

The suppression of intrinsic conductivity in p-Bi_{0.5}Sb_{1.5}Te₃ by the plastic deformation

B.M.Goltsman, V.A.Kutasov, L.N.Lukjanova
Ioffe Physical-Technical Institute, Russian Academy of Sciences,
Polytekhnicheskaya 26, 194021 St.-Petersburg, Russia
email: lidia.lukyanova@mail.ioffe.ru
Ph. +7 812 5159247, Fax +7 812 5156747

Abstract

The investigations of the Zeebeck coefficient temperature dependencies in the interval 300K - 480K of the solid solution p-Bi_{0.5}Sb_{1.5}Te₃ polycrystals, exposed by pressing, had shown, that the plastic deformation can increase the Zeebeck coefficient at the elevated temperatures. It may be connected with the suppressing of the intrinsic conductivity by the plastic deformation. The possible reasons of this effect are the change of the sample texture and the origin of the linear structural defects (the dislocations, the microcracks), that enhanced the minor current carriers scattering.

Introduction

One of the essential factors determining the thermoelectrical properties is the intrinsic conductivity. The intrinsic conductivity reduces the thermoelectric efficiency $Z = \alpha^2 \sigma / \kappa$ (α - the Zeebeck coefficient, σ - the coefficient of electric conductivity, κ - the coefficient of thermal conductivity), that is connected with the decrease of the Zeebeck coefficient and the increase of the thermal conductivity. Some electrical conductivity growth does not compensate the changes of the Zeebeck coefficient and the coefficient of thermal conductivity.

In our investigation the probability to suppress the intrinsic conductivity by the plastic deformation of the thermoelectric has been observed. Such deformation is able to change the texture of material and to create the structural defects, which may decrease the mobility mainly of the minor current carriers. The object of investigation is the solid solution p-Bi_{0.5}Sb_{1.5}Te₃, for which the intrinsic conductivity considerably influences on the thermoelectrical properties already at the temperatures higher, than 400K, due to the narrow energy gap ($E_{g,300K} = 0.12\text{eV}$ [1]).

Experiment

The initial samples of this material were obtained by the cutting of the ingots, prepared by zone melting. The samples had the cylindrical form and the polycrystalline columnar structure. The crystal grains were elongated in parallel to the cylinder axis (the L-direction). The orientation of the cleavage planes (these planes are characteristic for Bi_{0.5}Sb_{1.5}Te₃) was determined by the investigation of the angular distribution of the reflected laser beam by scanning of the beam on the surface, revealed by the sample cracking along the cylinder diameter. The normals to the cleavage planes were approximately perpendicular to the L-direction: The mean angle between normals and L-direction was 4°.

The samples were plastically deformed in the prefilling press, having the rectangular hole. The sample was disposed in the press so, that the direction L was perpendicular to the

direction of pressing (P-direction). The pressing was carried out at 400°C by the pressure 4t/cm². After the primary pressing it followed the repetitive one at the same conditions, but the direction of pressing had been turned through 90° (the L-direction was conserved). The deformed sample structure was described using the angular distribution of the normals to the cleavage surface, obtained by the sample cracking. The orientation of the normals was determined by the angles between the P-direction and the directions of normal projections on the PL-plane, (containing the P- and L-directions), or on the A-plane, (perpendicular to the L-direction). The investigation, using the laser beam, showed, that in the deformed samples the normals to the cleavage surface are oriented preferentially along the pressing direction. The directions of the projections on the PL-plane differed from P-direction much less than the directions of the projections on the A-plane. The mean angles between the P-direction and the directions of the pointed above two kinds of projections were 3° and 12°. The plastic deformation leads also to the bending of the cleavage planes. The bending of the cleavage surface of the deformed sample may be described by the curvatures of the intersections of the cleavage surface and the PL- or A-planes. The intersections of the cleavage surface and the PL-plane were bent much more, than the intersections of the cleavage surface and the A-plane (Fig.1).

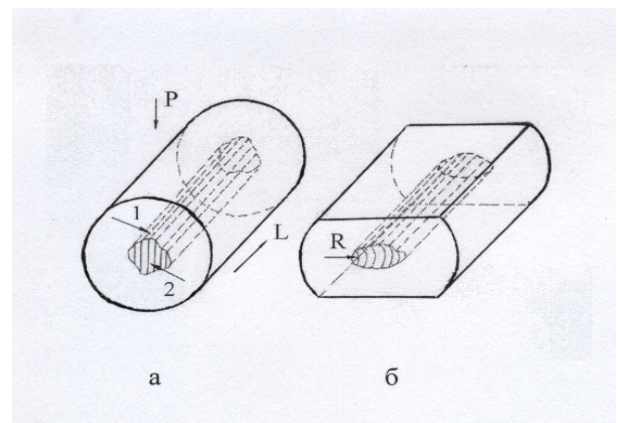


Fig.1. Bending of the crystal grains cleavage planes by the deformation. a) The sample before the deformation. b) The sample during the deformation. 1 - The crystal grain. 2 - The cleavage plane. R - The bend radii, lying in the crosswise section of the sample.

The influence of the plastic deformation on the intrinsic conductivity of p-Bi_{0.5}Sb_{1.5}Te₃ was determined by the comparison of the Zeebeck coefficient temperature

dependencies of the non-deformed and deformed samples (Fig.2).

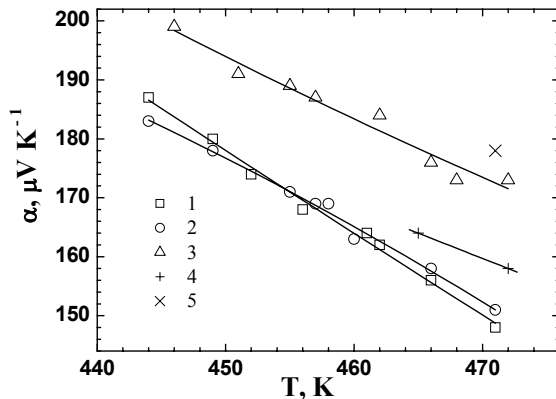


Fig.2. The Zeebeck coefficient temperature dependencies by the different orientations of the temperature gradient by the measurements. 1 - non-deformed sample, gradT is parallel to the L-direction. 2 - deformed sample, gradT is parallel to the L-direction. 3 - Deformed sample, gradT is perpendicular to the P- and L-directions. 4 - Singlecrystal, gradT is parallel to the cleavage planes. 5 - Singlecrystal, gradT is perpendicular to the cleavage planes.

All samples had at the lowest temperatures of measurement (300K) approximately equal values of Zeebeck coefficient ($224\text{--}227\mu\text{V/K}$), corresponded to the extrinsic conductivity of $\text{p-Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ at this temperature. The measurements of the Zeebeck coefficient temperature dependency of the non-deformed samples by the temperature gradient, oriented along the L-direction, had shown, that at the temperature 471K the Zeebeck coefficient decreases to $148\mu\text{V/K}$, due to the appearing of intrinsic conductivity. The measurements of the deformed samples were performed by the temperature gradient, lying in the plane, perpendicular to the P-direction, besides the temperature gradient either was oriented along the L-direction, or was perpendicular to the L-direction. In the first case the Zeebeck coefficient temperature dependence of deformed sample coincided with the temperature dependence of the non-deformed one (Fig.2), but in the second case the values of the Zeebeck coefficient at the elevated temperatures were considerably higher ($173\mu\text{V/K}$ at 471K). Simultaneously it was noted the weakening of the temperature dependence. The values of the Zeebeck coefficient at 300K after the temperature measurements coincided with the initial values at this temperature. As a result, the plastic deformation had enhanced the Zeebeck coefficient at 471K by 18%.

Discussion

So, we suppose, that the intrinsic conductivity is suppressed in deformed $\text{p-Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, when the thermal and electric flows during the Zeebeck coefficient measurements are perpendicular to the P- and L-directions. It leads to the origin of the anisotropy of the Zeebeck

coefficient in the plane, perpendicular to the P-direction. One of possible reasons of this anisotropy can be the texture, formed by the sample deformation. In the deformed sample, having the texture, described above, the electrical flow, oriented transversely to the P- and L-directions crosses the cleavage planes by the higher angle, than the flow, oriented along the L-direction. For the materials on the $\text{p-Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ basis the ratio of the mobilities along and crosswise to the cleavage planes (exceeding the unit) is higher for electrons, than for holes [1]. Therefore, in our case the minor current carriers will be scattered in the higher degree, when the temperature gradient is oriented crosswise to the P- and L-directions. For the estimation of the contribution of this factor it was measured the Zeebeck coefficient temperature dependence of the $\text{p-Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ singlecrystal with the insignificant violation of the cleavage planes orientation. In this extreme case the Zeebeck coefficient at 471K for the temperature gradient, perpendicular to the cleavage planes, was only by 13% higher, than the Zeebeck coefficient for the gradient, oriented along these planes. Thus there are other reasons of intrinsic conductivity suppression.

Such reason can be the preferential scattering of the electrons by the structural defects, arising due plastic deformation. Since we have the anisotropy of the Zeebeck coefficient in the plane, perpendicular to the P-direction, it is possible suppose, that we have the linear defects (the dislocations, the microcracks), located in this plane and oriented preferably along the L-direction. Such orientation agrees to the above-stated picture of the cleavage plane bending at the sample deformation (Fig.1). These defects may scatter the current carriers in the greatest degree, when the electronic flow in the Zeebeck coefficient measurements is perpendicular to the lines of defects (just as the maximal scattering takes place for the electronic flow perpendicular to the dislocation lines in the germanium crystal [2]).

Conclusions

It is shown that the intrinsic conductivity can be suppressed in the $\text{p-Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ plastically deformed samples for the certain direction of the electric current relative to orientation of a sample. This effect may be connected with the intensification of the minor current carriers scattering by the change of sample texture and by the origin of structural defects (the dislocations, the microcracks), as the result of the plastic deformation.

References

1. Goltsman B.M., Kudinov V.A., Smirnov I.A. Thermoelectric semiconductor materials on the Bi_2Te_3 basis, Science (Moscow, 1972), p. 143, p. 306.
2. Smith R.A. Semiconductors, Foreign Literature (Moscow, 1962), p. 158.