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Synthesis of the high-entropy $(BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$ compound promising for thermoelectric applications

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Abstract. Single phase and nanosized powders of high-entropy $(BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$ compound with x=0; 0.3, 0.6 were synthesized by using soft chemistry approaches. Owing to its low thermal conductivity, this compound is promising for thermoelectric applications. The synthesized powders were used to prepare bulk samples totally suitable for testing thermoelectric properties.

1. Introduction

It is known that large-scale commercial application of thermoelectric materials has been remarkably limited by their low energy conversion efficiency [1]. The efficiency is expressed by the dimensionless figure of merit, $ZT=S^2T/\rho k$, where S, T, ρ and k are the Seebeck coefficient, absolute temperature, specific electrical resistivity and total thermal conductivity, respectively. To enhance the thermoelectric conversion efficiency, many efforts based on various modern scientific and technological approaches, focusing on optimal S, ρ and k combination, have been made in recent decades [2-4]. The concept of high-entropy alloy is a new strategy to improve the thermoelectric efficiency of thermoelectric materials [5, 6]. High-entropy alloys are usually considered as solid solutions in which more than five principal elements each in a 5-35% molar ratio compete for the same crystallographic site, yielding a high entropy of mixing, that results in unusual and exciting properties. As for developing of thermoelectricity, the lattice thermal conductivity in high-entropy alloys can be remarkably reduced via severe lattice distortion effects, resulting in the enhancement of ZT. An important technological challenge in the development of high-entropy alloys, is to prepare single phase compound with a desired structure and elemental composition.

The aim of this work is to find a synthesis method based on soft chemistry approaches, which is suitable to prepare the high-entropy $(BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$ compound. This compound is a new high-entropy one, which seems to be promising for thermoelectric applications. Besides, the compound can be considered as a derivate from the Bi_2Te_3 compound, which is a typical low-temperature thermoelectric. It should be also underlined that, in contrast to common methods used to prepare high-entropy alloys, soft chemistry synthesis is implemented at rather low temperatures.

2. Materials and methods

A soft chemistry method was developed to synthesize starting $(BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$ powders with x=0; 0.3, 0.6. It is known that reducing the lattice thermal conductivity in high-entropy alloys is often accompanied by a degradation of the carrier mobility [5, 6]. To reduce the degradation, Cu doping was

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used. All the synthesis manipulations were carried out in a conic flask with reflux and constant stirring. In a typical procedure (for 2 g powder), high pure ($Bi(NO_3)_3$*$5H_2O$, SeO_2, TeO_2, $Cu(CH_3COO)_2$*H_2O) precursors were dissolved in 400 ml ethylene glycol in stoichiometric proportions, with 10 g of NaOH addition for controlling *pH*-value and heated to 373 K for 1 h . The obtained solution was cooled to room temperature. 10 ml of hydrazine hydrate was slowly added with stirring into the solution and heated to 433 K. The resulting dark solution was maintained at this temperature for 3 h. After the reaction process, black powder was precipitated. The powder was purified by centrifugation and washing for 3 times with ethanol and acetone. Then the powder was dried in an argon atmosphere at 523 K for 2 hours.

The powder was further used to compact bulk samples by cold pressing in a steel mold at 100 MPa. The compacted samples were finally annealed at 673 K for 2 h, as a result, samples suitable for the examination of the thermoelectric properties were obtained. The density of the bulk materials, measured by the Archimed method, was estimated to be ~90%.

The morphology and size of the powder particles were identified by transmission electron microscopy (Jeol JEM 2100 microscope).

The crystal structure was determined by the X-Ray diffraction method (Rigaku Ultima IV diffractometer).

The elemental composition and microstructure of the samples were examined by scanning electron microscopy (FEI Quanta 600 FEG microscope) with an energy dispersive spectroscopy (EDS) detector.

3. Results and discussion

XRD patterns for the starting $(BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$ powders with x=0; 0.3, 0.6 are shown in Figure 1.

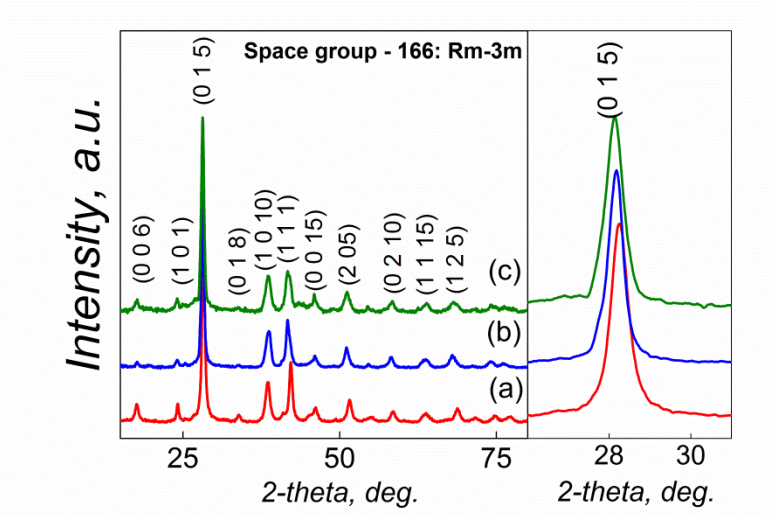

Figure 1. The XRD patterns of the $BiSbSe_{1.5}Te_{1.5}$ (a), $(BiSbSe_{1.5}Te_{1.5})_{0.7}Cu_{0.3}$ (b), $(BiSbSe_{1.5}Te_{1.5})_{0.4}Cu_{0.6}$ (c) powders.

According the XRD data, all the powders are single phase with tetragonal symmetry corresponding to the space *R*3*m* group. The lattice parameters were found to be slightly increased with increasing *x*, as shown, for instance, for the (015) peak. The incorporation of Cu atoms in the crystal structure can lead to this lattice expansion. As result, the diffraction peaks are shifted to low angles. No significant structure changes of the powders and bulk samples were observed while drying and annealing.

The use of $N_2H_4 \cdot H_2O$ as a common reducing agent results in simultaneously reducing the temperature and duration synthesis. The decomposition of hydrazine hydrate during synthesis to non-reactive gases (NH_3, N_2) and water does not pollute the resulted nanopowder. Ethylene glycol has the coordinating properties inducing surface functionalization and colloidal stabilization of nanosized particles. This

method of synthesis summarizes favorable properties of hydrazine hydrate and ethylene glycol, that, in turn, allows preparing single phase, highly-crystalline and nanosized ($BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$) powders for a short time and at low temperatures. The content of Bi, Sb, Se, Te, Cu in the powders with various x was determined by the EDS method. The element composition of all the powders was found to be corresponding to their nominal composition. The results of TEM-examination of the powders with various x demonstrated similar pattern for all the compositions. A typical morphology of the $(BiSbSe_{1.5}Te_{1.5})_{0.7}Cu_{0.3}$ powder is presented in Figure 2 (a). The powder consisted of irregularly shaped agglomerates of nanoplates.

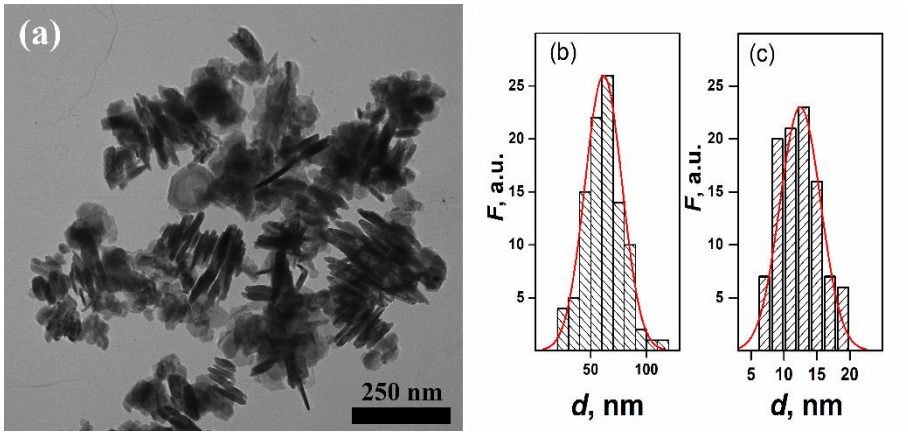

Figure 2. The TEM-image of the $(BiSbSe_{1.5}Te_{1.5})_{0.7}Cu_{0.3}$ powder (a) and histograms of the nanoparticles diameter size (b) and thickness (c) distributions.

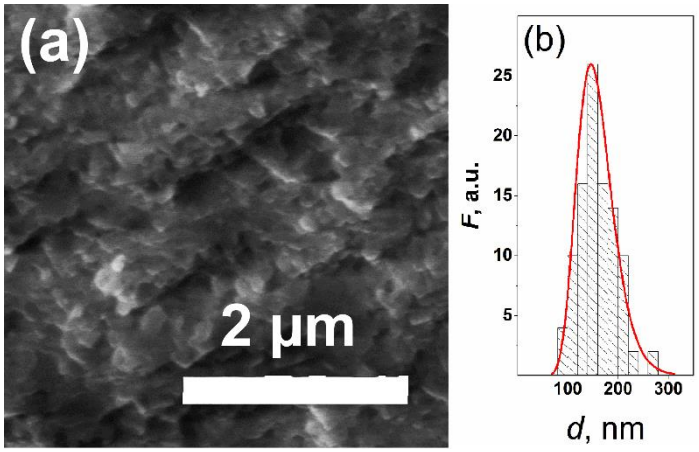

Figure 3. Typical microsctructure of the fractured surface for the bulk $(BiSbSe_{1.5}Te_{1.5})_{0.7}Cu_{0.3}$ sample (a) and the histogram of grain size distribution (b).

It was found that the probability density function, $P(d)$ for the histograms of the nanoparticles size distribution in Figure 2 (b) and (c) can be described by an unimodal lognormal distribution

$$P(d) = \frac{1}{\sqrt{2\pi}\sigma d} exp\left(\frac{-(lnd-lnd')^2}{2w^2}\right) \quad (1)$$

where *d* is the current nanoparticles size, *d'* is the average nanoparticles size, and *w* is the standard deviation of the logarithms of the particle sizes.

The analysis based on expression (1) of the experimental histograms of the nanoparticles size distribution in the powders material allowed estimating the average diameter size as ~ 60 nm and thickness size as ~ 12 nm.

It is known that nanocrystals of compounds based on Bi_2Te_3 usually form two-dimensional plates because of their crystal structure [7]. Bulk Bi_2Te_3 crystal has a layered structure that is composed of stacked two-dimensional layers of Te(1)−Bi−Te(2)−Bi−Te(1) with a Te(1)−Te(1) weak van der Waals interaction, leading to the ease of cleavage along the planes perpendicular to the *c*-axis.

The SEM-image taken from the fractured surface of the bulk $(BiSbSe_{1.5}Te_{1.5})_{0.7}Cu_{0.3}$ sample is shown in Figure 3 (a). All the bulk samples have a disordered grain structure with an average grain size of ~ 150 nm. The size was extracted from the analysis of histograms of the grain size distribution (figure 3 (b)). One can see that the the growth of grains occurred during the fabrication of material consisting of the starting nanosized powder. This phenomenon destroying the initial nanostructural state is characteristic of high-temperature sintering of nanomaterials [8].

4. Conclusion

Thus, a simple method based on soft chemistry approaches was developed to prepare the $(BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$ powders with x=0; 0.3, 0.6. The method allowed synthesizing single phase and nanosized starting powders. Then, bulk materials, suitable for examination of the thermoelectric properties, were prepared.

Acknowledgments

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References

[1] Nolas G S, Sharp J, and Goldsmid H J, Thermoelectrics Basic Principles and New Materials Developments, Springer, Berlin, 2001.
[2] Chen Z G, Han G, Yang L, Cheng L, and Zou J, "Nanostructured thermoelectric materials: current research and future challenge", Progress in Natural Science: Materials International, Vol. 22, pp. 535-549, 2012.
[3] Yaprintsev M, Lyubushkin R, Soklakova O and Ivanov O, "Effects of Lu and Tm doping on thermoelectric properties of Bi_2Te_3", Journal of Electronic Materials, Vol. 47, pp. 1362-1370 2018.
[4] Hu L, Zhu T, Liu X, and Zhao X, "Point defect engineering of high-performance bismuth-telluride-based thermoelectric materials", Advanced Functional Materials, Vol. 24, pp. 5211-5218, 2014.
[5] Fan Z, Wang H, Wu Y, Liu X J, Lu Z P, "Thermoelectric high-entropy alloys with low lattice thermal conductivity," RSC Advances, Vol. 6, pp. 52164-52170, 2016
[6] Fan Z, Wang H, Wu Y, Liu X J, Lu Z P "Thermoelectric perfomance of PbSnTeSe high-entropy alloys," Materials Research Letters, Vol. 5 No. 3, pp. 187-194, 2017.
[7] Goldsmid H J, "Bismuth telluride and its alloys as materials for thermoelectric generation", Materials, Vol. 7, pp. 2577-2592, 2014.
[8] Scheele M, Oeschler N, Meier K, Kornowski A, Klinke C, Weller H, "Synthesis and thermoelectric characterization of Bi_2Te_3 nanoparticles", Advanced Functional Materials, Vol. 19, pp. 3476-3483, 2009.