Properties of the Electron and Phonon Sub-systems of Tin-doped Bismuth Telluride-based Solid Solutions

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Abstract

We report the results of an experimental study of the thermal conductivity and other basic transport coefficients: electrical, Hall, Nernst-Ettingshausen and Seebeck coefficients and their anisotropy in $Bi_{2-x}Sn_xTe_{3-y}Se_y$ single crystals doped with Sn. All crystalls were grown by the Czochralski technique. The p-type samples show similar peculiarities in the temperature dependence of the transport coefficients that can be explained by the presence of resonant states of Sn. Improved thermoelectric properties of n-type $Bi_{2-x}Sn_xTe_{3-y}Se_y$ were found: a maximum of $Z = 3.3 \cdot 10^{-3}\ K^{-1}$ at 340-370 K which is a larger value compared to solid solutions without Sn. We observed a different influence of Sn atoms on the electron and phonon sub-systems: an increase of the thermal resistivity, whereas the electron mobility doesn't change simultaneously. Moreover, improved homogeneity of the carrier concentration distribution was detected by locally resolving measurement of the Seebeck coefficient by the scanning thermo-probe on these crystals. The obtained experimental data support to the point of view that the incorporation of Sn atoms into $Bi_2Te_{3-x}Se_x$ is accompanied by the formation of a band of Sn states against the background of the allowed valence-band spectrum that interact with basic electron states of these compounds.

Introduction

Traditional application of Bi_2Te_3-based solid solutions in thermoelectric converters gives rise to look for methods to improve their properties. To create materials having a high thermoelectric properties it is used the doping of these materials with various impurities. But the addition of impurities usually leads to a significant increase in fluctuations of thermoelectric properties that is associated with the statistical character of the spatial impurity distribution.

According [1-3] it was established that on introducing Sn impurity into Bi_2Te_3 quasilocal states appear within the valence band near of the top of the additional extremum. The presence of resonant states provides the positive effect of producing crystals with high electrical homogeneity. Resonant states lead to pinning of the Fermi level. Since the thermoelectric power is sensitive to variation of the Fermi level, the resonant states lead to its stabilization and to enhancement of the homogeneity that was testified by investigations of the distribution of the Seebeck coefficient on the surface of crystals with scanning microprobe [3] and by experiences on microrentgenostructure analyses [4]. This is particularly important for crystals of the A^VB^{VI} trigonal system that exhibit a pronounced anisotropy. Under real growth conditions, even the best single crystals of this compound contain a large amount of inhomogeneities. It is known that the thermoelectric figure of merit is higher in homogeneous crystals. Hence, different possibilities may be considered to obtain material with high homogeneity. One of them is to use the Czochralski technique [6]. Another way is to use doping impurities (Sn) creating resonant states in the compound. We used both of these approaches in our investigation.

It is known that the thermal conductivity is the important parameter in the expression for the thermoelectric figure of merit. So an experimental study on the influence of Sn doping on the thermal conductivity of. crystals lattices is important an object. The crystal lattice of bismuth telluride as well as the crystal lattices of lead chalcogenides, have a high polarizability. So the influence of impurities on the lattice thermal conductivity depends strongly on their charge state. The effective phonon scattering cross-section Φ of charged impurities in these compounds is several times greater than that of neutral impurities [5]. This fact we will use in this work to elucidate the charge state of an tin impurity and to verify the model of quasilocal impurity states in Bi_2Te_3- based solid solutions.

Experiment

All single crystals were grown by Czochralski technique with replenishment of the melt from a liquid phase [6]. The single crystals were grown in the [1010] direction normal to the main crystallographic axis *c*. Samples for measurement had different composition: 1. samples of Bi_2Te_3 doped only with tin were described by the chemical formula $Bi_{2-x}Sn_xTe_3$, were x = 0; 0.002; 0.004; 0.005; 0.007; 0.01 and 0.02 (x = 0.01 corresponds to a carrier density of $6.10^{19} cm^{-3}$); 2. samples Bi_2Te_3 codoped with tin and iodine have the formula of $Bi_{2-x}Sn_xTe_3$ +

$ySbJ_3$, where x = 0.005; 0.01; 0.02 and y = 0.05; 0.1; 0.15 wt%; 3. samples Bi_2Te_3 codoped with tin and lead have the formula $Bi_{2-x-z}Sn_xPb_zTe_3$ (x = 0.005; 0.01; 0.02 and z = 0.005; 0.01; 0.02; 0.03); 4. samples of solid solution p-$Bi_{2-x}Sn_xTe_{3-y}Se_y$ with x = 0; 0.01 and y = 0.06 and 0.12; 5. samples of solid solution n - $Bi_{2-x}Sn_xTe_{3-y}Se_y$ with x = 0; 0.002; 0.004 and y = 0.15. The tin content was determined by plasma atomic-absorption spectroscopy.

Measurements of thermal conductivity were carried out at room temperature using a normal kind of system. As well as thermal conductivity κ_{11} we measured the following independent components of the transport tensors: the Hall coefficient R_{321}, the thermoelectric power S_{11} and the electrical conductivity σ_{11}. In this notation the number 3 indicates the trigonal axis of a crystal. The measurements of transport coefficients were carried out mainly in the temperature range 77 - 420 K. The carrier density was determined from the expression $n, p = [q\, R_{321}(77\ \mathrm{K})]^{-1}$. The lattice resistivity W_l was determined from the lattice contribution to the thermal conductivity

$W_l = \kappa_l^{-1} = (\kappa - \kappa_e)^{-1}$. The electronic component of the thermal conductivity was calculated from formula $\kappa_e = (k_0/e)^2 L\sigma T$, where L is the Lorenz number.Thw Lorenz number was calculated taking account of the parabolic electron spectrum and dominant contribution from acoustic phonons to electron scattering at room temperature.

The spatial distribution of thermoelectric power over the surface of $Bi_2Te_{3-x}Se_x$:Sn single crystals was investigated by a 30 μm-resolution microprobe method described in [7]. The main advantages of this technique are the simple measuring conditions and high lateral resolution. In this method the applied temperature difference was 3-5 K. The accuracy of thermoelectric power measurements was better than 1%.

Bi_2Te_3

Investigations of thermal conductivity, carried out on specimens of Bi_2Te_3, doped only with tin [8], showed that the additional lattice scattering per impurity atom is 3-4 times less than for an iodine impurity. It can be assumed that this is due to the absence of electrical charge on the majority of Sn atoms. The exception is the part of curve at a light guantity Sn. At N_{Sn} = 0.2 at. % the thermal resistivity W_r increases the same manner as for scattering on a charge impurities. May be it is due to the light part of Sn atoms places on the $Te^{(2)}$ positions, where they are electrically active. As the concentration of tin is increased, the thermal resistivity decreases up to value of undoped Bi_2Te_3. Probably, the Sn atoms places on the $Te^{(1)}$ positions after filling of $Te^{(2)}$. Accordingly conclusion of [2], atoms Sn substituting for $Te^{(2)}$ in Bi_2Te_3 create a resonant states. There are atoms Sn neutral relatively of lattice at this positions. The results of measurements of thermoconductivity support this assumption.The thermal resistivity of lattice follows the low of phonon scattering on neutral impurity

(Fig. 1).

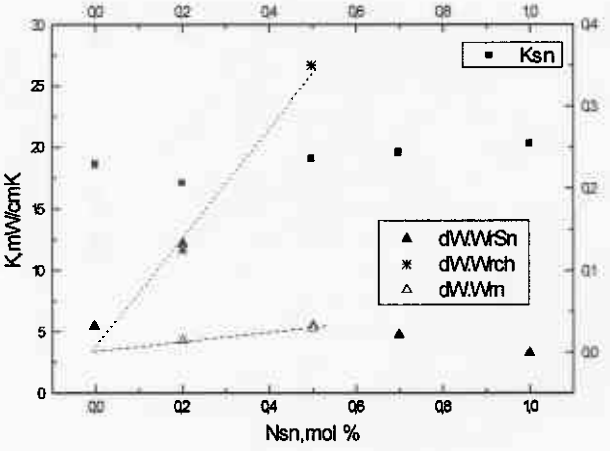


Fig.1. Dependences of the thermal conductivity $\kappa_{общ}$ (1) and relative value of additional lattice thermal resistivity dW/Wr (2-4) Bi_2Te_3 on the amount of doped impurity: 1,2 – Sn; 3 – charged I impurity, 4 – neutral Se impurity (3,4 - данные работы [7].

Results on the additional lattice resistivity W_l are more interesting. Consider the change of lattice thermal resistivity by codoping Bi_2Te_3 with tin and with acceptor (Pb) or donors (I, Cl). As seen from Fig.2 W_l is practically constant at codoping with acceptor, but W_l increases sharply at codoping with donor impurity.

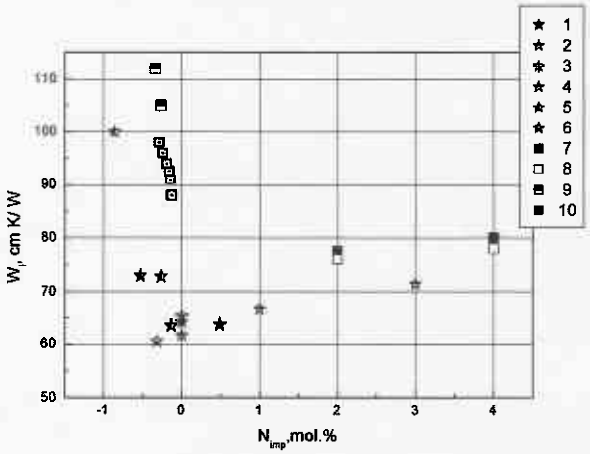


Fig.2. Dependences of lattice thermal resistivity W_l of Bi_2Te_3 (1–6) and $Bi_2Te_{3-y}Se_y$ (7-10) on the amount of doped impurity: only Sn (1-3,7); without Sn, only with acceptor Bi(Pb) (8) or with donor I (10); and codoped with Sn and acceptor (4) or with Sn and donor (5-6,9).

We shall analyze the $W_l = f(N_{imp})$ dependence obtained. We will consider that the change in W_l at doping with donors and acceptors is associated with features of phonon scattering in Bi_2Te_3 at additional doping. Then the phonon scattering cross-section Φ can be estimated from results on the thermal conductivity using the Ioffe's formula

$$k_0/k = W_l/W_0 = 1 + (N/N_0)\,\Phi\,(l_0/l) \qquad (1)$$

where N is the impurity concentration, N_0 is the number of atoms in the material per cm^3, a is nearest neighbor distance, l_0 is the phonon mean free path in

the impurity – free crystal, Φ is the coefficient in the relation $S = \Phi a^2$ (S is the phonon scattering cross-section of an impurity), k and k_0 , W_I and W_0 are the lattice thermal conductivity and resistivity in a crystal with and without impurity, respectively.

It turn out that the value of Φ is approximately constant and equal to 1.3 over the whole area of additional doping Bi_2Te_3:Sn with aceptor impurity (atoms Pb) and at codoping with donor impurity (atoms Cl or I) up to 0.5 mol.%. At N_{imp} = (0.5 – 1) mol.% phonon scattering cross–section increases up to Φ ~ 8. We note that the values of Φ, obtained in this work, agree well with literature values for Bi_2Te_3 for phonon scattering on neutral and charged impurities.

The result obtained are similar to the data observed in PbTe:Tl at additional doping with Na. The impurity Tl produces the resonant states in valence band of PbTe, and a strong acceptor impurity Na give possibility to empty these states and to take out Fermi level from the zone of resonant states [9]. The likeness of the experimental results obtained in this work on Bi_2Te_3:Sn lies in the fact that weak dependence W_I from additional impurity, when Fermi level is in a zone of resonant states: this is a zone of relatively stability of hole concentration and strong dependence W_I , when Fermi level is out a zone of resonant states.

$Bi_2Te_{2.85}Se_{0.15}$

At replace of the part of Te atoms on Se atoms in Bi_2Te_3, doped with Sn, we watched the same electrical properties as Bi_2Te_3:Sn. For example, we can see on the Fig.3 the dependences of hole concentration (p) on of doped Sn impurity amount. There are presented data of Bi_2Te_3 and of $Bi_2Te_{3-y}Se_y$, doped only with donor I(Cl) or acceptor Pb impurities and codoped with these impurities and Sn. We observe the low changes of hole concentration in tin-doped crystals. And we can see different action of donor impurities I (Cl) atoms at presence Sn and without it. The electron concentration changes much smaller at presence Sn.

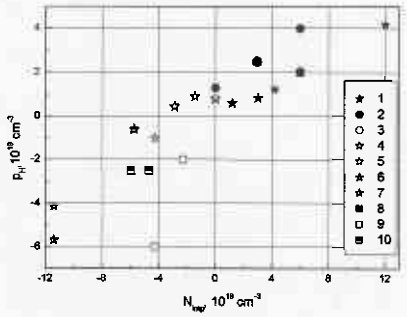


Fig.3. The dependence of hole concentration (p_H) against of impurity concentration (N_{imp}) of Bi_2Te_3 (1-7) and $Bi_2Te_{3-y}Se_y$ (8-10): only Sn (1,8); without Sn, only acceptor Bi,Pb (2) or donor I (3,9) impurity; and codoped with Sn and acceptor (4) or donor (5-7,10) impurity.

Electrical properties

p – type

A resonance states in the valence band of Bi_2Te_3 are leading to modifying the temperature dependences of the transport coefficients σ_{11}, R_{321}, S_{11} in these crystals drastically, similarly to as it was reported for Bi_2Te_3.

We can see this from the experimental data shown in Fig. 4. We observed the following changes:

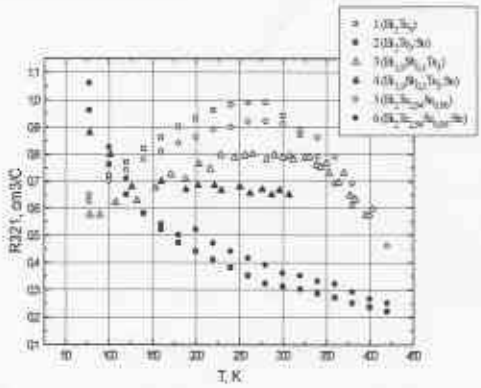
1. The temperature dependences ***R(T)*** of the samples containing Sn change from a rising pattern with a maximum typical for Bi_2Te_3 and $Bi_2Te_{3-x}Se_x$ to a strongly decreasing curve (Fig.1)

2. The Seebeck coefficient for tin containing samples is somewhat larger in the temperature region at T<200 K and at T>380 K and their dependence becomes more gently sloping with temperature (Fig.4).

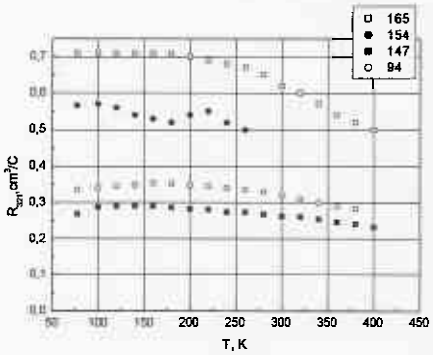
3.Considerable falloff of the electroconductivity σ (hole mobility) and Nernst is observed (Fig.4 a,b)

n - type

The doping with tin n-type solid solution does not change the character of the kinetic coefficients. But the anisotropy of the Hall and Nernst coefficients are reduced in Sn doping samples. Consequently, inhomogeneity in the distribution of the doping defects is reduced which results in a high electrical homogeneity.



a) p-type



b) n-type

Fig.4 **a)** R_{321} = f (T) for p-type Bi_2Te_3 (1), doped with Sn (2),under replace Sb → Bi (3,4) and under replace Se → Te (5,6); open symbol – without Sn, full symbol – doped with Sn. **b)**: R321 = f(T) for n-type $Bi_2Te_{3-y}Se_y$ with different electron concentration.

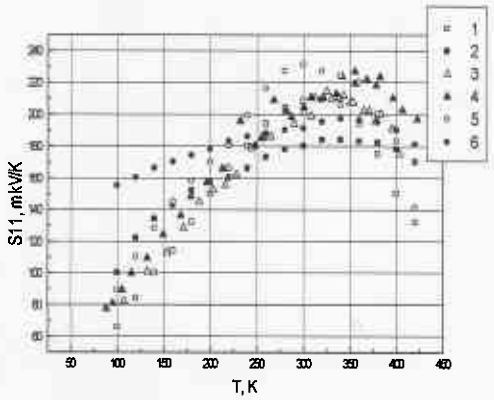


Fig.5a. Sij = f (T) for p-type Bi_2Te_3 (1), doped with Sn (2), under replace Sb → Bi (3,4) and under replace Se → Te (5,6); open symbol – without Sn, full
symbol – doped with Sn.

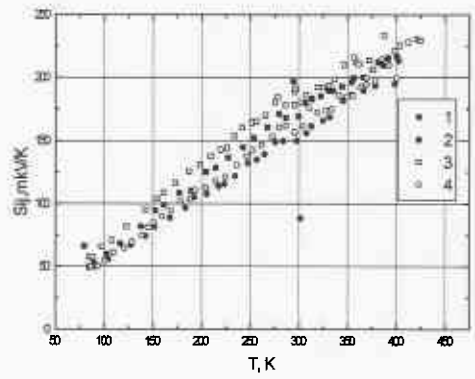


Fig.5.b Sij = f (T) for n-type Bi_2Te_3 (1), doped with Sn and with different electron concentration.

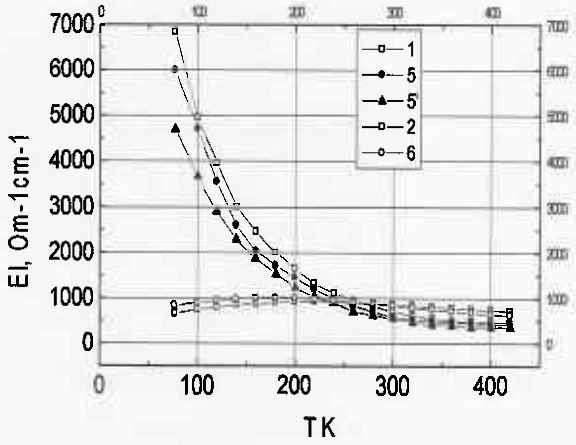


Fig.6a, Electroconductivity for p-type Bi_2Te_3 (1), doped with Sn (2), under replace Sb → Bi (3,4) and under replace Se → Te (5,6); open symbol – without Sn, full symbol – doped with Sn.

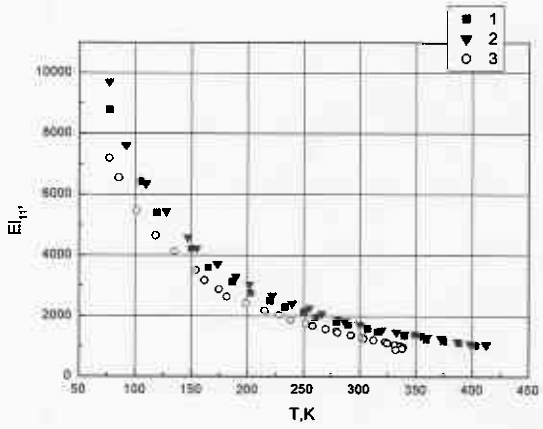


Fig.6b Electroconductivity for n-type Bi_2Te_3 (1), doped with Sn (2), under replace Sb → Bi (3,4) and under replace Se → Te (5,6); open symbol – without Sn, full symbol – doped with Sn.

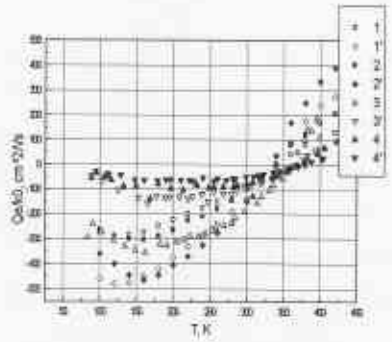


Fig 7a. The components of tensor Nernst-Ettingshausen effect Q_{ijk} = f (T) for p-type: Q_{321} – 1 and Q_{123} – 2 for crystal with Sn; Q_{123} – 3 without Sn

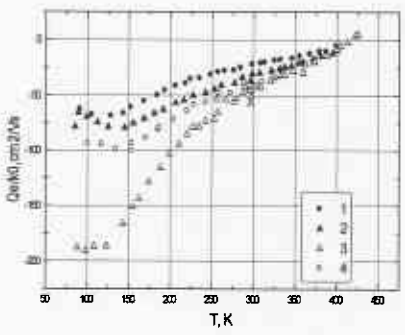


Fig 7b. The components of tensor Nernst-Ettingshausen effect Q_{ijk} = f (T) for n-type: Q_{321} – 1 and Q_{123} – 2 for crystal with Sn; Q_{123} – 3 without Sn

The spatial Seebeck coefficient distribution.

A resonance states in the valence band of Bi_2Te_3 are leading to the pinning of the Fermi level, to modifying the temperature dependence of the electrical properties and to extreme electrical homogeneity [3]. Similar behavior is observed in p-type $Bi_2Te_{3-y}Se_y$ [10]. However, in spite of the absence of any unusual transport effect in n-type $Bi_2Te_{3-y}Se_y$, but extreme electrical homogeneity of n-type crystals has been found as well [11] Fig.8.

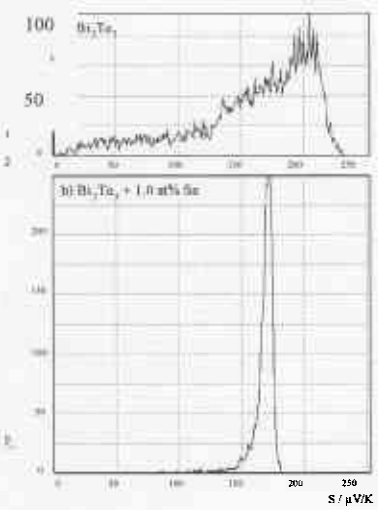


Fig. 8. The abundance plot of the Seebeck values contained in the 2D Seebeck scan of p-type (on the left) and n-type (on the right) $Bi_2Te_{2.88}Se_{0.12}$ without Sn(upper) and $Bi_{1.99}Sn_{0.01}Te_{2.88}Se_{0.12}$ doped with Sn(at the bottom). We can see extremely sharp distribution peak, indicating extreme homogeneity in the samples doped with Sn.

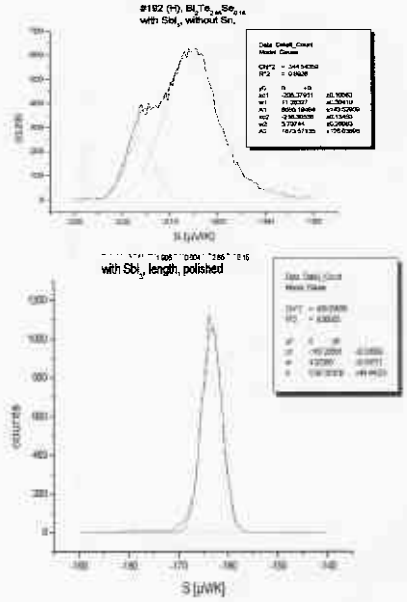
Tin is supporting improved crystallinity of $Bi_2Te_{3-y}Se_y$ thus suppressing the formation of scattering centers and improving the electron mobility in n-type solid solution. Sn addition leads to a decrease of the lattice thermal conductivity.

On the Fig.2 are also presented the results W_1 for $Bi_2Te_{3-y}Se_y$ doped and undoped with Sn together with data for Bi_2Te_3. W_1 for $Bi_2Te_{3-y}Se_y$ is practically constant at codoping with acceptor, but W_1 increases sharply at codoping with donor impurity the same way as for Bi_2Te_3.

We propose that there are only small part of atoms Sn charged in p–type solid solution. On the whole Sn atoms are neutral. So a phonones are scattering on neutral impurities and W_1 depends from amount impurity weakly. In the contrary, there are the change of charge states of atoms Sn takes place under influence of interaction with atoms iodine in n-type crystals. And the most part of Sn and all atoms iodine are charged in. A phonons are scattering on the charged impurities strongly.

Conclusion

The results obtained in this work on the influence of impurity Sn on lattice thermoconductivity and on electrical homogeneity of single crystals Bi_2Te_3 and $Bi_2Te_{3-y}Se_y$ argue for essential influence of Sn impurity states, placed within the valence band, on thermoelectric properties both on p-type and n-type crystals. It should be remarked that thermoelectric parameters of n-type crystals are more improved and reaches a value of $Z = 3.3*10^{-3}\ K^{-1}$ in the temperature range of 340 – 370 K.



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