

THE SPECTRA OF OPTICAL PARAMETERS OF  $\text{Bi}_2\text{Te}_3$  SINGLE CRYSTALS

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$R(E)$  reflection spectra of  $\text{Bi}_2\text{Te}_3$  single crystals of  $n$ - and  $p$ -types parallel and perpendicular to  $C$  axis and its film samples in beam energy interval  $1\div 6$  eV incident normally on the surface are measured in the work.

**Keywords:** optical spectra, reflection coefficient, optical conduction.

**PACS:** 535.3; 539.2/6; 539./04

## 1. INTRODUCTION

$R(E)$  reflection coefficients of material series (amorphous and single-crystal Se, Se-S,  $\text{InSnTe}_2$ ,  $\text{TlIn}_{0.9}\text{Ce}_{0.1}\text{Se}_2$ ,  $\text{TlInSe}_2\text{Ce}_{0.04}$ ,  $\text{TlInSe}_2$ ,  $\text{Cu}_3\text{GdTe}_3$ ,  $\text{Cu}_5\text{GdTe}_4$ ,  $\text{CuGdTe}_2$ ,  $\text{Se}_{95}\text{As}_5$  (with Sm impurity),  $\text{Bi}_2\text{Te}_3(\text{Ni}, \text{Cu}, \text{Zn})$ ,  $\text{Bi}_2\text{Te}_3$ ,  $\text{Bi}_2\text{Se}_3$ ) are measured by us and their optical parameters such as reflected light phase  $\theta$ , absorption index  $\kappa$  and refraction index  $n$ , real  $\varepsilon_1$  and imaginary  $\varepsilon_2$  parts of dielectric constant, absorption coefficient  $\alpha$ , the function of characteristic volume  $-\text{Im}g\varepsilon^{-1}$  and surface  $-\text{Im}g(\varepsilon+1)^{-1}$  electron losses, electrooptical differential functions ( $\alpha$ ,  $\beta$ ), optical conduction  $\varepsilon_2 E$ , integral function of bound state density  $\varepsilon_2 E^2$ , effective static dielectric constant  $\varepsilon_0(E)$ , effective number of valent electrons  $n_{\text{ef}}(E)$  [1] taking part in transitions up to the given energy  $E$  are calculated. The bismuth telluride is known as effective material for thermoelectric converters. This material can be easily prepared in the form of enough perfect single crystals and obtained both  $n$ - and  $p$ -types by doping [ 2, 6].

Crystals  $\text{Bi}_2\text{Te}_3$  have the packet structure and bond between neighbor packets has the mixed Van-der-Waals covalent character [7]. The additional bond takes place between packets because of transition of one  $p$ -electron on  $d$ -levels and overlapping of some  $d$ -levels with valence band. It causes the significant metal properties and comparably small values of its forbidden band energies in  $0,15\div 0,35$ eV interval.

$\text{Bi}_2\text{Te}_3$  and its analogues are uniaxial crystals at optical consideration. The dielectric constant in them is the tensor of second order and depends on incident wave direction in respect of  $C$  optical axis. The optical properties of bismuth telluride are investigated in region of higher frequencies in work [5].

The bound structure of  $\text{Bi}_2\text{Te}_3$  crystal is theoretically calculated in work [5]. The absence of data about the spin-orbital interaction value ( $\Delta$ ) and complexity of chemical bond character between  $\text{Bi}_2\text{Te}_3$  atoms present the significant difficulties.

The bismuth telluride and solid solutions on its base are applied at preparation of different energy converters. [7]. The monocrystalline or polycrystalline  $\text{Bi}_2\text{Te}_3$  and its solid solutions with  $\text{Bi}_2\text{Se}_3$  are mainly used in this preparing. The monocrystalline samples of  $\text{Bi}_2\text{Te}_3$  are easily chipped on cleavage plane [0001] forming the mirror surface which is stable to oxidation that is very

important for carrying out of optical measurements and it doesn't require the special chemical treatment.

The study of  $\text{Bi}_2\text{Te}_3$  band structure isn't achieved such level as germanium of  $A^{\text{III}}B^{\text{V}}$  compound that is connected with complexity of its crystal and band structure [3]. It causes the necessity to carry out the new investigations in this direction.

The measurement of  $\text{Bi}_2\text{Te}_3$  crystal reflection coefficient of  $n$ - and  $p$ -types parallel and perpendicular to  $C$  axis and also its polycrystalline film samples and also the spectrum definition of their optical parameters is the task of the given work.

## 2. EXPERIMENT TECHNIQUE

The chip of  $\text{Bi}_2\text{Te}_3$  single crystals having the mirror-smooth surface is used for measurement of reflection coefficient  $R(E)$ . The reflection coefficient is measured by method of double-beam spectroscopy. The crystals are doped by Cl impurities having the  $n$ -type conduction and Tb impurities having the  $p$ -type conduction.

The obtaining technology of single crystals and  $\text{Bi}_2\text{Te}_3$  films is described in works [8, 9, 10]. The single crystals are obtained by Bridgman methods as in work [3] and films by thickness 0,3mkm of polycrystalline  $\text{Bi}_2\text{Te}_3$  on the cleavage surface of rock salt crystals are obtained by its sublimation in vacuum.

The obtaining methods of optical parameters are given in work [11] and the procedure is described in work [12].

As usual, the special computer programs are used for calculation of optical parameters. The optical parameters of investigated materials are calculated by programs written by author of work [13]. These programs are checked at calculation of optical parameters of material series in works [14-18].

## 3. RESULTS AND THEIR DISCUSSION

The reflection coefficients  $R(E)$  of single-crystal  $\text{Bi}_2\text{Te}_3$  of  $n$ - and  $p$ -types parallel and perpendicular to  $C$  axis and also its film samples of  $n$ - and  $p$ -types are measured in work and the spectra of their optical parameters:  $\alpha$  absorption coefficient,  $\varepsilon_2$  imaginary and  $\varepsilon_1$  real parts of dielectric constant,  $\kappa$  absorption and  $n$  refraction indexes,  $n_{\text{ef}}(E)$  effective number of valence electrons taking part up to given energy  $E$ ,  $\varepsilon_{0,\text{eff}}(E)$  effective static dielectric constant, functions of

characteristic volume  $-Img \varepsilon^{-1}$  and surface  $-Img(\varepsilon+1)^{-1}$  electron losses,  $\theta$  reflected light phase,  $\varepsilon_2 E$  optical conduction, integral function of bound state density  $\varepsilon_2 E^2$  and electro-optic differential functions  $(\alpha, \beta)$ .

The presented data make it possible to compare the optical spectra, the transitions of single crystals and film samples of Bi<sub>2</sub>Te<sub>3</sub>. The authors [5] have found transitions 1.4 eV and 1.1 eV for the case of high energies for single-crystal Bi<sub>2</sub>Te<sub>3</sub>. As can be seen from Table 1, the same transitions are observed for n- and p-types, respectively. As noted in [18], the study of absorption transitions in materials is impossible in the energy range of interband transitions  $E > E_g$  ( $E_g$  is forbidden band width) because of the large absorption. The only effective method in this case is the reflection.

The analytic singularities of the imaginary part of  $\varepsilon_2(E)$  complex dielectric constant and the functions bond by the  $dN/dE$  state densities almost coincide, and the main contribution to  $dN/dE$  function is made by the interband distances gradient:

$$\frac{dN_{ij}}{dE} \sim \int \frac{dS_k}{|\nabla_k E_{ij}|}, \quad (1)$$

where  $E_{ij}(k) = E_j(k) - E_i(k)$  is the distance between the conduction and valence bands.

Theoretically,  $dN/dE$  values near the critical points in  $k$ -space, determined by the expression  $|\nabla_k E_{ij}|=0$ , and also the position of the critical points and the type of transitions can be calculated from the band structure.

Analysis of the function  $\varepsilon_2(E)$ ,  $dN/dE$ , and the reflection coefficient  $R(E)$  shows that the location and character of the maxima in their spectra are the same or very close ones. Therefore, by direct comparison of the experimental data in the region  $E > E_g$  with theoretical calculations of  $dN/dE$  function, it is possible to determine the values of the corresponding interband gaps and the band natures. The resonance frequency  $E_0$ , as noted in [18], is essentially the frequency at which the conductivity of  $2nk \cdot E$  reaches a maximum, over which the interband transitions are determined.

Non-crystalline materials are characterized by high transparency in a wide energy range  $E < E_g$ , and several methods for determining  $E_g$  are known. One of them is the estimation of it by the level of the absorption coefficient  $\alpha(E)$  of the long-wave edge.  $E_g$  exact value for non-crystalline semiconductors is debatable, and usually a discussion of  $\alpha(E)$  spectrum nature in the Urbach or Tautz models is performed without estimates of  $E_g$  [20, 21]. According to the Tautz model,  $E_g$  is determined for the value  $\alpha(E) = 10^3 \text{ cm}^{-1}$ . As noted in [20], the concept of density of states  $N(E)$  is equally suitable one for crystalline and non-crystalline substances. According to the available experimental data, the motion of the density of states in a non-crystalline body slightly differs from the corresponding one in the crystal. The fine structure in the first case can be blurred, and local states can appear in the forbidden band. The band structure is, in general, conserved, i.e. it is determined by the short-range order in the materials.

The author of [22] notes that it is impossible to draw a fundamental boundary between single-crystal,

polycrystalline and amorphous states of substances. The presence of the band structure including the band gap and the conduction band can be deduced from the fact of the existence of a short-range order and for such an output there is no need to require the periodic arrangement of atoms.

As the authors of [23-25] show, the structure of a disordered binary compound can be considered as a set of different basic clusters represented in a structural matrix with different static weight and immersed in an effective medium. As the authors of [26] note, the main contribution to the density of electronic states is given by the short-range order. However, since the short-range order in binary compounds can vary significantly from site to site in the structural matrix of an amorphous substance, it is the statistics of basis clusters that determine the final density of electronic states.

Thus, at melt cooling or during the formation of amorphous substances in another way, the low-molecular structural configurations may appear which is accompanied by a certain gain in energy.

Because such formations are characterized by a special symmetry, they can't serve neither as nuclei of crystals, nor as growth centers of solid amorphous phases.

The ambiguity of the structural ordering in composite amorphous solids of  $A_x B_{1-x}$  type can be considered as their common property.

The features of short-range order in the neighborhood of each node are caused, firstly, by the physical methods of  $A_x B_{1-x}$  system preparing and secondly, by the principle of chemical ordering taking into account the "8-N rule" [20] and by the binding energy value of neighboring atoms.

The destruction of an ideal structure in a non-crystalline solid takes place in systems involving atoms with unshared electron pairs. Often at bond breakage the electron pair stays on one of the fragments, i.e. the heterolytic bond break occurs.

In this case, one positively and one negatively charged defect centers arise in the short-range order regions.

The energy required to break the bond is partly compensated for by the existence of an unshared electron pair in atoms in the nearest environment, and the number of chemical bonds does not change in whole.

Thus, in homogeneous non-crystalline materials of stoichiometric composition, along with density fluctuations and the existing topological disordering of various types, there is also structural disordering. It manifests itself in the form of positively and negatively charged defect centers, as in the case of point defects in crystals. As a result, the defects of the reaction dominate, the formation of which is characterized by the least change in free energy. Thus, in homogeneous non-crystalline materials of stoichiometric composition, along with density fluctuations and the existing topological disordering of various types, there is also structural disordering. It reveals in the form of positively and negatively charged defect centers, as in the case of point defects in crystals. As a result, the defects of the reaction dominate, the formation of which is characterized by the least change in free energy.

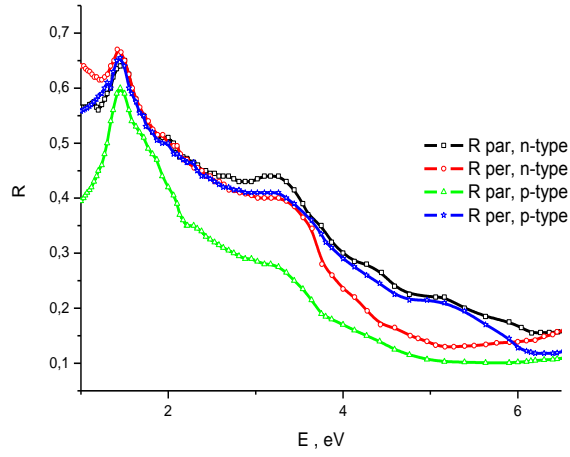


Fig.1.  $\text{Bi}_2\text{Te}_3$  reflection spectra of single crystals by  $n$ - and  $p$ -types parallel and perpendicular to C axis.

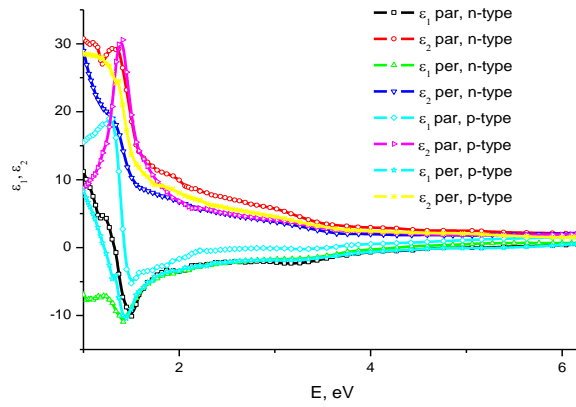


Fig.2. Coefficient spectra  $\varepsilon_1$  and  $\varepsilon_2$  of  $\text{Bi}_2\text{Te}_3$  single crystals by  $n$ - and  $p$ -types parallel and perpendicular to C axis.

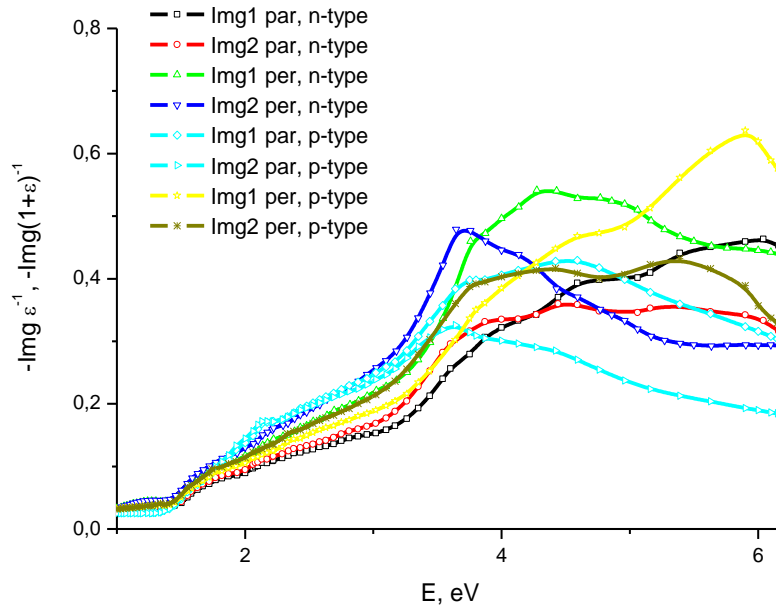


Fig.3.  $\text{Im}g_1 (-\text{Im}\varepsilon^{-1})$  and  $\text{Im}g_2 (-\text{Im}(1+\varepsilon)^{-1})$  spectra of  $\text{Bi}_2\text{Te}_3$  single crystals by  $n$ - and  $p$ -types parallel and perpendicular to C axis.

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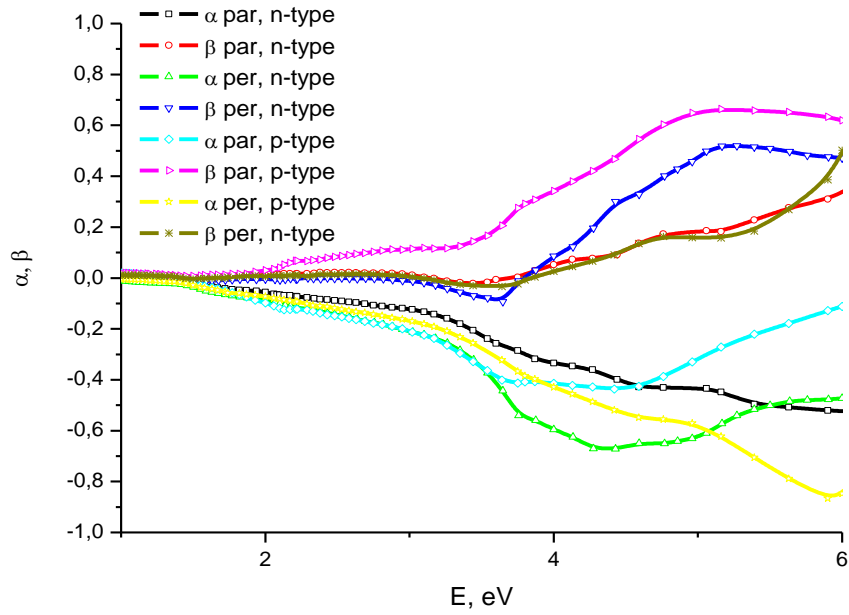


Fig.4. The spectra of  $\alpha$  and  $\beta$  electro-optic coefficients of  $\text{Bi}_2\text{Te}_3$  single crystals by  $n$ - and  $p$ -types parallel and perpendicular to C axis.

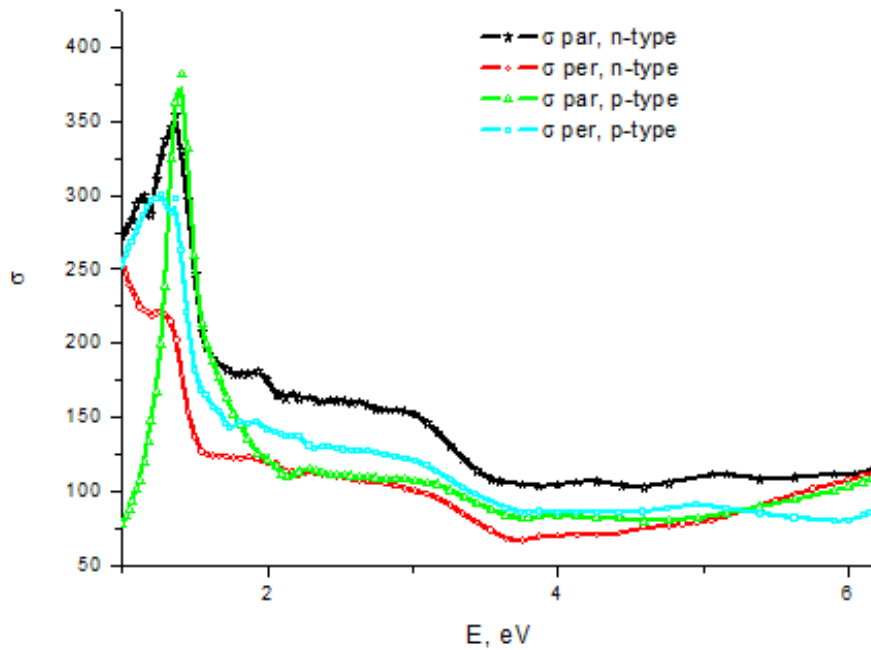


Fig.5. The spectra of  $\sigma$  optical conduction of  $\text{Bi}_2\text{Te}_3$  single crystals by  $n$ - and  $p$ -types parallel and perpendicular to C axis.

One of the fundamental concepts in the physics of disordered systems is the idea of short-range order at the formation of electronic energy zones. This idea has been experimentally and theoretically confirmed on the example of numerous non-crystalline solid and liquid semiconductors [27]. The formation mechanism of valence and conduction bands in non-crystalline semiconductors is formulated mainly by the authors of [28, 29]. In the works of these authors, the similarity of the spectral dependence main features of the imaginary

part of the dielectric constant  $\varepsilon_2(E)$  for non-crystalline semiconductors and their crystalline analogs is emphasized. This similarity in the example of selenium is demonstrated by the author [28]. A similar entry is made also with respect to  $a\text{-As}_2\text{S}_3$  and  $a\text{-As}_2\text{Se}_3$  works [28, 29]. In the case of amorphous materials, only a smoothing of the maximum occurs in their  $\varepsilon_2(E)$ , but the similarity of the curves for amorphous and crystalline samples remains similar.

The optical transitions in Bi<sub>2</sub>Te<sub>3</sub> single crystals in energy interval 1÷6 eV by *n*- and *p*-types parallel and perpendicular to C axis defined by maxima of optical conduction.

<i>n</i> - type parallel to C axis	<i>n</i> – type perpendicular to C axis	<i>p</i> - type parallel to C axis	<i>p</i> - type perpendicular to C axis
1.01	0.70	1.41	1.19
1.10	0.79	2.02	1.27
1.14	1.29	2.29	1.37
1.36	1.86	2.96	1.81
1.94	2.07	3.18	1.92
2.16	2.17	7.21	2.10
2.28	2.31	7.41	2.23
2.44	2.58	-	2.42
2.61	2.71	-	2.99
3.02	3.09	-	4.95
4.24	3.95	-	6.98
5.06	4.61	-	7.10
7.08	6.45	-	-
7.22	6.81	-	-
7.38	6.97	-	-
7.69	7.12	-	-
8.10	7.41	-	-
-	8.08	-	-
-	8.32	-	-

Now it is established that, with a change in the chemical composition, as well as the introduction of impurities, the optical, photoelectric, and electrical properties of non-crystalline semiconductors can be specifically directed. In this case, the concentration of charged defect centers D<sup>+</sup> and D<sup>-</sup> (U<sup>-1</sup>-centers) changes in them and these defects are formed from initial neutral defects D<sup>0</sup> by the reaction:



which can be intrinsic, impurity or mixed defects that make it possible to control their physical properties.

Thus, *R* (*E*) reflection coefficients of single crystals and Bi<sub>2</sub>Te<sub>3</sub> film samples of *n*- and *p*-types in the beam

energy interval 1 ÷ 6 eV normally incident on the surface are measured. For the case of Bi<sub>2</sub>Te<sub>3</sub> single crystals, measurements are made in parallel and perpendicular to C axis. It is shown that for some non-crystalline samples the values of some optical transitions of Bi<sub>2</sub>Te<sub>3</sub> from the crystalline to the non-crystalline state are preserved.

Only reflection coefficient spectra *R*(*E*), imaginary  $\epsilon_2$  and real  $\epsilon_1$  parts of dielectric constant, functions of characteristic volume  $Img \epsilon^{-1}$  and surface  $-Img(\epsilon+1)^{-1}$  electron losses, the spectra of electro-optical spectral functions ( $\alpha$ ,  $\beta$ ),  $\sigma$  optical conduction of massive samples are shown in fig.1-5 for short and the values of interband optical transitions defined by maxima of  $\sigma$  optical conduction are given in tables 1 correspondingly.

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*Recevid:27.03.2017*