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CONDUCTIVITY OF IRON DOPED Bi_2TeO_5 SINGLE CRYSTALS

The Bi_2TeO_5 crystals doped with iron (10^{-3} mol% Fe_2O_3) were grown by Czochralski method. The electrical conductivity of obtained crystals was studied in the range of temperatures from 20 to 300°C and fields up to 1300 kV/m. The ohmic and space charge limited currents regions were observed at the current-voltage characteristics. In Bi_2TeO_5:Fe was not observed the region of sharp increase of current, as in undoped Bi_2TeO_5. The effective mobility of charge carriers was calculated from the current-voltage characteristics on the basis of the model of monopolar injection. The mobility of charge carriers in Bi_2TeO_5:Fe crystals in all temperature range was higher than the same for undoped crystals. Two regions with activation energies of 0.85 eV (up to 150°C) and 1.32 eV (from 150 to 350°C) were revealed on the temperature dependence of the mobility. The stimulation of conductivity in Bi_2TeO_5:Fe crystals was not observed in the studied ranges of temperatures and fields. The exponential character of temperature dependency of mobility and its low value suggest the hopping mechanism of conductivity in Bi_2TeO_5:Fe.

Keywords: Bi_2TeO_5:Fe, current-voltage characteristic, photorefractive crystals.

1. Introduction

Bismuth tellurite is a crystal of an orthorhombic fluorite-type structure and a space group of Abm2 with parameters of an elementary cell a= 11,602 Å, b = 16,461 Å and c = 5,523 Å [1]. It has a layered structure with a cleavage plane (100). Bismuth tellurite has a number of interesting properties, such as photorefractive, photochromic and photovoltaic ones that may have practical application [2-4]. The doping by ions of transition metals and rare earths can vary the manifestation of these properties. The photorefractive effect in bismuth tellurite crystals is distinguished by intensity and duration in comparison with other photorefractive crystals. In bismuth tellurite, to preserve the holographic image, a constantly applied external field is not needed. According to [4], Bi_2TeO_5 single crystals doped with iron have photorefractive sensitivity, which is an order of magnitude higher than in pure crystals.

It is assumed that the nature of the photorefractive effect in bismuth tellurite is not related to its ferroelectric properties. The ferroelectric and piezoelectric properties of Bi_2TeO_5 crystals have been studied in the papers [1, 5]. It is established that the Bi_2TeO_5 belongs to the class of improper ferroelectrics with a phase transition at 780 °C [5]. Nevertheless, studies of the kinetics of the photorefractive effect in bismuth tellurite led the authors [4] to the conclusion that this effect is related to the diffusion of charge carriers. The results of investigation of ac and dc conductivities of undoped Bi_2TeO_5 crystals are given in [6, 7]. Since the photorefractive properties of iron-doped bismuth tellurite differ substantially from the properties of undoped crystals, it is of interest to study the processes of charge transfer in them. In this paper, the results of studying the current-voltage characteristics (I-V) of Bi_2TeO_5: Fe crystals are presented.

2. Experimental procedure

Bi_2TeO_5:Fe single crystals were grown by the Czochralski method from a melt containing 1×10^{-3} mol. % Fe_2O_3. The starting materials for the growth of doped bismuth tellurite single crystals were tellurium dioxide (TeO_2), bismuth sesquioxide (Bi_2O_3) and iron sesquioxide (Fe_2O_3), all of 5N purity.

The oxides were dried thoroughly mixed in a ratio of 53 mol% TeO_2, 47 mol% Bi_2O_3. The admixture of iron was calculated as the isovalent substitution of bismuth. The resulting mixture was exposed to a two-stage synthesis. The first stage was annealing at temperatures of 400 – 600 °C for 24 hours. After thorough grinding of the mixture a second annealing followed at temperatures of 600 – 800 °C for 24 hours. The resulting material was melted homogeneously at 920 °C, X-ray phase analysis showed the correspondence of the mixture to the formula of the compound Bi_2TeO_5. The mixture in a platinum crucible was placed in the growth furnace with the temperature gradient of 10º – 25 ºC/cm above the crucible. The seeds were cut perpendicularly to the cleavage plane (100) and along the direction of extinction in polarized light. The crystals were grown at a rotation speed of 25 – 40 rpm. The pulling speed of the crystal was from 1 to 4 mm/h. The obtained crystals had the form of plates of a light yellow color, transparent, without gas pores. The grown crystals are shown in Fig. 1.

For I-V characteristics measurements the plane-parallel single crystal plates were used. The samples of 0.75 mm thickness were obtained by cleaving along (100) plane. The In-Ga electrodes of 4,5 mm^2 square were deposited on both sides of the sample. Before the measurements, the sample was heated to 450 °C and cooled to room temperature with short-circuited electrodes. When measuring the I-V characteristic, the sample exposed by voltage for 10 minutes after which the current was gauged. After each measurement cycle, the sample with short-circuited contacts was heated up to 450 °C. The studies were carried out in the voltage range up to 1000 V and temperatures from 20 to 300 °C.

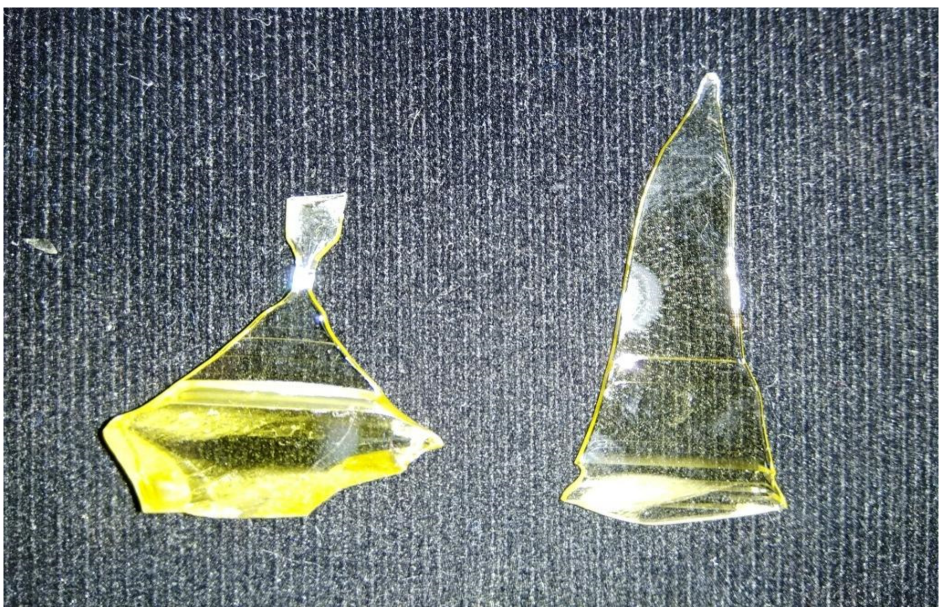

Fig. 1. Bismuth tellurite single crystal doped by Fe_2O_3 grown by Czochralski method.

2. Results and discussion

The obtained results of the studies of I-V characteristic are presented at Fig. 2. In the investigated range of temperatures, ohmic and quadratic sections are observed. It is noteworthy that forward and reverse processes of the I-V curves are very close.

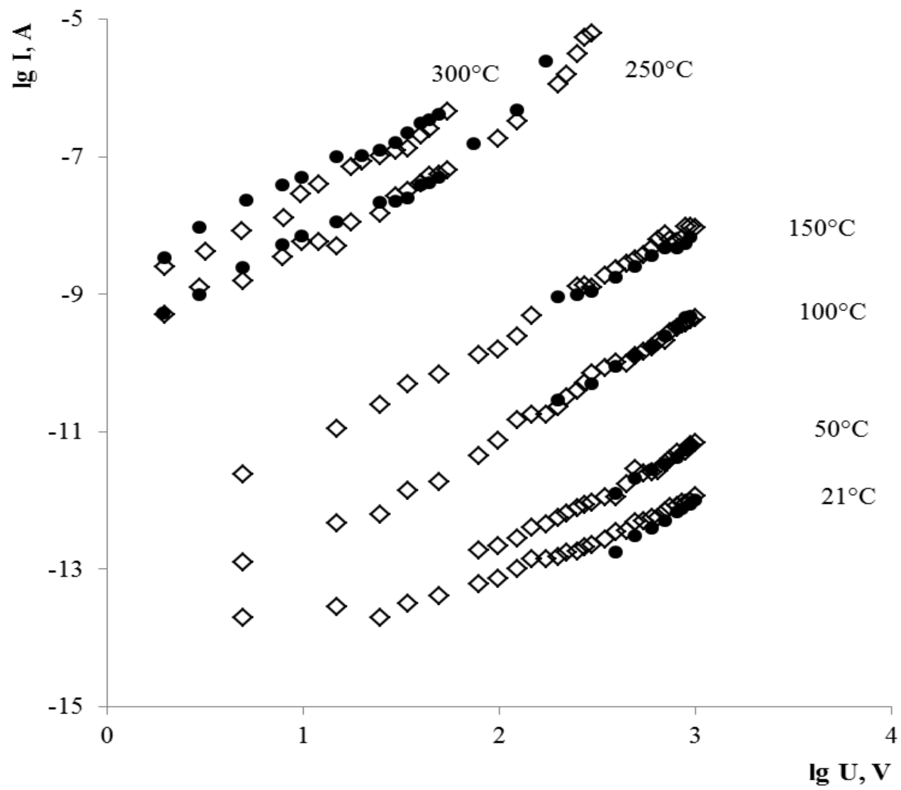

Fig. 2. The current-voltage characteristics at different temperatures of Bi_2TeO_5:Fe single crystals. White markers – forward process, black markers – backward process.

The presence of quadratic sections of the I-V characteristic indicates the existence of space charge limited currents (SCLC) in the crystal sample, which can be the result of charge carrier injection.

According to the SCLC theory [8], the I-V characteristic for monopolar injection has the following features. For low fields, the process of the I-V characteristic is determined by the concentration of free thermally generated carriers n_0. So, here the Ohm's law is observed. The Ohm's law is fulfilled until the voltage U_x, at which the average density of injected carriers n_i becomes comparable with n_0. At $U > U_x$, when the concentration of injected carriers becomes larger than n_0, the current is limited by the space charge and the I-V characteristic is described by the quadratic law:

$$J = (9/8)\varepsilon\varepsilon_0\mu U^2/d^3, \quad (1)$$

where J – the current density; ε, ε_0 – the relative and absolute permittivities respectively; μ – the effective drifting mobility; U – the applied voltage; d – the sample thickness of the sample.

The drift mobility of the charge carriers μ was determined from the quadratic sections of the I-V characteristics using the formula:

$$\mu = 8Id^3/9\varepsilon\varepsilon_0 SU^2, \quad (2)$$

where I – the current passing through the crystal sample; d – the thickness of the sample; ε, ε_0 – the relative and absolute permittivities respectively; S – the electrode square of the sample; U – the applied voltage.

The temperature dependence of the mobility is shown in Fig. 3. The mobility at low temperatures (50°C, see Fig. 3) is 2.1×10^{-8} $cm^2V^{-1}s^{-1}$ and its further variation is described by two sections with charge carrier activation energies of 0.85 eV (up to 150°C) and 1,32 eV (from 150 to 350°C).

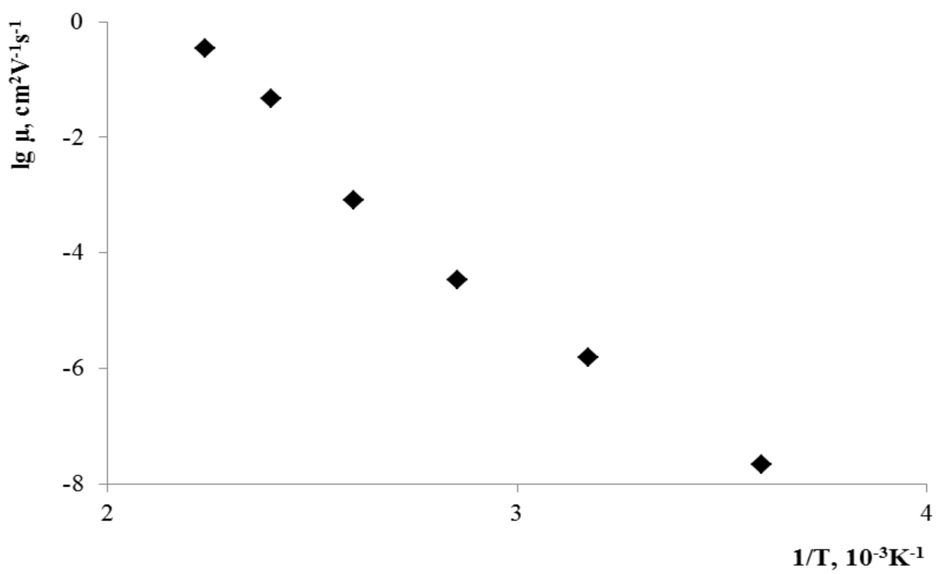

Fig. 3. The temperature dependence of the mobility of Bi_2TeO_5:Fe single crystals.

Low values of mobility and its exponential increase with temperature are typical for hopping charge transfer over localized states [6], which is also true for undoped bismuth tellurite crystals. Comparing the obtained I-V characteristics for Fe-doped samples of Bi_2TeO_5 crystals with the dependences for a pure crystal given in [7, 8], we note the following.

4. Conclusions

1. For Fe-doped crystals, the curves of the I-V characteristic with increasing (forward processes) and decreasing (reverse processes) voltage practically coincide in the whole investigated temperature range. For undoped crystals, even at T > 100°C, the reverse process is much higher than the forward process [6].

2. In all the investigated range of fields (in Ohm's and quadratic laws), the conductivity of Fe-doped crystals is an order of magnitude higher than that of undoped ones.

3. In Fe-doped crystals, there are no regions of sharp increase of current that occurs in undoped crystals.

4. At 100°C, the mobility of charge carriers in Fe-doped crystals is higher than in undoped ones (1.6×10^{-6} $cm^2V^{-1}s^{-1}$ and 6.8×10^{-7} $cm^2V^{-1}s^{-1}$, respectively), but in the high-temperature region the activation of the mobility of charge carriers approximately coincides.

Thus, doping of bismuth tellurite crystals with small iron additives affects its conductive properties, but does not change the conduction mechanism (hopping). In the investigated temperature and field range, the effect of stimulation, which was noted for pure crystals, practically does not appear for doped ones.

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