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Effect of dendritic inhomogeneity on the thermoelectric properties of $Bi_{0.88}Sb_{0.12}$ crystals

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The effect of dendritic inhomogeneity in $Bi_{0.88}Sb_{0.12}$ crystals on the transport properties and thermoelectric Q-factor was studied by experiment. It was found that the thermoelectric Q-factor of dendritic $Bi_{0.88}Sb_{0.12}$ crystals grown at a molten zone displacement rate of 1 cm/h exceeds the Q-factor of homogeneous crystals of the same composition by up to 20%.

Key words: bismuth, antimony, dendritic inhomogeneity, thermoelectric properties.

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1. Introduction

The thermoelectric Q-factor Z of crystals of $Bi_{1-x}Sb_x$ system was studied in detail depending on the ratio of alloy components and temperature [1–5], as well as on dopants content [6]. Previous studies [7,8] shown the possibility of Z increasing of inhomogeneous bismuth−antimony crystals in comparison with homogeneous crystals at low temperatures. Due to the practical interest in low-temperature materials based on bismuth−antimony crystals [9], we carried out systematic studies of the effect of composition inhomogeneity on their thermoelectric properties. This paper presents the results of an experimental study of $Bi_{0.88}Sb_{0.12}$ crystals in the temperature range 77−300 K.

2. Experimental results and discussion

The crystals for the study were grown by the method of horizontal zone recrystallization [10]. Homogeneous single crystals were grown at a molten zone passage speed of $v \leq 0.05$ cm/h and a temperature gradient at the crystallization front of $G \cong 20$ K/cm [4,11]. Due to the significant effect of low concentrations of dopants on the thermoelectric properties of bismuth−antimony crystals, the growth was carried out with additional use of the purified bismuth [6]. Inhomogeneous crystals were grown by the same method, but in different modes. As in papers [7,8], in such crystals a dendritic-type inhomogeneity was created, the degree of which was controlled by changing the speed of the molten zone passage $(0.05 < v < 10)$ cm/h during crystal growth.

The coefficients of thermoelectric EMF (α), electrical resistance (ρ) and thermal conductivity (κ) of grown crystals were measured using stationary methods in the temperature range 77−300 K. The thermoelectric Q-factor $Z = \alpha^2/\kappa\rho$ was determined from the results of measuring the corresponding transport coefficients. For crystals with an average content of $Bi_{0.88}Sb_{0.12}$ components, the data of the antimony concentration in dendrites and interdendritic layers and of their relative volumes, obtained using X-ray and metallographic methods, are given in the Table depending on the crystal growth rate.

Bismuth−antimony crystals are anisotropic, their thermoelectric Q-factor takes the highest values for the direction of heat and electric charge flows along C_3 axis, therefore $Z_{max} = Z_{33}$. Figures 1−3 show the results of experimental measurements in $Bi_{0.88}Sb_{0.12}$ crystals for a given crystallographic direction of resistivity (ρ_{33}), thermoelectric EMF (α_{33}) and thermal conductivity (κ_{33}).

The resistivity vs. temperature of all investigated crystals (Fig. 1) has two sections: characteristic for semiconductors at $T < 140$ K and characteristic for metals at $T > 200$ K. The resistivity of homogeneous single crystals ($v = 0.05$ cm/h) changes the form of the temperature dependence at the highest temperature $T = 200$ K. The transition temperature decreases as the growth rate increases to $T = 120$ K for $v = 10$ cm/h. At $T < 200$ K the resistivity of crystals grown at $v = 1$ cm/h is significantly lower than the resistivity of homogeneous crystals ($v = 0.05$ cm/h), which is due to the difference in nature and value of temperature dependencies of the resistivity of dendrites and interdendritic layers.

In general, the reason for the resistivity decreasing depending on the degree of inhomogeneity is the growing inhomogeneity of the antimony distribution over volume, which leads to a decrease in the antimony content in interdendritic interlayers and an increase in their volume fraction in the crystal (see Table).

Antimony distribution in inhomogeneous $Bi_{0.88}Sb_{0.12}$ crystals

Growth rate, cm/p	Dendrite cell		Inter-dendritic layer	
	Occupied volume, %, (±3%)	Concentration of antimony in center, at%, (±0.5%),	Occupied volume, %, (±3%)	Concentration of antimony, at%, (±0.5%)
1	80	14.3	20	8.8
2.5	69	15.9	31	7.1
5	61	18.2	39	5.0
10	46	22.1	54	3.2

Fig. 2 shows the results of the concentration and mobility of electrons calculation from experimental data of the resistivity, Hall coefficient, and magnetoresistance in a weak magnetic field of homogeneous single crystals of bismuth–antimony solid solutions grown at low zone passage speeds $\upsilon \leq 0.05$ cm/h. The Figure shows that at

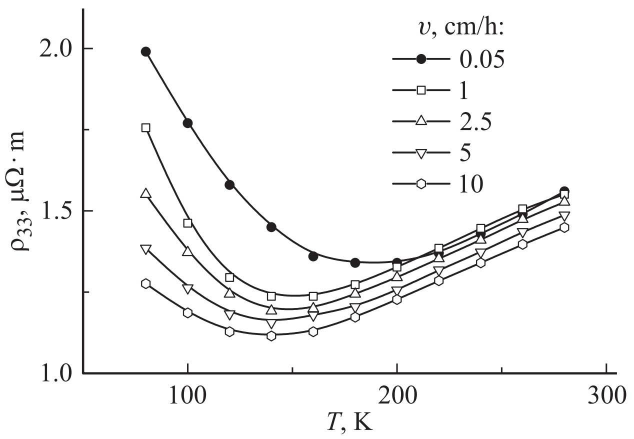

Figure 1. Resistivity vs. temperature of $Bi_{0.88}Sb_{0.12}$ crystals grown at different rates υ.

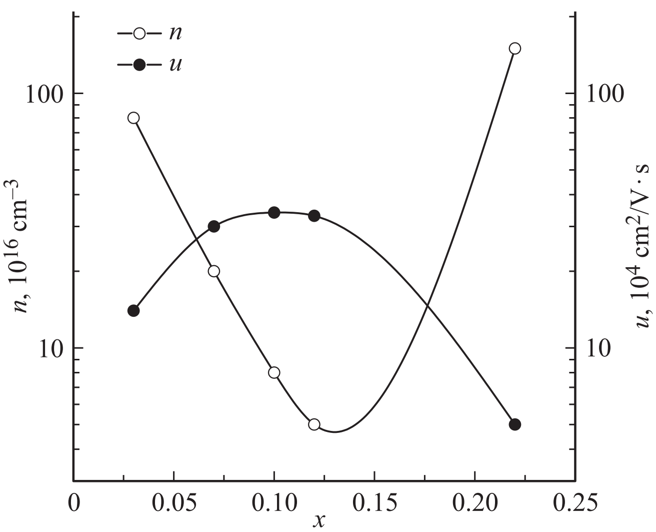

Figure 2. Concentration n and mobility u vs. composition of L-electrons in crystals of $Bi_{1-x}Sb_x$ system.

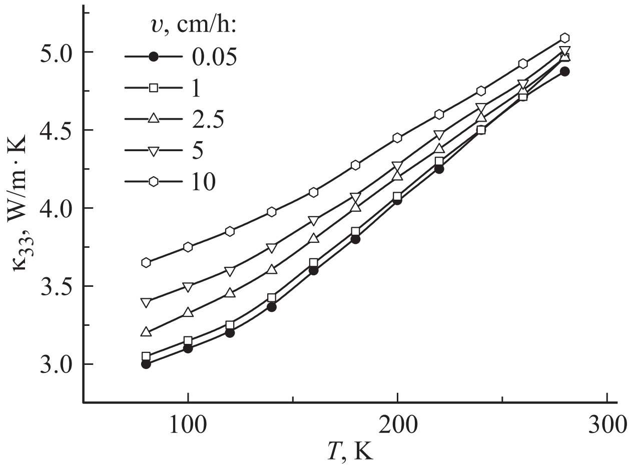

Figure 3. Thermal conductivity vs. temperature of $Bi_{0.88}Sb_{0.12}$ crystals grown at different rates υ.

comparable mobility the concentration of charge carriers differs significantly in dendrites and interdendritic layers. At the growth rate of 10 cm/h, both dendrites, and interdendritic layers have a high concentration of charge carriers, so the electrical resistance of such a crystal is the lowest.

For the same reason the thermal conductivity continuously increases with the growth rate increasing (Fig. 3). But growth is slow due to additional scattering of phonons at the boundaries of dendrites and interdendritic layers.

The thermoelectric EMF decreases with the crystal growth rate increasing (Fig. 4) due to the averaging of the distribution of transfer coefficients over the volume, additional scattering of carriers and eddy currents in inhomogeneous crystals. In the range of rates 0.05–1 cm/h the change in thermoelectric EMF and thermal conductivity is insignificant.

As a result, this leads to the thermoelectric Q-factor Z_{33} increasing up to 20% for crystals grown at rate of 1 cm/h, as compared to homogeneous crystals (Fig. 5). A further increasing of the growth rate and the degree of crystal inhomogeneity leads to decreasing of the thermoelectric EMF and the thermoelectric Q-factor. Thus, depending on the growth rate and the degree of inhomogeneity of bismuth–antimony crystals caused by it, the thermoelectric Q-factor passes through a maximum.

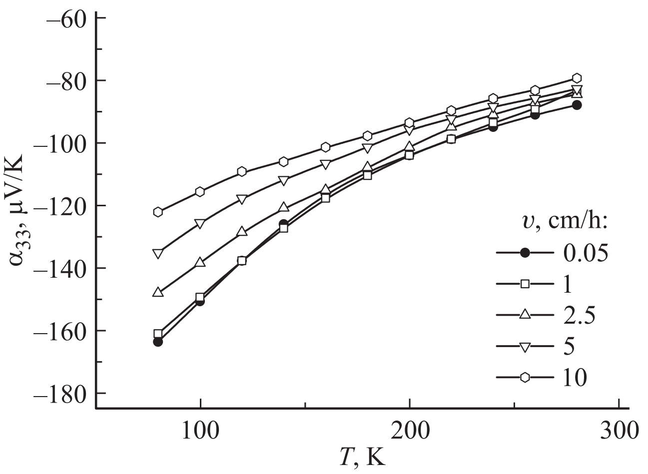

Figure 4. Thermoelectric EMF vs. temperature of $Bi_{0.88}Sb_{0.12}$ crystals grown at different rates υ.

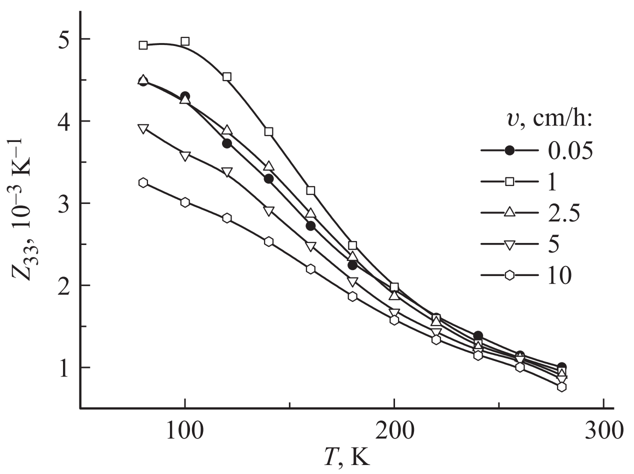

Figure 5. Thermoelectric Q-factor vs. temperature of $Bi_{0.88}Sb_{0.12}$ crystals grown at different rates υ.

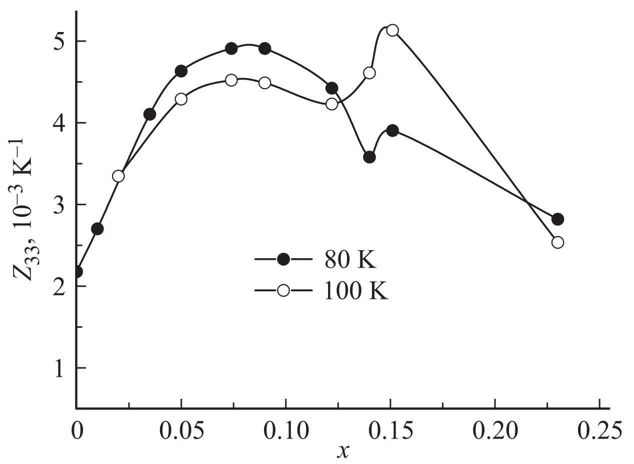

Figure 6. Thermoelectric Q-factor Z_{33} vs. antimony concentration at low temperatures.

The observed changes in the transport properties and thermoelectric Q-factor are associated with a complex change in the zone structure of crystals of the bismuth−antimony system depending on composition, and with nonmonotonic dependence of the thermoelectric Q-factor of homogeneous bismuth−antimony crystals on the content of antimony (Fig. 6). It can be seen that the maxima of the thermoelectric Q-factor are located on the graph to the right and to the left of the $Bi_{0.88}Sb_{0.12}$ crystal Q factors. Therefore, when grown at the rate of 1 cm/h, the dendrites with Sb concentration of 14.3%, and interdendritic interlayers with Sb concentration of 8.8% have Q-factor Z_{33} higher than the homogeneous $Bi_{0.88}Sb_{0.12}$ crystal.

Inhomogeneous $Bi_{1-x}Sb_x$ crystals are two-component structures, a detailed theoretical analysis of their Q-factor was carried out in the paper [12], and the results obtained by us do not conflict with the results of this paper.

3. Conclusion

When used in thermoelectric converters, the inhomogeneous $Bi_{1-x}Sb_x$ crystals grown at the rate of $\upsilon = 1$ cm/h have advantages over homogeneous ones ($\upsilon = 0.05$ cm/h). They have high values of Z_{33}, comparable with the values of the most efficient homogeneous $Bi_{1-x}Sb_x$ crystals, are more resistant to chipping, require less cost for growth, and are therefore economically preferable.

Using the example of bismuth−antimony solid solutions, the possibility of a practically significant increasing of the thermoelectric Q-factor of thermoelectric materials that are inhomogeneous in composition as compared to homogeneous ones is experimentally shown.

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Conflict of interest

The authors declare that they have no conflict of interest.

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