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Unipolar injection currents in $Bi_4Ge_3O_{12}$ crystals

T.M. Bochkova, S.N. Plyaka, G.Ch. Sokolyanskii
Dniepropetrovsk National University, 13, Naukova str., 49050 Dniepropetrovsk, Ukraine
Phone: +380 (562) 465597; E-mail: tbochkova@ff.dsu.dp.ua

Abstract. Current-voltage characteristics of bismuth orthogermanate ($Bi_4Ge_3O_{12}$) single crystals have been measured at different temperatures under conditions of unipolar injection of charge carriers. It has been found that conduction is characterized by the existence of two channels of the percolation. The temperature dependencies of the conductivity, mobility and concentration of the electrons and holes are considered. The obtained results are discussed in terms of hopping transport model of charge carriers in doped heavily compensated semiconductors.

Keywords: hopping conductivity, current-voltage relations, bismuth orthogermanate.

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1. Introduction

Crystalline bismuth orthogermanate, ($Bi_4Ge_3O_{12}$, named as BGO) was initially synthesized and studied as an electrooptical material, then it was considered as perspective laser host for rare-earth elements and now it is one of the most effective scintillators for the detection of ionizing radiations. At present time BGO is widely used in high-energy physics and computer tomography. According to priority directions of BGO technical applications, the most attention of the scientists was concentrated on the study of its structure and growth procedures, optical and scintillation performances [1, 2]. At the same time in literature there are not enough data about local centers in a crystal lattice of BGO, phenomena of charge transport and mechanisms of a recombination. There are different opinions in respect of a luminescence mechanism: some authors suppose exciton nature [3–5], other ones presume the recombination mechanism of the luminescence [3, 6, 7]. Physical properties of BGO caused by processes of charge transfer (photoconductivity, photochromism, emissive recombination) were considered only from conduction band model positions [8]. And current-voltage characteristics of BGO samples measured at room temperature were ohmic [9]. But thermal depolarization investigation have shown that in BGO simultaneous formation of homo- and heterocharge takes place due to the accumulation of carriers on the spatially and in energy separated energy levels [10]. It is agreed with the data of our work [11], where the investigations of the conductivity of BGO have been carried out in wide temperature, field and frequency ranges. Results have shown that BGO crystals one can consider as partially compensated semiconductors. The transport of charge carriers is realized by hopping from one localized state to another. Gradual transition from pair jumps near Fermi level to multiple jumps with frequency is shifted to higher temperatures. It points out the existence of quasicontinuous distribution of localized states in the forbidden band. Current-voltage characteristics of BGO studied in [11] were typical for space-charge-limited currents (SCLC) and had a series of features, viz.: the field hysteresis of the direct and reverse currents with increase of temperature not only decreases but also changes a sign; the temperature dependence of concentration of the equilibrium charge carriers, calculated from I–V relations transits through a maximum. It had allowed to assume presence of double injection of charge carriers from electrodes into the samples.

This paper is the natural continuation of the work [11]. We present the results of the study of current-voltage relations in BGO single crystals in a mode of unipolar injection.

2. Experimental

Studied BGO single crystals of a good optical quality were grown by Czochralski technique from high-purity Bi_2O_3 and GeO_2 oxides. The material and quality of the contacts are of great importance. In the work [9] the careful examination of I–V characteristics of BGO samples at room temperature was carried out both in the dark and under light exposure. The semitransparent Al, Cr electrodes thermally sputtered and transparent high frequency sputtered In_2O_3 + 9%SnO_2 electrodes were used for measurements [9]. In our work we used liquid In-Ga electrodes. It was found that all considered metals at room temperature form neutral type of contacts with BGO.

Asymmetrical contacts were used for measurements of I–V characteristics in the unipolar injection mode. As injection electrode was In-Ga one. On the other side of the sample the thin layer of silicate glass Na_2SiO_3 was put between the electrode and the crystal. The conductivity of such glasses has ionic nature and is a few orders of magnitude higher than the conductivity of the investigated samples. Application of this layer allows to eliminate the double injection.

I–V relations were studied in (10^2–10^4 V/cm) range of electric fields at temperatures 25–400°C. Measurements of a current have carried out for steady-state achieved after application of voltage during 5 minutes. Low values of the currents were measured with electrometer BK2-16. Q-meter BM-311G was used for measurements of the conductivity at frequency of 20 MHz. The influence of space charge was avoided by employing a preliminary annealing of the samples with shorted electrodes at 400^0C during 2 hours.

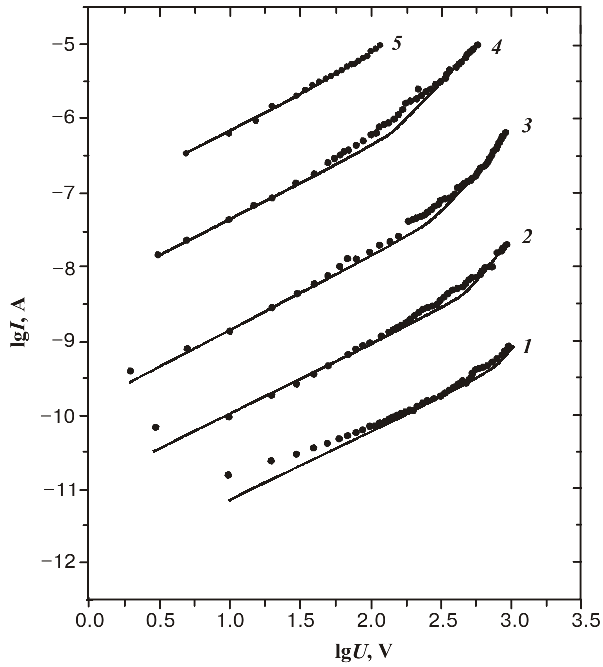

Fig. 2. Current-voltage characteristics of $Bi_4Ge_3O_{12}$ crystals measured in a mode of unipolar injection of holes: 1 – 100°C, 2 – 150°C, 3 – 200°C, 4 – 250°C, 5 – 300°C.

3. Results and discussions

Results of measurements of I–V relations in BGO under conditions of unipolar injection of electrons and holes are shown in Figs 1, 2. In both cases in an explored interval of voltages up to temperatures ~100°C I–V relations are ohmic and values of the currents are low, that agree well with data of [9]. Above 100°C the regions of linear, quadratic and steep rise of currents are observed on the I–V curves. It is typical for space-charge limited currents in dielectrics with traps [12].

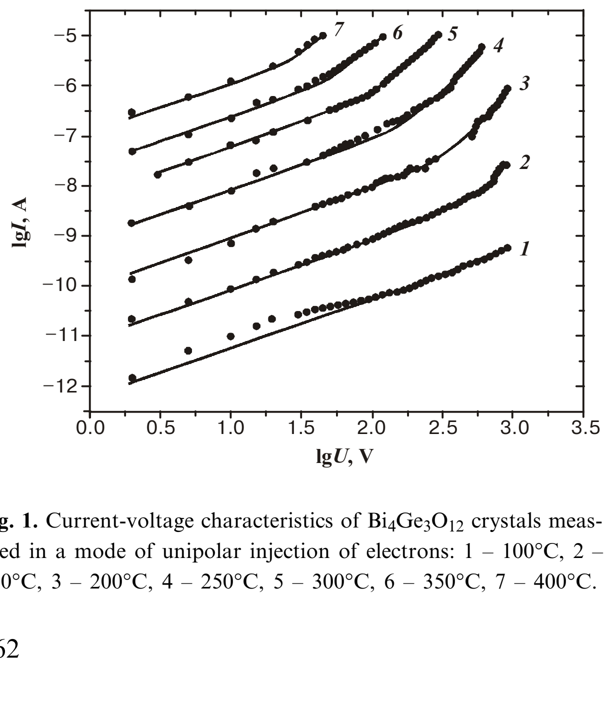

Fig. 1. Current-voltage characteristics of $Bi_4Ge_3O_{12}$ crystals measured in a mode of unipolar injection of electrons: 1 – 100°C, 2 – 150°C, 3 – 200°C, 4 – 250°C, 5 – 300°C, 6 – 350°C, 7 – 400°C.

Values of a specific conductivity (σ_n and σ_p), concentrations of equilibrium carriers of charge (n_0 and p_0) and effective mobility (μ_n and μ_p) are presented in Fig. 3.

Comparison of these data and values of analogous parameters obtained by us earlier for the case of double injection [11] allows to note that absolute values of conductivity in all three cases are rather close. Invariable there is also an activation character of temperature dependence of conductivity (Fig. 3*a*). Up to ~200°C temperature dependencies of electronic and hole conductivity coincide, the activation energy $\Delta E_\sigma = 0.9$ eV, Above 200°C the hole conductivity is predominant and the activation energy of holes rises up to 1.32 eV. These values of the activation energy are less than half of a forbidden gap width in BGO (4.5 eV [1, 2]), i.e. charge transport is realized with the participation of local centers.

The effective mobilities (μ_n and μ_p) of charge carriers up to ~200°C also practically coincide in magnitude (Fig. 3*b*). Above this temperature the effective mobility of holes rises more quickly. The activation energy of electrons and holes ΔE_μ in the first region is 1.11eV, in the second region, for holes, $\Delta E_\mu = 1.72$eV. Lack of the coincidence of the activation energies of the conductivity and mobility (in our case $\Delta E_\sigma > \Delta E_\mu$) testifies about the distribution of the traps in energy in the forbidden band. In particular, at Gaussian distribution of the density of localized states N(E), the activation energy of mobility $\Delta E_\mu = E_t + \delta/2kT$, where E_t – energy of maximum, δ – parameter of Gaussian distribution of the traps [13]. In the injection process the quasi-Fermi level, shifting through Gaussian dumbbell, can lie lower or higher E_t, but only in a case $\delta = 0$ (a monoenergetic level) $\Delta E_\sigma = \Delta E_\mu = E_t$.

The temperature dependencies of the experimentally obtained eqiulibrium concentrations of electrons n_0 and holes p_0 are presented in Fig. 3*c*. Using known relations

$$\sigma = \sigma_0 \exp(-\Delta E_\sigma / kT),\ \mu = \mu_0 \exp(-\Delta E_\mu / kT),$$

$$n = n_0 \exp(-\Delta E_n / kT)$$

and taking into consideration the equality $\sigma = en\mu$, one obtains $\Delta E_n = \Delta E_\mu - \Delta E_\sigma$.

Actually, with increase of temperature the concentration as electrons, and holes decreases exponentially with the positive activation energy making 0.19–0.21 eV both for electrons and holes in the temperature range up to ~250°C. At the further rise in temperature the hole concentration falls more sharply with the activation energy 0.40 eV. The values obtained are agreed with experimental values $\Delta E_\mu - \Delta E_\sigma$, which are equal 0.21 eV and 0.38 eV for electrons and holes in corresponding temperature ranges.

On the basis of the experimental results one can conclude that in BGO crystals charge carriers are simultaneously both electrons and holes. Values of mobility and conductivity for electrons and holes are close. Activation rise of mobility with temperature for both types of carriers and its low values confirm hopping mechanism of the conduction. Such processes and high values of the activation energy ΔE_σ for electrons and holes are typical for hopping conduction involving impurity centers and ΔE_σ is governed by the position of quasi-Fermi level relatively the percolation level [14]. This mechanism of the conduction is widespread enough for strongly compensated semiconductors with a wide band gap [15, 16]. Its activation temperature dependence is usually connected with the "smearing out" of discrete impurity levels involved into "hopping" due to the presence of charged impurities, random distribution of which creates a large-scale fluctuations of electrostatic potential of a crystal lattice. Though we have investigated the nominally pure crystals, the existence of the proper defects in BGO grown by Czochralski method, have been established by many authors. So, wide bands in the optical absorption spectra observed after an irradiation with UV-light or X-ray were connected with the color centers forming from the defects-precursors. [17,18]. The investigations of the local centers in the crystals, carried out by methods of thermally stimulated luminescence and photoconductivity [17, 19], thermally stimulated exoelectronic emission [20] and thermal depolarization [10] have confirmed the existence of the wide energetic spectrum of local states in $Bi_4Ge_3O_{12}$.

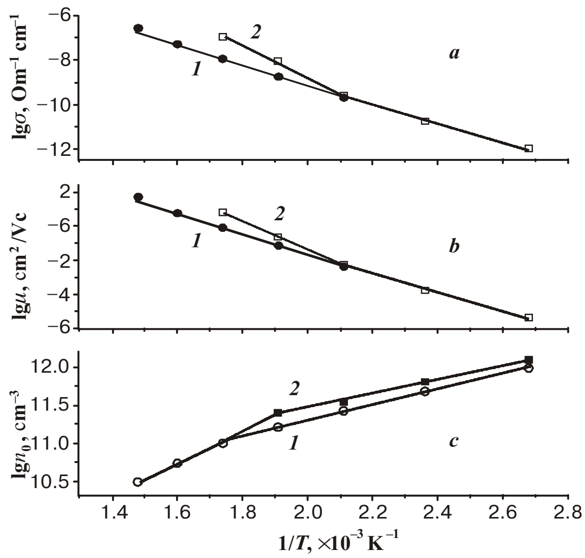

Fig. 3. Temperature dependences of conductivity (a), mobility (в) and concentration (c) of charge carriers in $Bi_4Ge_3O_{12}$ crystals: 1 – electrons; 2 – holes.

Values of the concentration of traps N_t obtained by us from voltage-current curves for electrons as well as values of the concentration of the equilibrium carriers of charge (n_0, p_0) are close (~10^{12} cm^{-3}) and are obviously understated in comparison with really existing in the crystal the concentration of uncontrolled impurities and other electrically active defects. It takes place because at temperatures of experiment hopping of charge carriers may occur inside clusters of finite sizes, i.e. infinite cluster for percolation of charge is not formed yet. The accumulation of charge at the ends of the clusters leads to peculiar migration polarization of the sample. Thus, moving of the charge carriers inside of clusters of different sizes may give a contribution into dielectric permittivity and conductivity of semiconductors [21] and the estimation of concentration of electrons and holes $n(p)$ shall be more correct, if we use values of ac-conductivity and dielectric permittivity measured at high frequency, when more considerable amount of charge carriers takes part in the transfer.

The existence of clusters of different sizes in BGO crystals was experimentally found in [11] from temperature dependences of ac-conductivity at different frequencies. The estimation of the chain length of jumps performed according to [22], have shown that at 20–180°C jumps of charge carriers near quasi-Fermi level occur inside of the pair centers, at higher temperatures the transport of charge is realized by multiple jumps. And, the increase of frequency leads to rise of $\sigma_\sim$ due to decrease of cluster sizes.

Measurements of dielectric permittivity and conductivity were performed at 20 MHz and have shown that they vary in this temperature range a little: $\varepsilon = 66–73$, $\sigma_\sim = (2–6)\cdot 10^{-4} Ohm^{-1} cm^{-1}$. Computed values n and p are given in the table.

Using obtained values of the concentration of electrons and holes, it is possible to estimate also concentration of the basic impurities (proper defects). It is known that value of hopping conductivity and its activation energy depend on an impurity concentration and a degree of compensation of donors and acceptors ($K = N_d/N_a$). In case of strong compensation ($K \to 1$) following expression was obtained in [14, 23] :

$$\sigma = \sigma_0 \exp\left[-\left(\frac{\alpha}{N_d^{1/3} a} + \frac{e}{\varepsilon\varepsilon_0}\frac{N_d^{1/3}}{(1-K)^{1/3}\cdot kT}\right)\right],$$

where α – the coefficient dependent on a degree of compensation, a – Bohr radius. Considering temperature dependence of conductivity and taking into account, that at strong compensation concentration of the free charge carriers $n = N_d - N_a$, we shall find:

$$N_d = \left(\frac{E_\sigma \varepsilon\varepsilon_0}{e}\right)^{3/2} \cdot n^{1/2}.$$

Values of N_d, N_a, calculated for electrons and holes are presented in the table. Apparently, values of a degree of compensation K are close to 1, i.e. $Bi_4Ge_3O_{12}$ crystal really is strongly compensated semiconductor. That fact, that on the direct current both electrons and holes are mobile, and also distinctions in values of N_d and N_a for electrons and holes at temperatures above 200°C demonstrated presence of two channels of percolation of the charge, parted recombination barriers. Therefore, the cause of described above the exponential decrease of concentration of equilibrium charge carriers may be their mutual recombination through barriers. Obviously, that feather study of a nature of local centers and electron-hole processes in $Bi_4Ge_3O_{12}$ is necessary as for the solution of a problem of growth of the perfect crystals, understanding of regularities of the radiation defect formation and mechanisms of luminescence, and for development of the modern model of conduction in wide band semiconductors of complex oxides.

Table. The calculated parameters of hopping conductivity in $Bi_4Ge_3O_{12}$.

t°C	The electrons			
	n, cm^{-3}	N_d, cm^{-3}	N_a, cm^{-3}	K
200	$5.21\cdot10^{17}$	$7.273\cdot10^{19}$	$7.221\cdot10^{19}$	0.993
250	$3.38\cdot10^{16}$	$1.853\cdot10^{19}$	$1.850\cdot10^{19}$	0.996
300	$2.86\cdot10^{15}$	$6.978\cdot10^{18}$	$6.951\cdot10^{18}$	0.998
	The holes			
	p, cm^{-3}	N_a, cm^{-3}	N_d, cm^{-3}	K
200	$5.63\cdot10^{17}$	$7.561\cdot10^{19}$	$7.508\cdot10^{19}$	0.993
250	$3.12\cdot10^{15}$	$9.998\cdot10^{18}$	$9.995\cdot10^{18}$	0.999
300	$2.80\cdot10^{14}$	$3.879\cdot10^{18}$	$3.8787\cdot10^{18}$	0.999

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