SOME TRANSPORT PROPERTIES OF $CoGe_{1.5}Te_{1.5}$

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N-type $CoGe_{1.5}Te_{1.5}$ compound was for the first time studied as a potential thermoelectric material. Due to the specific way of preparation, the samples of $CoGe_{1.7}Te_{1.47}$ composition with high overstoichiometry of Ge and some substoichiometry of Te were prepared. From x-ray diffraction pattern it looks the compound is of cubic structure but some of lower symmetry (space groups No. 195 - P23, No. 200 - P2/m3 or No. 201- P2/n $\bar{3}$) unlike the most of other skutterudite compounds (space group $Im3$). Tellurium vacancies or ionized surplus Ge atoms are proposed to be responsible for observed n-type conductivity. Two regions corresponding to extrinsic and intrinsic conductivity were identified on the temperature dependence of electrical conductivity. The potential possibility to change quantity of the incorporated Ge and Te in wide range around stoichiometric composition ($CoGe_{1.5}Te_{1.5}$) together with possibility to influence its thermoelectric properties by proper doping and void filling is therefore of interest of further thermoelectric research.

1. Introduction

Compounds with the skutterudite structure ($CoAs_3$) have attracted the attention of thermoelectric research since the early 1990s in its pursuit for new generation of thermoelectric materials [1]. Due to their structure, containing two large voids in the unit cell which could be "filled" with foreign ions acting here as effective phonon-scattering centres, skutterudites serve as a very typical example of "an ideal thermoelectric material" defined according to PGEC (phonon-glass electron-single-crystal) concept proposed by Dr. Slack [2]. During of decade of intensive study skutterudites proved to be prospective material for further research [3-5].

One of the possibilities in optimizing of transport properties of skutterudites for thermoelectric applications is an isostructural replacement of pnicogen atoms with the atoms of groups IV and VI. Such skutterudite materials should be semiconductors, as they are isoelectronic with $CoSb_3$. The fact was confirmed in the studies of $CoSn_{1.5}Te_{1.5}$ [6] and of $CoGe_{1.5}Se_{1.5}$ [7]. In our article we present some transport properties of polycrystalline $CoGe_{1.5}Te_{1.5}$ samples. The compound was identified in [8] in the study of Co-GeTe system. The material with skutterudite structure has never been studied from point of view of its thermoelectric properties. This work is the first one dealing with some thermoelectric properties of the material.

2. 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 870 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

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(7190 kg.m^{-3}) and typical grain sizes of 10 µm. 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). 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~10^{-4} Pa) quartz ampoules. The pellets were stacked in columns in the ampoules and the ampoules were placed in horizontal furnace. 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. In this article we will be engaged in the samples with surplus of Ge. We would like to remark that all the samples were single-phased, as we will discuss below, and also their measured transport properties were the same.

3. Results and discussion

As it was mentioned above, we observed in most of our samples surplus of Ge atoms in comparison with weighed CoGe$_{1.5}$Te$_{1.5}$ composition. Relatively high Te vapour pressure resulted in a reduced amount of Te as compared to Ge content in our samples. The composition of the presented samples, determined by EDX microanalysis, was CoGe$_{1.7}$Te$_{1.47}$. The samples contained well-formed grains with typical sizes between 5 to 10 µm (see Fig. 1).
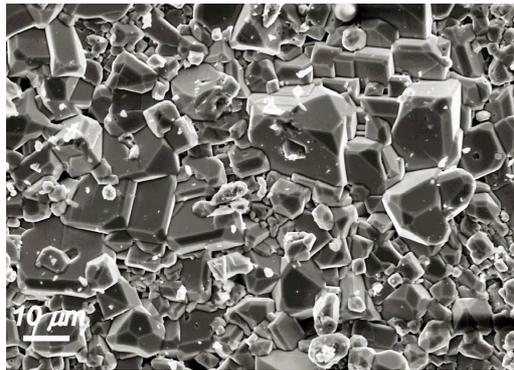

Fig. 1. SEM image of CoGe$_{1.7}$Te$_{1.47}$ sintered sample.

The x-ray diffraction pattern was indexed to a cubic unit cell corresponding to the skutterudite structure, space group *Im3*. The measured lattice constant at room temperature of the powdered sample was $a_0 = 8.7174$ *Å*. The value well corresponds with findings of Jet Propulsion Laboratory (JPL) [9] ($a_0 = 8.7270$ *Å*). Diffraction pattern of the sample is presented on Fig. 2. There is evident from the Fig. 2 that beside of lines corresponding to *Im3* space group (only lines with even sum of $h+k+l$ – labels printed in bold on Fig. 2), typical for most of skutterudites materials, also other lines occurs (labels printed in italic on Fig.2). They could be indexed as lines corresponding to cubic space group but some of lower symmetry.

That means that studied material could have cubic structure corresponding to one of the following space groups: No. 195 - P23, No. 200 - P2/m3 or No. 201- P2/n 3 . The emerging of these lines is probably connected with considerable difference in values of atomic scattering factors of Ge and Te. The other similar compounds where simultaneous substitution of group IV and VI atoms on the pnicogen sites - CoGe$_{1.5}$Se$_{1.5}$ [7] and CoSn$_{1.5}$Te$_{1.5}$ [6] – was used, 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.
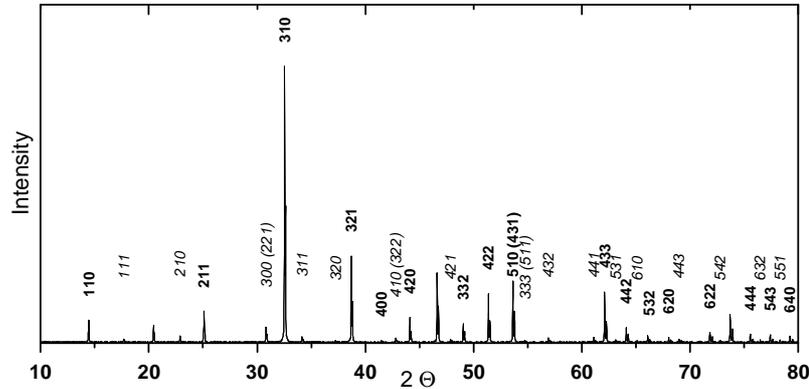

Fig. 2. Diffraction pattern of $CoGe_{1.7}Te_{1.47}$ sample.

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. In the studied material ($CoGe_{1.7}Te_{1.47}$) corresponds the surplus approximately just two atoms of Ge per unit cell.

On the Fig. 3 the temperature dependence of Seebeck coefficient in 120-600 K temperature range is presented. There is evident from the Fig. 3 that prepared material of $CoGe_{1.7}Te_{1.47}$ composition is of n-type electrical conductivity. The observed n-type of electrical conductivity could be explained both by the deficit of tellurium in the lattice (tellurium vacancies) and partial ionization of surplus Ge atoms incorporated in the above mentioned voids presented in skutterudite structure. The Seebeck coefficient reaches its maximal value -540 $\mu V.K^{-1}$ at 380 K. Above this temperature it tends to decrease. This is, in our opinion, due to an increase in concentration of thermally excited minority carriers which cause a decrease in its magnitude.
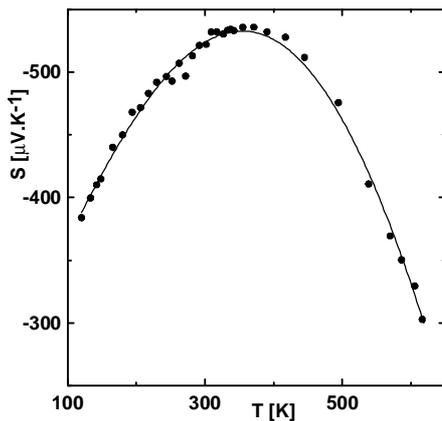

Fig. 3. Temperature dependence of Seebeck coefficient of $CoGe_{1.7}Te_{1.47}$ sample.

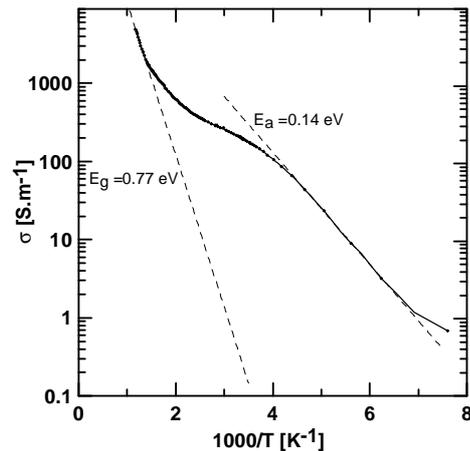Fig. 4. Electrical conductivity of $CoGe_{1.7}Te_{1.47}$ sample vs. inverse temperature

The electrical conductivity values presented on Fig. 4 increases with temperature over the whole temperature range of measurement. Two dashed lines in the Fig. 4 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 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 are in good agreement with authors [6], who obtained for sample $CoSn_{1.5}Te_{1.5}$ value of $E_g=0.7$ eV.

On Fig. 5 temperature dependence of power factor ($S^2.\sigma$) is given. The dependence reaches its maximal value of 1.4 $\mu W.m^{-1}.K^{-2}$ around 500 K. From thermoelectric point of view the value is not too interesting, but one has to realize that thermoelectric properties of the studied basic material could be in further research enhanced e.g. with proper doping and with voids filling.
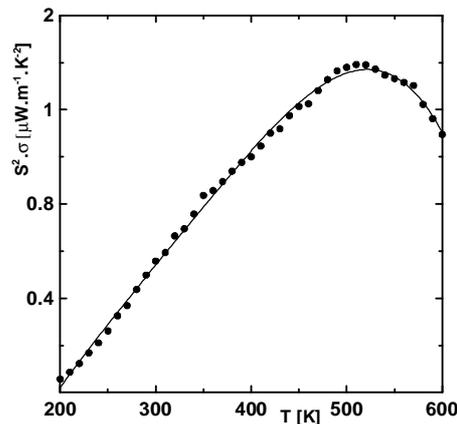

Fig. 5. Power factor ($S^2.\sigma$) of $CoGe_{1.7}Te_{1.47}$ sample vs. temperature.

4. Conclusions

Some thermoelectric properties of compounds of $CoGe_{1.7}Te_{1.47}$ composition were for the first time described. Deviation from stoichiometric composition ($CoGe_{1.5}Te_{1.5}$) was due to the specific way of preparation. From x-ray diffraction pattern analysis it looks the material is of cubic structure but unlike the most of skutterudite materials (space group *Im3*) one of with the lower symmetry. N-type electrical conductivity was ascribed to the existence either of tellurium vacancies or incorporation of surplus Ge into voids presented in the skutterudite structure. The activation energies corresponding to extrinsic electrons transitions (0.14 eV) and those of corresponding to activation of the charge carriers across the intrinsic energy gap (E_g=0.77 eV) were identified in temperature dependence of electrical conductivity.

The possibility to change content of incorporated Ge and Te in wide range around stoichiometric composition ($CoGe_{1.5}Te_{1.5}$) together with possibility to influence its thermoelectric properties by proper doping and void filling could lead to enhancement of thermoelectric properties of the compounds.

References

[1] T. Caillat, A. Borschevky, J. P. Fleurial, Proc. 27th Intersoc. Energ. Conv. Engin. Conf., San Diego, California, August 3-7, (3), 499 (1992).
[2] G.A. Slack, CRC Handbook of Thermoelectrics, Ed. D.M. Rowe, CRC Press, Boca Raton (1995).
[3] D.T. Morelli, G. P. Meisner, J. Appl. Phys. **77**, 3777 (1995).
[4] C. Uher, Semiconductors and Semimetals **69**, 139 (2001).
[5] G. S. Nolas, J. W. Sharp, J. H. Goldsmid, Thermoelectrics: Basic Principles and New Materials Development, Springer-Verlag, Heidelberg (2001).
[6] Y. Nagamoto, K. Tanaka and T. Koyanagi, Proc. 16th Int. Conf. Thermoelectrics, Dresden, Germany, August 26-29, 330-334 (1997).
[7] G. S. Nolas, J. Yang, R. W. Ertenberg, Phys. Rev. **B68**, 193206 (2003).
[8] N. C. Abrikosov, L. I. Petrova, L. D. Dudkin, V. M. Sokolova, G. I. Schmelev, Neorg. Mater. **18(3)**, 376 (1982).
[9] J. P. Fleurial, T. Caillat, A. Borschevky, Proc. 16th Int. Conf. Thermoelectrics, Dresden, Germany, August 26-29, 1-11 (1997).