

<https://doi.org/10.15407/ujpe66.11.988>

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## THERMODEPOLARIZATION OF $\text{Bi}_{12}\text{SiO}_{20}$ CRYSTALS DOPED WITH Fe

*The polarization processes in  $\text{Bi}_{12}\text{SiO}_{20}$  crystals doped with Fe ( $\text{Bi}_{12}\text{SiO}_{20}:\text{Fe}$ ) in the temperature interval 300–800 K are studied by the thermoactivation spectroscopy methods. The temperature dependences of the thermostimulated depolarization (TSD) currents and the dependences of the intensities of TSD current peaks on the polarization conditions are obtained. The mechanisms of space charge and quasidipole polarizations are revealed. The temperature dependences of the optical absorption of  $\text{Bi}_{12}\text{SiO}_{20}:\text{Fe}$  crystals are also investigated.*

*Keywords:* polarization, thermostimulated depolarization, optical absorption,  $\text{Bi}_{12}\text{SiO}_{20}$  crystals doped with Fe.

### 1. Introduction

The modification of the properties of crystals that belong to the family of  $\text{Bi}_{12}\text{MO}_{20}$  sillenites (BMO, where  $M = \text{Si, Ge, Ti}$ ) by doping is of unremitting scientific and practical interests [1]. These crystals, being wide-band semiconductors, are important for solving the problem of deep centers in solid state physics. The unique combination of many practically useful properties allows us, by their modification, to count on expanding the scope of using BMO as an active medium in functional devices of the electronics. To date, the extensive studies of BMO doped with single and multiply charged impurities have been performed. The influence of a number of impurity ions (Al, Ga, Cr, Mn) on the totality of the optical [2–4], photoelectric [5], and electrophysical [6, 7] properties of BMO is already known. Despite this, the insufficient attention is paid to Fe ions. It is known that they cause the low-temperature photochromic effect (PCE), which can be erased by the heating to room temperature [8]. According to the EPR studies, the excitation of PCE and its erasure are accompanied, respectively, by a decrease and restoration of the concentration of Fe ions, which in the charge state  $\text{Fe}^{3+}$  occupy the positions of  $M^{4+}$  ions in the BMO oxygen tetrahedra [9]. It seems important to study

the role of  $\text{Fe}^{3+}$  ions in electrophysical phenomena in BMO.

Our paper presents the results of thermostimulated polarization and depolarization studies, as well as the temperature dependences of the optical absorption of  $\text{Bi}_{12}\text{SiO}_{20}$  (BSO) crystals doped with Fe ions (BSO:Fe).

### 2. Experiment

Optically homogeneous BSO:Fe crystals were grown by the Czochralski method. The impurity was incorporated into the burden in the form of  $\text{Fe}_2\text{O}_3$  oxide. The so-called isotopic effect, according to which the incorporation of  $^{57}\text{Fe}$  isotopes into BSO crystals improves their optical quality and enhances PCE in comparison with the  $^{56}\text{Fe}$  isotope [8], was taken into account. A similar effect of increasing the EPR signal intensity was also noted in [9]. According to the spectral emission analysis, the studied crystals contained 0.02 mass. % of  $^{57}\text{Fe}$  ions. The samples for the electrical measurements were prepared in the form of carefully polished parallelepipeds,  $(1 \div 1.5) \times 3 \times 9 \text{ mm}^3$  in size and with (001) faces. The Pt electrodes were deposited on both  $3 \times 9 \text{ mm}^2$  surfaces by the dc ion-plasma sputtering at a pure Ar pressure of 10 mTorr. With regard for the data [10] and relatively large values of the electron work function of platinum ( $\sim 5 \text{ eV}$ ), we assume that the Pt-BSO:Fe contacts were of the barrier type. In view of the high

( $\rho \sim 10^{14} \Omega \cdot \text{cm}$ ) dark resistivity of BSO, we used a special sample holder with sapphire insulation ( $\rho \sim 10^{19} \Omega \cdot \text{cm}$ ) in order to measure the polarization and depolarization currents. To bring the electronic subsystem to the same initial state before measurements, the samples were heated to 900 K and then slowly cooled to 300 K for 24 h in air and with short-circuited electrodes. This procedure ensured the reproducibility of results.

The samples were polarized at a constant voltage applied to the Pt electrodes. The field strength  $E_p$  and the polarization temperature  $T_p$  varied within the intervals:  $E_p = 0.1 \div 5 \text{ kV} \cdot \text{cm}^{-1}$  and  $T_p = 350 \div 750 \text{ K}$ . The polarization duration in all cases was 30 min. The thermostimulated polarization (TSP) and depolarization (TSD) currents were measured in the temperature interval 300–800 K in the linear heating mode at a rate of  $\beta = 0.16 \text{ K} \cdot \text{s}^{-1}$ . A computerized measuring system was used for electrical measurements.

The transmission spectra  $t(\nu)$ , where  $\nu = 1/\lambda$  and  $\lambda$  is the wavelength, in the optical interval  $\nu = 11000\text{--}8000 \text{ cm}^{-1}$  were measured by a spectrophotometer Specord M40 in the temperature interval 85–700 K. The samples for optical measurements were prepared as a collection of polished plates with (001) face and with the thickness  $d = 0.1 \div 5 \text{ mm}$ . The optical absorption spectra  $\alpha(\nu)$  were calculated from the relation [11]:

$$t(\nu) = \frac{(1-R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)}, \quad (1)$$

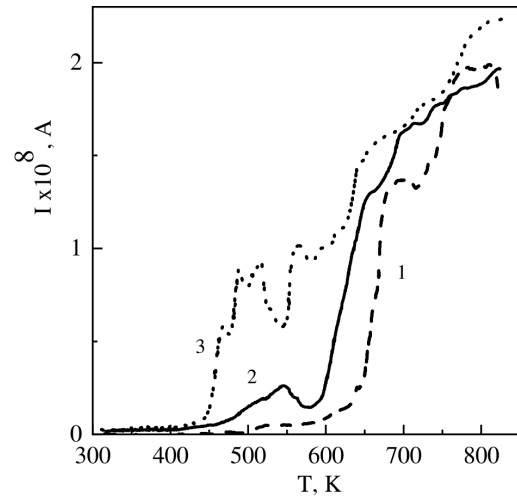
with regard for the reflection spectra  $R(\nu)$ :

$$R(\nu) = \frac{(1-n)^2}{(1+n)^2}, \quad (2)$$

where  $n$  is the refractive index [11]. To determine  $n$ , a prism with a refractive angle of  $15^\circ$  was made from a BSO:Fe crystal. The spectra  $n(\nu)$  were measured in the range  $\nu = 25000\text{--}16000 \text{ cm}^{-1}$  using a GS-5 goniometer and an MDR-12 monochromator. The experimental spectra  $n(\nu)$  in the indicated range agree with the spectra calculated from the relation [12]:

$$n^2(\nu) - 1 = \frac{a \lambda_0^2 \lambda^2}{(\lambda^2 - \lambda_0^2)} + \frac{b \lambda_1^2 \lambda^2}{(\lambda^2 - \lambda_1^2)}, \quad (3)$$

with the values of the free parameters  $a = 92.22 \mu\text{m}^{-2}$ ,  $b = 0.534 \mu\text{m}^{-2}$ ,  $\lambda_0 = 0.22 \mu\text{m}$ , and



**Fig. 1.** Effect of the polarizing field strength on the TSD current  $I^{\text{TSD}}(T)$  of BSO:Fe crystals:  $E_p = 0.4$  (1),  $1.7$  (2),  $5.8 \text{ kV} \cdot \text{cm}^{-1}$  (3);  $T_p = 350 \text{ K}$

$\lambda_1 = 0.37 \mu\text{m}$ . The calculated spectrum obtained in this way made it possible to expand the range of  $n(\nu)$  dependences to  $\nu = 25500\text{--}12000 \text{ cm}^{-1}$ . Note that the values of  $a$ ,  $b$ ,  $\lambda_0$  are equal to the corresponding values found in [13] for undoped BSO crystals, and  $\lambda_1$  is slightly different from  $\lambda_1 = 0.378 \mu\text{m}$  given in [13].

### 3. Experimental Results and Discussion

The results obtained are as follows. The temperature spectra of the TSD currents  $I^{\text{TSD}}(T)$  of BSO:Fe crystals were very sensitive to the conditions of preliminary polarization. The TSD currents curves were most structured after the polarization in a strong electric field (Fig. 1). At the same time, the structure of the TSD current spectra is weakly expressed with an increase of the polarization temperature to  $T_p \approx 520 \text{ K}$  at relatively weak polarizing fields (Fig. 2).

An increase of the number of the peaks (components) in TSD current spectra  $I^{\text{TSD}}(T)$  in the interval  $\Delta T_1 = 400\text{--}550 \text{ K}$  with an increase of the polarizing field strength  $E_p$  is a distinctive feature of BSO:Fe crystals, in contrast with undoped BSO crystals (Fig. 1).

Such behavior of the spectra is typical of the peaks possessing the quasidipole nature and called the strong field effect. The quasidipoles are reoriented as a result of the displacement of weakly bound ions (or

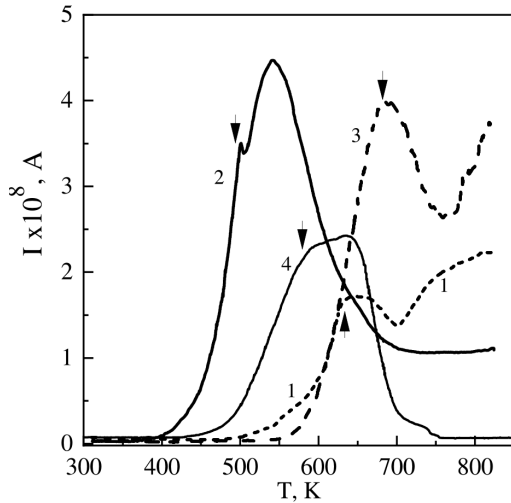


Fig. 2. Effect of the polarization temperature  $T_p$  on the TSD current spectra  $I^{TSD}(T)$  of BSO:Fe:  $T_p = 370$  (1), 520 K (2) and BSO:  $T_p = 370$  (3), 520 K (4);  $E_p = 89 \text{ V} \cdot \text{cm}^{-1}$

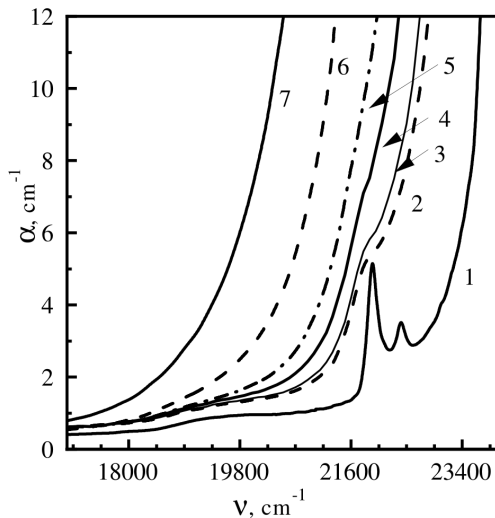


Fig. 3. Optical absorption spectra of BSO:Fe crystals obtained at  $T = 85$  (1), 300 (2), 320 (3), 370 (4), 420 (5), 520 (6) and 670 K (7)

Parameters of electrically active defects \*

Crystals	$T_{max}, \text{K}$	$E_a, \text{eV}$	$\omega_{ef}, \text{cm}^{-1}$	$T_p, \text{K}$
BSO	68	1.37	$7.02 \cdot 10^7$	370
	503	0.59	$3.1 \cdot 10^3$	520
BSO:Fe	647	0.89	$3.02 \cdot 10^5$	370
	499	0.68	$9.59 \cdot 10^3$	520

\* $E_p = 89 \text{ V} \cdot \text{cm}^{-1}$ .

vacancies) from one equilibrium position to another one. If there are several positions, then there will be several quasidipoles with different thermal activation energies and different frequency factors. With an increase in  $E_p$ , quasidipoles are gradually included in the polarization process, and then demonstrate themselves in the thermal depolarization [14]. The quasidipoles in BSO:Fe crystals can be distorted oxygen tetrahedra, in which, according to [9],  $\text{Si}^{4+}$  ions are replaced by  $\text{Fe}^{3+}$  ions, and the charge compensation is carried on by the oxygen vacancy  $\text{O}^-$ . The oxygen vacancies can be located in different nodes of the tetrahedron and can move from one node to another one.

In the interval of relatively higher temperatures  $\Delta T_2 \approx (550-800) \text{ K}$ , the structure of broad peaks on the  $I^{TSD}(T)$  curves practically did not change with an increase in  $E_p$  (Fig. 1). However, after the polarization in weak fields ( $E_p \leq 1 \text{ kV} \cdot \text{cm}^{-1}$ ), the peaks experienced a significant low-temperature shift with an increase of the preliminary polarization temperature  $T_p \geq 370 \text{ K}$  (Fig. 2). The shift was accompanied with an increase of the released thermoelectric charge  $Q = \int_{T_1}^{T_2} I(T) dT$ , which reached a maximum at  $T_p = 520 \text{ K}$ . The response to an increase of  $T_p$  was different from that for undoped BSO crystals, where the charge  $Q$  decreased (Fig. 2).

This behavior of BSO:Fe crystals is a characteristic feature of the space-charge mechanism of charge relaxation in the case of bimolecular recombination kinetics [14]. The fact is that, for the bimolecular kinetics of the recombination, the effective frequency factor  $\omega_{ef}$  of the capture centers (traps in the band gap) depends on the initial concentration  $n_{t0}$  of the traps filled with charge carriers in the process of thermostimulated polarization:  $\omega_{ef} \sim n_{t0}$ . The value of  $n_{t0}$  grows with  $T_p$ , when an additional condition is realized: there is a strong recapture of charge carriers by traps. The latter circumstance leads to a low-temperature shift of the peaks of the TSD spectra. The shape of the peaks should be asymmetric with a overextended high-temperature slope [14], which was observed in our experiments (Fig. 2). Charge carrier traps in the band gap of BSO:Fe crystals arise due to intrinsic defects and uncontrolled impurities [10].

Using the “initial slope” method [14], the thermal activation energy  $E_a^T$  of quasidipoles and traps for some peaks (indicated by arrows in Fig. 2) was deter-

mined as:

$$E_a^T = \frac{d(\ln(I^{\text{TSD}}))}{d\left(\frac{1}{kT}\right)}, \quad (4)$$

where  $k$  is the Boltzmann constant. The obtained values of  $E_a^T$  are shown in Table.

Taking into account that, during the bimolecular recombination, for the TSD current peaks, the condition for the peak maximum is

$$\omega_{\text{ef}} = \frac{E_a}{kT_{\text{max}}^2} \beta \exp\left(\frac{E_a}{kT_{\text{max}}}\right) \left[1 + \frac{2kT_{\text{max}}}{E_a}\right]^{-1}, \quad (5)$$

where  $T_{\text{max}}$  is the temperature of the TSD current peak maximum [14], was determined the values  $\omega_{\text{ef}}$  for traps with the values of  $E_a^T$ , listed in the Table. As we can see, the values of the effective frequency factor  $\omega_{\text{ef}}$  in weak fields  $E_p$  at a low polarization temperature  $T_p$  for BSO crystals fall into the theoretically justified range  $\omega_{\text{ef}} = 10^6\text{--}10^{12} \text{ s}^{-1}$  [14], and, for BSO:Fe values of  $\omega_{\text{ef}}$  approach it. There is a sharp decrease of the  $\omega_{\text{ef}}$  values for the peaks of the TSD current, shifted to low temperatures, with an increase of  $T_p$ . This fact indicates a change in the mechanism of recombination from the monomolecular to bimolecular one, which is possible with a strong re-capture of charge carriers in traps. It should be noted that the error in determining the  $E_a$  values for the shifted TSD current peaks increased significantly.

The presence of  $\text{Fe}^{3+}$  ions with coordination number 4 in the studied BSO:Fe crystals was evidenced by the optical absorption spectrum obtained at  $T = 85 \text{ K}$ . The measured spectra contain a doublet absorption band with  $\nu_{\text{max}} = 21970$  and  $22400 \text{ cm}^{-1}$  (Fig. 3, curve 1), which is characteristic of intracenter transitions of electrons in  $\text{Fe}^{3+}$ . All specific features of the low-temperature absorption spectra of BSO:Fe crystals were analyzed by us earlier in the framework of the crystal field theory [8]. It was shown that they are caused by spin-forbidden  $d-d$  transitions in  $\text{Fe}^{3+}$  ions (electronic configuration  $3d^5$ ) from the ground state ( ${}^6A_1$ ) to excited ones:  ${}^4T_1(t_2^2 e^2)$ ,  ${}^4T_2(t_2^2 e^2)$ ,  ${}^4A_1$ ,  ${}^4E(t_2^3 {}^2E, e^2 {}^3H_2)$ ,  ${}^4T_2(t_2^3 e^2)$ ,  ${}^4E({}^4D)$ .

As can be seen from Fig. 3, the doublet band is located near the fundamental optical absorption edge of BSO crystals (the band gap at room temperature is  $\approx 3.25 \text{ eV}$ ). In addition, these crystals have a high concentration of intrinsic point defects

( $\sim 10^{18} \text{ cm}^{-3}$ ). In other words, they can be considered as heavily doped. Defects are responsible for the presence of many local energy levels in the BSO band gap [10].

With an increase of the temperature ( $T \geq 300 \text{ K}$ ), the absorption increases, the  $\alpha(\nu)$  spectra shift to the low-energy region. This indicates a narrowing of the band gap. The doublet band from  $\text{Fe}^{3+}$  ions becomes indistinguishable (Fig. 3). The spectra  $\alpha(\nu)$  can be described by the well-known Urbach rule [11]:

$$\alpha(\nu) \sim \exp\left(\frac{h\nu}{E_0}\right), \quad (6)$$

where  $E_0 \approx kT$  is some specific energy. This situation is typical of heavily doped semiconductors. Such semiconductors have the so-called ‘‘tails’’ of the local levels state density, which exponentially decreases into the forbidden band. The high temperature leads to a redistribution of electrons on these levels. The concentration of electrons  $n_{t0}$  on deeper levels (traps) increases, which contributes to the space-charge polarization, when an electric field is applied.

#### 4. Conclusions

Thus, as a result of studying the TSD currents obtained by varying the conditions of preliminary polarization, the mechanisms of quasidipole and space-charge polarizations in BSO:Fe crystals are identified. These mechanisms are responsible for the low- and high-temperature peaks of the TSD current spectra in the intervals  $\Delta T_1 = 400\text{--}550 \text{ K}$  and  $\Delta T_2 \approx (550\text{--}800) \text{ K}$ , respectively.

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Received 31.03.21

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ТЕРМОДЕПОЛЯРИЗАЦІЯ  
КРИСТАЛІВ  $\text{Bi}_{12}\text{SiO}_{20}$ , ЛЕГОВАНИХ Fe

Методами термоактиваційної спектроскопії в інтервалі температур 300–800 К досліджено поляризаційні процеси в кристалах  $\text{Bi}_{12}\text{SiO}_{20}:\text{Fe}$ . Одержано температурні залежності струму термостимульованої деполіризації (ТСД) та залежності інтенсивності піків струму ТСД від умов поляризації, ідентифіковано механізми об'ємно-зарядової та квазідипольної поляризації. Досліджено також температурні залежності оптичного поглинання кристалів  $\text{Bi}_{12}\text{SiO}_{20}:\text{Fe}$ .

*Ключові слова:* поляризація, термостимульована деполіризація, оптичне поглинання, кристали  $\text{Bi}_{12}\text{SiO}_{20}:\text{Fe}$ .