POLARIZATION FEATURES OF $Bi_{12}SiO_{20}$:Cr AND $Bi_{12}SiO_{20}$:Mn CRYSTALS

T.V. Panchenko[1]*, L.M. Karpova[2], Yu.N. Potapovich[1], M.P. Trubitsyn[1]

[1]*Oles Honchar Dnipro National University, Dnipro, Ukraine*
[2]*Ukrainian State University of Chemical Technology, Dnipro, Ukraine*
**e-mail: panchtv141@gmail.com*

The effect of impurity ions and polarization conditions on the dielectric characteristics and polarization features of $Bi_{12}SiO_{20}$ crystals doped with Cr and Mn ions is studied by dielectric spectroscopy in the sound frequency range and by thermoactivation spectroscopy in the temperature range 280 ÷ 800 K. The mechanisms of the observed phenomena are discussed at the atomic level.

Keywords: $Bi_{12}SiO_{20}$:Cr and $Bi_{12}SiO_{20}$:Mn crystals, dielectric permittivity, thermoelectret state, polarization mechanism.

Received 30.10.2022; Received in revised form 07.12.2022; Accepted 23.12.2022

1. Introduction

$Bi_{12}SiO_{20}$ (BSO) silicosillenite crystals have a unique set of practically useful properties. Due to the photorefractive effect and high light sensitivity ($\sim 10^{-6}$ J·cm^{-2}), BSO is successfully used as a functional material in devices for recording, storing, and processing of optical information. The field of BSO applications is continuously expanding [1]. However, electrophysical properties of BSO have not been systematically studied up to now. It is known that silicosillenites have high dielectric permittivity ($\varepsilon \sim 50$ at room temperature and in the frequency range 10^2–10^4 Hz) and electret properties. Thermodepolarization analysis of undoped and doped with Al and Ga crystals of BSO has shown that the contributions of the space-charge and quasi-dipolar polarization mechanisms to the electret state formation depend on the impurity ion type and polarization conditions [2]. Further study and understanding of polarization mechanisms is of interest since that can help to propose the ways of obtaining the doped BSO crystals with targeted dielectric properties.

In this work we investigated the influence of pre-polarization conditions on the dielectric and electret properties of BSO crystals doped with multivalent chromium (BSO:Cr) and manganese (BSO:Mn) ions.

2. Experiment

The BSO:Cr and BSO:Mn doped single crystals were grown by Czochralski method. The impurity content was 0.02 mass % (Cr) and 0.3 mass % (Mn). The samples were prepared as parallelepipeds with polished faces and edges of typical sizes $(1\div1.5)\times3\times9$ mm^3. Pt electrodes were deposited on the 3×9 mm^2 faces. Polarization was carried out without illumination under voltage $U_p = 100$ V at temperatures $T_p = 300 \div 600$ K. Dielectric measurements were performed in the frequency range $f = 10^2 \div 10^5$ Hz. The effect of polarization temperature T_p on the temperature-frequency behavior of the real part of the complex permittivity $\varepsilon'(T)$ as well as on the currents of thermostimulated depolarization $i^{TSD}(T)$ was studied in the temperature range 280 ÷ 800 K.

3. Results and discussion

The dependences $\varepsilon'(T)$ and $i^{TSD}(T)$ of BSO:Cr and BSO:Mn crystals are essentially different from the known ones for undoped BSO [3]. Both crystals have weak (BSO:Cr) or pronounced (BSO:Mn) peaks of $\varepsilon'(T)$ curves (Fig. 1). Previously it was shown [3] that in BSO:Cr crystals with an increase of measuring field frequency the peculiar relaxation dispersion of dielectric loss tangent $\mathrm{tg}\delta(T)$ was observed. This made it possible to calculate thermoactivation barriers and frequencies of relaxators. In BSO:Mn crystals the $\varepsilon'(f)$ dispersion is close to quasi-resonant with frequency $\sim 10^3$ Hz [3].

The change of the dispersion mechanism in crystals doped with Mn and with Cr may be due to higher electrical conductivity $\sigma \approx 9.7\cdot10^{-13}\,\Omega^{-1}\cdot\mathrm{cm}^{-1}$ in BSO:Mn versus $\sigma\approx9.9\cdot10^{-14}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ in BSO:Cr ($T = 300$ K).

Now in our experiments, the influence of pre-polarization conditions consists in the following. In BSO:Cr crystals, an increase of T_p as well as measuring field frequency f growth lead to the decrease of $\varepsilon'(T)$ peak intensity (Fig. 1, a). In BSO:Mn crystals, T_p growth increases the magnitude of $\varepsilon'(T)$ peaks at $f\leq10^3$ Hz and vice versa suppresses $\varepsilon'(T)$ peaks at $f>10^3$ Hz (Fig. 1, b). The character of $\varepsilon'(f)$ dispersion in both cases does not change.

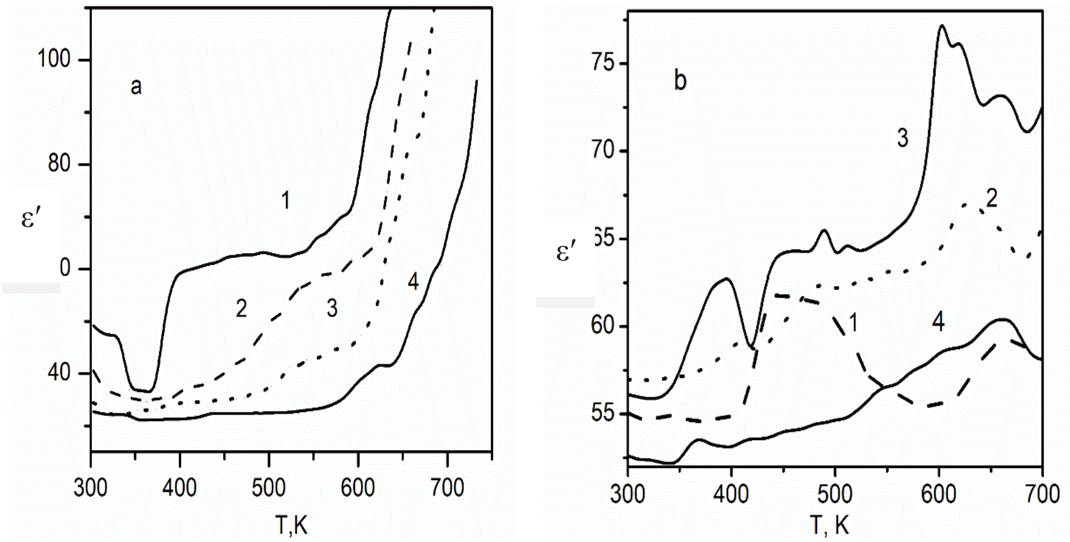

Fig. 1. The effect of polarization temperature on the ε′(*T*) dependences in BSO:Cr (a) and BSO:Mn (b). Polarization conditions: T_p= 320 K (Fig. 1, a – curve 1; Fig. 1, b – curve 1), 420 K (a – curve 2; b – curves 2, 4), and 520 K (a – curves 3, 4; b – curve 3); U_p = 100 V. Measuring field frequency *f* = 700 Hz (a – 1, 2, 3; b – 1, 2, 3) and 10^4 Hz (a – 4; b – 4).

The study of thermodepolarization (TSD) currents $i^{\mathrm{TSD}}(T)$ has shown that pre-polarization of BSO:Cr and BSO:Mn crystals results in formation of the thermoelectret state (TES) caused by accumulation of heterocharge. Full depolarization occurs at $T \geq 900$ K. The groups of the following peaks are registered: weak *A*-peaks in the range of 300 – 400 K and more intense П-shaped *B*-peaks in the range of 500 – 600 K. In the interval of 600 – 900 K, the $i^{\mathrm{TSD}}(T)$ curves become dome-shaped, weakly structured, and represent envelopes of *C*-peaks (Fig. 2, a, b). In undoped BSO crystals, the intensities of the TSD current peaks are much weaker, as we have shown in the previous studies [2, 3].

A large number of new peaks in the $\varepsilon'(T)$ and $i^{\mathrm{TSD}}(T)$ dependences of BSO:Cr and BSO:Mn crystals as compared to undoped BSO [2] reflects the presence of electrically active defects (relaxators) with different parameters (Figs. 1, 2). The thermodepolarization analysis made it possible to determine the energy of thermal activation of electroactive defects E_a (Table 1) and the electret charge Q_{el} accumulating in the regions of *A*, *B* and *C* peaks groups. The value of the electret charge is in the range $Q_{el} = 10^{-7} - 10^{-5}\,\mathrm{Q\cdot cm^{-2}}$.

The authors of [4] showed that the close relationship between the temperature behavior of dielectric permittivity and thermal depolarization currents made it possible to recalculate the dependences of the imaginary part of permittivity $\varepsilon''(T)$ into the $i^{\mathrm{TSD}}(T)$ dependence and vice versa. By using the well-known relation $\varepsilon''(T) = [\varepsilon'(T) - \varepsilon_\infty]\omega\tau$, where the value of high-frequency component ε_∞ is assumed as temperature independent, it is also possible to recalculate the real part of dielectric permittivity $\varepsilon'(T)$ into $i^{TSD}(T)$ within those temperature ranges where the relaxation time $\tau(T)$ changes weakly.

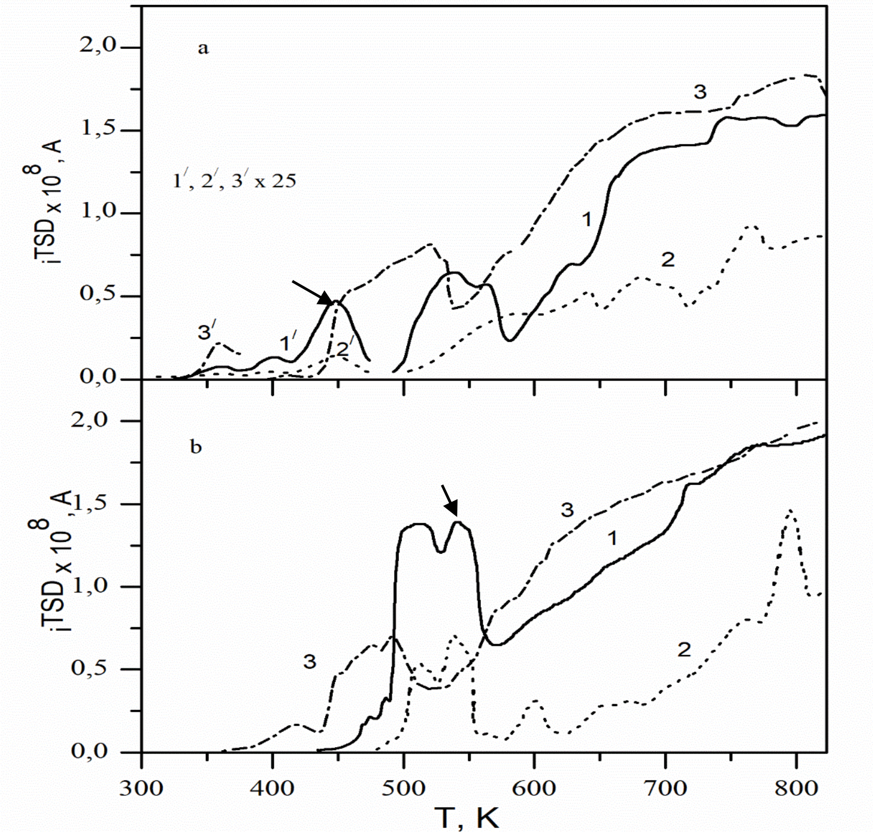

Fig. 2. The effect of the polarization temperature on the $i^{TSD}(T)$ dependences in BSO:Cr (a) and in BSO:Mn (b). Polarization conditions: T_p= 320 K (a – 1; b – 1), 420 K (a – 2, b – 2), and 520 K (a – 3, b – 3); U_p = 100 V.

Table 1

The parameters of electrically active defects that manifest themselves in the $i^{TSD}(T)$ spectra of BSO:Cr and BSO:Mn crystals

BSO:Cr		BSO:Mn	
T_m, K	E_a, eV	T_m, K	E_a, eV
360	0.85	691	1.14
406	0.95	650	1.25
531	1.27	703	1.54

Relative to each other, the $\varepsilon'(T)$ and $i^{TSD}(T)$ spectra should be shifted along the temperature axis, since $i^{TSD}(T)$ is measured under stationary conditions, whereas $\varepsilon'(T)$ is measured in alternating electric field. With an increase in the measuring frequency, we observe a high-temperature shift of the $\varepsilon'(T)$ curves (Fig. 1 a, b).

The above considerations make it possible to analyze the dependences of maximum values ε'_m for individual peaks or envelope groups of peaks on the polarization temperature $\varepsilon'_m(T_p)$. It is important that the character of current dependences $i_m^{TSD}(T_p)$ provides an opportunity to identify the polarization mechanism as dipole or space-charge.

According to [5], the curves of dipole polarization have two branches: the low-temperature branch where $i_m \sim (T_p)^{-1}\cdot\exp(-E_a/kT_p)$ and the high-temperature branch where $i_m \sim (T_p)^{-1}$. In general, the dependence $i_m^{TSD}(T_p)$ passes through the maximum, and we found similar dependences for some peaks of the TSD current (Fig. 3).

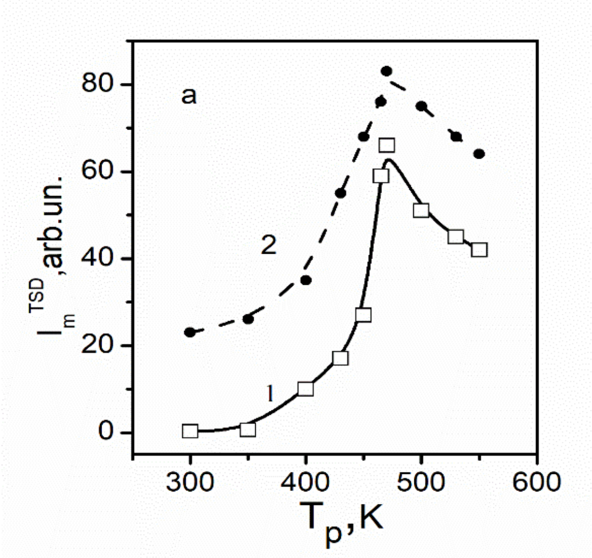

Fig. 3. The dependences of $i_m^{TSD}(T_p)$ of BSO:Mn (1) and BSO:Cr (2) crystals for TSD current peaks with T_m = 548 K (BSO:Mn) and T_m = 450 K (BSO:Cr), U_p = 100 V. TSD current peaks are indicated by arrows in Fig.2.

Studies of the dielectric permittivity show the following. For BSO:Mn crystals in the range T=400 – 500 K, the curves $\varepsilon'_m(T_p)$ can be described as $\varepsilon'_m(T_p) \sim (T_p)^{-1}(\exp(-E_a/kT_p)$ (Fig. 4, curve 3), i.e. as low-temperature branches of $i^{TSD}_m(T_p)$ dependences of BSO:Cr and BSO:Mn crystals (Fig. 3).

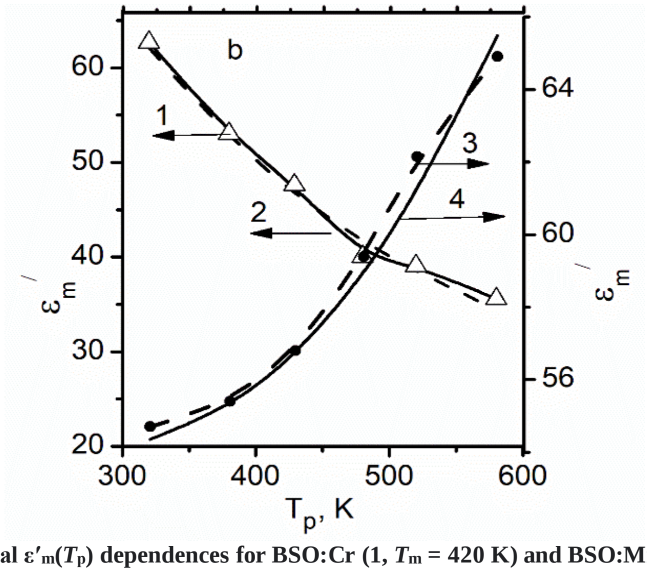

Fig. 4. The experimental $\varepsilon'_m(T_p)$ dependences for BSO:Cr (1, T_m = 420 K) and BSO:Mn (3, T_m =530 K). The curve 2 is calculated as $\varepsilon'_m(T_p) = B(T_p)^{-1}$, $B = 2\cdot10^4$. The curve 4 is calculated as $\varepsilon'_m(T_p) = A(T_p)^{-1}(\exp(-E_a/kT_p))$ where $A = 5.6\cdot10^5$, E_a = 0.25 eV. U_p = 100 V.

For BSO:Cr crystals, the $\varepsilon'_m(T_p)$ curves in the same range obey the relation $\varepsilon'_m \sim (T_p)^{-1}$ (Fig. 4, curve 1) corresponding to the high-temperature branches of the $i^{TSD}{}_m(T_p)$ dependences of BSO:Cr and BSO:Mn: $i^{TSD}{}_m(T_p) \sim (T_p)^{-1}$ (Fig. 3). The calculated dependences $\varepsilon'_m(T_p)$ agree well with the experimental ones (Fig. 4, curves 2, 4).

The regularities of the polarization temperature effect on the dielectric permittivity $\varepsilon'_m(T_p)$ confirm the conclusion about the dipole (quasi-dipole) polarization mechanism in BSO:Cr and BSO:Mn crystals, which follows from the analysis of $i^{TSD}{}_m(T_p)$ curves.

The additional information on the polarization mechanism can be obtained by studying the response of the $i^{TSD}(T)$ and $\varepsilon'(T)$ spectra to photopolarization, i.e., polarization that occurs due to illumination by light in the visible wavelength range. It should be taken into account that multivalent 3*d*-ions of chromium and manganese can create local energy levels in the band gap of BSO:Cr and BSO:Mn crystals. Accumulation of electrons on these levels leads to the appearance of space-charge polarization. Illumination of the crystal increases the concentration of electrons at these levels. As a result, according to [5], the $i^{TSD}(T)$ and $\varepsilon'(T)$ spectra peaks caused by the space-charge polarization, should grow in the intensity, and shift to low-temperature side.

In our experiment photopolarization was induced by light with energy of quanta ~ 3 eV, which was close to the BSO bandgap width. Nevertheless, we did not observe in the spectra of $i^{TSD}(T)$ and $\varepsilon'(T)$ the described above manifestations of space-charge polarization. Such behavior testifies in favor of the quasi-dipole nature of the observed polarization phenomena. This conclusion is also supported by the fact that doping with Cr and Mn ions sharply decreases photoconductivity in BSO:Cr and BSO:Mn crystals in the entire visible wavelength range [6].

Using the obtained results and the photochromic effect study [7, 8], we can clarify the nature of the quasi-dipoles. We suppose that the quasi-dipoles belong to the "impurity-compensators" type where the impurity is Cr^{2+}_{Bi} or Mn^{4+}_{Bi} ions which substitute for Bi^{3+} within oxygen pseudo-octahedrons in BSO structure. At the same time, hole O^{-} center or F^{+} center can be proposed as the charge compensators for Cr^{2+}_{Bi} impurity (here F^{+} center represents one electron captured by an oxygen vacancy V_O). The excess charge of Mn^{4+}_{Bi} center can be compensated by a defect pair consisting of bismuth vacancy V_{Bi} and oxygen vacancy V_O. The moments of impurity-compensator quasi-dipoles are oriented under the action of polarization voltage U_p and temperature T_p. Polarization is carried out as thermally activated relaxation process.

The moments of the quasi-dipoles can be increased under the exposure of T_p due to oxygen-based defects (O^{-}, F^{+} or V_O) jumping to new non-equivalent positions, which are accompanied by the appearance of quasi-elastic force of Coulomb nature. The polarization has quasi-elastic nature, but the quasi-dipoles are rather inert, that leads to a low quasi-resonant frequency (~10^3 Hz). The influence of T_p is associated with thermally activated jumps of charge-compensating defects.

4. Conclusions

1. The doping of BSO crystals with Cr and Mn ions and variation of polarization conditions allow to significantly modify the temperature-frequency behavior of dielectric characteristics of BSO crystals in a sound frequency range and in the temperature interval 280 ÷ 800 K.

2. The TES charge of BSO:Cr and BSO:Mn crystals is much higher than that of undoped BSO crystals. It is close to the charge of the best inorganic electrets ($SrTiO_3$, $CaTiO_3$ etc.) and can vary over a wide range by changing the pre-polarization conditions.

3. The dependences of dielectric permittivity and thermodepolarization currents on the polarization temperature indicate a dipole (quasi-dipole) mechanism of polarization in BSO:Cr and BSO:Mn crystals.

4. The obtained characteristics of dielectric and electret properties of BSO:Cr and BSO:Mn crystals may be of interest for functional electronics devices.

References

1. Photorefractive Materials and Their Applications 1. Basic Effects / Eds. P. Gunter, J.-P. Huignard // Springer Science+Business Media (New York). – 2006. –.423 p. doi.org/10.1007/b106782

2. **Panchenko, T.V.** Photoelectret state in Al, Ga-doped $Bi_{12}SiO_{20}$ crystals / T. V. Panchenko, G. V. Snezhnoy // Ferroelectrics. – 1995. – Vol. 174. – P. 51 – 59.

3. **Panchenko, T.V**. Dielectric properties crystals of silicosillenite doped with chromium and maganese ions / T. V. Panchenko, L. M. Karpova // Journal of Physics and Electronics. –2020. – Vol. 28 (1). – P. 25 – 28. https://doi: 10.15421/332994

4. Electrets (Topics in Applied Physics, Volume 33) / Ed. G. M. Sessler // Springer-Verlag (Berlin – Heidelberg – New York), 1987 – 446 p.

5. **Gorokhovatsky, Yu.A.** Termoaktivatsionnaya tokovaya spektroskopiya vysokoomnykh poluprovodnikov i dielektrikov / Yu. A. Gorokhovatsky, G. A. Bordovsky. – M.: Nauka, 1991. – 245 p.

6. **Panchenko T.V.** Photoelectric properties of $Bi_{12}SiO_{20}$ crystals / Panchenko T.V., Yanchuk Z.Z. // Phys. Stat. Sol. – 1996. – V. 38. – № 10. – P. 3041 – 3046.

7. **Panchenko T.V.** Optical absorption and photochromic effect in Cr and Mn doped $Bi_{12}SiO_{20}$ single crystals / Panchenko T.V., Truseyeva N.A // Ferroelectrics.– 1991. – V.115. – P. 71 – 80.

8. **Panchenko, T.V.** Thermally activation spectroscopy of optical absorption in the $Bi_{12}SiO_{20}$ crystals / T.V. Panchenko, L.M. Karpova // Ukr. J. Phys. Opt. – 2020. – Vol. 21, No. 2. – P. 84 – 92. http://info.lviv.ua/jo urnal/2020/2020n2v21.html