EFFECT OF PARTIAL La FILLING OF $Co_4Ge_6Te_6$ TERNARY SKUTTERUDITE ON THEIR THERMOELECTRIC PROPERTIES

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Abstract

The partially filled $La_xCo_4Ge_6Te_6$ (x=0 – 0.5) ternary skutterudite compounds were prepared to study influence of La filling on some thermoelectric properties. The complex changes in their final stoichiometry due to the La incorporation caused even change of the electrical conductivity type for $La_{0.4}Ge_6Te_6$ sample. The power factor of La filled ternary skutterudites decreased for all prepared samples.

1. Introduction

$CoSb_3$ skutterudite compounds belongs to a most promising thermoelectric materials that are adequate for the thermoelectric power generation using heat resources with temperatures of 600 to 800 K. Uher [1] provided an in-depth review on skutterudite materials. Some of the compounds have relatively good thermoelectric properties, i.e. high Seebeck coefficient and electrical conductivity. However, they do not demonstrate sufficient thermoelectric performance, because of a relatively high thermal conductivity. Lowering the thermal conductivity of skutterudite materials by phonon scattering is a very useful means to improve the thermoelectric performance [1].

Besides of traditional approach of lowering thermal conductivity by formation of solid solutions of two or more binary skutterudites [e.g. 2] there are other possibilities to lower lattice part of thermal conductivity at skutterudites. One of them is "filling" of large voids inside of their structure with heavy atoms (mostly lanthanides) [e.g. 3] and the other of the possibilities to lower thermal conductivity is formation of ternary skutterudites, i.e. an isoelectronic replacement either on the cation site (e.g. Fe^{2+} and Ni^{4+} instead of Co^{3+} in $Fe_{0.5}Ni_{0.5}Sb_3$ [4]) or on the anion site.

The later of the possibilities, i.e. an isoelectronic replacement of pnicogen atoms with the atoms of groups IV and VI, was studied e.g.for $CoSn_{1.5}Te_{1.5}$ [5] or $CoGe_{1.5}Se_{1.5}$ [6] and it was confirmed that such compounds are of the skutterudite structure and exhibit semiconducting behaviour.

In our previous studies we prepared $CoGe_{1.5}Te_{1.5}$ ternary skutterudite [7], we studied its thermoelectric properties when part of Co was substituted with Ni atoms [8] and finally we prepatred thermoelectrically optimized material combining both above mentioned strategies [9]. In this study we present our first results on thermoelectric properties of this material partially filled with La atoms.

2. Experimental

Co powder of 3N-purity (Aldrich, 3N-purity) was at first heated at 870 K for 2 hr in H_2/Ar atmosphere (15:85) to remove oxides. The treated Co powder was

together with Ge and Te (both of 5N-purity from Research Institute of Metals, Panenske Brezany, CR) and with Yb (Aldrich, 3N-purity) weighed in stoichiometric ratio into graphitized quartz ampoules and after evacuation ($<10^{-2}$ Pa) the ampoules were sealed. Further details of synthesis of the samples are described in our previous papers [e.g. 9].

Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using CuK_α radiation with secondary graphite monochromator. Diffraction angles were measured from 10° to 80° (2Θ). The morphology and the contents of cobalt, germanium and tellurium were determined by an electron scanning microscope JEOL JSM-5500LV and energy-dispersive X-ray (EDX) microanalyzer IXRF Systems (detector GRESHAM Sirius 10). The accelerating voltage of the primary electron beam was 20 kV.

Electrical conductivity was measured with four-probe method using Lock-In Amplifier (EG&G model 5209). The Seebeck coefficient was determined using temperature gradient on the samples ± 2K in the temperature range 200-800 K.

Results and Discussion

In series of the samples of $La_xCo_4Ge_6Te_6$ composition we obtained up to x=0.3 single-phased diffractograms corresponding to rhombohedral structure (space group $R\bar{3}$ - *No. 148).* For x= 0.4 and 0.5 we observed in diffractograms also small amount of GeTe phase (see Fig. 1).

We calculated lattice parameters of all prepared samples for the above mentioned rhombohedral structure $R\bar{3}$. The results of the calculations are given in Table 1. As follow from the Table incorporation of La atoms into voids of the $Co_4Ge_6Te_6$ ternary skutterudites does not change significantly lattice parameters of their structure. Only inconsiderable change is at sample 4 in *c*-parameter.

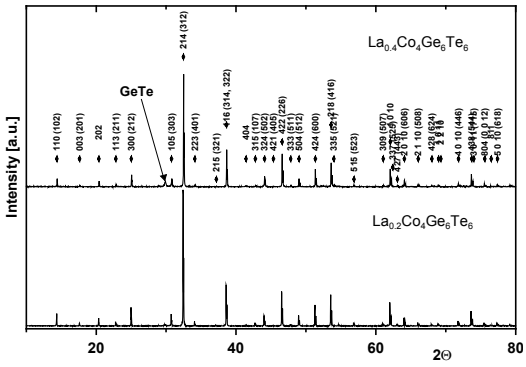

Fig.1: X-ray diffraction patterns of two samples filled with La atoms. At higher concentrations of La a small quantity of GeTe is observed. Diffraction lines corresponding to $R\bar{3}$ structure are presented.

Table 1: Lattice parameters of the $La_xCo_4Ge_6Te_6$ (x≤0.5) samples (space group $R\bar{3}$).

No.	Weighed composition	*a* [Å]	*c* [Å]
0	$Co_4Ge_6Te_6$	12.3295(3)	15.0998(5)
1	$La_{0.1}Co_4Ge_6Te_6$	12.3301(3)	15.0983(3)
2	$La_{0.2}Co_4Ge_6Te_6$	12.3308(3)	15.0983(3)
3	$La_{0.3}Co_4Ge_6Te_6$	12.3314(2)	15.0994(4)
4	$La_{0.4}Co_4Ge_6Te_6$	12.3312(4)	15.1054(3)
5	$La_{0.5}Co_4Ge_6Te_6$	12.3311(2)	15.0989(7)

As we mentioned in our previous work [9], EDX analysis of the samples consisting of small grains (< 5 μm) can, according [10], introduce quite large deviations in the relative intensities measured by EDX when analysing elements with significantly different atomic numbers. That is why we are very careful to make any conclusions on real stoichiometry of the prepared samples. Despite of these limitations, we dare to make make some conclusions following from the Table 2. where the EDX results are presented. We observed increasing content of La in the samples. The most striking fact following from the results is

the ratio Ge/Te. We always in our previous works [7-9] observed some overstoichiometry of Ge over Te, but for the sample number 4 is the overstoichiometry even higher than for the other samples. Also ratio Co/Ge was lower then theoretical.

Table 2: EDX analysis results (stoichiometric ratios Co/Ge = 0.66 and Ge/Te=1).

No.	La (at.%)	Co/Ge	Ge/Te
0	0	0.60	1.08
1	0.9	0.59	1.11
2	1.4	0.57	1.07
3	2.1	0.58	1.09
4	2.9	0.54	1.21
5	3.3	0.57	1.05

From the below presented temperature dependencies of Seebeck coefficient (see Fig.2) of the $La_xCo_4Ge_6Te_6$ samples one can see that incorporation of La atoms into voids of the *skutterudite-like* structure is accompanied with increase of Seebeck coefficient values at lower temperatures (below 400 K), while at higher temperatures the values decrease with increasing La content. For sample 4 ($La_{0.4}Co_4Ge_6Te_6$) we observed p-type of electrical conductivity, while for sample 5 ($La_{0.5}Co_4Ge_6Te_6$) is n-type again.

From the shapes of these dependencies we think that at least one type of electrons and one type of holes participates in the charge transport processes. We expect that incorporating La atoms acts as donors, but their incorporation into voids of the structure influences also occupancy of surrounding sites with other participating atoms. As we wrote our previous work [7-9] some part of overstoichiometric Ge atom probably also enters into the voids. Entering of La atoms drive these Ge atoms out of the voids. To explain p-type of electrical conductivity observed at sample 4 we have to admit that some part of these Ge atoms could substitute Co atoms. Their substoichiometry in this compound is also one of the typical features we observed during the study of the basic compound $Co_4Ge_6Te_6$. The probability of this substitution is supported with not very different covalent radii of both atoms (Co ~116 pm vs. Ge ~ 122 pm). Just the ratios Ge/Te and Co/Ge presented at Table 2 are for sample 4 quite different than at the other samples.

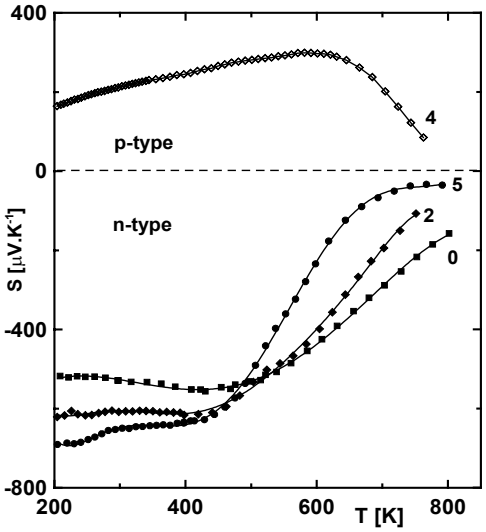

Fig.2: Temperature dependence of Seebeck coefficient of $La_xCo_4Ge_6Te_6$ samples (samples numbered according Table 1).

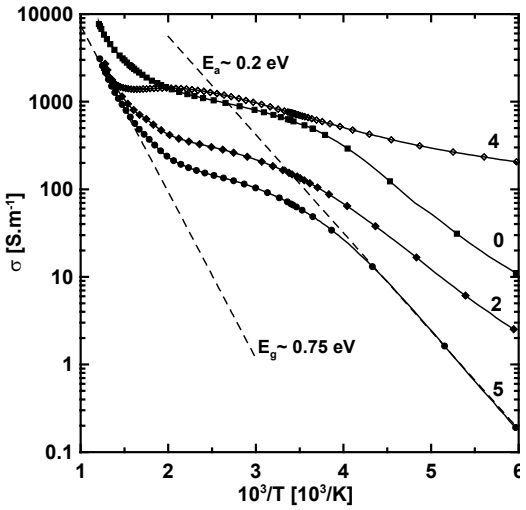

Fig. 3: Temperature dependence of electrical conductivity of $La_xCo_4Ge_6Te_6$ samples (samples numbered according Table 1).

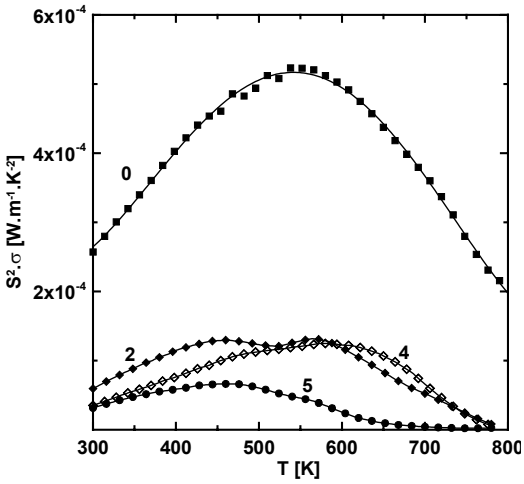

Fig. 4: Temperature dependence of *power factor* $S^2.\sigma$ of $La_xCo_4Ge_6Te_6$ samples (samples numbered according Table 1).

The electrical conductivites of some samples are presented in Fig. 3 as a function of inverse temperature. The exponential increase of the electrical conductivities of n-samples at lower temperatures represents the activation of the extrinsic electrons and calculated activation energy according $\sigma = \sigma_0.e^{-E_a/kT}$ is for all n-samples about 0.2 eV. The same dependence reveals existence acceptor level close to the valence band ($E_a \sim 0.05$ eV) in p-type material ($La_{0.4}Co_4Ge_6Te_6$).

The increase of the electrical conductivity above 600 K indicates at all samples the activation of the charge carriers across intrinsic band gap E_g. The estimated value for all samples is about 0.75 eV.

In the last Fig. 4 tempature dependencies of *power factor* $S^2.\sigma$ of the above presented materials are presented. Incorporation of La atoms into voids of their structure causes lowering of these values.

Conclusions

La atoms partially filled into voids of ternary *skutterudite* material $Co_4Ge_6Te_6$ act as donors, but their incorporation influences also stoichiometry of the other participated elements. At composition $La_{0.4}Ge_6Te_6$ even so much that we observe change of electrical conductivity type (p-type). One of the possible explanations of this fact is due to the substation of part of Co atoms with overstoichiometric Ge.

Ackowledgement

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