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

J. Navrátil$^1$, T. Plecháček$^1$, Beneš L.$^1$, Vlček M.$^1$ and Laufek F.$^2$

$^1$Joint Laboratory of Solid State Chemistry of IMC AS CR and University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic
$^2$Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic
Jiri.navratil@upce.cz, Phone: +420 46 603 6152, Fax: +420 46 603 6011

Abstract
The mixed anion skutterudite Co$_4$Ge$_6$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 Yb$_{0.2}$Co$_{3.98}$Ni$_{0.02}$Ge$_6$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 $\lambda_L$ and superior thermoelectric properties [e.g. 3,4].

Other of the possibilities of decreasing in $\lambda_L$ is formation of ternary skutterudites, i.e. isostructural 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. Ru$_{0.5}$Pd$_{0.5}$Sb$_3$) [5], structural studies carried out on materials prepared by anion substitution (e.g. CoGe$_{1.5}$Se$_{1.5}$) [6] suggest a lowering of the cubic symmetry of their structure.

Another of such compounds is CoGe$_{1.5}$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$ar{3}$ space group to rhombohedral one $R\bar{3}$ (Fig.1) was confirmed.

Fig.1: The representation of the structure of the skutterudite-related phase Yb$_{0.2}$Co$_{3.98}$Ni$_{0.02}$Ge$_6$Te$_6$ (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 CoGe$_{1.5}$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 (~7190 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 CuKα 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 CuKα 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 ±2 K in the temperature range 200-800 K.

Results and Discussion

Our x-ray powder diffraction data indicate that samples of YbₓCo₄Ge₆Te₆ 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.

Table 1: Weighed and analysed compositions of the samples.

<table>
<thead>
<tr>
<th>Weighed composition</th>
<th>EDX analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₄Ge₆Te₆</td>
<td>Co₄Ge₆.65Te₆.13</td>
</tr>
<tr>
<td>Yb₀.₁Co₄Ge₆Te₆</td>
<td>Yb₀.1₃Co₄Ge₆.65Te₅.₈₅</td>
</tr>
<tr>
<td>Yb₀.₂Co₄Ge₆Te₆</td>
<td>Yb₀.₂₄Co₄Ge₆.₅₄Te₅.₉₈</td>
</tr>
<tr>
<td>Yb₀.₃Co₄Ge₆Te₆</td>
<td>Yb₀.₃₅Co₄Ge₆.₃₆Te₅.₃₃</td>
</tr>
<tr>
<td>Yb₀.₂Co₄Ge₆.₈₅Ni₀.₀₈Ge₆Te₆</td>
<td>Yb₀.₂₉Co₄Ge₆.₈₅Ni₀.₀₈Ge₆.₈₅Te₆.₀₇</td>
</tr>
</tbody>
</table>

Table 2: Weighed composition

<table>
<thead>
<tr>
<th>Weighed composition</th>
<th>a [Å]</th>
<th>c [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₄Ge₆Te₆</td>
<td>12.3265(3)</td>
<td>15.0998(5)</td>
</tr>
<tr>
<td>Yb₀.₁Co₄Ge₆Te₆</td>
<td>12.3299(3)</td>
<td>15.0985(5)</td>
</tr>
<tr>
<td>Yb₀.₂Co₄Ge₆Te₆</td>
<td>12.3300(3)</td>
<td>15.0987(5)</td>
</tr>
<tr>
<td>Yb₀.₃Co₄Ge₆Te₆</td>
<td>12.3381(3)</td>
<td>15.0924(5)</td>
</tr>
</tbody>
</table>

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

The crystal structure of CoGe₁.₅Te₁.₅ 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 Co₄Ge₆Te₆ by Vaqueiro et al. [10]. The pseudo-Voight 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 Co₄Ge₆Te₆. The vertical bars indicate the positions of Bragg reflections.](image-url)

Table 2: Lattice parameters of the YbₓCo₄Ge₆Te₆ (x≤0.3) samples (space group R 3).

![Fig.2 shows the temperature dependence of the conductivity of all the studied samples including the sample](image-url)
in which part of the Co atoms was substituted with Ni atoms. We used the substitution for Yb$_{0.2}$Co$_4$Ge$_6$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 - Yb$_{0.2}$Co$_4$Ge$_6$Te$_6$ – the value increase up to about 700 $\mu$V.K$^{-1}$ at 350 K and then rapidly decreases. For sample doped with Ni - Yb$_{0.2}$Co$_3.92$Ni$_{0.08}$Ge$_6$Te$_6$ – is the value in whole temperature range more or less stable – about 300 $\mu$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 CoGe$_{1.5}$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 Co$_4$Ge$_6$Te$_6$. In Yb$_x$Co$_4$Ge$_6$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 Co$_4$Ge$_6$Te$_6$ structure together and their donor effects sum up. Above certain concentration (x<0.2) built-in 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 – Yb$_x$Co$_4$Ge$_6$Te$_6$ (for x ≤ 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 Yb$_{0.2}$Co$_3.92$Ni$_{0.08}$Ge$_6$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 $\mu$W.m$^{-1}$.K$^{-2}$. This value is only 2-3 times worse then value of one of the...
best n-type skutterudite materials Yb\(_{0.19}\)Co\(_4\)Ge\(_6\)Te\(_6\) [15] (see Fig. 6).

![Graph showing the comparison of power factors for Yb\(_{0.2}\)Co\(_3.92\)Ni\(_{0.08}\)Ge\(_6\)Te\(_6\) and Yb\(_{0.19}\)Co\(_4\)Sb\(_{12}\) [15].](image)

Fig. 6: The comparison of power factors for Yb\(_{0.2}\)Co\(_3.92\)Ni\(_{0.08}\)Ge\(_6\)Te\(_6\) and Yb\(_{0.19}\)Co\(_4\)Sb\(_{12}\) [15].

Conclusions

We report on the synthesis and some transport properties of the partially filled ternary skutterudites Yb\(_x\)Co\(_4\)Ge\(_6\)Te\(_6\) (x\(<\)0.3). We verified latest findings [10] concerning the structure of this compound. Unlike binary skutterudites the Co\(_4\)Ge\(_6\)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 Co\(_4\)Ge\(_6\)Te\(_6\) structure. For samples (x\(<\)0.2) their donor effects sum up and the electrical conductivity increases. At higher concentrations the built-in Yb atoms prevent the 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 (Yb\(_{0.2}\)Co\(_3.92\)Ni\(_{0.08}\)Ge\(_6\)Te\(_6\)) to optimize carrier concentration. The power factor values of this compound increased few times and peaked up to 1400 \(\mu\)W.m\(^{-1}\).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 Yb\(_{0.19}\)Co\(_3\)Sb\(_{12}\).

Acknowledgments

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References