Influence of Bismuth on the Kinetic Parameters of Lead Telluride

T. A. Christakudi, G. Ch. Christakudis, L. D. Borisova**

Institute for Foreign Students, G. A. Naser, Sofia 1111
**Faculty of Physics, Sofia University, Sofia 1126*

Polycrystalline lead telluride samples doped with low bismuth concentration (0 –1 at. %) havbeen obtained. The mobility, thermoelectric power coefficient, Hall coefficient, current carrier cone centration, Fermi level and the effective mass of the density of states are studied as a function of the amount of dopant. The results obtained confirm the donor action of bismuth. The increase in Bi concentration up to 0.3 at. % produces a strong effects on the parameters of the materials, whereas the further increase is more weakly expressed on the properties of the samples. The observed behaviour of the studied quantities as a funcfion of the sample composition could be explained in terms of the impurity atom introduced in the cationic sublattice of lead telluride and the formation of electroneutral complexes on the basis of bismuth telluride.

1. Introduction

The narrow band materials based on lead chalkogenides, doped with different impurities are of great interest for science and technology in relation to their application to fabricate thermoelectric devices, receivers of light in the infrared region, tunable lasers for the IR spectroscopy [1]. This finding, as well as the possibility to create active and near-contact regions of laser structure based on PbTe ⟨Bi⟩ defines the interest in studying the properties of these materials [8].

From studies on the properties of solid solutions in the system Pb-Te-Bi it is known certainly that the bismuth acts as donor [2—4]. It may be introduced into lead telluride as pure element or as BiTe and Bi_2Te_3 compounds [6], the solubility of the first compound being up to 1 at. % and the second compound up to 5 % [2, 6, 9].

The published results for the electric and thermoelectric properties of the system PbTe⟨Bi⟩ refer mainly to composition with high bismuth concentration [2—12], a number of problems referring to the variation of the kinetic parameters and the charge carrier scattering mechanism with changes in the composition are not sufficiently elucidated.

The purpose of the present work is to study the influence of small amounts of bismuth, introduced as BiTe on the kinetic parameters and the current carrier scattering mechanism of lead telluride.

2. Experiment

By the method of direct ampoule single temperature synthesis, polycrystalline lead telluride samples with small amounts of doped bismuth (from 0 to 1 at. % BiTe) have been prepared. The direct synthesis of the studied solid solutions was carried out at 1300 K. To homogenize the materials, the samples were treated at 873 K for the duration of 150 hours, subsequently cooled down sharply in an ice bath.

The polycrystalline samples were used to measure the electric conductivity, Hall coefficient and the thermoelectric power at 300 K. The measurements were carried out using an automated system for measuring the thermoelectric parameters of semiconducting substances [13] using the van der Pau d. c. method and classical methods with 5 % and 2 % accuracy, respectively.

3. Results and discussion

Figures 1—3 show the variations of the mobility, thermoelectric power and Hall coefficient with the amount of introduced impurity. Since bismuth was introduced as BiTe compound, the parameter expressing the composition in the formula $(PbTe)_{1-x}(Bi_2Te_3)_x$ characterizes also the amount of bismuth atoms introduced in the system.

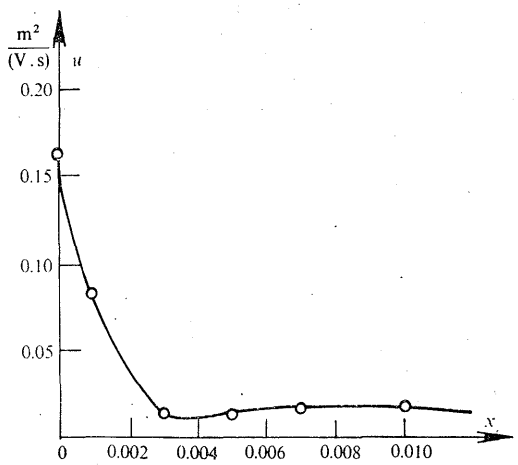

Fig. 1. Variation of mobility with composition

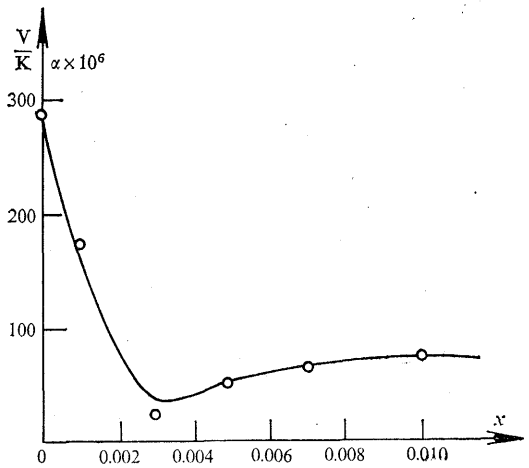

Fig. 2. Variation of thermal power with composition

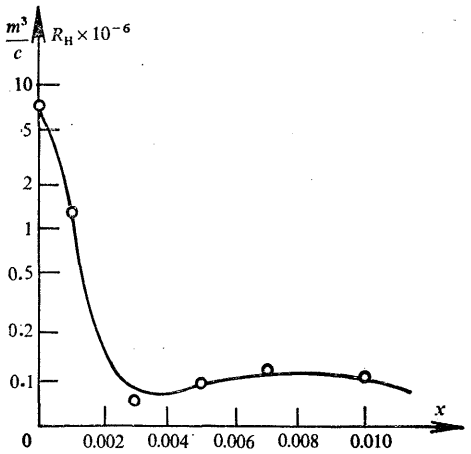

Fig. 3. Variation of the Hall coefficient with composition

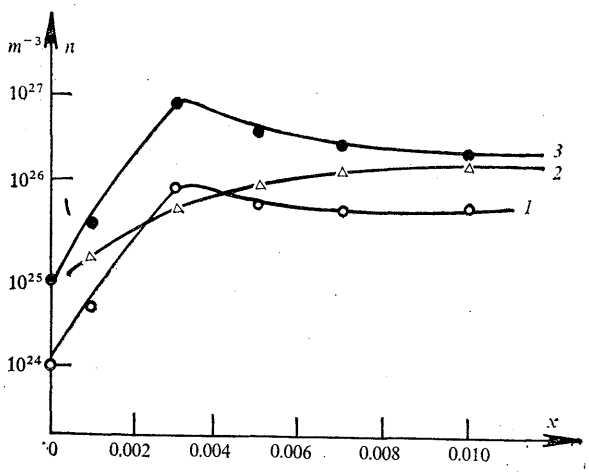

Fig. 4. Variation of the concentration with composition

The variation of the current carrier concentration with the composition is shown in Fig. 4. Curve *1* is the Hall concentration calculated from the experimental values of the Hall coefficient R_H according to the relation

$$n=\frac{r_H}{eR_H}, \tag{1}$$

where the Hall factor r_H is assumed to be unity.

The free current carrier concentration in doped PbTe is defined by the ratio between the number of lead and telluride vacancies and the bismuth impurity atoms, being incorporated into the lead sites in the cationic sublattice. These quantities are related by the equation for electroneutrality of the crystal [16]

$$n+V_{Pb}^{2-}=p+V_{Te}^{2+}+Bi_{Pb}^{3+}, \tag{2}$$

where n is the free electron concentration and p is the p-carrier concentration. The lead vacancies V_{Pb}^{2-} and the telluride vacancies V_{Te}^{2+} are doubly ionized and Bi_{Pb}^{3+} stands for the concentration of the bismuth positive ions at the lead sites. Curve 2 in Fig. 4 shows the dependence of the calculated current carrier concentration on the composition according to (2) under the assumption of defect-free crystal lattice, incorporation of all bismuth atoms in it and the release of a single electron per atom in the conduction band.

The Fermi level determined from the thermoelectric power coefficient under the assumption that the effective mass of the density of states is equal to the free electron mass m_0, using (4) has been employed to calculate the corresponding current carrier concentrations for the different compositions. The results are presented in Fig. 4, curve 3.

The location of the reduced Fermi level F is determined from experimental data on the thermoelectric power using the relation

$$\alpha=\frac{k}{e}\left[\frac{{}^{1}L_2^{r+1/2}(F,\beta)}{{}^{0}L_2^{r+1/2}(F,\beta)}-F\right]. \tag{3}$$

Here $F=F^*/kT$, F^* is the Fermi level, and r is a parameter that characterizes the current carrier scattering mechanism, $\beta=kT/E_g$ is the non-parabolicity coefficient,

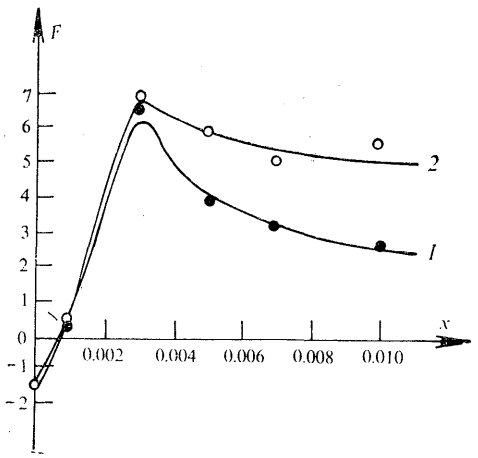

Fig. 5. Variation of the Fermi level with composition

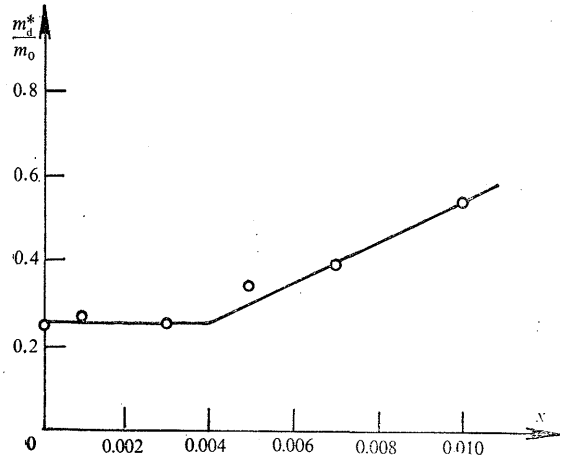

Fig. 6. The dependence of the effective mass of the density of states on the composition

${}^{n}L_2^r$ are the two-parameter Fermi integrals. The calculations have been performed according to the Kane model, modified in [15]. The computational procedure is described in Ref. [13]. Due to the low impurity concentration, we assume that the energy band gap width is the same as for PbTe, namely $E_g=0.32$ eV. The results from the calculations are presented in Fig. 5, curve 1. The calculated Fermi level from the experimental Hall coefficient at $m_d^*=\text{const}=0.25\,m_0$ according to equation (4) is given in Fig. 5, curve 2.

From the Fermi level (Fig. 5, curve *1*) and the carrier concentration, determined from the Hall coefficient, we calculated the effective mass of the density of states (Fig. 6). The concentrational and the temperature dependence of the effective mass of the density of states provide information on the dispersion law $E(k)$ defining the shape of the isoenergy surface about the band edge.

According to the Kane model in the presence of non-parabolicity of the bands, elastic scattering, weak magnetic field, impurity conductivity and arbitrary degeneracy, the effective mass of the density of states is given by the expression [1]

$$m_d^* = \frac{\hbar^2 (3\pi^2)^{2/3}}{2k_0 T} \left[\frac{n}{{}^0L_0^{3/2}} \right]^{2/3}. \tag{4}$$

Here k_0 is the Bolzmann constant, T is the temperature and n is the current carrier concentration.

It is seen from Fig. 1 that the introduction of small amounts of bismuth ($0 \leq x \leq 0.003$) the mobility is changed strongly, whereas the further increase in the impurity concentration produces a comparatively weaker change. The thermoelectric power coefficient data (Fig. 2) and the Hall coefficient (Fig. 3) show that all compositions display n-type conduction which confirms the donor action of bismuth that is known in the literature [1—4]. A behaviour similar to the concentrational course of the mobility is also observed for these two coefficients. The changes in the three parameters as to their nature are intercorrelated.

A similar behaviour of the numerated kinetic parametars with the composition is observed also when studying the metal-ceramic samples made out of lead telluride doped with Bi_2Te_3 [14].

It is seen from Fig. 4, curve *1* that the Hall concentration increases with increasing x and after passing through a maximum at $x=0.003$ slightly decreases. According to the electroneutrality equation (2) the increased current carrier concentration could be attributed to the donor action of bismuth. Since bismuth is in oxidation state 5, an excess electron is obtained from every added bismuth atom, which increases the current carrier concentration. However, under this assumption the calculated and measured concentrations are in poor agreement: The measured values are smaller than the calculated ones (Fig. 4, curves *1* and *2*). The only exception is the $x=0.003$ composition.

A possible explanation of this variance between the two curves may be as follows. When adding bismuth to lead telluride, the homogeneity region is shifted towards tellurium [6], i. e. there is more tellurium in the equilibrium phase. Since the studied compositions refer to stoichiometric amounts of Pb and Te, in order to retain the equilibrium, the excess lead atoms should create an additional number of tellurium vacancies. These vacancies are positively charged hence the electron concentration would exceed the bismuth concentration which explains the deviation observed for $x=0.003$ (Fig. 4, curves *1* and *2*).

In this way it may be claimed that at low impurity concentrations the impurity atoms are incorporated as substituting the main atoms in the PbTe crystal lattice. At high impurity concentrations and especially when one component is in excess, their incorporation would depend on the ratio and the nature of the other defects and it may not correspond to the formation of single vacancies, producing an increased free carrier concentration [16]. In some cases [3, 5] it is energetically more favourable to form complexes of defects between the vacancies of the main compound and the impurity ions. Thus, at $x \geq 0.003$, the formation of electroneutral complexes such as Bi_2Te_3 or $Pb\,Bi_4Te_7$ is possible thereby leaving the carrier concentration constant or even decreasing with increasing x (Fig. 4).

The lower Hall concentration than the bismuth atom concentrations at low impurity contents is probably a result of the compensation since the number of own lead vacancies is still greater than that of the tellurium vacancies.

It is seen from the Fermi level data (Fig. 5, curve *1*) that the $x=0$ and $x=0.001$ compositions are nondegenerate or slightly degenerate, the remaining compositions being located in the mixed region, tending to a totally degenerate semiconductor. From the variation of the Fermi level with increasing impurity amount one can judge about the dependence of the carrier concentration n on the composition (Fig. 4, curve *3*). As seen, these n values are considerably higher than the values measured for all compositions, but the shape of the dependences is the same. This implies that the effective mass of the density of states should be lower than the free electron mass.

It is seen from the variation of the effective mass with the composition, presented in Fig. 5, that for x ranging from 0 to 0.003 this mass is constant and the values coincide within the error limits with the literature data published for undoped PbTe. For $x>0.003$, the effective mass of the density of states increases up to about $0.5\,m_0$. If this course is really such, this would imply that the band structure of these compositions is changed considerably which is less probable for such a small impurity concentration.

The last result provides the basis to calculate the Fermi level at $m_d^*=\text{const}=0.25\,m_0$ (Fig. 5, curve *2*). The measured value and that calculated with the F values thus obtained coincide due to which we assume that these values are closer to reality.

For impurity doped lead telluride the current carrier mobility is defined mainly by scattering from acoustic phonons, impurity atoms free current carriers, etc. The observed strong dependence of mobility on the composition (Fig. 1) cannot be explained only in terms of scattering by the acoustic phonons, since the lattice changes inessentially with variable x [10].

The decreased mobility with introduction of bismuth is connected with the increase in number of the scattering impurity centers. However, due to the high dielectric constant of these materials, the impurity atoms are screened and they behave as electroneutral and for this reason the drop in mobility should be smoother and monotonous.

The increased current carrier mobility at $x>0.003$ may be explained by assuming the presence of considerable scattering by the free carriers. Since for these compositions, the carrier concentration is comparatively high, the mobility is defined in this case by the concentration, i. e. the observed decrease in concentration (Fig. 4) would produce increased mobility.

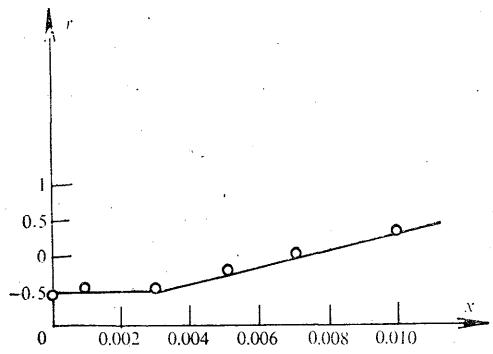

Fig. 7. Variation of the parameter r with composition

For scattering by free current carriers the dependence of the wave vector on energy cannot be written as a power function with r exponent. This is manifested in an effective increase of the r parameter that characterizes the mechanism of scattering of the current carriers. To check the last assumption, the parameter r (Fig. 7) was calculated from equation (3) and the Fermi level data, obtained from the Hall coefficient (Fig. 5, curve 2). For $0\leq x\leq 0.003$ we obtained $r=-0.5$, i. e. the predominant role is played by scattering from acoustic phonons, point defects and electroneutral impurities. The increase of the r parameter at $x>0.003$ demonstrates that another mechanism of scattering intervenes and this is most probably scattering by the free current carriers.

In this way the analysis of the results from the comprehensive complex study of the kinetic parameters of the system $(PbTe)_{1-x}$ $(BiTe)_x$ as a function of composition shows that the limit of bismuth solubility in this case is about $x=0.003$ at. % and the mechanism of incorporation of the impurity atoms is rather complicated.

4. Conclusions

The following conclusions may be drawn from the results presented in this work:

1. The data on the experimental measurements of the kinetic parameters confirm the effective and stable donor action of bismuth in lead telluride, which is due to the high similarity in the characteristic of the bismuth and lead atoms — namely their similar electronic configurations, close atomic radii and electronegativity, as well as the similar electronic structures of bismuth and lead telluride, the boundary solubility being $x=0.003$.

2. Small amounts of bismuth affect strongly the kinetic parameters of lead telluride whereas for high bismuth concentrations ($x>0.003$) the effect is weak probably due to the formation of electroneutral complexes.

3. The variation of the current carrier concentration with the composition is related to the incorporation of bismuth into the lead telluride lattice.

4. The main mechanisms that define the mobility of the current carriers are scattering by the acoustic phonons, impurity atoms and free current carriers.

References

1. Равич, Ю. И., Б. А. Ефимова, И. А. Смирнов. Методы исследования полупроводников в применении к халькогенидам свинца PbTe, PbSe, PbS. М., Наука, 1968.
2. Ефимова, Б. А., Г. Ф. Захарюгина, А. А. Коломоец. — Изв. АН СССР, Неорганич. материалы, 4, 1968, 1, 32—38.
3. Кайданов, В. И., Р. Б. Мельник, Л. А. Шапиро — ФТП, 6, 1972, 11, 2140—2143.
4. Борисова, Л. Д. Канд. Дисертация, С., 1983.
5. Айтикеева, Т. Д., Н. С. Голованова, В. П. Зломанов, И. А. Лебедев, О. И. Тананаева — ФТП, 20, 1986, 1, 44—47.
6. Рогачева, Е. И., С. А. Лаптев, В. С. Плоская, Б. А. Ефимова. — Изв. АН СССР, Неорганич. материалы, 20, 1984, 8, 1350—1353.
7. Бытенский, Л. И., В. И. Кайданов, Р. Б. Макеенко, Р. Б. Мельник, С. А. Немов — ФТП, 18, 1984, 3, 489—492.
8. Горина, Ю. И., Г. А. Калюжная, К. В. Киселева, В. М. Сальман, Н. И. Строганкова — ФТП, 13, 1979, 2, 305—310.
9. Абрикосов, Н. Х., Е. В. Скуднова, Л. В. Порецкая, Т. Осипова — Изв. АН СССР, Неорганич. материалы, 5, 1969. 10, 1682—1683.
10. Schenk, M., H. Berger, C. Kleint, N. S. Golowanova, O. I. Tananaeva, V. P. Zlomanov. — Phys. stat. sol. (a), 91, 1985, K35—K39.
11. Елагина, Е. И., Н. Х. Абрикосов. — Журнал неорганической химии, 4, 1959, 7, 1638—1642.
12. Голованова, Н. С., В. П. Зломанов. О. И. Тананаева, Л. Д. Личева — Изв. АН СССР Неорганич. материалы, 20, 1984, 4, 574—577.
13. Христакудис, Г. Х. Канд. Дисертация, С., 1987.
14. Borissova, L. D., S. K. Dimitrova, G. Ch. Christakudis, T. A. Christakudi — Bulg. J. Phys., 9, 1932, 3, 291—294.
15. Vassilev, L. V., G. Ch. Christakudis — Phys. stat. sol. (b), 117, 1983, 1, K53—K55.
16. Крегер, Ф. Химия несовершенных кристаллов, Мир, М., 1969.

Received August 5, 1988

Влияние висмута на кинетические параметры теллурида свинца

Т. А. Христакуди, Г. Х. Христакудис, Л. Д. Борисова

(Резюме)

Получены поликристаллические образцы теллурида свинца, легированного маленькими количествами висмута (от 0 до 1 ат. %). Исследована зависимость по-