Some Thermoelectric Properties of $CoGe_{1.5}Te_{1.5}$

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Abstract

From weighed composition $CoGe_{1.5}Te_{1.5}$ two different materials were prepared. They were different both in composition and structure. Probably due to the diffusion of Ge atoms in the stack of pellets, on one side of the stack samples with surplus of Ge ($CoGe_{1.7}Te_{1.47}$) were found, while on the other side of stack had pellets with distinct deficit both Ge and Te ($CoGe_{1.15}Te_{1.05}$) in comparison with weighed composition. Both materials were characterized with x-ray diffraction and their probable structures and structural parameters were proposed. According to the results, the $CoGe_{1.7}Te_{1.47}$ material has cubic structure, but some of lower symmetry (No. 200 – *P2*/*m*3 or No. 195 – *P*23). The $CoGe_{1.15}Te_{1.05}$ seems to be of rhombohedral structure (No. 47 - *P mmm*). Measurements of some transport and thermo-electric properties of both materials are presented and discussed in the paper.

Introduction

During one decade, compounds with the skutterudite structure ($CoAs_3$) have attracted a lot of attention of themoelecrics community due to their promising thermoelectric properties [1]. Although the binary skutterudites have excellent electronic transport properties, their thermal conductivity is too high for thermoelectric applications. Fortunately, unique structure of the compounds allows a few ways how to fight against the problem, i.e. how to lower rather high values of the thermal conductivity. Most common ways are filling of empty voids located inside the structure with foreign ions [e.g. 2, 3] or formation of solid solutions from isostructural binary compounds [e.g. 4]. 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 $Fe_{0.5}Ni_{0.5}Sb_3$ [5]) 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 $CoSn_{1.5}Te_{1.5}$ [6] or $CoGe_{1.5}Se_{1.5}$ [7] and it was confirmed that such compounds are of the skutterudite structure and exhibit semiconducting behaviour.

In this contribution we present the continuation of our study of the $CoGe_{1.5}Te_{1.5}$ compound [8]. The compound was for the first time identified by Abrikosov *et al.* [9] in the study of the Co-GeTe system. As a possible candidate for the thermoelectric studies was the compound proposed by Fleurial *et al.* [5]. However, no information is available in the literature on the thermoelectric properties of the compound. We have found that the compound can be prepared, due to the used technology, with some surplus or deficit of Ge and/or Te. Two different compositions of the compound were prepared. Some of their thermoelectric properties were measured and the properties are discussed from point of view of the composition and structure of the compound.

Experimental

GeTe compound was prepared from Ge and Te of 5N-purity with their direct reaction at 1120 K for 24 hr in evacuated quartz ampoules. Co powder of 3N-purity (Atlantic Equipment Engineers) was at first heated at 1070 K for 2 hr in H_2/Ar atmosphere (15:85) to remove oxides. Starting GeTe and Co were ground and mixed together 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. The prepared samples were found to be approximately 80% of theoretical density (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 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 STADI P STOE diffractometer in transmission geometry using $CoK_{\alpha1}$ 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 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 not exceeding 10 K in the temperature range 100-570 K.

The final composition of the prepared material was significantly influenced by the preparation method. As we mentioned in the experimental part, we have used cold-pressed pellets which were loaded into evacuated ($p{\sim}10^{-4}$ Pa) quartz ampoules. The pellets were stacked in columns in the ampoules and the ampoules were placed in horizontal furnace. Probably due to existence of the small temperature gradient in the furnace some part of Ge diffused from pellets on one side of the ampoule towards the other side. That is why, in our opinion, we observed surplus of the Ge atoms in comparison with weighted $CoGe_{1.5}Te_{1.5}$ composition in the most of prepared samples, while in the samples from the other side of the ampoule we observed both Ge and Te deficit.

Results and Discussion

As it was mentioned above, we prepared two different materials - probably due to the existence of some temperature gradient along a stack of pressed pellets inside the quartz ampoule during the final sintering process. The temperature gradient, in our opinion, forced diffusion of some Ge towards the one side of the stack. That is why we observed on one side of the stack pellets with surplus of Ge atoms (composition about $CoGe_{1.7}Te_{1.47}$ – sample No.1), in comparison with weighted $CoGe_{1.5}Te_{1.5}$ composition, while on the other side we obtained pellets with both Ge and Te deficit (typical composition about $CoGe_{1.15}Te_{1.05}$ – sample No.2). As one can see from Fig. 1, both types of samples were different not only in composition, but also in the structure.

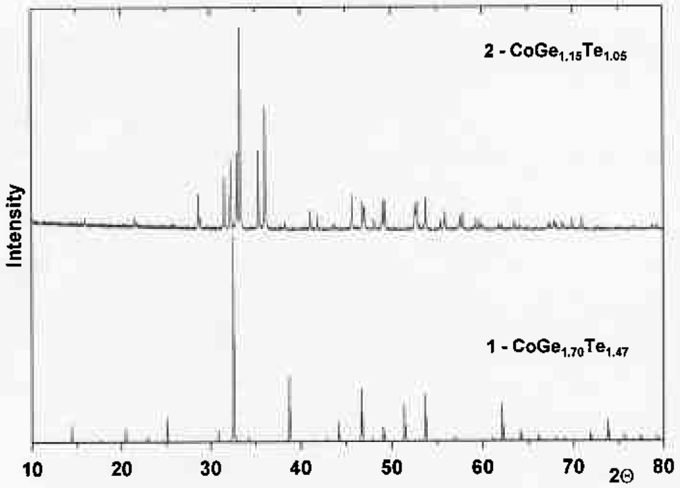

Fig.1: XRD patterns of the prepared samples

The x-ray diffraction pattern of the sample No.1 was indexed with DICVOL [10] to a cubic unit cell corresponding to the skutterudite structure, space group *Im3*, with unit cell dimension $a_0=8.696$ *Å* and with figures of merit $M_{20}=12.9$ and $F_{20}=10.4$ (0.050; 38). The obtained value of structural parameter $a_0=8.696$ *Å* well corresponds with previous findings of Fleurial *et al.* [5], i.e. $a_0=8.7270$ *Å*. However, besides lines corresponding to *Im3* skutterudite structure space group (only lines with even sum of $h+k+l$ – labels printed in bold in Fig. 2), there are also other lines in the presented diffraction pattern. These lines could be indexed as lines corresponding to a cubic space group, but some of lower symmetry. The lines printed in italic in Fig.2 are the ones with odd sum of $h+k+l$. The emerging of the lines is, in our opinion, connected with considerable difference in values of atomic scattering factors of Ge and Te. The similar above mentioned compounds $CoSn_{1.5}Te_{1.5}$ [6] or $CoGe_{1.5}Se_{1.5}$ [7] were reported to be of skutterudite structure (space group *Im3*). This is not surprising as the differences in values of the above mentioned factors between Ge – Se and Sn – Te respectively, are very small.

The X-ray diffraction pattern was refined with the cell found by DICVOL and using „profile matching"option [11] of the program FullProf [12], in order to determine the space group. The profile-shape function used to approximate peaks in the powder pattern was of pseudo-Voight type. The refined parameters included those describing peak shape and width, peak asymmetry, unit cell dimension and zero correction term. In total, we refined 10 parameters. Lattice parameter a_0 was refined to *8.7205(3) Å*. No systematic absences were observed. That means that material could have cubic structure to one of the following space groups: No 200 – *P*2/*m*3 or No. 195 – *P*23. Space group No.200 - *P*2/*m*3 was preferred, due its group – subgroup relations (*Im*3 – *P*2/*m*3). The final Le Bail fit is shown on Fig.2.

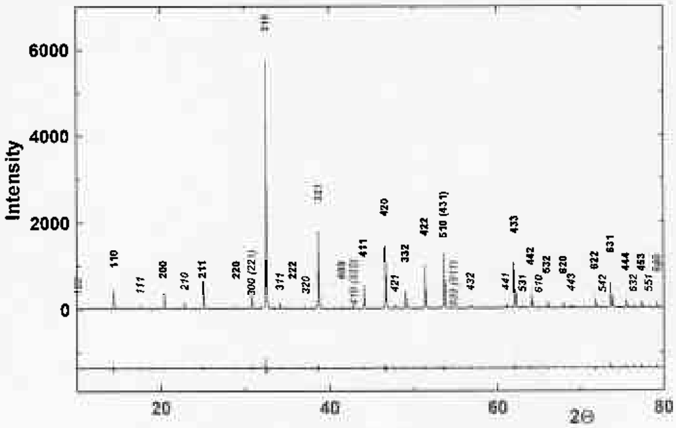

Fig.2: Final Le Bail plot of $CoGe_{1.7}Te_{1.47}$ sample (Rp=13.8%, Rwp=22.6%, Rexp=16.22%) - CuK_α radiation.

According EDX microanalysis there is quite high surplus of Ge atoms in the studied material in comparison with weighed $CoGe_{1.5}Te_{1.5}$ composition. In our opinion the surplus 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. Incorporating Ge atoms inside the voids of $CoSb_3$ has been recently confirmed by Nolas *et al.* [15]. In the studied material ($CoGe_{1.7}Te_{1.47}$) corresponds the surplus approximately 1.6 atoms of Ge per unit cell.

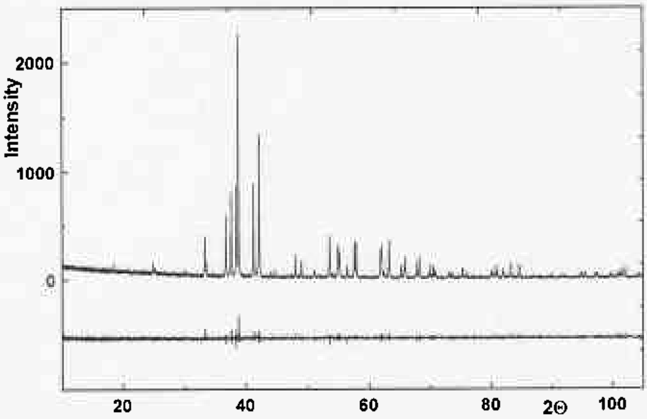

Fig.3: Final Le Bail plot of $CoGe_{1.15}Ge_{1.05}$ sample (Rp=9.94%, Rwp=13.7%, Rexp=13.08%) - CoK_α radiation.

Indexing of pattern No.2 with DICVOL [10] led to orthorhombic solution with unit cell dimensions *a=11.134 Å*, *b=6.233 Å*, *c=6.194 Å* and with figures of merit $M_{20}=29.9$ and $F_{20}=25.8$ (0.011; 67). Profile matching [11] was carried out with FullProf program [12]. The profile shape function was a pseudo-Voight type. In total, we refined 14 parameters. Lattice parameters were refined to: *a=11.1396(4) Å*, *b=6.2373(1) Å*, *c=6.1979(1) Å*. No systematic absences were observed. The space group of this material could be *P mmm* (No. 47) or *P* 222. Refinement was carried in a space group *Pmmm* (No. 47), due its group-subgroup relations (*Im*3 – *Pmmm*). The final Le Bail fit is shown on Fig.3.

From the results of EDX microanalysis of the sample No. 2 ($CoGe_{1.15}Ge_{1.05}$) together with determined probable crystal structure (orthorhombic space group) we are inclined to think that the second compound could be actually isoelectronic compound derived from $CoSb_2$, where antimony atoms are almost equally replaced with Ge and Te atoms. According Siegrist *et al.* [13] high-temperature modification of $CoSb_2$ is of orthorhombic structure (marcasite). The exact solution of the structures of both prepared materials calls for preparation of single crystalline grains of larger dimensions.

On Fig. 4 values of electrical conductivity *vs.* reciprocal temperature of both studied samples are presented. As follows from the figure electrical conductivity of sample No. 1 increases with temperature over the whole temperature range of measurement. Two dashed lines on the dependence represent fits using equation $\sigma=\sigma_0 . exp(-E_a/kT)$, where k is the Boltzman constant and E_a is the activation energy. The E_a value (0.14 eV) at lower temperatures is well comparable with value obtained for $CoGe_{1.452}Se_{1.379}$ [7]. Unlike the authors [7], who assigned the energy to intrinsic semiconducting band gap, we think that it probably represents the activation energy of the extrinsic electrons. The increase of the electrical conductivity above 550 K indicates, in our opinion, the activation of the charge carriers across the intrinsic energy gap E_g=0.77 eV. Here we got a good agreement with authors [6], who obtained for sample $CoSn_{1.5}Te_{1.5}$ value of E_g=0.7 eV.

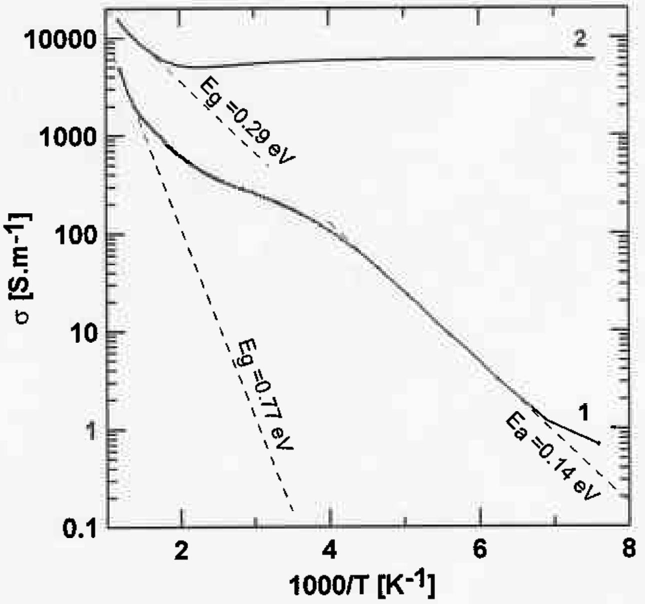

Fig. 4: The electrical conductivity dependence *vs.* reciprocal temperature of $CoGe_{1.7}Te_{1.47}$ (No.1) and $CoGe_{1.15}Te_{1.05}$ (No.2). Dashed lines present fits of the form $\sigma=\sigma_0 . exp(-E_a/kT)$

The course of reciprocal temperature dependence of electrical conductivity of the second sample (No. 2) is totally different from the course of the first sample. At lower temperatures the course is more or less constant and above 500 K it starts to increase. This increase is, similarly like in the case of the sample No.1, connected probably with crossing of charge carriers via intrinsic band gap. Applying the same fit ($\sigma=\sigma_0 . exp(-E_a/kT)$) as for the first sample we got value of E_g=0.29 eV. Interesting is, in our opinion, both the similarity of the shape of electrical conductivity dependence with the one for $CoSb_2$ (e.g. [14]) and also comparison of E_g-value of our material with those ones for $CoSb_2$ (E_g=0.17 eV [13]) or $CoAs_2$ (E_g=0.3 eV [13]).

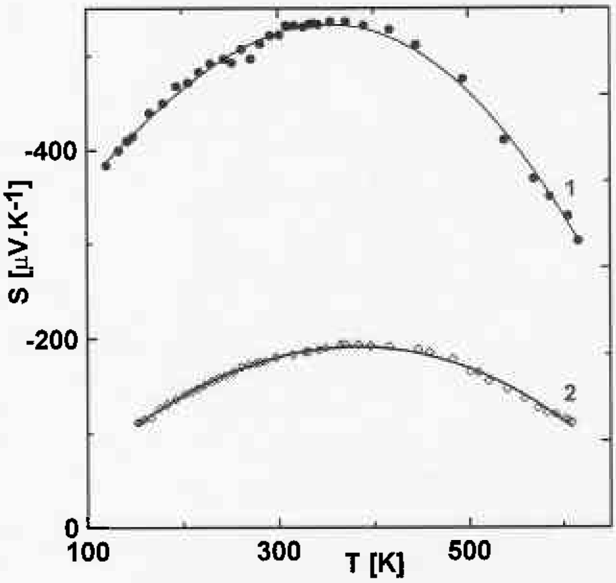

Fig. 5: Temperature dependence of Seebeck coefficient of $CoGe_{1.7}Te_{1.47}$ (No.1) and $CoGe_{1.15}Te_{1.05}$ (No.2).

Temperature dependencies of Seebeck coefficient (S) for both studied samples in 120-600 K temperature range are presented in Fig. 5. The negative S-values of both samples indicate that electrons are the majority carriers. Large Seebeck coefficient value (maximum -540 $\mu V.K^{-1}$ at 360 K) was observed on the sample No.1. Basing on results of EDX analysis ($CoGe_{1.7}Te_{1.47}$), N-type electrical conductivity of the sample could be explained both by the deficit of tellurium in the lattice (tellurium vacancies) and partial ionization of surplus Ge atoms residing inside the interstitial voids of the skutterudite crystal structure. Thermal excitation of minority carriers at higher temperatures causes decrease of Seebeck coefficient values.

As for the shape, the temperature dependence of S for $CoGe_{1.15}Te_{1.05}$ is similar to that observed for $CoGe_{1.7}Te_{1.47}$, but the values are lower (maximum -195 $\mu V.K^{-1}$ at 380 K). We think that also here electrons are produced by ionisation of Ge atoms located probably in interstitial positions of the material structure.

As for the thermoelectric properties, we have tried to compare $S^2.\sigma$ products (power factor) of both materials. One can see from the Fig.6 that large value of S for sample No.1 (in comparison with No.2) is compensated by considerably lower values of electrical conductivity, and final magnitudes of the product $S^2.\sigma$ are actually the same, as for the maxima.

Quite different is, however, location of the maxima (530 K for sample No.1 vs. 360 K for sample No.2). The values are, from thermoelectric point of view quite small. One has to realize that our samples prepared by cold pressing technology have only 80% of theoretical density (in case of sample No. 1). We expect that using of hot-pressing technique can considerably improve values of electrical conductivity without more distinct worsening of Seebeck coefficient values. In this case one can expect increase of power factor values.

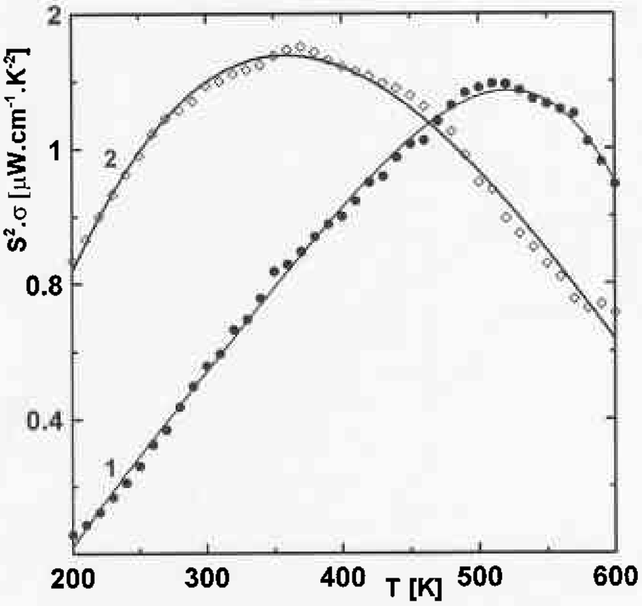

Fig.6: Power factor ($S^2.\sigma$) values as a function of temperature for $CoGe_{1.7}Te_{1.47}$ (No.1) and $CoGe_{1.15}Te_{1.05}$ (No.2) samples.

Conclusions

Two different materials were prepared from weighed composition $CoGe_{1.5}Te_{1.5}$ due to the diffusion of Ge through stack of pellets during the preparation. The materials were different both in composition and structure. While the first material ($CoGe_{1.7}Te_{1.47}$) was proposed to be of cubic structure (either *P2/m*3 or *P*23 space group), the second one ($CoGe_{1.15}Te_{1.05}$) seems to be of rhombohedral structure (probably *P mmm* space group). Both materials are of n-type electrical conductivity. From temperature dependence of electrical conductuctivity, energies of their band gaps were derived ($CoGe_{1.7}Te_{1.47}$ - E_g=0.77 eV, $CoGe_{1.15}Te_{1.05}$ - E_g=0.29 eV).

Acknowledgments

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