

Conductivity Effects in Bi_2TeO_5 Single Crystals

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The current–voltage characteristics (I – V) of non-stoichiometric bismuth tellurite crystals were studied in a range of temperatures from 150 °C to 350 °C and fields up to 2.5 kV/cm with asymmetric contacts (In–Ga eutectic and Na_2SiO_3). The I – V curves and observed monopolar injection are described by the approximation of space charge limited currents. In the composition of 47% Bi_2O_3 –53% TeO_2 electronic conduction is prevailed. In the composition 43% Bi_2O_3 –57% TeO_2 the conductivity is contributed by electrons and holes. The spectrum of local states in the band gap of the studied crystals is quasicontinuous, which cannot be described by models of a discrete or exponential distribution.

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1. Introduction

The tellurites of metals have attracted an attention as perspective acousto-optic materials [1]. The study of the $\text{Bi}_{1-x}\text{Te}_x\text{O}_{(3+x)/2}$ system showed that the compositions with x from 0.33 to 0.5 formed a non-stoichiometric phase and melted congruently at $x = 0.33$, which corresponded to Bi_2TeO_5 . Bismuth tellurite is a nonlinear crystal with orthorhombic fluorite-type structure of $Abm2$ space group with unit cell parameters $a = 1.1602$, $b = 1.6461$, and $c = 0.5523$ nm [2]. It has a layered structure with a cleavage plane (100). The crystal of bismuth tellurite became of interest as a promising material with photorefractive, photochromic and photovoltaic properties [3–5]. Many features of these properties were associated with the energy states in the band gap of crystal. Various aspects of charge transport processes in bismuth tellurite had been considered in a number of papers [6–9]. The experimental results of dc and ac conductivity studies were associated with carrier's injection, captures, hops on the local states, and the long-term conservation of stimulated conductivity due to the presence of deep defect levels [6–8]. Because of the reversibility of stimulated conductivity and the occurrence of photoconductivity [10], it was assumed that carrier transport in Bi_2TeO_5 had an electronic nature. The results of the studies mentioned above were obtained in the temperature range up to 300 °C. The results of conductivity studies in the range up to 900 °C were given in [9]. It was shown that at high temperatures, Bi_2TeO_5 single crystals had mixed conductivity (electronic and ionic), whereas at low temperatures (below 600 °C) the conductivity was considered as mainly electronic.

Extensive information on charge transport in Bi_2TeO_5 single crystals was obtained from an analysis of I – V characteristics, which were interpreted on the basis of space charge limited currents (SCLC) theory in the case

of monopolar injection. All of the above studies were performed on the samples with two injecting electrodes. This made it impossible to determine the contribution of electrons and holes to the electrical conductivity of bismuth tellurite crystals. In this work, I – V curves were measured using asymmetric contacts, only one of which was an injector. This made it possible to eliminate the double injection and to obtain information on the type of the majority carriers.

One of the components (TeO_2) of the compound is characterized by high vapor pressure in the melting region (51 Pa at 733 °C). This changes the component ratio and shifts the melting point of the compound. Therefore, the growth of Bi_2TeO_5 crystals was carried out from a melt containing an excess of tellurium dioxide. Initially, we obtained single crystals of excellent quality with the component ratio 43% Bi_2O_3 to 57% TeO_2 (hereinafter be referred to as T-57). Subsequently, Bi_2TeO_5 single crystals with a smaller excess of TeO_2 were grown by authors of [11]. Taking into account the results of that work, we also obtained high quality crystals with the same ratio of the components (47% Bi_2O_3 –53% TeO_2 , hereinafter be referred to as T-53). In this paper, we study I – V curves of both crystals (T-57 and T-53) with one injecting contact.

2. Experimental

The T-57 and T-53 single crystals were grown by the Czochralski method. The oxides of bismuth (Bi_2O_3) and tellurium (TeO_2) of 5N pure were used as initial components. The main features of growth process were considered in [12]. X-ray studies had shown that T-53 and T-57 crystals had orthorhombic symmetry and the lattice parameters corresponded to the Bi_2TeO_5 compound. The differences of the lattice parameter values, as shown by X-ray studies, did not exceed the value of the experimental error. At the same time, the crystals were of different colors. The T-53 crystals were colorless or had a light yellow color. The T-57 crystals were characterized by intense yellow color and more pronounced layered structure.

The procedure for measuring I – V characteristics was described in [8]. We studied I – V curves in the tempera-

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ture range from 150°C to 350°C and in the fields up to 2.5 kV/cm. The magnitude of the currents was gauged with the help of an electrometric amplifier U5-11. The temperature regulator RIF-101 made it possible to control the temperature with an accuracy of 0.02°C. The voltage was applied to (100) cleavage plane. The eutectic of indium-gallium was used as an injecting contact (25% In, 75% Ga by weight, melting point — 15.5°C). The second contact was a layer of silicate glass Na_2SiO_3 . In [13], conductive properties of Na_2SiO_3 electrodes as contacts to $\text{Bi}_{12}\text{SiO}_{20}$ crystals were investigated. It was found that the conductivity of Na_2SiO_3 glass was several orders of magnitude higher than the conductivity of $\text{Bi}_{12}\text{SiO}_{20}$ crystals. The I - V characteristics with two electrodes from Na_2SiO_3 obeyed Ohm's law, i.e. these electrodes did not inject electrons. The absence of charge injection from Na_2SiO_3 electrodes was also observed in Bi_2TeO_5 crystals.

3. Results and discussion

The obtained I - V curves of T-53 and T-57 crystals were typical for SCLC in dielectrics at the presence of traps [14]. There were several regions of the power law dependences ($I \sim U^\gamma$) on I - V curves in the studied temperature range: $\gamma = 1$ (Ohm's law), $\gamma = 2$ (quadratic range), $\gamma > 2$ (sharp rise range). Such I - V curves were observed for T-53 and T-57 samples at both polarities of the In-Ga electrode. It should be noted that similar I - V curves were observed in the case of two injection electrodes [6, 8]. It was shown in [14] that the barrier conduction and the ionization of local states by the field were lead to qualitatively identical I - V curves for monopolar and double-injection cases.

From the ohmic parts of the I - V characteristics the conductivity values (σ) were calculated, which agreed well with the results obtained from measurements of $\sigma(T)$ in low fields [6, 8]. The existence of nonlinear ranges on the I - V curves of both polarities of In-Ga contact shows that this electrode injects both electrons and holes into the samples. From quadratic region of I - V characteristics it is possible to calculate the effective mobilities of electrons (μ_-) and holes (μ_+) at various temperatures. According to [14]

$$\mu = 8jd^3/9\varepsilon\varepsilon_0U^2, \quad (1)$$

where j — current density in sample, U — voltage, applied to the sample, d — thickness of the sample, ε , ε_0 — dielectric permittivities of crystal and vacuum, accordingly.

These results for T-53 and T-57 crystals are represented in Fig. 1 and the activation energies of conductivity and mobility are presented in Table I.

The received values show that the effective mobility is low and exponentially increases with temperature. These results coincide with the conclusion about the hopping conductivity mechanism, which is made in [7]. As can be seen from Fig. 1 and Table I, a change of bismuth tellurite component ratio leads to a substantial change in the charge transport parameters. For T-57 crystals, the

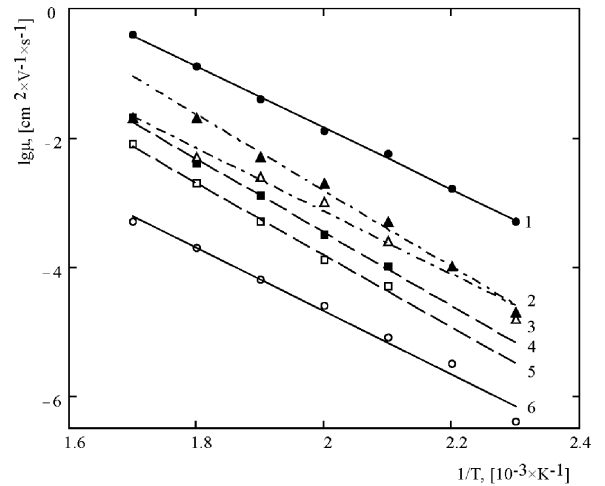


Fig. 1. The temperature dependences of carrier mobilities of bismuth tellurite crystals. 1 — electron mobility in T-53 sample, 2 — mobility in T-53 sample, according to [8], 3 — mobility in T-57 sample, according to [8], 4 — electron mobility in T-57 sample, 5 — hole mobility in T-57 sample, 6 — hole mobility in T-53 sample.

TABLE I

The activation energies [eV] of conductivity and mobility of electrons and holes in bismuth tellurite crystals

	In-Ga contact, cathode		In-Ga contact, anode	
	σ [$\frac{1}{\Omega\text{cm}}$]	μ [$\frac{\text{cm}^2}{\text{Vs}}$]	σ [$\frac{1}{\Omega\text{cm}}$]	μ [$\frac{\text{cm}^2}{\text{Vs}}$]
T-53				
$E_a(\sigma)$	0.77	0.9	1.13	0.92
E_{80}	0.62		1.09	
T-57				
$E_a(\sigma)$	0.94	1.09	1.1	1.24
E_{80}	1.0		1.12	

effective mobilities of carriers of both signs are close in magnitude and they have the same pattern of their temperature changes. For T-53 μ_- exceeds μ_+ by 3 orders in all temperature range and by an order of magnitude higher than the mobility of both type carriers in T-57 crystals. These results do not coincide with the data of [8], where the samples with two injecting contacts are studied. For comparison, the carrier mobilities of T-53 and T-57 are presented in the case of two injection contacts according to [8] (Fig. 1, curves 2 and 3). These mobilities are not only close in value to each other, but also close to the mobilities for T-57 crystals with one injection electrode.

In real crystals, especially with a well-defined layered structure, a significant concentration of different type of defects is observed. The presence of a cleavage plane in the structure of Bi_2TeO_5 crystals can lead to the existence of potential barriers for charge carriers and cause the formation of space charges within the layers when an electric field is applied. In addition, bismuth tellurite belongs to the group of the continuous solid solu-

tions $\text{Bi}_{1-x}\text{Te}_x\text{O}_{(3+x)/2}$ ($0.33 \leq x \leq 0.5$), that leads to chaotic micro-deviations of the component concentration from the stoichiometric composition. Such deviations can cause fluctuations of lattice electric potential. Potential fluctuations can be the cause of formation of smeared local states in the band tails. This can be manifested in the processes of carrier excitation and transport (absorption spectra and hopping conductivity in Bi_2TeO_5 [5, 6]).

On the experimental I - V curves, the smearing of the local levels is manifested in a monotonic increase of the slope angle γ ($\gamma = \text{d}I/\text{d}U$), in contrast to the sharp increase of the current for the case of discrete distribution of levels. The observed monotonic increase of γ cannot be related to the exponential distribution of states with the energy $N(e)$, since a constant slope of γ is necessary to such a model in a wide range of fields. The most acceptable is the Gaussian model of the distribution of local states, which is described accordingly [15] by the formula:

$$N(e) = \frac{N_t}{\delta\sqrt{2\pi}} \exp\left(-\frac{(E - E_t)^2}{2\delta^2}\right), \quad (2)$$

where δ — dispersion parameter, N_t — concentration of the local states, E_t — position of the Gaussian distribution maximum in the band gap.

For such a model, it is necessary to know a number of parameters: δ , N_t , E_t . E_t can be determined from the experimental data by studying the dependence of the activation energy of the conductivity $E_a(\sigma)$ at different voltages [16]. The temperature dependences of the currents in the T-53 and T-57 samples were obtained at voltages up to 80 V. The activation energies of conductivity at a voltage $U = 80$ V (E_{80}) for the samples of bismuth tellurite are given in Table I.

Comparison of the values $E_a(\sigma)$ shows that in T-53 crystals $E_a(\sigma)$ decreases slightly for both polarities of In-Ga electrode with increasing field. However, for samples T-57 $E_a(\sigma)$ varies little and even slightly increases with electric field increase (Table I). This does not allow to uniquely connect the obtained values of the activation energies of conductivity with the maximum of the Gaussian distribution and, accordingly, to obtain the rest of characteristics (δ , N_t) which are calculated on the basis of the experimentally determined E_t .

4. Conclusions

The investigations of conductivity of bismuth tellurite crystals with one injecting contact show that both electrons and holes are mobile carriers. Since the mobility of electrons in T-53 samples is much higher than

the mobility of holes, it can be assumed that the conductivity in these samples is determined by electrons. In T-57 samples there are contributions to the conductivity of carriers of both types.

According to X-ray diffraction data, the studied samples corresponded to the Bi_2TeO_5 formula. However, the chaotic distribution of lattice defects associated with different crystal growth conditions leads to a violation of lattice periodicity and causes a difference of electrical conductivity in T-53 and T-57 samples. A quasi-continuous distribution of levels in the band gap of Bi_2TeO_5 crystals is observed when both electrons and holes are injected. The most probable description of such distribution is the Gaussian approximation of the local states.

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