoretical curve describes quite well, within an experimental error, experimental values for 300 K. Results of computations for higher temperatures are slightly elevated in comparison to values obtained from measurements. It can be an effect of simplified assumption concerning constant, independent of temperature, scattering factors and carrier mobility, which can lead to overestimation of *ZT* results. However, it can be noted that the position of the theoretical curve maximum is in good agreement with experimental data.

The maximum value ZT_{max} for model curves corresponds to the Fermi energies η_{opt} close to 0 which is a typical case for most of thermoelectric materials. The determined optimal values α_{opt}, corresponding for ZT_{max}, are about 175 μV·K^{-1} at 300 K and carriers concentration n_{opt} of about $1.3 \cdot 10^{20}$ cm^{-3}.

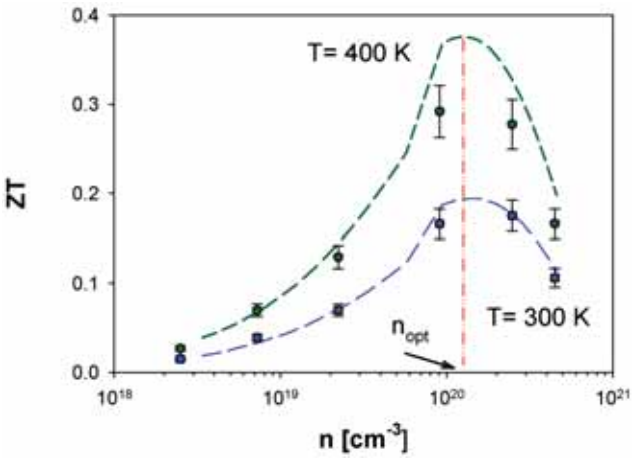

Fig. 4. Calculated theoretical dependences (lines) and experimental values (markers) of ZT parameter on reduced Fermi energy η for selected compositions x of $CoSb_3$ samples.

4. Conclusions

The optimal carrier concentration corresponding for the maximum value of the thermoelectric figure of merit is about $1.3 \cdot 10^{20}$ cm^{-3}. Such a high doping leads to shifting of the Fermi energy η into conduction bands and degeneration of the semiconductor. The highest values of *ZT* parameter correspond to Fermi level position at which it crosses flat bands responsible for large effective masses of carriers of about 3 to 5 m_0.

Acknowledgments

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