

Transport Properties of Partially Filled $\text{Yb}_x\text{Co}_4\text{Ge}_6\text{Te}_6$ -Based Skutterudites

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Abstract

The mixed anion skutterudite $\text{Co}_4\text{Ge}_6\text{Te}_6$ was synthesized and characterized with XRD. An influence of partial filling of empty voids of its structure with Yb atoms on some transport properties (electrical conductivity and Seebeck coefficient) has been studied. These properties were measured in 200–800 K temperature range on hot-pressed samples of these compounds. Coming out of EDX results N-type conductivity of unfilled sample can be attributed partly to the tellurium vacancies in anion lattice and partly to the surplus of Ge atoms, which probably enters empty voids of the basic structure and acts here as donors. Yb atoms entering the voids are donors too. The values of the power factor $S^2\sigma$ stay practically the same with incorporation of the Yb atoms and increase almost three times with replacing part of Co atoms with Ni atoms at $\text{Yb}_{0.2}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Ge}_6\text{Te}_6$ composition.

Introduction

Since the beginning of 1990's, when a major rejuvenation of interest in search for new types of thermoelectric materials has started and after an critical assessment of broad range of the prospective materials conducted by researchers from Jet Propulsion Laboratory, the skutterudites turned out to be as prime candidates for novel thermoelectrics [1]. Just skutterudites, thanks to the presence of large voids in their structure, fulfill at least one of the conditions for PGEC (Phonon-Glass Electron Crystal) defined by Slack [2]. These empty voids can be filled with various atoms which are believed to produce important phonon scattering, resulting in a significant reduction in lattice thermal conductivity λ_L and superior thermoelectric properties [e.g. 3,4].

Other of the possibilities of decreasing in λ_L is formation of ternary skutterudites, i.e. isoelectronic replacement either on cation site or anion site of binary skutterudite MX_3 (where M is one of the group 9 transition metals Co, Rh or Ir and X stands for P, As or Sb). While ternary skutterudites formed by cation substitution appear to be isostructural to the their binary analogues (e.g. $\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$) [5], structural studies carried out on materials prepared by anion substitution (e.g. $\text{CoGe}_{1.5}\text{Se}_{1.5}$) [6] suggest a lowering of the cubic symmetry of their structure.

Another of such compounds is $\text{CoGe}_{1.5}\text{Te}_{1.5}$ which was for the first time identified by Abrikosov *et al.* [7] in the study of the Co-GeTe system and mentioned as a possible candidate for the thermoelectric studies in J.P. Fleurial's list of prospective ternary skutterudites [8]. In one of our first

studies on the material [9] we suggested some lowering of the cubic symmetry. The structure was recently refined by powder neutron diffraction [10] and lowering the symmetry from cubic $Im\bar{3}$ space group to rhombohedral one $R\bar{3}$ (Fig.1) was confirmed.

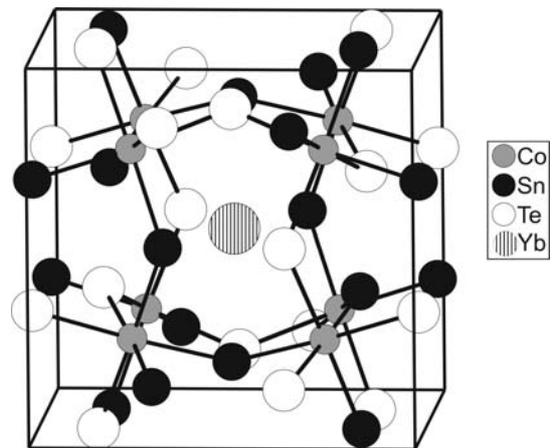


Fig.1: The representation of the structure of the skutterudite-related phase $\text{Yb}_x\text{CoGe}_{1.5}\text{Te}_{1.5}$, $R\bar{3}$ (rhombohedral setting).

Our next contribution [11] in the study of the material dealt with a study of influence of substitution of part of Co-atoms with Ni-atoms. In this paper we studied some thermoelectric properties of partially filled $\text{CoGe}_{1.5}\text{Te}_{1.5}$ with Yb atoms.

Experimental

Co powder of 3N-purity (Atlantic Equipment Engineers) 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. At first the content of the ampoules were heated above 1400 K for 24 hrs. Obtained ingots were pulverized in agate mortar under pure acetone to prevent oxidation. After blowing of acetone away by Ar, the starting powder was loaded in a steel die and cold pressed into cylindrical pellets. The pellets were then sealed into evacuated quartz ampoules. The ampoules were then heated at 873 K for 3 days. The resulted material was once more grounded under acetone and the above mentioned process was repeated. After verification of the completion of the solid state reaction with powder x-ray diffraction were

powder finally hot-pressed at 500°C (HP-samples) and 50MPa for one hour. HP-pellets were about 96-98% of theoretical (X-ray) densities ($\sim 7190 \text{ kg.m}^{-3}$). The density of samples was measured by immersion technique using distilled water as the liquid.

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). Data for sample No.2 were verified on a PANalytical diffractometer using CuK_α radiation. Diffraction angles were measured from 10° to 105° (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 $\pm 2\text{K}$ in the temperature range 200-800 K.

Results and Discussion

Our x-ray powder diffraction data indicate that samples of $\text{Yb}_x\text{Co}_4\text{Ge}_6\text{Te}_6$ are in range $x=0-0.3$ single-phased. At higher values of x the additional reflections corresponding to the YbTe and GeTe compounds start to appear in diffractograms. In this contribution we will discuss only single-phased samples, with $x=0,0.1,0.2,0.3$.

Weighed composition	EDX analysis
$\text{Co}_4\text{Ge}_6\text{Te}_6$	$\text{Co}_4\text{Ge}_{6.65}\text{Te}_{6.13}$
$\text{Yb}_{0.1}\text{Co}_4\text{Ge}_6\text{Te}_6$	$\text{Yb}_{0.13}\text{Co}_4\text{Ge}_{6.6}\text{Te}_{5.85}$
$\text{Yb}_{0.2}\text{Co}_4\text{Ge}_6\text{Te}_6$	$\text{Yb}_{0.24}\text{Co}_4\text{Ge}_{6.54}\text{Te}_{5.98}$
$\text{Yb}_{0.3}\text{Co}_4\text{Ge}_6\text{Te}_6$	$\text{Yb}_{0.35}\text{Co}_4\text{Ge}_{6.36}\text{Te}_{6.35}$
$\text{Yb}_{0.2}\text{Co}_{3.92}\text{Ni}_{0.08}\text{Ge}_6\text{Te}_6$	$\text{Yb}_{0.29}\text{Co}_{3.92}\text{Ni}_{0.08}\text{Ge}_{6.8}\text{Te}_{6.07}$

Table 1: Weighed and analysed compositions of the samples.

We realize that EDX analysis results (see Table 1) suffer from problem arising as a consequence of small grain sizes ($< 5 \mu\text{m}$). According [12] this fact can introduce quite large deviations in the relative intensities measured by EDX when analysing elements with significantly different atomic numbers. Despite of the uncertainties we can make some conclusions concerning with the composition of the samples. In accordance with our previous article on the compound [9] it seems to be probable that all samples exhibits some overstoichiometry of Ge, while Te is presented in the samples at slightly substoichiometric content. In our opinion, the surplus of Ge atoms can enter into one or both of large voids, which are located in the unit cell and are typical for materials with skutterudite structure. The same

incorporation into the voids was observed by Nolas *et al.* [13]. The qualitative estimate of the Ge content in the voids is due to the above mentioned facts doubtful. The same is valid also for Yb contents in the samples as it lies close to the detection limits of the EDX analyser. Nevertheless the observed values of the Yb content correspond well with weighed amounts.

The crystal structure of $\text{CoGe}_{1.5}\text{Te}_{1.5}$ was refined by the Rietveld method (Fig.2) for X-ray powder diffraction data using the FullProf program [14]. The starting model of the structure was derived from the data published for $\text{Co}_4\text{Ge}_6\text{Te}_6$ by Vaqueiro *et al.* [10]. The pseudo-Voigt function was used to describe the peak profiles. The refined parameters include those describing peak shape and width, peak asymmetry, unit-cell parameters, fractional coordinates and isotropic displacement factor. In total, 22 parameters were refined.

The final cycles converged to residuals of $R_p = 0.043$, $R_{wp} = 0.065$ and $R_B = 0.087$. The structural model proposed by Vaqueiro *et al.* [10] was confirmed; no significant deviations from starting structural parameters were observed. Besides, the Rietveld analysis revealed good crystallinity of the sample.

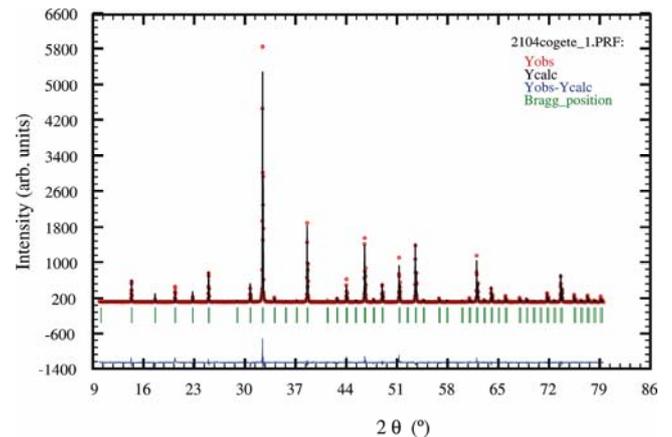


Fig.2: Observed (dots), calculated (solid line) and difference Rietveld profiles (the lowest line) for $\text{Co}_4\text{Ge}_6\text{Te}_6$. The vertical bars indicate the positions of Bragg reflections.

As follows from Table 2, all studied samples have very similar lattice parameters with respect to experimental uncertainty.

Weighed composition	a [Å]	c [Å]
$\text{Co}_4\text{Ge}_6\text{Te}_6$	12.3265(3)	15.0998(5)
$\text{Yb}_{0.1}\text{Co}_4\text{Ge}_6\text{Te}_6$	12.3299(3)	15.0985(5)
$\text{Yb}_{0.2}\text{Co}_4\text{Ge}_6\text{Te}_6$	12.3300(3)	15.0987(5)
$\text{Yb}_{0.3}\text{Co}_4\text{Ge}_6\text{Te}_6$	12.3381(3)	15.0924(5)

Table 2: Lattice parameters of the $\text{Yb}_x\text{Co}_4\text{Ge}_6\text{Te}_6$ ($x \leq 0.3$) samples (space group $R\bar{3}$).

Fig.2 shows the temperature dependence of the conductivity of all the studied samples including the sample

in which part of the Co atoms was substituted with Ni atoms. We used the substitution for $\text{Yb}_{0.2}\text{Co}_4\text{Ge}_6\text{Te}_6$ sample, where we observed highest values of the power factor $S^2\sigma$ [11]. One can see from the Fig. 3 that electrical conductivity slightly increases at first with the increasing content of incorporated Yb and then it falls down. As we expected, substitution of Co with Ni atoms caused relatively high increase of the electrical conductivity.

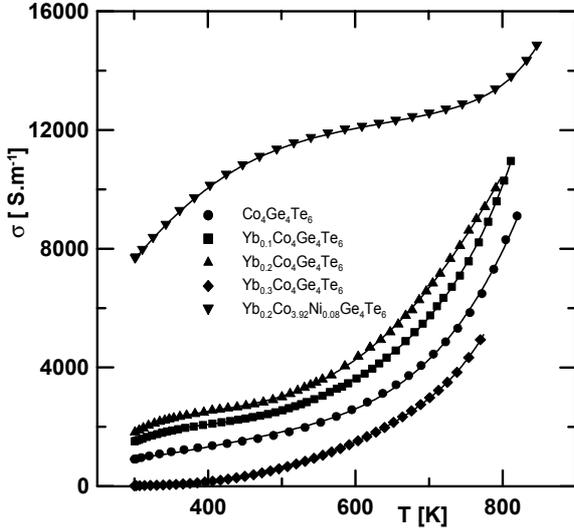


Fig.3: Electrical conductivity of the studied samples vs. temperature from 200 to 800 K.

As follows from Fig. 4, where temperature dependencies of Seebeck coefficient of the studied samples are presented, all sample are of n-type electrical conductivity. At lower temperatures (300 - 500 K) the values of Seebeck coefficient decrease at first with increasing Yb content and at last sample - $\text{Yb}_{0.3}\text{Co}_4\text{Ge}_6\text{Te}_6$ - the value increase up to about $700 \mu\text{V.K}^{-1}$ at 350 K and then rapidly decreases. For sample doped with Ni - $\text{Yb}_{0.2}\text{Co}_{3.92}\text{Ni}_{0.08}\text{Ge}_6\text{Te}_6$ - is the value in whole temperature range more or less stable - about $300 \mu\text{V.K}^{-1}$.

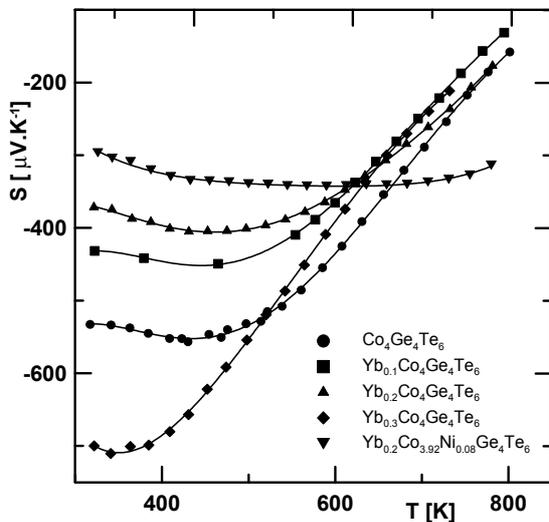


Fig. 4: Seebeck coefficient of the studied samples vs. temperature from 200 to 800 K.

As it was mentioned above we expect from EDX results that overstoichiometric Ge can enter into voids of the $\text{CoGe}_{1.5}\text{Te}_{1.5}$ structure similarly like at CoSb_3 [13]. Authors [13] suppose that the Ge atoms act here as donors. In our opinion, mainly this incorporation of Ge atoms is responsible for of n-type electrical conductivity of the undoped and unfilled $\text{Co}_4\text{Ge}_6\text{Te}_6$. In $\text{Yb}_x\text{Co}_4\text{Ge}_6\text{Te}_6$ compounds we expect that Yb atoms behave in this compound similarly like in case of CoSb_3 [15], i.e. they are electron donors. Coming out the EDX results (see Table 1), the observed changes in electrical conductivity and in Seebeck coefficient can be explained as follows: at first Yb atoms and overstoichiometric Ge atoms occupy empty voids of the $\text{Co}_4\text{Ge}_6\text{Te}_6$ structure together and their donor effects sum up. Above certain concentration ($x < 0.2$) inbuilt Yb atoms prevents incorporation of the Ge atoms into the voids and these ones enter their regular positions. In such case one can expect decrease of donor concentration and also decrease in electrical conductivity. As it was mentioned above substitution of Co atoms with Ni atoms leads to the increase in electrical conductivity mainly due to the donor effect of the Ni atoms similarly like in the case of CoSb_3 [16].

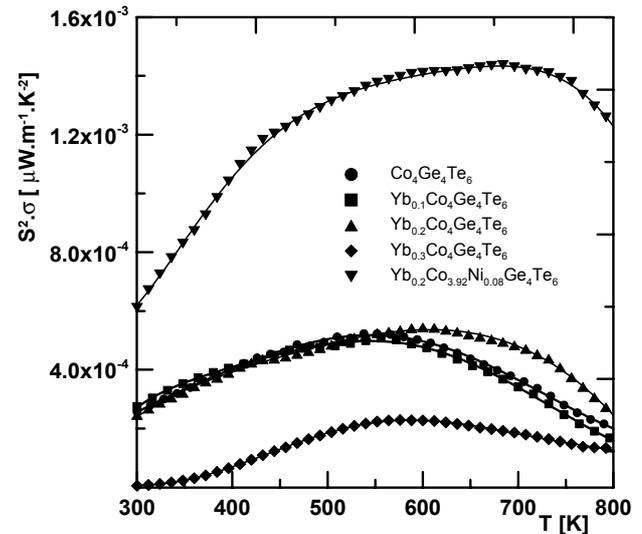


Fig. 5: Temperature dependence of power factor $S^2\sigma$ of the studied samples

To evaluate “thermoelectric quality” of the studied samples we calculated temperature dependencies of their power factor, i.e. product $S^2\sigma$. These dependencies are given in Fig. 5. At Yb-filled samples - $\text{Yb}_x\text{Co}_4\text{Ge}_6\text{Te}_6$ (for $x \leq 0.2$) - increase in electrical conductivity is compensated by decrease of Seebeck coefficient values and it results in more or less the same dependencies of $S^2\sigma$ -product. At sample $\text{Yb}_{0.2}\text{Co}_{3.92}\text{Ni}_{0.08}\text{Ge}_6\text{Te}_6$, where part of Co atoms is substituted with Ni atoms we observed distinct increase of the power factor values in quite broad range of temperatures. Between 600-700 K the value peaks up to $1400 \mu\text{W.m}^{-1}\text{K}^{-2}$. This value is only 2-3 times worse than value of one of the

best n-type skutterudite materials $\text{Yb}_{0.19}\text{Co}_4\text{Ge}_6\text{Te}_6$ [15] (see Fig. 6).

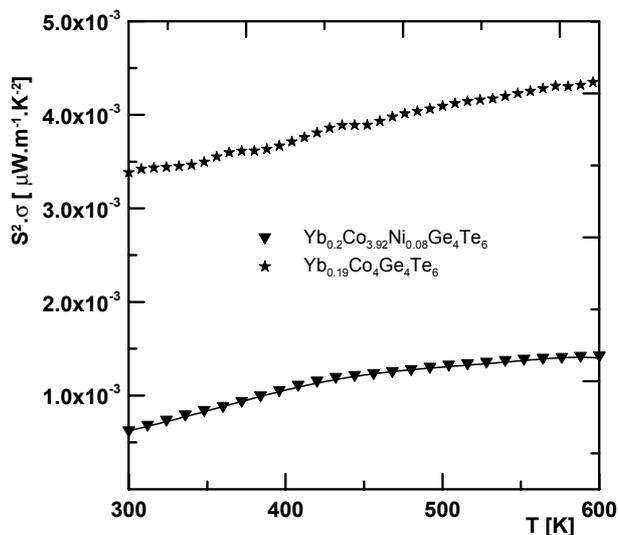


Fig.6: The comparison of power factors for $\text{Yb}_{0.2}\text{Co}_{3.92}\text{Ni}_{0.08}\text{Ge}_6\text{Te}_6$ and $\text{Yb}_{0.19}\text{Co}_4\text{Sb}_{12}$ [15].

Conclusions

We report on the synthesis and some transport properties of the partially filled ternary skutterudites $\text{Yb}_x\text{Co}_4\text{Ge}_6\text{Te}_6$ ($x \leq 0.3$). We verified latest findings [10] concerning the structure of this compound. Unlike binary skutterudites the $\text{Co}_4\text{Ge}_6\text{Te}_6$ grows in rhombohedral structure $R\bar{3}$. All prepared samples were of n-type electrical conductivity mainly due to the donor effects of Yb and overstoichiometric Ge located inside the voids of the $\text{Co}_4\text{Ge}_6\text{Te}_6$ structure. For samples ($x \leq 0.2$) their donor effects sum up and the electrical conductivity increases. At higher concentrations the inbuilt Yb atoms prevent to overstoichiometric Ge atoms to incorporate into voids and these ones occupied their regular sites. We doped the sample with best thermoelectric properties with Ni atoms ($\text{Yb}_{0.2}\text{Co}_{3.92}\text{Ni}_{0.08}\text{Ge}_6\text{Te}_6$) to optimize carrier concentration. The power factor values of this compound increased few times and peak up to $1400 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ between 600-700 K, which is the value only 2-3 times lower than the value of power factor of one of the best n-type skutterudite $\text{Yb}_{0.19}\text{Co}_4\text{Sb}_{12}$.

Acknowledgments

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