

***I*–*V* CHARACTERISTICS OF $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ – Mn CRYSTALS IN THE UNIPOLAR INJECTION MODE**

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Current-voltage relations in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ – Mn crystals were measured under the conditions of unipolar injection of charge carriers. The characteristics obtained for electrons and holes are different. *I*-*V* curves in the case of electron injection contain ohmic, quadratic regions and regions of a sharp increase in current. This indicates the formation of a space charge enriched in electrons. The values of conductivity, effective drift mobility, and electron concentration calculated at different temperatures are close to the values obtained for pure crystals. In the case of hole injection *I*-*V* curves are characterized by the presence of sublinear regions. It is assumed that injection of the holes causes the formation of a space charge layer depleted in electrons due to the recombination. It is shown that doping with manganese does not change the nature of conductivity in bismuth germanate crystals and strongly affects the recombination processes.

Keywords: $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, current-voltage relations, unipolar injection, space charge.

Received 30.10.2019; Received in revised form 02.12.2019; Accepted 23.12.2019

1. Introduction

Bismuth orthogermanate crystals ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) are among the most efficient scintillators for detecting ionizing radiation and are widely used in high-energy physics and computed tomography. The structure and growing methods, optical and scintillation properties of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ are well studied [1, 2]. At the same time bismuth orthogermanate is a photorefractive material with applicable properties. The band gap of it according to optical measurements exceeds 4.5 eV and dark conductivity is $\sim 10^{-13}$ Ohm⁻¹m⁻¹ at room temperature. The crystals have cubic symmetry. Space group $I\bar{4}3d$ (T_d^6). The tensor of the linear electro-optical effect is characterized by a nonzero coefficient $r_{41} = r_{52} = r_{63}$. For a wavelength of 0.63 μm , the refractive index $n = 2.09$ and $n^3 r_{41} = 8.8 \cdot 10^{-12}$ m/V, the half-wave voltage $V_{\lambda/2} = 48.5$ kV [2]. The possibility to grow large crystals of high quality, their transparency and non-hygroscopicity are favorable for the use of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystals in optical information processing devices, in particular, for recording holographic gratings at various wavelengths [3]. Doping of crystals with transition metals, in particular, Mn, leads to the appearance of a photochromic effect [4], which increases the efficiency of holographic recording. However, there is extremely little information about the influence of the iron group impurities on the charge transfer processes in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystals. This paper presents the results of studying the unipolar injection currents in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystals doped with manganese.

2. Samples and experimental details

The crystals of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ doped with Mn were grown from the melt by Czochralski method using double recrystallization technology. The Mn content in the crystals according to spectral analysis was 0.01 – 0.03 weight%. The thickness of the samples was about 0.40 mm.

Asymmetric contacts were used for current-voltage dependency measurements in the unipolar injection mode. In–Ga was chosen as the injection electrode. In order to avoid double injection of charge carriers, a thin layer of silicate glass (Na_2SiO_3) was applied between the sample and the electrode on the other side of the sample. (Glass conductivity is ionic and significantly exceeds the conductivity of the crystal studied).

The measurements of *I*-*V* characteristics were carried out in electric field (10^2 – 10^4 V/cm) and temperature (25 – 400 °C) ranges in accordance with the procedure described in [5-6].

3. Results and discussion

The results of current-voltage dependency measurements of the crystals of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ doped with Mn are presented in Figs. 1, 2. Previously, the authors studied I - V characteristics in nominally pure crystals $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ [5-6]. They became a good tool for studying the processes of space charges formation in bismuth orthogermanate crystals.

I - V characteristics measured in the samples with two metal electrodes (Pt, Ag, In—Ga) have a number specific features. In the temperature range up to 150°C , regions with a linear ($I \sim U^m$, $m=1$) and superlinear ($I \sim U^m$, $m>1$) increase in current are observed. The presence of a quadratic regions indicates the ohmic nature of the contacts and also that the concentration of charge carriers injected from the contacts becomes comparable with the concentration of equilibrium ones. It is typical for space-charge limited currents (SCLC) in dielectrics with traps. At temperatures of $150 - 250^\circ\text{C}$, regions with negative differential resistance (NDR) of the N-type are observed. And at temperatures above 250°C we see extended sublinear ($I \sim U^m$, $m=1/2$ or $0 < m < 1$) regions, which, with increasing voltage, are again replaced by ohmic and superlinear characteristics.

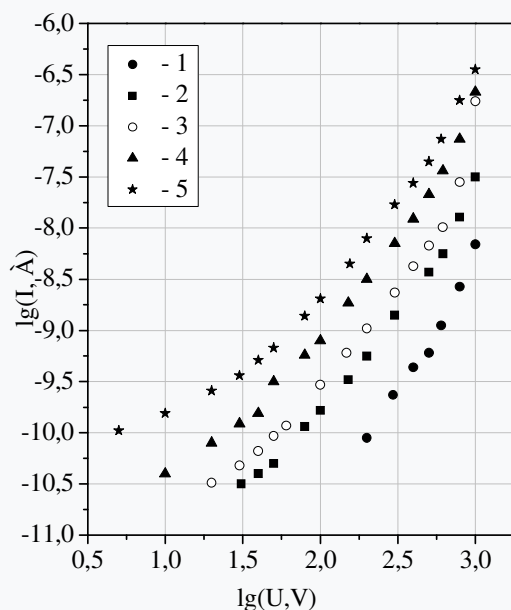


Fig. 1. Current-voltage characteristics of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ – Mn crystals measured in the mode of unipolar injection of electrons: 1 – 160°C , 2 – 175°C , 3 – 200°C , 4 – 225°C , 5 – 250°C .

To explain the complex behavior of the family of current-voltage curves for $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, measurements were performed on the samples with asymmetric electrodes [5]. It was shown that the I - V dependencies taken under such conditions correspond to the case of currents limited by the space charge for both electrons and holes. Further studies made it possible to determine that $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ is a relaxation type semiconductor [7].

It was found that in the temperature range up to $150 - 175^\circ\text{C}$ the injection of the main charge carriers (electrons) dominates and the space charge enriched in the electrons is formed. Above this temperature, the injection of minority charge carriers (holes) becomes noticeable. The recombination begins. The number of main carriers sharply decreases and a space charge layer is formed, depleted in the main carriers. It is due to

recombination in the space charge layer we can observe NDR and sublinear regions in $I-V$ characteristics.

The recombination process is highly dependent on the presence of impurities, since the existence of traps can significantly affect the lifetime of charge carriers and, accordingly, the recombination rate.

A comparison of the current-voltage characteristics of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystals, pure and doped with manganese ions, measured in the double injection mode was performed in [8]. It was shown that the presence of the impurity of manganese does not change the nature of electrical conductivity, but affects the formation of space charge and the processes of recombination, which, at temperatures above 250 °C, limit the current in the range of applied voltage of 10 – 850 V forming the $I-V$ dependencies with a small slope.

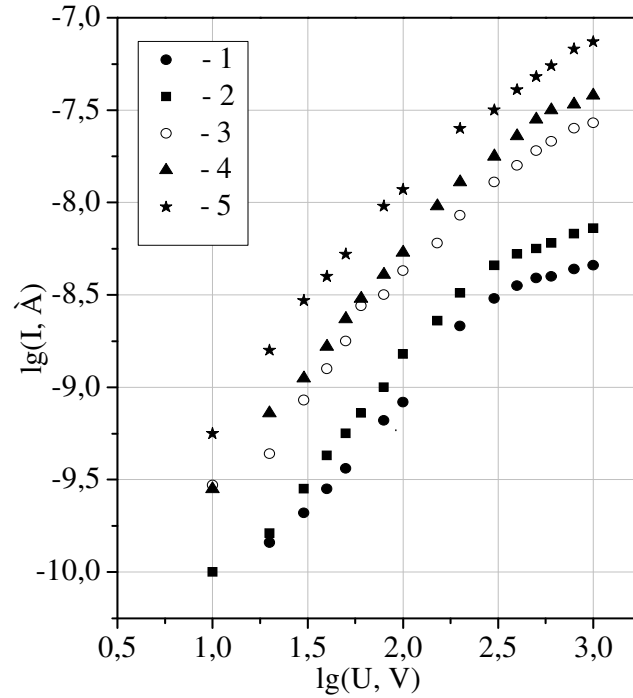


Fig. 2. Current-voltage characteristics of $\text{Bi}_4\text{Ge}_3\text{O}_{12} - \text{Mn}$ crystals measured in the mode of unipolar injection of holes: 1 – 150 °C, 2 – 175 °C, 3 – 200 °C, 4 – 225 °C, 5 – 250 °C.

The current-voltage characteristics presented in Fig. 1 (injection of electrons) correspond to the case of SCLC. The conductivity, effective drift mobility, and concentration of electrons were calculated according to formulas SCLC (Table 1). They completely correlate with the data obtained for pure crystals. The conductivity and mobility are very small and have an activation character. These features are inherent in hopping conduction.

Let us consider the $I-V$ dependences in Fig. 2. They fundamentally differ both from the $I-V$ relations shown in Fig. 1, and from the $I-V$ relations measured in the unipolar hole injection mode for pure crystals [6]. The formation of a space charge enriched in holes does not occur. The slope of the curves decreases to sublinear. It means that currents are limited by recombination processes. Obviously, recombination centers in crystals $\text{Bi}_4\text{Ge}_3\text{O}_{12} - \text{Mn}$ are associated with the introduction of manganese.

Table 1

The parameters of the electron conductivity in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ – Mn crystals

$t, ^\circ\text{C}$	$\sigma_n, \text{Ohm}^{-1}\cdot\text{cm}^{-1}$	$\mu_{\text{ef}}, \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{c}^{-1}$	n_0, cm^{-3}
175	$2,41 \cdot 10^{-11}$	$0,94 \cdot 10^{-3}$	$8,0 \cdot 10^{11}$
200	$2,03 \cdot 10^{-10}$	$2,94 \cdot 10^{-3}$	$6,43 \cdot 10^{11}$
225	$1,76 \cdot 10^{-9}$	$7,15 \cdot 10^{-3}$	$4,13 \cdot 10^{11}$
250	$1,15 \cdot 10^{-9}$	$4,46 \cdot 10^{-2}$	$2,87 \cdot 10^{11}$

4. Conclusions

In bismuth orthogermanate crystals doped with manganese, the charge carriers are both electrons and holes. I - V relations measured under the conditions of unipolar injection of electrons corresponding to the case of space-charge limited currents. The values of conductivity, effective drift mobility, and electron concentration calculated for different temperatures are close to the corresponding values in pure crystals and are characteristic for hopping conductivity. Therefore, the introduction of Mn does not change the nature of the conductivity in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. In the case of hole injection, I - V dependencies show sublinear rise of the current with voltage increase. We attribute this phenomenon to the effect of manganese on recombination processes.

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