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SEMICONDUCTORS

# Isothermal Relaxation of Current in Doped $Bi_{12}SiO_{20}$ : Ge Sillenite Single Crystals

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**Abstract**—This paper presents the results of studying transient isothermal currents in germanium-doped $Bi_{12}SiO_{20}$ : Ge bismuth silicate single crystals at different stresses and temperatures. It has been found that electronic processes caused by the accumulation of considerable charges occur in the samples under investigation in a dc electric field. The relaxation of current at different temperatures corresponds to the mechanism of charge transfer formed at the energy level in the band gap. The microscopic parameters of the crystals characterizing the processes that occur in the material under investigation, in particular, the activation energy of the local level and the frequency factor, have been determined.

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## 1. INTRODUCTION

Single crystals with the sillenite-type structure $Bi_{12}MO_{20}$ (here, $M$ is Si, Ge, Ti, etc.) exhibit a set of physical properties, including the manifestations of piezoelectric, electro and magneto-optical effects, photorefraction, and photoconductivity in a wide spectral range. This allows considering these materials as promising media for making piezo and optical detectors, modulators of laser light, and a number of other optoelectronic devices [1, 2]. Despite such a wide field of applications, information on a possible defect structure determining the distribution of energy levels in the band gap and on the mechanisms of charge transfer in compounds of the Bi–$M$–O system is incomplete. The emergence of local states in the band gap, which affect the electrophysical properties, is facilitated by the presence of impurities and stoichiometric defects of the structure associated with a complex composition of sillenites and with the presence of an active lone electron pair belonging to the bismuth ions $Bi^{3+}$ [3, 4].

Inertia and electric characteristics of devices based on wideband semiconductors, which include the crystals with a sillenite structure, are largely determined by the rate of charge carrier generation from the energy levels in the band gap and by trapping to these levels. Studying the relaxation electronic processes is one of the basic methods to obtain information on mechanisms of charge accumulation and transfer and to establish the nature of degradation of semiconductor structures and electronic units on their basis under the action of the electric field [5].

The oxygen-containing compound of the sillenite system Bi–Si–O (BSO), $Bi_{12}SiO_{20}$, has been actively studied recently. Interest in this compound is primarily associated with its implementation as an optically active medium for recording 3D holograms and with the opportunity of building optical memory systems [6, 7]. However, expanding the application field of bismuth silicate crystals is hindered by the absence of detailed information on the mechanisms of charge transfer in the BSO semiconductor system in the dc electric field.

This work is aimed at studying the relaxation phenomena in germanium-doped $Bi_{12}SiO_{20}$ single crystals by current transient spectroscopy.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Investigation was carried out on BSO : Ge single crystals grown in air by the Czochralski method along the crystallographic direction [001] in a platinum crucible. The samples were 1 × 3 × 5-mm polished bars with a Henkel AquaDag E conducting paste as contact plates.

The measurements were performed with the use of a Keithley-6517A electrometric amplifier with a variable voltage applied to the samples. During the experiments, the samples were heated in air to a specified temperature ranging from 293 to 340 K at a rate of ~0.5 K/min in a Nabertherm muffle furnace equipped with a temperature controller. The composition and the presence of an impurity (Ge) were detected by

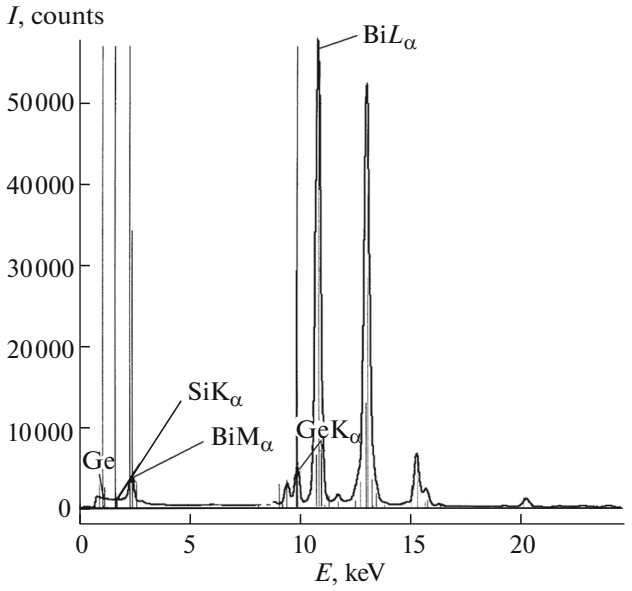


**Fig. 1.** X-ray fluorescence spectrum of the $Bi_{12}SiO_{20}$ : Ge sample.

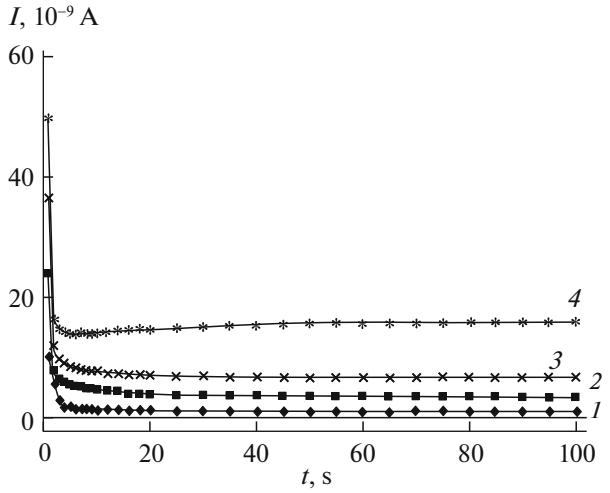


**Fig. 2.** Time dependence of the current passing through the $Bi_{12}SiO_{20}$ : Ge sample at voltages $U$ = (*1*) 20, (*2*) 40, (*3*) 60, and (*4*) 80 V and $T$ = 296 K.

X-ray fluorescence analysis (on an X-ART M setup), the results of which are shown in Fig. 1.

## 3. RESULTS AND DISCUSSION

Since the crystal lattice of BSO is highly polarizable owing to the presence of $Bi^{3+}$ ions containing a lone electron pair, one can assume the probability of active relaxation processes that occur in the volume of the samples under investigation. Figure 2 presents the results of the experimentally measured time dependence of the isothermal current $I(t)$ passing through the BSO : Ge single-crystal sample under different voltages. At a dc voltage applied to the samples under investigation, the current in the outer circuit first sharply increased, then exhibited a decrease and stabilized after some time at a steady-state value. The decreasing relaxation of the current, which revealed fast and slow stages of the relaxation process in the samples under investigation, led to a weaker power dependence of the current on the voltage. The transient current increased and the character of kinetics in the time interval under consideration changed with an increase in the voltage. More specifically, the length of the initial part of the kinetics of the polarization current decreased and the decay rate of the function $I(t)$ increased.

The shape of the shown dependences allows assuming the existence of a set of dielectric relaxation time constants in the compound under investigation corresponding to a non-Debye model, which is seemingly associated with the presence of carriers released from traps, which are characterized by a high level of emission at a given temperature. The fast component of the current kinetics conformed with the exponential dependence and the further variation of the current followed a hyperbolic relation.

The analysis of the experimental data indicates that the initial part of the time dependence of the current satisfies the expression [8]

$$I(t) = (e\mu\tau_e nSE/\tau)\exp(-t/\tau), \quad (1)$$

where $q$ is the unit charge, $\mu$ is the drift mobility of charge carriers, $\tau$ is the relaxation time constant, $\tau_e$ is lifetime of the charge carriers, $n$ is the carrier density in the traps, $S$ is the contact area, $E$ is the applied electric field.

The presence of two components of the time dependence of the relaxation current was observed in many semiconductors with different degrees of structural ordering [9] and the manifestation of slow current relaxation is usually interpreted as the formation of a space charge owing to trapping of charge carriers to local levels with a subsequent thermal emptying of increasingly deeper traps, which leads to deceleration of the process. In this case, a charge is formed in the sample, the electric field of which acts in the direction opposite to the applied voltage.

An increase in temperature leads to an increase in the relaxation current in the entire time interval (Fig. 3). The analysis of the data of the current kinetics at different temperatures allows finding the depth of local levels. This parameter was computed from the slope of the Arrhenius dependence $\ln I(10^3/T)$ (inset in Fig. 3) and appeared to be 0.60 eV at a given voltage (20 V).

According to the theory of isothermal currents describing the transition of the sample from a nonequilibrium to equilibrium state [10], the analysis of the $It(t)$ curve, i.e., of the time dependence of the

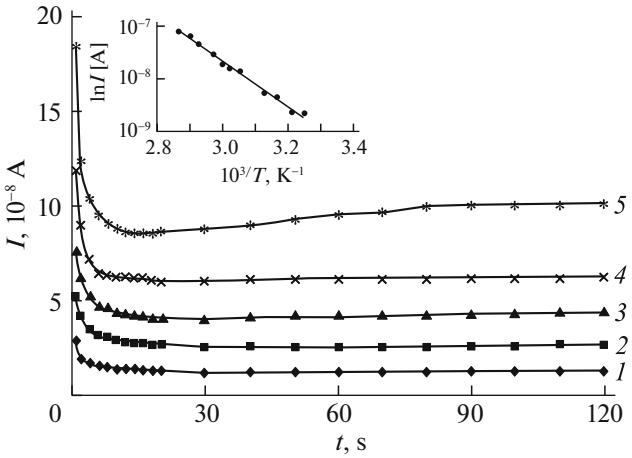


**Fig. 3.** Time dependence of the current passing through the $Bi_{12}SiO_{20}$ : Ge sample at the voltage $U = 20$ V and temperature $T$ = (*1*) 300, (*2*) 308, (*3*) 318, (*4*) 328, and (*5*) 340 K. The inset shows the temperature dependence of the steady-state current.

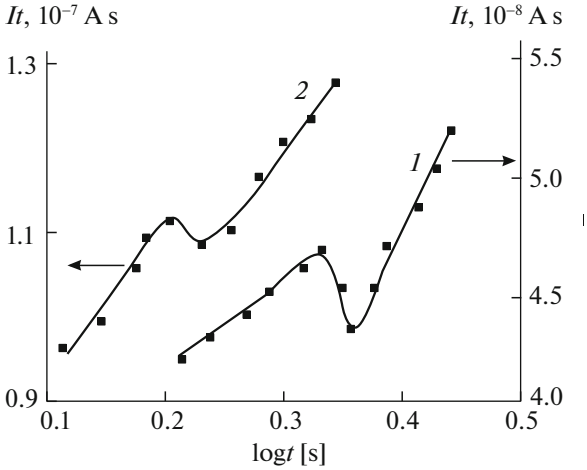


**Fig. 4.** The $It$–log$t$ curve for $Bi_{12}SiO_{20}$ : Ge at the temperatures $T$ = (*1*) 300 and (*2*) 318 K.

accumulated charge, allows finding the distribution of levels in the band gap. Figure 4 shows the dependences of this kind for the samples of the BSO crystal under investigation at two temperatures. An increase in temperature leads to a shift of the $It$ maxima toward shorter times.

The maximum of the $It$(log$t$) curve corresponding to the value $t = \tau$ is related to the depth of the trap level via the expression [11]

$$E_t = kT \ln \nu\tau, \qquad (2)$$

where $\nu$ is the frequency factor.

The average value of the frequency factor obtained according to Eq. (2) with the calculated $E_t$ value at a given temperature appeared to be $\nu = 4.8 \times 10^9$ s$^{-1}$.

Structural changes in $Bi_{12}SiO_{20}$ : Ge can be caused by the substitution of embedded germanium for bismuth in distorted oxygen octahedra during doping with the formation of oxygen vacancies [12]. According to the condition of charge compensation, the latter vacancies can capture electrons and lead to the emergence of the electric current in the opposite direction and, consequently, to the current relaxation.

## 4. CONCLUSIONS

Thus, we studied the kinetics of the current relaxation in BSO : Ge single crystals based on the theory of isothermal currents depending on the effects of the electric field and temperature. The measured time dependences of the current have three basic regions: a sharp increase, a decay, and a stationary region. It was found that the slow relaxation of current is associated with the accumulation of charge on traps with the energy $E_t = 0.60$ eV below the bottom of the conduction band at the frequency factor $\nu = 4.8 \times 10^9$ s$^{-1}$. The obtained data indicate that the investigation of the isothermal current relaxation is a promising method of revealing the structure of localized states in the band gap of BSO : Ge single crystals. On the other hand, further experiments are required for a detailed study of mechanisms responsible for the formation of the space charge and slow decay of current in doped compounds with the sillenite structure.

## REFERENCES

1. P. Gunter and J. P. Huignard, *Photorefractive Materials and Their Applications* (Springer-Verlag, Berlin, 1988–1989), Vols. 61–62.
2. V. K. Malinovskii, O. A. Gudaev, V. A. Gusev, and S. I. Demenko, *Photoinduced Phenomena in Sillenites* (Nauka, Novosibirsk, 1990) [in Russian].
3. S. F. Radaev and V. I. Simonov, Sov. Phys. Crystallogr. **37** (4), 482 (1992).
4. A. V. Egorysheva, Inorg. Mater. **45** (10), 1175 (2009).
5. V. T. Avanesyan and M. P. Sevryugina, Phys. Solid State **53** (5), 939 (2011).
6. V. T. Avanesyan and N. M. Abramova, Phys. Solid State **57** (6), 1100 (2015).
7. T. V. Panchenko, A. A. Dyachenko, and O. V. Khmelenko, Phys. Solid State **57** (4), 771 (2015).
8. G. Micocci, A. Rizzo, P. Siciliano, and A. Tepore, Phys. Status Solidi **114** (1), 253 (1989).
9. A. K. Jonscher, *Universal Relaxation Law* (Chelsea Dielectric Press, London, 1996).
10. E. V. Zenova, N. D. Karpechenkov, and V. A. Chernyshev, Meas. Tech. **51** (5), 516 (2008).
11. G. S. Nadkarni and J. G. Simmons, Phys. Rev. B: Solid State **7** (8), 3719 (1973).
12. T. I. Milenov, M. N. Veleva, D. P. Petrova, M. M. Gospodinov, V. M. Skorikov, A. V. Egorysheva, Yu. F. Kargin, and A. Ya. Vasil'ev, Inorg. Mater. **41** (2), 152 (2005).

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