The Bismuth and Antimony Chalcogenides Solid Solutions Single Crystals with Gradient Carrier Concentration

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Abstract

Purpose of the work – receive the legs with a gradient carrier concentration along legs for thermoelectric modules. We have developed the way of preparation of bismuth and antimony chalcogenide solid solution single crystals with a gradient longitudinal carrier concentration profile. The Seebeck gradient (α) in the crystals is 40–70 µV/K over a distance 1–1.5 mm. The shape of the crystallization front of the crystals was determined. The gradient legs have optimal carrier concentrations for different working temperatures of multistage thermoelectric coolers (the thermoelectric power at hot end is from 230 to 270 µV/K).

Introduction

Thermoelectric materials based on solid solutions between antimony and bismuth chalcogenides are widely used to fabricate thermoelectric coolers and generators operating in the range 200–500 K. In the best devices it is obtained the maximum temperature difference of 73-75 K across single-stage modules on cooling from room temperature. According to earlier results [1-4], the use of legs with a graded carrier concentration profile markedly enhances the performance of thermoelectric modules. In the case of inhomogeneous legs, the Peltier heat is absorbed not only by the cold junction of the thermo-couple but also in the bulk of the leg, which further reduces the temperature of the cold junction in compar-ison with thermocouples consisting of homogeneous legs. In [3] and [4] investigated modules that employed composite legs produced by soldering two segments of materials based on Czochralski technique grown solid solutions between bismuth and antimony chalcogenides. The composite legs were mounted so that the regions with low carrier concentration (high Seebeck coefficient) were located in the hot zone. The maximum temperature difference across such modules increases by about 10% at a hot-junction temperature of 300 K. At the same time, the use of composite legs may give rise to losses at the junction between regions differing in carrier concentration. In this context, it is of interest to produce legs with a carrier concentration gradually varying within preset limits (so-called gradient legs).

Experimental

High-quality gradient p-type single crystals based on bismuth and antimony chalcogenide solid solution are grown by the Czochralski technique with supplementary feeding of liquid melt. The process offers the possibility of growing high-quality single crystals in a crystallographic direction predetermined by the seed crystal. Figure 1 shows a schematic of the floating crucible system. The floating crucible (*2*) insures temperature stabilization in the growth zone and a nearly flat growth interface. Moreover, the melt coming from the main crucible (*4*) though the capillary is free of insoluble oxide particles. When present on the melt surface, such particles may impair the quality of growing crystal. The crucibles we used were fabricated from dense extrapuregrade graphite. The heater and thermal shields were also made of graphite. The process was run in a high-purity helium atmosphere at a pressure of 1.6×10^5 Pa. The pulling, crystal rotation and crucible rotation rates were set by an operator, who could observe the process and optimize the process parameters.
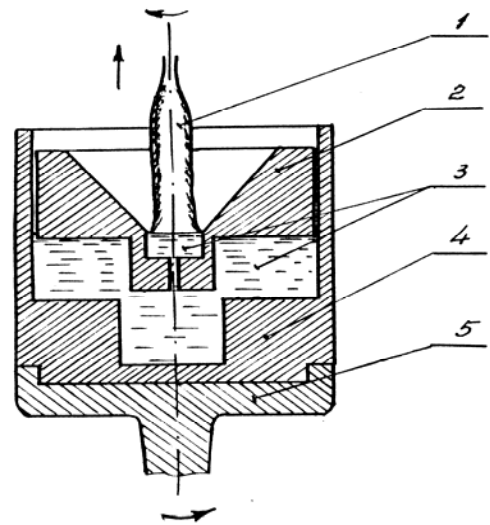

ig.1. Schematic illustrating crystal growth through a floating crucible: (*1*) crystal, (*2*) floating crucible, (*3*) melt, (*4*) main crucible, (*5*) holder.

The gradient of carrier concentration along the crystals is obtained by growing parts of the crystal from a melt with different content of tellurium. The Seebeck coefficient (α) is very sensitive to changes of carrier concentration, which is determined by the deviation from stoichiometric composition of solid solutions of bismuth and antimony chalcogenide. As it was shown in [5] for

equilibrium alloys of solid solution of $Bi_{0.5}Sb_{1.5}Te_3$, a change in the content of tellurium by no more than 0.2 at. % causes a change of Seebeck coefficient by about 100 µV/K (from 120 up to 230 µV/K), i.e. very small deviations of the content of tellurium lead to a significant change of the Seebeck coefficient. To reduce deviations from stoichiometry, we added selenium in form of Bi_2Se_3 (4 mol %) to the melt. Varying the concentration of excess tellurium in the melt during crystal growth, we obtained a gradient in carrier concentration along the crystal axis. The gradient regions of single crystals of $Bi_{0.5}Sb_{1.5}Te_{2.88}Se_{0.12}$ solid solution is present in fig.2.
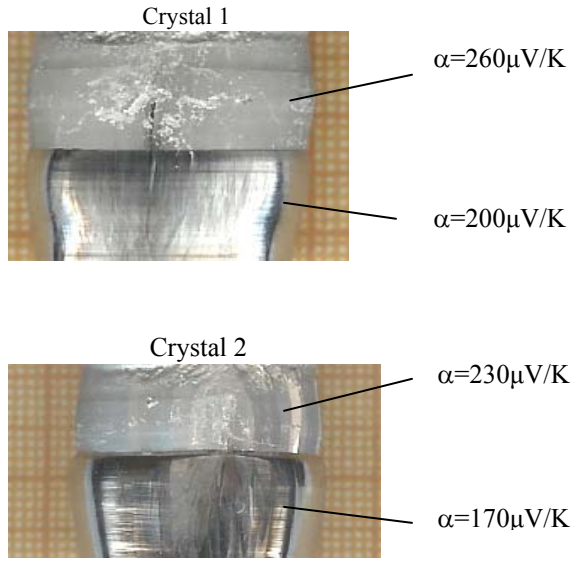
Crystal 1

α=260µV/K

α=200µV/K

Crystal 2

α=230µV/K

α=170µV/K

Fig.2. Regions of the single crystals of $Bi_{0.5}Sb_{1.5}Te_{2.88}Se_{0.12}$ with gradient Seebeck coefficient.

The electrical conductivity, thermal conductivity, carrier concentration were determined for samples cut from different parts of the crystals along the cleavage plane. The longitudinal Seebeck coefficient profile was measured by the several methods. Firstly, we measured the Seebeck coefficient by the help of bringing copper-constantan thermocouples to opposite faces and producing a temperature gradient of ~30 K. In this way, α was determined with an accuracy of ±2 µV/K over an area of ~0.8 cm^2. Secondly, we measured α of single crystals over an area of ~0.1cm^2 using copper-constantan thermocouples and indium spacers. Third, the Seebeck coefficient was measured using a hot probe in order to more accurately determine the α profile between regions differing in carrier concentration. In that case, we measured the relative value of α around the contact area between the crystal and a 0.3-mm-diametrer steel ball heated to about 330 K. Overall, the α profile was determined with an accuracy of ~2%. The variations in the Seebeck coefficient and the thermoelectric figure of merit along the gradient crystals in room temperature are present in fig. 3.
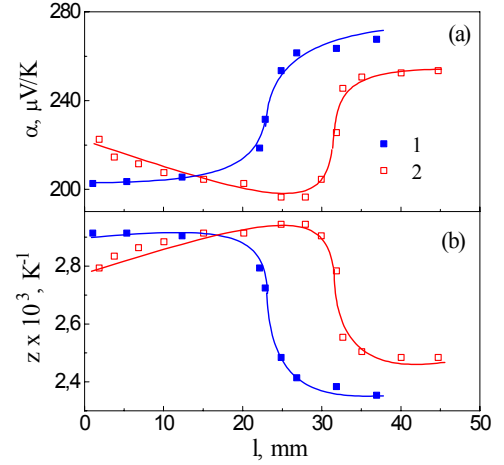

Fig.3. The variations in Seebeck coefficient (a) and thermoelectric figure of merit (b) along crystals 1 and 2.

The variation in α is 60 µV/K (from 270 to 210 µV/K) over distance of 4 mm in crystal 1 and 65 µV/K (from 250 to 185 µV/K) over 5 mm in crystal 2 and Z varies in the ranges $(2.3–2.8) \times 10^{-3}$ and $(2.5-3.0) \times 10^{-3}$ K^{-1}, respectively.

The gradient of carrier concentration of gradient plate cross sections is determined by measuring the Seebeck coefficient with a microprobe. Plates are cut from gradient regions of single crystals and the distribution of the Seebeck coefficient over their cross section is studied. The thickness of the plates was 2.5 mm. The variations in α of gradient plate cross sections on high- and low-α surface are present in fig. 4.
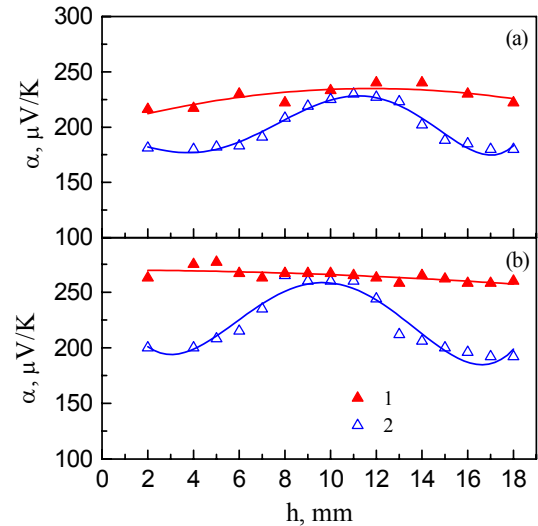

Fig.4. The variations in Seebeck coefficient of gradient plate cross sections (a, b) on (1) high- and (2) low-α surfaces.

This gradient plate was cut symmetrically about the junction. It is established that the crystallization front of the single crystals is not plane. For p-type single crystals it is convex. The distribution of Seebeck coefficient over the high-α surface was uniform. On the low-α surfaces, α

is higher in the central part. As a result, there is no axial gradient in α in that region, which is due to convex shape of the growth interface. The sag in the growth interface toward the melt was about 1 mm in central part. Subsequently, gradient plates were cut asymmetrically about the junction, displacing the cuts so as to reduce the zero-gradient region in the central part of the plate.

The gradient legs (1.4x1.4 mm and 0.6×0.6 mm in cross-section dimensions) that were cut from gradient plates and had no mechanical damage were used to evaluate the longitudinal gradient in carrier concentration. The gradient legs had the optimal carrier concentrations for different working temperatures of multistage thermoelectric coolers. The Seebeck coefficient at room temperature was measured about 0.5 mm away from the ends of the leg. The legs had different Seebeck coefficients at hot end and gradient of Seebeck coefficient $\Delta\alpha = 40\div70$ µV/K (α in hot end was from 230 to 270 µV/K).

The measurements of the Seebeck coefficient also were made along the length of the legs at 0.25-mm intervals. The measurement results for legs cut from two plates are presented in fig.5.
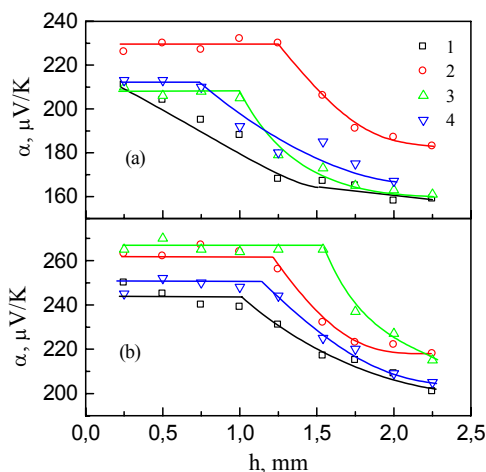

Fig.5. The variations in Seebeck coefficient on heights of gradient legs (1-4) cut from two plates (a, b).

The results demonstrate that α varies in gradient legs over distance 1−1.5 mm.

Microstructures were examined on lateral leg surfaces parallel and perpendicular to the cleavage plane after etching in aqueous 50% HNO_3 for 20s. The investigations of gradient legs with different carrier concentration (different α values) indicated the presence of Te-based eutectic precipitates along the cleavage plane in regions with low carrier concentration (α>220 µV/K). This explains that the composition of the regions was beyond the solubility limit of tellurium. Fig.6 illustrates, at different magnifications, the microstructure of the lateral surface of a gradient leg in which α varies from 250 to 200 µV/K. The presence of Te-based eutectic reflects in the crystal morphology: regions containing eutectic precipitates have rough lateral surfaces (fig.2).
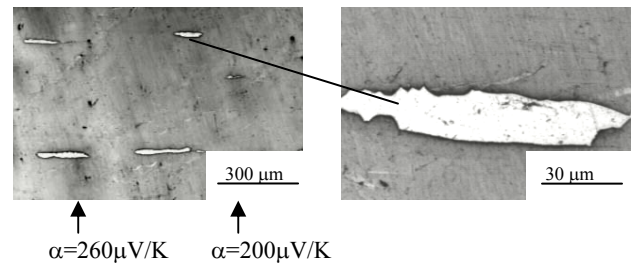

α=260µV/K   α=200µV/K

Fig.6. Microstructure of a gradient leg.

Conclusions

It was received high-efficient gradient single crystals based on bismuth and antimony chalcogenide solid solution. The carrier concentration gradient along crystals was obtained by varying the tellurium content of the melt during crystal growth.

The crystallization front of the single crystals was shown to be convex, with a sag of about 1mm in its central part.

We produced the gradient legs with optimal carrier concentrations for different working temperatures of multistage thermoelectric coolers. The Seebeck coefficient at hot end of the legs change from 230 to 270 µV/K.

It were received the gradient legs with the $\Delta\alpha = (40\div70)$ µV/K along legs on a distance 1−1.5 mm.

Regions with low carrier concentration (α>220 µV/K) were found to contain Te-based eutectic precipitates along the cleavage plane.

References

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