

STRUCTURAL, THERMOELECTRIC AND GALVANOMAGNETIC PROPERTIES OF PbTe-BiTe SEMICONDUCTOR SOLID SOLUTIONS

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Abstract

The concentration dependences of unit cell parameter a , width of diffraction reflections B , electrical conductivity σ , the Seebeck coefficient S , the Hall coefficient R_H , charge carrier mobility μ , and thermoelectric power factor $P = S^2 \cdot \sigma$ for the $Pb_{1-x}Bi_xTe$ ($x = 0 \div 0.05$) alloys were obtained. A non-monotonic character of the concentration dependences of properties was detected and attributed to a change in the defect formation in the PbTe-BiTe system under increasing BiTe concentration.

1. Introduction

Investigations of lead chalcogenides doped with different impurities are stimulated by their wide applications in optoelectronics and thermoelectricity [1].

PbTe crystallizes in the NaCl-type structure with lattice parameter $a = 6.46 \text{ \AA}$ [2], melts congruently at 1197 K [2] and has a narrow double-sided homogeneity region (HR). BiTe has the BiSe-type structure with lattice parameters $a = 4.4 \text{ \AA}$ and $c = 24.0 \text{ \AA}$ [2] and melts incongruently at 813 K [2]. The data on the equilibrium diagrams of the $Pb_{1-x}Bi_xTe$ system and the extension of HR are rather contradictory (from 0.2 to 2 mol.% BiTe in the PbTe-BiTe system [3-6]). The PbTe-BiTe section is known to be non-quasibinary [6].

Influence of Bi on properties of PbTe has been studied in [3-8]. When studying solid solutions PbTe-Bi₂Te₃ and PbTe-BiTe [5,8], deep donor action of Bi and sharp drop in the charge carrier mobility, more significant in the last case, were revealed. The bend in the concentration dependence of charge carrier concentration in PbTe-BiTe solid solutions at 0.1 at.% Bi was found out [5,8]. This fact was interpreted by formation of the second phase (Pb) and appearance of Bi₂Te₃ neutral complexes [5], or, within the framework of two-band model of the conduction band, by growth in a number of electrons, which fall in the second extremum and give a small contribution to the Hall constant due to their low mobility [8].

Since properties of doped PbTe strongly depend on the scheme of Bi introduction (in the form of Bi, BiTe or Bi₂Te₃), it is necessary to study the mechanism of defect formation under impurity introduction in each case. To the best of our knowledge, the works using direct structural methods for this purpose are practically absent.

In this work, some experimental results concerning the effect of BiTe on the thermoelectric (electrical conductivity σ , the Seebeck coefficient S , thermoelectric power factor $P = S^2 \cdot \sigma$) and galvanomagnetic (Hall coefficient R_H , charge carrier mobility μ) properties of PbTe are presented. The detailed investigation of the crystal structure (precise determination of unit cell parameter a and width of diffraction reflections B) with a view toward clarifying the mechanism of defect formation in PbTe-BiTe solid solutions was performed.

2. Experimental details

Polycrystalline samples of $\text{Pb}_{1-x}\text{Bi}_x\text{Te}$ alloys ($x = 0-0.05$) were prepared by direct melting of high-purity elements in evacuated down to $\sim 10^{-3}$ Pa quartz ampoules at 1300 ± 10 K and subjected to homogenizing annealing at 820 K during 200 h with subsequent cooling down with the furnace. All alloys were prepared simultaneously to ensure identity of the preparation conditions. The composition of each sample was controlled using chemical analysis as well as X-ray spectroscopy. X-ray diffraction study was performed using DRON-2 diffractometer and Ni-filtered Cu K_α -radiation. The lattice parameter a was determined using (644)+(820) reflections with an accuracy of $\Delta a = 1 \cdot 10^{-4}$ Å. The temperature dependences of σ and R_H were obtained in the temperature range of 80-300 K by conventional direct-current method in a magnetic field of 1 T. Six ohmic contacts were prepared by soldering In to the surface of rectangle-shaped sample. The error in the measurement of σ and R_H did not exceed 5 %. On the basis of the values of σ and R_H , the temperature dependences of μ were calculated as $\mu = \sigma \cdot R_H$. The Seebeck coefficient was measured with regard to copper with an accuracy of not less than 3 %.

3. Results and discussion

The analysis of the X-ray powder diffraction data showed that all samples crystallize in the NaCl-type structure. No extra lines corresponding to Bi, BiTe, Bi_2Te_3 , Bi_2Te , Bi_3Te_4 , Bi_4Te_5 , Bi_4Te_3 or $\text{Bi}_{14}\text{Te}_6$ phases [9-11], which are possible when introducing BiTe into PbTe, were observed in the X-ray powder diffraction patterns even under maximum BiTe content ($x = 0.05$). To reveal the limit of PbTe homogeneity region in the PbTe-BiTe system it is necessary to use more sensitive methods, for example precise determination of unit cell parameter.

In fig. 1,a, b, the concentration dependences of a and B for the PbTe-BiTe solid solutions are presented. It is seen, that the substitution $\text{Pb} \rightarrow \text{Bi}$ upon the introduction of BiTe into PbTe causes a decreasing a , but with bigger changes at higher Bi concentration (above $x \sim 0.015$). Maximum in B in the vicinity of $x \approx 0.0075$ and further narrowing of the X-ray lines above $x \sim 0.015$ (fig. 1,b) are observed. The decrease in B indicates a reduction in the degree of lattice distortion during the introduction of impurity defects.

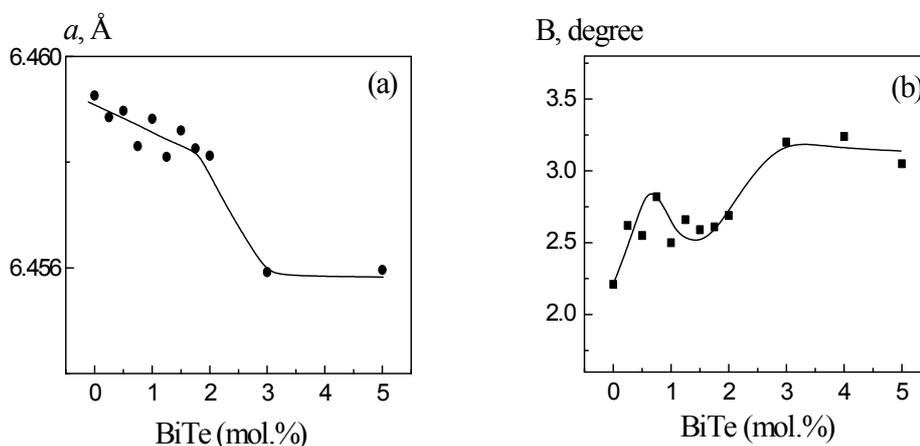


Fig. 1. The concentration dependence of unit cell parameter (a) and width of diffraction reflections (644)+(820) (b) in the $\text{Pb}_{1-x}\text{Bi}_x\text{Te}$ alloys.

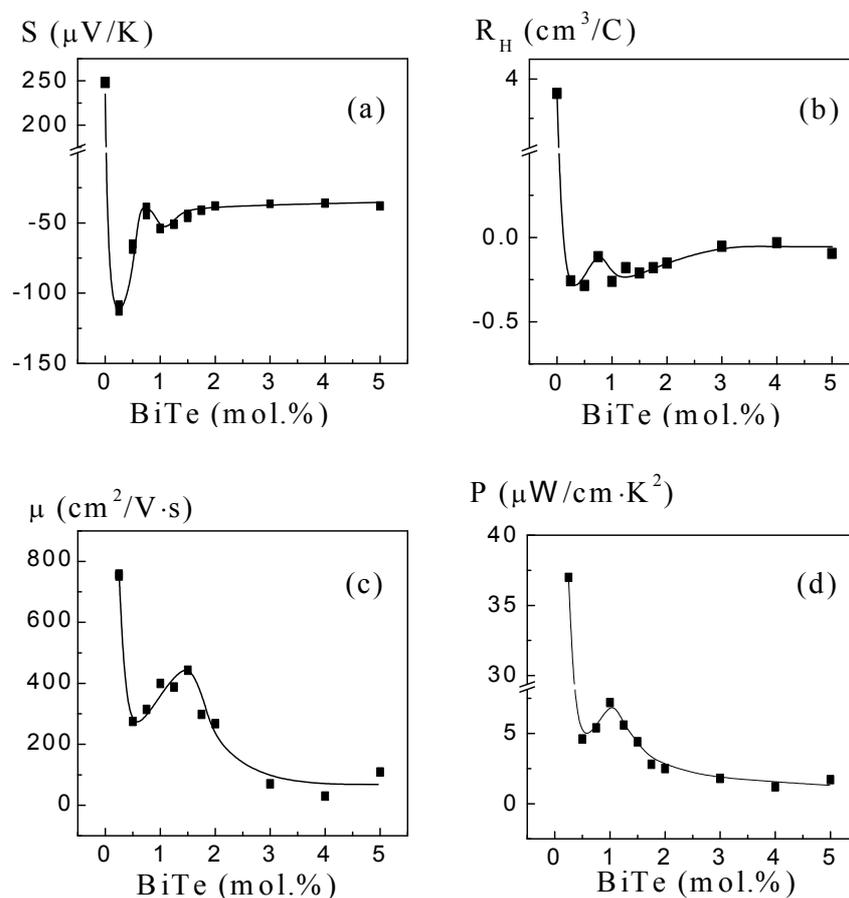


Fig. 2. Room temperature Seebeck coefficient (a), Hall coefficient (b), charge carrier mobility (c), and thermoelectric power factor $P = S^2 \cdot \sigma$ (e) vs. BiTe content in the PbTe-BiTe solid solutions.

Measurements of S and R_H (fig. 2, a, b) revealed that PbTe exhibits p -type conductivity (the hole concentration at room temperature is $p \sim 1.6 \cdot 10^{18} \text{ cm}^{-3}$), but doping of the stoichiometric PbTe with BiTe leads to an inversion of the dominant carrier sign from p to n already under introduction of first portions of BiTe ($x = 0.0025$). The electron concentration n at this reaches $n \sim 2 \cdot 10^{19} \text{ cm}^{-3}$. As it seen from fig. 2 a, S regularly decreases under increasing BiTe concentration above $x = 0.0025$, reaching saturation at $x > 0.0015$. After decreasing μ when increasing first portion of BiTe (fig. 2, c) a growth in μ is observed up to $x \sim 0.015$.

The maximum value of thermoelectric power factor $P = S^2 \cdot \sigma$ ($\sim 37 \text{ } \mu\text{W/cm}\cdot\text{K}^2$ at room temperature at $x = 0.0025$ (fig. 2, d)) in the studied PbTe-BiTe alloys exceeds P value of undoped PbTe (~ 8 and $\sim 34 \text{ } \mu\text{W/cm}\cdot\text{K}^2$ for p - and n -PbTe, correspondingly).

The character of the concentration dependences of properties allows us to suppose that BiTe solubility in PbTe does not exceed 3 mol.% after described heat treatment.

Non-monotonic character of the concentration dependences of a , B , σ , R_H , μ , S in the range of HR is an evidence of complicated character of Bi solubility in PbTe. The existence of bends in the dependences of properties on BiTe content within the HR allows to connect them with a change in the defect formation mechanism which depends on BiTe concentration.

Doping of PbTe with BiTe must cause the formation of Bi_{Pb} substitution defects. However, deviations of $a(x)$ dependence from Vegard's law and $n(x)$ dependence from theoretical one, calculated under condition of the $\text{Pb} \rightarrow \text{Bi}$ substitution in accordance to

introduction of one electron per one atom of Bi, are observed. Taking into account the amphoteric property of Bi [12] the process of partial transition of Bi atoms from Pb sublattice into Te sublattice can be quite likely. One should not exclude the possibility of partial distribution of Bi atoms in tetrahedral voids of the compact packing of Te atoms. Formation of such non-perfect solid solutions can be explained by growing of the entropy part in the free energy expression of a crystal due to formation of defects of new types (for example Bi atoms in Te sublattice or/and Bi interstitials). Further growth in concentration of such defects under increasing of doping degree may become thermodynamically unfavorable, and a change in the defect formation mechanism will take place. Pb→Bi substitution can occur. The existence of two regions with different mechanisms of defect formation within the HR will be shown in appearance of bends in the concentration dependences of properties (fig. 1, 2).

Assuming simple Pb→Bi substitution, one should not exclude the possibility of formation of BiTe or/and Bi₂Te₃ complexes. With increasing BiTe content the probability of the formation of such electrically neutral complexes increases. Tying together atoms into neutral complexes leads to at least partial compensation of lattice distortion and can explain the narrowing of the X-ray lines in the vicinity of $x \sim 0.0015$ (fig. 1, b). An increase in μ within HR (fig. 2, c) can be connected with decrease in number of ionized Bi atoms due to formation of indicated neutral complexes.

4. Conclusions

The results of a complex study of crystal structure, galvanomagnetic and thermoelectric properties of polycrystalline samples of Pb_{1-x}Bi_xTe ($x = 0 \div 0.05$) alloys are presented. Non-monotonic character of the concentration dependences of properties within the homogeneity region was revealed and attributed to a change in defect formation mechanism under increasing BiTe concentration (above $x \sim 0.0015$).

Introduction of BiTe into PbTe leads to increase in thermoelectric power factor at room temperature up to $P = 37 \mu\text{W}/\text{cm}\cdot\text{K}^2$ at $x = 0.0025$.

Existence of two regions with different defect formation mechanisms and caused by that peculiarities of properties in the range of homogeneity region should be taken into account while designing and fabricating devices based on PbTe-BiTe solid solutions.

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