UDC 537.632.3

A.V. Ilinsky [1], R.A. Castro [2], L.A. Nabiullina [2], M.E. Pashkevich [3], E.B. Shadrin [1]

[1] Ioffe Physical Technical Institute of the Russian Academy of Sciences
26 Polytekhnicheskaya St., St. Petersburg, 194021, Russia
[2] Herzen State Pedagogical University of Russia
48 Moika Emb., St. Petersburg, 191186, Russia
[3] St. Petersburg State Polytechnical University,
29 Politekhnicheskaya St., St. Petersburg, 195251, Russia

DIELECTRIC SPECTROSCOPY AS THE MEANS OF DIAGNOSTICS OF ELECTRONIC STATES OF SILLENITS

А.В. Ильинский, Р.А. Кастро, Л.А. Набиуллина, М.Э. Пашкевич, Е.Б. Шадрин

ДИЭЛЕКТРИЧЕСКАЯ СПЕКТРОСКОПИЯ КАК СРЕДСТВО ДИАГНОСТИКИ ЭЛЕКТРОННЫХ СОСТОЯНИЙ СИЛЛЕНИТОВ

The physical parameters of impurity centers of $Bi_{12}SiO_{20}$ crystals have been determined by the dielectric spectroscopy method.

DIELECTRIC SPECTROSCOPY, SILLENITES, THERMO-STIMULATED CURRENTS.

Методом диэлектрической спектроскопии определены физические параметры примесных центров кристаллов $Bi_{12}SiO_{20}$.

ДИЭЛЕКТРИЧЕСКАЯ СПЕКТРОСКОПИЯ, СИЛЛЕНИТЫ, ТЕРМОСТИМУЛИРОВАННЫЕ ТОКИ.

I. Introduction

Sillenite crystals have been drawing the attention of scientists for a long time. It is due to the unique physical properties of sillenites: easiness of the synthesis of big crystals, high optical transparency in visible and near infrared ranges, high dark resistance and photosensitivity, high electro-optical (EO) effects, and big optical rotatory power. It is possible to use sillenites for recording, processing and storage of an optical information, including recording holograms [1].

In recent times, the attention of scientists has been concentrated on the research of magneto-optical properties of sillenites [2, 3]. Nonlinear properties of Faraday and magneto-optical Kerr effects in undoped $Bi_{12}SiO_{20}$ have been found out. The results of these researches are interpreted with the use of electro-magneto-gyration model. The electro-gyration part of common effects is caused by the formation of the internal electric field induced by optical orientation of spins. It has been shown that magnetism of not lone-electron pair of Bi-O-heptahedron in crystal lattice brings the contribution to total optical rotatory power. In connection with this creation of the algorithm of the express-analysis of optoelectronic parameters of sillenites is very topical.

The proposed paper is devoted to the express analysis of $B_{12}SiO_{20}$ (BSO) crystals by dielectric spectroscopy methods. These methods are widely applied by research of temperature and light influence on physical properties of many materials [4, 5].

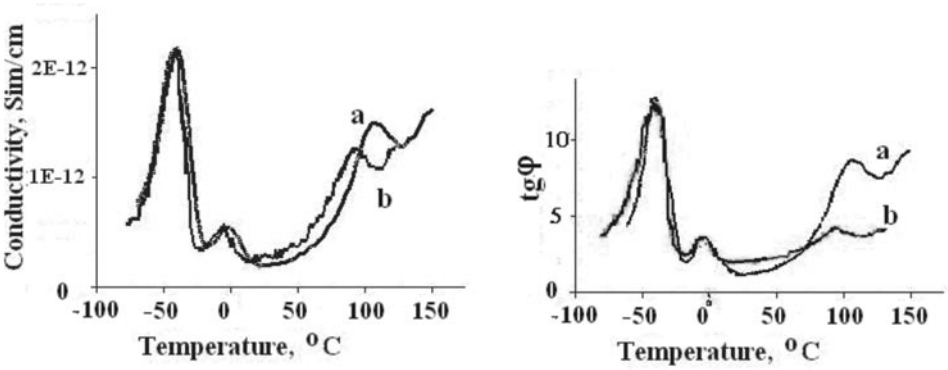

Fig. 1. Temperature dependences of conductivity σ (left) and dielectric loss tangent tg φ (right) of BSO-samples at 100 Hz (*a*) and 10 Hz (*b*) frequencies

II. Samples and the Technique of the Experiment

Investigations were provided on undoped BSO samples which had been grown by Chokhralsky method. The sizes of the samples were 10×10×1 mm. Dark specific resistance was 10^{13} Ω·m. Researches of dielectric spectra and thermo-stimulated currents (TSC) were carried out with the use of dielectric spectrometer «Alpha-Beta Impedance Analizer» produced by the Novocontrol Technologies firm. The temperature T of the sample during the TSC-measurements at frequencies of 10 Hz and 100 Hz changed from −50 °C up to +150 °C with the constant speed of 5 °C/min. Furthermore, the measurements of temperature and frequency dependences of a dielectric loss tangent, and also of the real and imaginary parts of the dielectric constant in the range from 10^{-2} to 10^{5} Hz were made. The sample was located between the facings of the condenser. The amplitude I_0 of a current through the sample was measured at the application of a sine voltage $U(t)$ to the sample. The phase difference φ between oscillations $U(t)$ and $I(t)$ was measured, too. With the use of a special converter, these data were transformed into the data on physical characteristics of the sample, using computer programs developed by the Novocontrol Technologies firm.

During the analysis of the experimental data it was assumed that the equivalent circuit of the crystal was parallel connection of the resistance R_x and electrocapacity C_x of the sample. At the initial stage the values of the real and imaginary parts of the dielectric constant were calculated using the following formula:

$$|\varepsilon'| = I_0 \mathrm{tg}\varphi / [(1 + \mathrm{tg}^2\varphi)^{1/2} \omega C_0 U_0];$$

$$|\varepsilon''| = |\varepsilon'| / \mathrm{tg}\varphi,$$

where ω is the registration frequency, and C_0 is the capacity of the empty measuring cell.

It was possible to calculate, at the subsequent stage, the value of Maxwell relaxation time

$$\tau_M = R_x C_x = |\varepsilon'| / |\varepsilon''| \omega.$$

At the last stage the values of $R_x = \tau_M / C_0 |\varepsilon'|$ and $C_x = \tau_M / R_x$ were calculated.

III. Results of the Experiment

Measurements were carried out on the samples prepared in an ordinary way, and this guaranteed the reproducibility of the results. Namely, at first the sample was heated up from the room temperature to +150 °C with the purpose of emptying the traps of various types. After that the sample was cooled up to −50 °C, and after that it was illuminated during 20 min with photoactive light (λ = 470 nm) of constant intensity. Further, the sample was kept in darkness without illumination for 20 min to except the influence of activity of super shallow traps. After that the measurements of electric parameters of the sample were carried out at heating with a constant speed of 5 °C/min in the range from −50 °C to +150 °C.

The temperature dependences of the conductivity and dielectric loss tangent of BSO samples at the frequencies of 100 Hz and 10 Hz are shown in Fig. 1, *a* and *b*, accordingly. In Fig. 2, *a* and *b*, the dielectric spectra at temperature 0 °C of not illuminated and illuminated samples are shown.

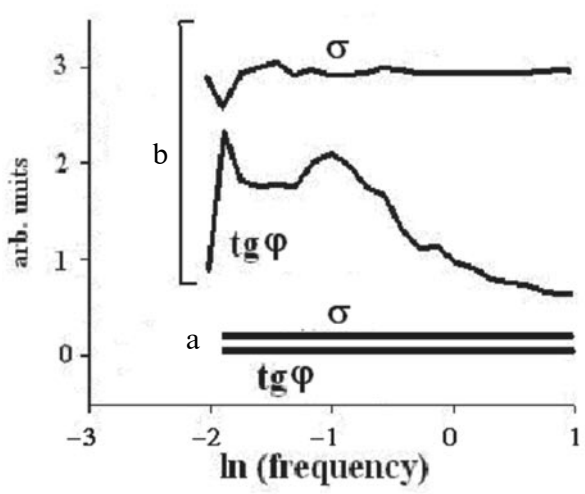

Fig. 2. Spectra of the conductivity σ and dielectric loss tangent tg φ of BSO-samples at 0 °C obtained before (a) and after (b) photoactive illumination

The temperature dependence of Maxwell relaxation time of preliminary illuminated BSO samples is shown in Fig. 3.

In Fig. 1, *a* and *b*, in the range from −50 °C up to +15 °C, we can see two TSC maxima at the temperatures of −40 °C (233 K) and −2 °C (271 K).

The comparison of Fig. 1, *a* and *b* shows that the change of the frequency of registration from 10 Hz to 100 Hz does not lead to the maxima parameters changes. The reason is that small concentration of free electrons $n(t)$

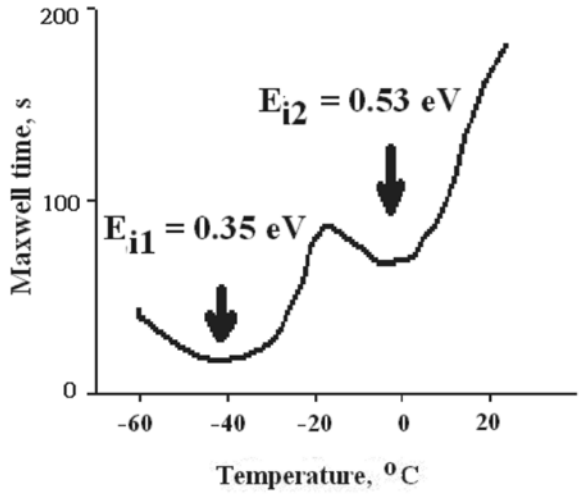

Fig. 3. Temperature dependence of Maxwell relaxation time of BSO-samples

in a conductivity band at TSC measurement is realized. Under these conditions the Maxwell relaxation time τ_M is very large and is fixed in the range from tens up to hundreds of seconds. That is why the working frequencies of 10 Hz and 100 Hz used in our research are many times more than the value $1/\tau_M$ and, consequently, the deduced results of TSC measurements reflect the undistorted value $n(t)$. Such conclusion is confirmed by the comparison of the dielectric spectra of Fig. 2, *a* and *b* obtained before and after photoactive illumination. Namely, only at the frequencies less than one Hertz, the influence of illumination on the dielectric spectrum is observed.

IV. Discussion of the Results

A. Qualitative Model

BSO crystal is a high-resistance photoconductor, electrooptical (EO) properties of which allow observing evolution of spatial charge area in the volume of crystal [6]. In Ref. [6] the evolution of a spatial charge zone of BSO crystal after photoactive illumination was observed. On the basis of this information we can say the following.

It is known [1] that in the gap of BSO crystals there are levels of traps and levels of the deep recombination centers. We have experimentally found out two TSC maxima. For this reason, at the analysis of our experimental results we consider the energy circuit (Fig. 4) that has two levels of tr1 and tr2 traps and one deep recombination *R* level.

According to executing the algorithm of our experiment, preliminary warming the sample up to 150 °C led to full emptying the traps and to the recombination of electrons with holes on *R* centers. Heating up to 150 °C, cooling of the sample in darkness up to −50 °C and keeping the sample at −50 °C without illumination provided reproducibility of the results.

Illumination of a BSO sample with photoactive light (λ = 470 nm) at low temperatures (−50 °C) within 20 min caused the transitions of electrons from the *R* centers through the gap to the traps (Fig. 4, *a*). Subsequent keeping the sample in darkness fixed metastable quasi-equilibrium station at which the concentration of electrons in the

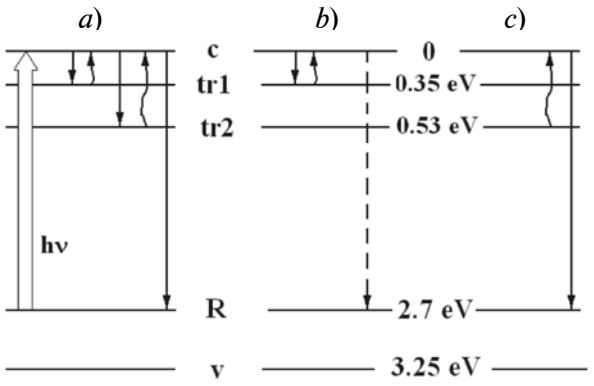

Fig. 4. The scheme of the levels of local centers in BSO: *a* – preliminary illumination of the sample at low temperature $T = -50$ °C; *b* – the scheme of electronic transitions in the range of the first (low temperatures) TSC-maximum; *c* – the scheme of electronic transitions in the range of the second (high temperatures) TSC-maximum

conduction band was small. For this reason, when an external alternate voltage was applied to the crystal, the registered current was small too. By rising the temperature at constant speed $b = 5$ °C/min, the shallow tr1 traps were ionized at first. It generated charge carriers in a conduction band and that is why a thermo-stimulated current (TSC) is now visible.

Initial range of TSC maximum was generated by approaching kT (k – Boltzmann constant) to the ionization energy (E_{i1}) of tr1 traps. According to electrooptical data [6] for tr1 traps, the drift of free electrons in an external electric field is accompanied by effective reoccupation and weak recombination processes (see Fig. 4, *b*). It provided in EO experiments the expansion of the spatial charge area. Such expansion is typical for strong reoccupation of the traps by electrons at weak recombination processes. By continued rise of the temperature, the recombination processes empty the tr1 centers despite effective reoccupation and cause the decrease of TSC with the formation of low temperature TSC maximum. Shallow tr1 traps are empty. It is necessary to notice that tr2 traps remain filled with electrons.

Ionization of electrons from deep tr2 traps begins with continued rise of temperature. It creates high-temperature TSC maximum. For tr2 traps, in contrast to tr1 traps, reoccupation of carriers is small (Fig. 4, *c*). It is established in electrooptical experiments [6]. Namely, for tr2 traps, narrowing the spatial charge area was observed [6], but an expansion did not appear.

B. Mathematical TSC Description

According to our model, the results of TSC measurements are described by the system of equations (1). The system (1) describes the change of electronic concentration in conduction band $n(t)$ and electrons concentration $n_{tr}(t)$ in the traps. The temperature T is fixed. We can write:

$$\begin{aligned} dn(t)/dt &= An_{tr}(t) - Bn(t) - Cn(t); \\ dn_{tr}(t)/dt &= Bn(t) - An_{tr}(t). \end{aligned} \qquad (1)$$

Here $A = 1/\tau_T$ is the probability of thermal ionization of the traps, $B = 1/\tau_{tr}$ – the probability of the capture of a free electron by a trap, $C = 1/\tau_R$ is the probability of recombination of free electrons with holes on the R centers.

Generally, the system (1) has an analytical solution with the initial conditions $n_{tr}(0) = n_{tr0}$ and $n(0) = n_0$, and at the assumption that A, B, C do not depend on time:

$$n_{tr}(t) = [(n_{tr0}\lambda_2 - Bn_0 + An_{tr0})/(\lambda_2 - \lambda_1)]\exp(\lambda_1 t) + \\ + [(Bn_0 - n_{tr0} - An_{tr0})/(\lambda_2 - \lambda_1)]\exp(\lambda_2 t);$$

$$n(t) = [(n_{tr0}\lambda_2 - Bn_0 + An_{tr0})/(\lambda_2 - \lambda_1)] \times \\ \times [\exp(\lambda_1 t)](\lambda_1 + A) + [(Bn_0 - n_{tr0} - \\ -An_{tr0})/(\lambda_2 - \lambda_1)][\exp(\lambda_2 t)](\lambda_2 + A),$$

where

$$\lambda_1 = (1/2)\{-(A + B + C) + \\ + [(A + B + C)^2 - 4AC]^{1/2}\};$$

$$\lambda_2 = (1/2)\{-(A + B + C) - \\ - [(A + B + C)^2 - 4AC]^{1/2}\}.$$

In a limiting case, when strong reoccupation of carriers is small, that is at $B >> C$ ($\tau_R >> \tau_{tr}$), the system (1) becomes simpler. In initial range of a TSC maximum, its solution looks:

$$n(T) = n_{tr}(0)\tau_{tr}/\tau_T = t_{tr}\omega T n_{tr}(0)\exp(-E_i/kT), \qquad (2)$$

where $1/\tau_T = \omega_T \exp(-E_i/kT)$.

The formula (2) does not describe completely the form of TSC maximum. The reason for this is that the neglect of recombination processes is powerless at the top and slope of a TSC maximum.

In the other limiting case at strong recombination $C >> B$ ($t_R << t_{tr}$) without reoccupation processes, the system of Eq. (1) becomes simpler too. With the assumption $t = (T - T_0)/b$, (b is the speed of heating), the expression for electronic concentration in the conduction band looks like

$$n(T) = (\tau_R/\tau_T)n_{tr}(0)\exp[-(T - T_0)/(b\tau_T)]. \quad (3)$$

The system of Eq. (1) has the generally analytical solution with the assumption, as has already been told, that probabilities $A = 1/\tau_{tr}$, $B = 1/\tau_T$, $C = 1/\tau_R$ do not depend on time. This solution allows performing the full description of the process of TSC occurrence. The comparison of the theory with the experiment can be performed with the use of computer software packages. However, at the initial stage of processing of the results, it is reasonable to use the expressions (2) and (3).

C. Processing the Experimental Results

Fig. 5 shows the result of definition E_i in initial temperature ranges of TSC maxima. The low temperature maximum 1 accords with the case of a strong reoccupation of electrons by shallow tr1 traps and small recombination probability of electrons on the R centers. Thus, it corresponds to the case of deep tr2 traps inaction. For the low temperature maximum 1, from expression (2) it follows that

$$\ln[n_1(T)] = -E_{itr1}/kT + \ln[\tau_{tr1}\omega_T n_{tr1}(0)].$$

Using Arrenius coordinates leads to linearization of the initial range. By means of the tangent of an angle of inclination of a linear site we determine the ionization energy of shallow traps E_{i1} = 0.35 eV. The high-temperature maximum 2 accords to the case of thermal ionization of deep tr2 traps. After ionization from tr2 traps, electrons recombine with holes on R centers. Repeated capture of electrons on tr2 traps is absent. Shallow traps tr1 are completely empty.

The analysis of the initial range of the second TSC maximum gives

$$\ln[n_2(T)] = -E_{i2}/kT + \ln[\tau_R\omega_T n_{tr2}(0)].$$

In Arrenius coordinates, we determine energy E_{i2} of the ionization of tr2 traps: E_{i2} = 0.53 eV. Notice that the methods of

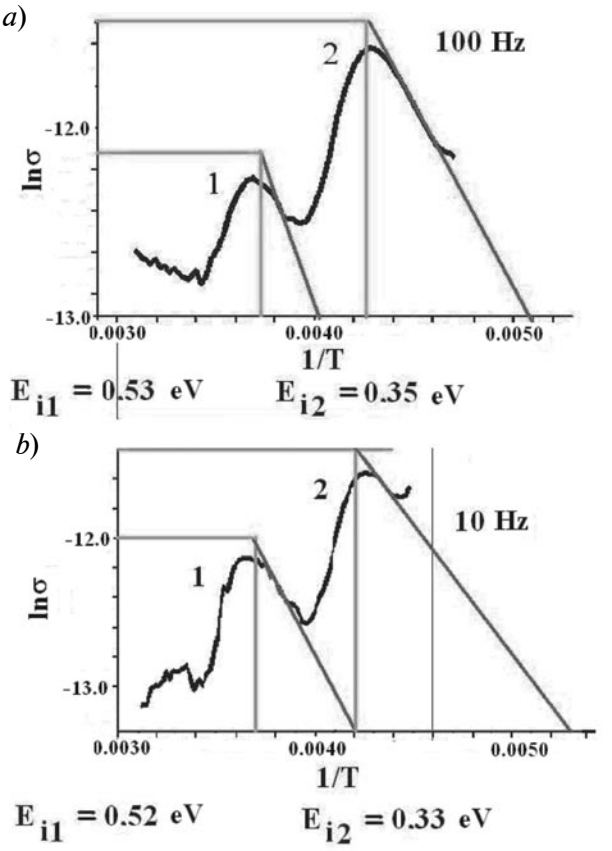

Fig.5. Definition of E_i (ionization energy) of the impurity centers (traps) in BSO crystals by TSC method on the base of dielectric spectroscopy data for frequencies100 Hz (*a*) and 10 Hz (*b*)

defining E_i in the initial range of TSC maxima accord with the methods described in Ref. [5].

The method of the analysis of an initial range allows estimating the relation of probabilities $B = 1/\tau_{tr}$ and $C = 1/\tau_R$. Actually, from the Eq. (2) and (3) in view of crossing points $\ln[n_1(T \to \infty)]$ and $\ln[n_2(T \to \infty)]$ by the linear sites of an ordinates axis ($1 / kT \to 0$), we have the following:

$$\ln[n_1(T)] - \ln[n_2(T)] = \ln[\tau_{tr1}\omega_T n_{tr1}(0)] - \\ - \ln[\tau_R\omega_T n_{tr2}(0)] = 2.4.$$

From here follows $C/B = \tau_{tr1}/\tau_R = 3$. The relation $n_{tr1}(0)/n_{tr2}(0)$ of degrees of initial filling the tr1 and tr2 traps at illumination is equal to 3. This value is determined using the area relation covered with 1 and 2 TSC maxima. τ_{tr1}/τ_R parameter derived in such measurements is important for the estimation of optoelectronic properties of sillenits. This parameter

directly reflects mutual ability of the impurity centers to capture electrons.

V. Conclusion

In the present work we demonstrate the possibility of application of dielectric spectroscopy to estimating Maxwell relaxation time of high-resistance semiconductors with the use of ε(ν) and tg φ spectra. It is shown that the reasonable choice of frequency of registration allows determining key parameters of impurity centers. The algorithm of starting preparation of the samples, excluding the distortion of the data is developed. It is essentially important in the area of using sillenits as sensors of physical parameters.

REFERENCES

1. **Osugi Y., Minemoto T.** Increase the size of Bi12Si020 real-time hologram for three-dimensional display. *Optical Review*, Vol. 3, No. 6B (1996), pp. 552–555.

2. **Petrov M.R., Stepanov S.I., Khomenko A.V.** Fotochuvstvitel'nye elektroopticheskie sredy v golografii i opticheskoi obrabotke informatsii. Leningrad, Nauka, 1983, 270 p. (rus)

3. **Ilinskyi A.V., Castro R.A., Nabiullina L.A., Pashkevich M.E., Shadrin E.B.** Magneto-optical effects in undoped bismuth silicate crystals. *St. Petersburg State Polytechnical University Journal: Physics and Mathematics*, 2013, No. 4-1(182), pp. 9–20. (rus)

4. **Nabiullina L., Shadrin E.** Magnetic resonance properties of single crystals $Bi_{12}SiO_{20}$:Fe. *Izvestia: Herzen University Journal Of Humanities & Sciences*, 2012, No. 147, p. 63–72.

5. **Bordovskii G.A., Castro R.A.** Photoinduced changes in optical and contact properties of chalcogenide glasses. *Optics and Spectroscopy*, 2001, Vol. 90, Iss. 6, pp. 884–886.

6. **Castro R.A. Bordovsky G.A., Bordovsky V.A., Anisimova N.I.** Correlation between bismuth concentration and distribution of relaxators in As_2Se_3(Bi)(x) layers. *Journal of Non-Crystalline Solids*, 2006, Vol. 352, Iss. 9–20, pp. 1560–1562.

7. **Astratov V.I., Il'inskii A.V., Furman A.S.** Dinamika ekranirovaniia elektricheskogo polia v fotorefraktivnykh kristallakh $Bi_{12}SiO_{20}$. *Technical Physics Letters*, 1988, Vol.14, Iss.14. (rus)

8. **Gorokhovatskii Yu.A., Bordovsky G.A.** Termoaktivatsionnaia tokovaia spektroskopiia vysokoomnykh poluprovodnikov i dielektrikov. Moscow, Nauka, 1991, 245 p. (rus)

СПИСОК ЛИТЕРАТУРЫ

1. **Osugi Y., Minemoto T.** Increase the size of Bi12Si020 real-time hologram for three-dimensional display. *Optical Review*, Vol. 3, No. 6B (1996), pp. 552–555.

2. **Петров М.Р., Степанов С.И., Хоменко А.В.** Фоточувствительные электрооптические среды в голографии и оптической обработке информации. Л.: Наука, 1983. 270 с.

3. **Ильинский А.В., Кастро Р.А., Набиуллина Л.А., Пашкевич М.Э., Шадрин Е.Б.** Магнитооптические эффекты в недопированных кристаллах силиката висмута // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2013. № 4-1(182). С. 9–20.

4. **Набиуллина Л.А., Шадрин Е.Б.** Магниторезонансные свойства монокристаллов $Bi_{12}SiO_{20}$: Fe // Известия РГПУ им. А.И. Герцена. 2012. № 147. С. 63–72.

5. **Бордовский Г.А., Кастро Р.А.** Фотоиндуцированные изменения оптических и контактных свойств халькогенидных стекол // Оптика и спектроскопия. 2001. Т. 90. Вып. 6. С. 884–886.

6. **Castro R.A. Bordovsky G.A., Bordovsky V.A., Anisimova N.I.** Correlation between bismuth concentration and distribution of relaxators in As_2Se_3(Bi)(x) layers. *Journal of Non-Crystalline Solids*, 2006, Vol. 352, Iss. 9–20, pp. 1560–1562.

7. **Астратов В.Н., Ильинский А.В., Фурман А.С.** Динамика экранирования электрического поля в фоторефрактивных кристаллах $Bi_{12}SiO_{20}$ // Письма в Журнал технической физики. 1988. Т. 14. Вып. 14. С. 1330–1334.

8. **Гороховатский Ю.А., Бордовский Г.А.** Термоактивационная токовая спектроскопия высокоомных полупроводников и диэлектриков. М.: Наука, 1991. 245 с.

ИЛЬИНСКИЙ Александр Валентинович – *доктор физико-математических наук, старший научный сотрудник Физико-технического института им. А.Ф. Иоффе РАН.*

194021, Россия, г. Санкт-Петербург, Политехническая ул., 26

ilinskiy@mail.ioffe.ru

КАСТРО Арата Рене Алехандро – *доктор физико-математических наук, профессор кафедры физической электроники Российского государственного педагогического университета им. А.И. Герцена.*
191186, Россия, г. Санкт-Петербург, наб. реки Мойки, 48
recastro@mail.ru

НАБИУЛЛИНА Лилия Ансафовна – *аспирантка Российского государственного педагогического университета им. А.И. Герцена.*
191186, Россия, г. Санкт-Петербург, наб. реки Мойки, 48

ПАШКЕВИЧ Марина Эрнстовна – *старший преподаватель кафедры высшей математики Санкт-Петербургского государственного политехнического университета.*
195251, Россия, г. Санкт-Петербург, Политехническая ул., 29
marpash@yandex.ru

ШАДРИН Евгений Борисович – *доктор физико-математических наук, заведующий лабораторией физики фазовых переходов в твердых телах Физико-технического института им. А.Ф. Иоффе РАН.*
194021, Россия, г. Санкт-Петербург, Политехническая ул., 26
shadr.solid@mail.ioffe.ru