Effective Mass and Mobility in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ Solid Solutions below Room Temperature

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Abstract

An effective density-of-states mass m/m_0, mobility of charge carriers calculated with account of degeneration μ_0, and lattice heat conductivity κ_L have been studied in the multicomponent p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions based on bismuth and antimony chalcogenides with substitutions of atoms in cationic ($1 \leq x \leq 1.3$) and anionic ($0.04 \leq y \leq 0.09$) sublattices of bismuth telluride in the (80K-340K) temperature range.

These studies show that the main reasons for rising of thermoelectric efficiency Z at temperatures below 220 K are the features of behavior of m/m_0 and μ_0 on temperature, composition and concentration of charge carriers, because the change of κ_L value in the compositions of solid solutions under consideration is weak.

Introduction

Bismuth and antimony chalkogenides thermoelectrics are widely applied in various cooling devices operating at the range close–to-room temperatures. The development of HTSC-material applications and development of the different sensor devices with high sensitivity at low temperatures have lead to appearance of a new trend of researches in the region of low temperatures (<200K) down to 120-130 K.

The increase of thermoelectric efficiency Z at low temperatures can be achieved by two ways: decreasing of charge carriers concentration, and also modification of composition of solid solution by means of substitution of atoms in Bi_2Te_3 sublattices as compared with compositions, which is optimal for temperatures, close to room. Now perspective thermoelectrics for low temperatures are the p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions with substitutions of atoms (Sb → Bi) and (Se → Te) [1, 2].

Further, the relations of an average effective mass (m/m_0), mobility of charge carriers with allowance for degeneration μ_0, and lattice heat conductivity of a crystal lattice κ_L on temperatures, charge carriers concentrations and compositions of solid solutions are studied.

Theory

The solid solutions based on Bi_2Te_3 have a complex band structure described in terms of the six-valley energy-band model, both for main, and for second valence band [3-6]. The second valence band in the solid solutions has an influence on thermoelectric properties owing to change of parameters of ellipsoidal surfaces of a constant energy and scattering mechanisms of charge carriers.

The main scattering mechanisms in these thermoelectrics are scattering on acoustic phonons, on ionization impurities, and on atoms of the second components of solid solutions [7]. These scattering mechanisms are usually characterized by scattering parameter close to $r = -0.5$ in terms of a simple parabolic model of an energy spectrum with isotropic scattering of charge carriers. However, the results of galvanomagnetic effect and the data on Seebeck coefficient researches are shown that the value r differs from -0.5 in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$, as well as in n-$(Bi, Sb)_2(Te, Se)_3$ solid solutions [8-11].

The calculated effective scattering parameter (r_{eff}) was determined together with a reduced Fermi level η from the expressions for Seebeck coefficient $\alpha = f(r_{eff}, \eta)$ and a degeneracy factor $\beta_d = f(r_{eff}, \eta)$ in the same way as for n-type materials. The β_d values were defined from the data on galvanomagnetic effects for the p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions. Thus, the temperature and concentration relations of r_{eff}, and also dependence of Seebeck coefficient from a Fermi level and carriers concentration [8] were obtained.

The parameter r_{eff} was determined to be equal to (-0.35)—(-0.4) [8-10] at low carrier concentrations (about (3-4) 10^{18} cm^{-3}). At these carrier concentrations the second band in the valence band of Bi_2Te_3 and based on solid solutions starts to fill [3-6]. The value of $|r_{eff}|$ increases with growth of carrier concentrations and temperatures and then it stabilizes achieving the values about (- 0.7) – (-0.8). Thus, the dependence of r_{eff} on carrier concentration shows the concentrations range, in which the second valence band is filling. The parameter r_{eff} has close values in the materials of n- and p-type [8-10] and these data are in agreement with Ref. [11] for n- and p-$Bi_2Te_{3-y}Se_y$ (y=0.15).

Experiment and Discussion of the Results

1. Doping

The optimal hole concentration for range of low temperatures can be obtained by substitutions of atoms (Sb → Bi), (Se → Te) in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ and by adding excess Te, as compared with stoichiometric composition of solid solution. Such changes of composition increase in mobility due to polarity of chemical bonds, lowering of the concentration of antisite defects (Bi → Te) and of an acceptor type [12].

Samples for study were prepared by the method of directed crystallization (vertical zone equalization).

During crystallization the precision adjustment of temperature (with high accuracy up to ±1°C) was applied that allows to grow homogeneous ingots of multicomponent solid solutions [13].

2. Seebeck Coefficient and Electrical Conductivity

Fig. 1 plots the temperature dependences of the Seebeck coefficient α and electrical conductivity σ in the solid solutions p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ at $(1 \le x \le 1.3)$ and $(0.07 \le y \le 0.09)$. These data are used for definition of average effective mass (m/m_0) and mobility μ_0 with allowance for the effective scattering parameter r_{eff} on method used in Ref. [14, 15].

A decrease in contents of Sb atoms from x =1.3 to 1 leads to weakening of $\alpha=f(T)$ relation at composition near the middle of the system Bi_2Te_3-Sb_2Te_3. Such feature of $\alpha=f(T)$ relation shows the possibility of thermoelectric efficiency Z increasing in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ at low temperatures. Thus, the angular coefficient $s_\alpha=d\ln\alpha/d\ln T$ is weakly decreased in the samples for close carrier concentrations with decrease in contents of Sb atoms in the solid solution [8].

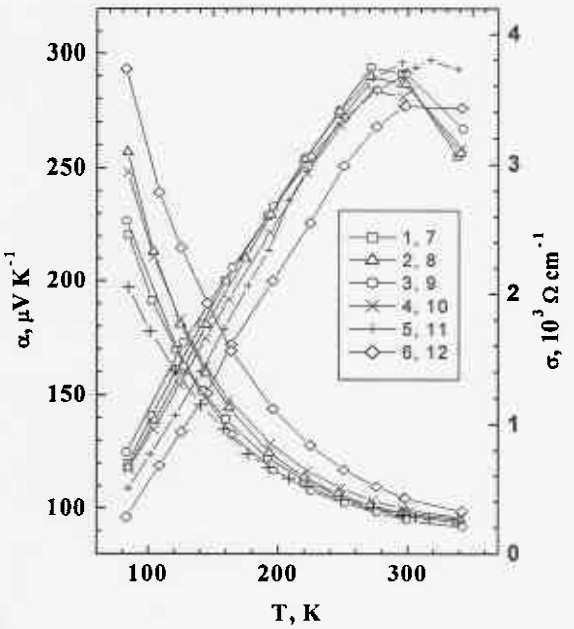

Fig. 1. Temperature behavior of the Seebeck coefficient α (1-6) and electrical conductivity σ (7-12) in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions.

1, *7* - (x=1, y=0.06), *2*, *8* - (x=1.1, y=0.06), *3*, *9* - (x=1.2, y=0.06), *4*, *10* - (x=1.2, y=0.09), *5*, *11* - (x=1.3, y=0.09), *6*, *12* - (x=1.3, y=0.07).

The temperature dependence of σ (Fig. 1) becomes weaker with increase in x and y for the solid solutions owing to additional scattering on Sb and Se atoms. The relation of σ on T determines variation of mobility with temperature due to very weak dependence of carrier concentration from T through the interval 80-300 K [8].

3. An average effective density-of-states mass

The temperature dependence of the effective density-of-states mass (m/m_0) in the p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ is shown in Fig. 2. The value of m/m_0 has very weak dependence on temperature in the interval 80K-150K. Then, with temperature rise the relation $m/m_0=f(T)$ becomes sharper right up to temperatures, at which the intrinsic conductivity begins, therefore the effective mass is decreased. Thus, peculiarities of variation in m/m_0 from T in the different temperature intervals for materials of p- as well as n- type may be described in the form $m \sim T^{s(T)}$.

An angular coefficient $s_m=d\ln m/m_0/d\ln T$ for the interval $150K$-$220K$ increases from 0.35 to 0.75 with increase of contents of Sb atoms (x=1-1.3) in the solid solution (Fig. 2). The effective mass increases with growth of contents of the second components in solid solution in the samples with close carrier concentrations (Fig.2, curves *1-3*).

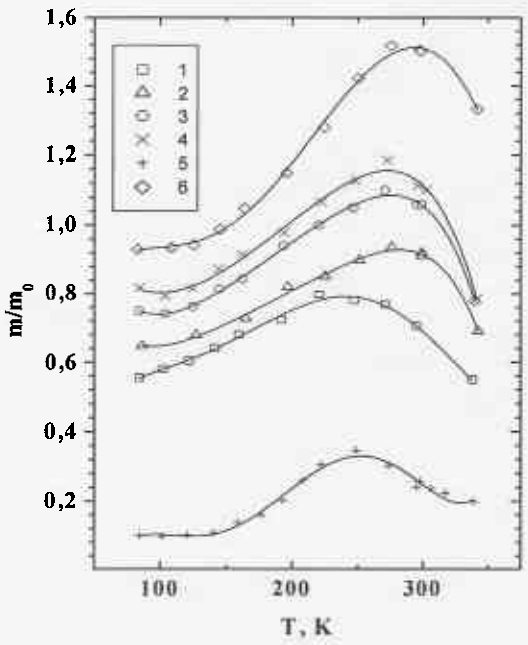

Fig. 2. Temperature dependence of the effective density-of-states mass m/m_0 in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions.

n, 10^{18} cm^{-3}: (x=1, y=0.06) *1* - 4, (x=1.1, y=0.06) *2* - 5, (x=1.2, y=0.06) *3* - 4, (x=1.2, y=0.09) *4* - 7, (x=1.3, y=0.09) *5* - 3, (x=1.3, y=0.07) *6* - 9.

As carrier concentration increases, m/m_0 rises as it is observed in n-type solid solutions [15]. The large increase in m/m_0 with growth of the hole concentration from 3 $10^{18}cm^{-3}$ to (4-5) $10^{18}cm^{-3}$ might be explained by filling of the second valence band in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$

solid solution (Fig. 2, curves 1, 2). At higher concentration the increase in m/m_0 connected with non-parabolic the valence bands of the p-type solid solutions.

As known, that the average effective density-of-states mass in terms of many-valley energy-band model [11, 33] with isotropic scattering of charge carriers is given by $m=N^{2/3}(m_1\ m_2\ m_3)^{1/3}$, where N is a number of valleys, and m_1 m_2 and m_3 are the principal components of the effective mass tensor. The components m_1 m_2, and m_3 depend on the parameters u, v, w, which describe the shape of the constant-energy ellipsoids and on degeneracy factor $\beta_d(r_{eff},\ \eta)$. Therefore the features of average effective mass (m/m_0) dependences on temperature, composition and carrier concentration are explained by changes in the parameters u, v, w, and β_d.

4. Mobility of Charge Carriers

The mobility with accounting of degeneration μ_0 decreases with growth of quantity of substituted atoms of Sb and Se and carrier concentration due to increase of the number of scattering centers (Fig. 3).

As the effective mass temperature dependence, $\mu_0(T)$ relation can be presented in the form $T^{s(T)}$ for different temperature intervals. Angular coefficient $|s_\mu| = d\mu_0 / d \ln T$ is reduced in the interval 80-150 K compared to higher value of $|s_\mu|$ at the temperatures 150K-220 K [8].

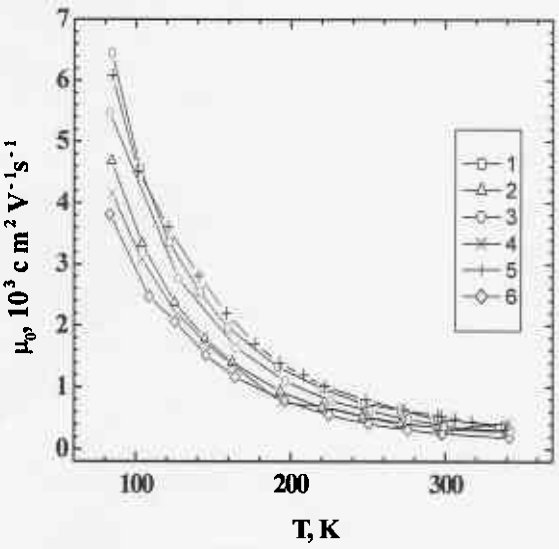

Fig. 3. Temperature dependence of the mobility μ_0 in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions.
Sample notation is the same as in Fig. 2.

A high mobility at (x=1.3, y=0.09) in the sample with low carrier concentration (Fig. 3, curve *5*) is explained by absence of inter-band scattering of charge carriers, since the second band in a valence band of the solid solution is not yet filled.

In the samples of different composition and close carrier concentrations the decrease in the mobility and in angular coefficient $|s_\mu|$ is observed with increase of Sb contents in the solid solution, when x changes from 1 up to 1.3 at T> 150 K, Fig. 3, curves *1-3*.

The coefficient $|s_\mu|$ increases as s_m in the temperature range 150K-220K with growth of Sb contents. The largest value of $|s_\mu|$ was found at x=1.3 composition. Such changes of s_m and $|s_\mu|$ values promote to increase of m/m_0 and μ_0 at the temperatures 150K-220K in the solid solution at x=1.3 compared to solid solutions with the smaller of Sb contents.

5. Lattice Heat Conductivity

Full (κ) and lattice heat conductivities (κ_L) in the $Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions are decreased compared with composition p-$Bi_{2-x}Sb_xTe_3$ owing to substitution of atoms in cationic (Sb→Bi) and anionic (Se→Te) sublattices of Bi_2Te_3. These substitutions result in an increase of phonon scattering that in turn leads to the decrease in κ and κ_L values. Heat conductivity of the crystal lattice κ_L was calculated as the way: $\kappa_L=\kappa-L(r_{eff},\ \eta)\ \sigma T$, where $L(r_{eff},\ \eta)$ – is the Lorentz number calculated with account of the effective scattering parameter r_{eff}.

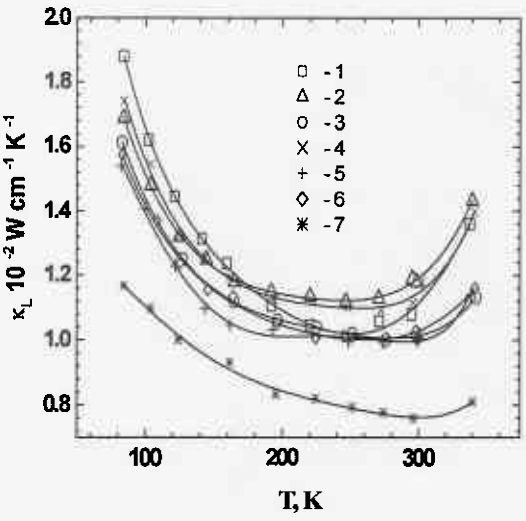

Fig. 4. Temperature dependence of heat conductivity of a crystal lattice κ_L in p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions.
Sample notation is the same as in Fig. 2.

As shown in Ref. [16], the lattice heat conductivity κ_L at the room temperature in the compositions close to middle of the system Bi_2Te_3 – Sb_2Te_3 depends on x very

weakly. Therefore, the increase in x from 1.1 to 1.3 and hole concentration from 3 up to 9 10^{18}cm^{-3} in the region of low temperatures result in a weak decrease of κ_L and the angle coefficient $|s_{\kappa L p}|$ with growth of Sb contents in the solid solutions (Fig. 4, curve 5, 6).

Further increase of the hole concentration (up to 1.8 $10^{19} cm^{-3}$) in the composition (x=1.3, y=0.09) at introduction excess of Se atoms in the solid solution leads to the considerable decrease of the lattice heat conductivity κ_L (Fig. 8, curve *7*). However, additional scattering on Se atoms result in to reduce of mobility.

Conclusions

As a result of studying of the p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions at $(1 \le x \le 1.3)$ and $(0.04 \le x \le 0.09)$ the features of the effective mass m/m_0, mobility μ_0 and lattice heat conductivity κ_L on temperature, composition, and hole concentration are determined.

In the temperature range (150K>T>220K) the increase in angular coefficients of the temperature dependences of the effective mass s_m and mobility $|s_\mu|$ (Fig. 2, 3, curves *6*) together with a weak decrease of a lattice heat conductivity (Fig. 4, curve *6*) were shown to promote increasing of thermoelectric efficiency Z in the solid solution at x=1.3 and hole concentration 9 10^{18} cm^{-3} in comparison with compositions with the smaller contents of Sb atoms.

High mobility and increase in angular coefficients s_m through the interval 80K<T<150K promote to growth of Z in the compositions at x=1.1 and 1.2 for low hole concentrations (Fig.3, 4, curves *2*, *3*) despite of weak growth in the lattice heat conductivity.

Thus, our study of the effective mass m/m_0, mobility μ_0 and lattice heat conductivity κ_L in the p-$Bi_{2-x}Sb_xTe_{3-y}Se_y$ solid solutions permits to explain appropriate modification of thermoelectric efficiency *Z* in considered temperature ranges.

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