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DIELECTRIC PROPERTIES OF $Bi_{12}SiO_{20}$ CRYSTALS DOPED WITH Al

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The temperature-frequency dependences of the complex dielectric permittivity ε and the voltage-farad characteristics of undoped and aluminum doped $Bi_{12}SiO_{20}$ crystals are studied before and after their polarization. It is shown that Al ions in the $Bi_{12}SiO_{20}$ dielectric matrix provide a significant increase as well as nonlinearity of ε in the temperature range 300 – 800 K and electric field strengths $E = 10^3 – 10^4$ V/cm. It is shown that polarization causes the appearance of dielectric hysteresis loops. Al impurity significantly affects the appearance and parameters of these loops. The role of Al ions in increasing the contribution of the quasi-dipole mechanism in the polarization processes is revealed.

Keywords: complex dielectric permittivity, voltage-farad characteristics, $Bi_{12}SiO_{20}$ crystals, Al impurity.

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1. Introduction

$Bi_{12}MO_{20}$ (BMO, where M = Si, Ge, Ti) crystals of the sillenite family are relevant materials of functional electronics. Today, about 60 species of sillenites have been synthesized, where M cations are replaced by Al, P, Fe, V, etc. ions [1]. Such a replacement made it possible to expand the range of characteristics of practically useful properties of sillenites (of photorefractive, acousto-optical, piezoelectric, photo- and dielectric). However, the presence of defects in such crystals limits their practical use. At the same time, the effectiveness of doping BMO is shown, while their optical quality is preserved. In particular, doping with Al, Ga, Cr, Mn, Sn ions significantly affects the optical absorption, photoconductivity, photo- and thermochromic effects in BMO crystals [2, 3]. This is of interest for the development of devices for recording, storage, processing and transmission of optical information. Lately, the temperature dependences of dielectric and piezoelectric characteristics of undoped and doped BMO crystals are studied [4, 5]. It was shown, for example, that the Co impurity allows controlling the dielectric properties of $Bi_{12}GeO_{20}$ (BGO) crystals in the temperature range $T \geq 300$ K [5] at frequencies $1 – 10^5$ Hz.

This paper presents the results of studying the effect of Al ions on the temperature-frequency dependences of the complex dielectric permittivity ε and on the voltage-farad characteristics of undoped and Al-doped $Bi_{12}SiO_{20}$ crystals in the non-polarized and thermoelectret state.

2. Experiment

Undoped $Bi_{12}SiO_{20}$ (BSO) and doped Al $Bi_{12}SiO_{20}$:Al (BSO:Al) crystals were grown by the Czochralski method. The content of Al in the crystals according to spectral-emission analysis was $6 \cdot 10^{-2}$ mass.%. Samples were prepared in the form of polished bars in sizes 0.1×0.1×0.8 cm. On the crystallographic surfaces (001) 0.1×0.8 cm in size, Pt electrodes were deposited by cathode sputtering in a vacuum. In the temperature range T = 300 – 800 K at frequencies $f = 10^2 – 10^3$ Hz, the temperature-frequency dependences of the real and imaginary parts of the complex dielectric permittivity ε′ (T, f) and ε″ (T), respectively, were measured. Samples were used in a non-polarized and polarized (thermoelectret) state. The thermoelectret state (TES) was formed at the temperature T_p = 300 K, voltage U_p = 500 V, and polarization time t_p = 30 min. In addition, the voltage-farad characteristics (VFCs) – the dependences of the sample capacitance on the value of the applied constant voltage of bias C (U_b) – were measured. The voltage U_b was varied discretely with a step of ± 5 V, it increased and decreased with reversal of the sign in the range: U = 0 – 200 – 0 and 0– -200 – 0 V for

the direct and reverse branches of the voltage-farad characteristics. The measurements were carried out at T = 300 K. The measurements were automated using a microcomputer.

3. Experimental results and discussion

For BSO and BSO:Al crystals, the ε′ (T, f) dependences in the range of 500 – 800 K have the form of structured dome-shaped curves, while the ε″ (T) dependences are in the form of exponentially increasing curves. Note that doping of BSO crystals with aluminum leads to a significant increase (by 1 – 2 orders of magnitude) of the dielectric permittivity ε′ (Figs. 1, 2) and to an anomalous increase in dielectric loss ε″ (T) with increasing temperature. The latter is probably due to an increase of the dark conductivity σ^T due to doping of BSO: Al crystals. The σ^T when measured with alternating current at the frequency of 100 Hz at room temperature is ~ 10^{-13} and ~ 10^{-7} $Ohm^{-1}\cdot cm^{-1}$ for BSO and BSO: Al, respectively [6].

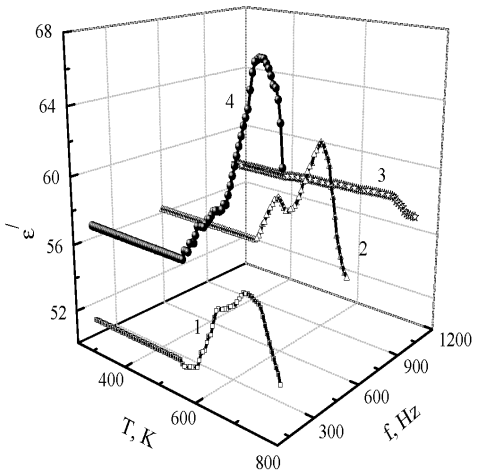

Fig. 1. Temperature-frequency dependences of the real part of the complex dielectric permittivity of BSO crystals in the non-polarized (1, 2, 3) and polarized state (4) at f = 100 (1, 4), 500 (2) and 10^3 Hz (3).

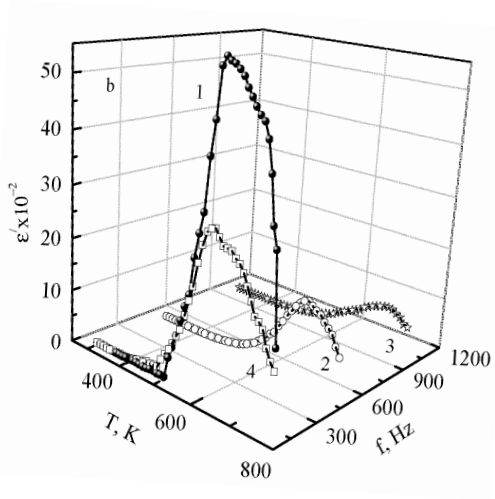

Fig. 2. Temperature-frequency dependences of the real part of complex dielectric permittivity of BSO:Al crystals in the non-polarized (4) and polarized state (1, 2, 3) at f = 100 (1, 4), 500 (2), and 10^3 Hz (3).

However, we note that the values ε′ ~ 10^4 – 10^5 at 300 K < T < 500 K were already observed at measuring frequencies from 1 to 10^3 Hz for undoped and cobalt doped BGO crystals, similar in structure and close in properties to BSO [5]. The authors of [5] attribute the high values of ε′ and the features of dielectric relaxation with the intrinsic defects in the BGO crystals and the incorporation of cobalt in the form of metal nanoparticles into the dielectric BGO matrix.

This seems unlikely, since metal ions usually react with the matrix and form oxide inclusions. In addition, when studying the thermal stability of the piezoelectric coefficients and dielectric constants of BSO crystals, which were measured in different crystallographic directions, it was found that they had small maxima at T > 300 K. The reasons for the appearance of maxima have not been studied [7].

It is noteworthy that, for both BSO and BSO:Al crystals, the polarization and formation of TEC entails an increase in the numerical values of ε′ up to ~ 10^4 for BSO:Al

and ~ 10^2 for BSO obtained in the temperature range 500 – 800 K at frequencies f ~ 10^3 Hz. For non-polarized BSO:Al crystals, the dependences ε′ (T, f) are shifted to the low-temperature region relative to those for BSO crystals. After polarization, the shift of the ε′ (T, f) curves for BSO:Al crystals increases (Figs. 1, 2).

The frequency behavior of ε′ is also unusual for undoped BSO. The numerical values of ε′ pass through a maximum in the frequency range 500 – 700 Hz and decrease at f ≥ 10^3 Hz. In other temperature ranges, ε′ monotonically increases with increasing frequency (Fig. 1).

For BSO:Al crystals, the numerical values of ε′ monotonically decrease with increasing frequency even at f >10^2 Hz (Fig. 2). At the same time, the dependence ε′ (T) disappears (for BSO) or significantly weakens (for BSO:Al) (Figs. 1, 2). This behavior of ε′ (T, f) is not typical for the low-frequency induced relaxation polarization. Most likely, an elastic orientation mechanism with the participation of quasidipoles takes place. The contribution of quasidipoles of the "impurity – vacancy" type to polarization processes during the formation of TES is indicated by the results of thermo-depolarization analysis performed in [8].

Interesting evidence of the dielectric nonlinearity of the investigated crystals is demonstrated by the voltage-farad characteristics. In both cases, BSO and BSO:Al, the obtained dependences $C(U_b)$ are nonlinear, asymmetric with respect to the vertical (C) and horizontal axes (U_b), and are characterized by hysteresis. The transition in TES is accompanied by an increase in the capacity of the investigated samples, while the indicated features of the voltage-farad characteristics are enhanced. In addition, to these features of the $C(U_b)$ curves, it is necessary to add a dependence of their form on the number of measurement cycles with reversal of the voltage sign U_b and, especially, on the presence of Al impurity ions. These ions change the character of the nonlinearity of the forward branches of the VFCs, whereas the branches of the VFCs for the back strokes of measurements change a little (Fig. 3). The type of hysteresis also depends on the presence of Al. For undoped BSO, there is an excess of the capacity of the back strokes of measurements over the capacity of the forward strokes ("positive hysteresis"). For BSO:Al, on the contrary, the capacity of the forward strokes of measurements exceeds the capacity of the back strokes ("negative hysteresis"). Measurement cycle repeating leads to a decrease in the area of the hysteresis loops of the VFCs, which determines the energy dissipation in crystals, and the loops become more symmetrical (Fig. 3).

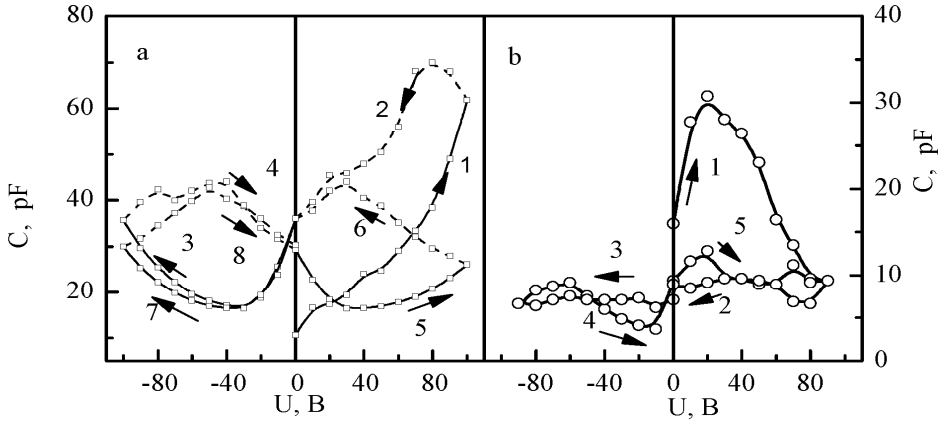

Fig.3. VFCs of BSO (a) and BSO:Al (b) crystals in the thermoelectret state for the first (a, curves 1, 2, 3, 4; b, curves 1, 2) and the second (a, curves 5, 6, 7, 8; b, 3, 4, 5) measurement cycles.

To analyze the results, it is necessary to take into account the mechanisms of TES formation and the conditions at the contacts of the investigated structures of Pt–BSO–Pt and Pt–BSO:Al–Pt. Taking into account that the work function from BSO is $A_1 = 4.5$ eV, and from the Pt electrodes $A_2 = 5.6$ eV, we see that Schottky barriers should appear on the Pt–BSO contacts. However, due to the higher electrical conductivity of BSO:Al crystals, the ratio between A_1 and A_2 at the Pt–BSO: Al contacts may not be the same as mentioned above, which does not exclude the injection of electrons from Pt. This entails a change in the nature of the hysteresis from positive to negative. The observed metamorphosis of the ε' (T, f) dependences may be due to different contributions to the polarization of electrically active defects in the form of quasidipoles with different thermal activation energies E_a and different accumulated polarization charge Q_p.

4. Conclusions

1. In the temperature range 400 – 800 K, anomalous temperature-frequency dependences of the real part of the complex permittivity of undoped and Al-doped BSO crystals were found.

2. It was established that doping BSO with Al, as well as the polarization of BSO and BSO:Al crystals in weak electric fields with strengths $E = 10^3 – 10^4$ V/cm, allowed controlling the numerical values of the dielectric permittivity of such crystals efficiently (up to three orders of magnitude).

3. It was shown that the polarization of BSO and BSO:Al crystals in weak electric fields causes their nonlinearity, which demonstrates itself in the form of dielectric hysteresis loops.

References

1. **Skorikov, V.M.** Growth of Sillenite-Structure Single Crystals / V.M. Skorikov, Yu.F. Kargin, A.V. Egorysheva, V.V. Volkov, M.M. Gospodinov // Inorganic Materials, Suppl.1. – 2005. – Vol .41. – P. S24 – S46.

2. **Panchenko, T.V.** The effect of doping on the properties of single crystals / T.V. Panchenko, A.Yu. Kudzin, N.A. Truseyeva // Inorganic Materials. – 1983. – Vol. 19, No 7. – P. 1144 – 1147.

3. **Panchenko, T.V.** Excitation and erasure of photochromic effect in the $Bi_{12}SiO_{20}$ crystals doped with Al, Ga and Sn / T.V. Panchenko, A.O. Dyachenko // Ukrainian Journal of Physical Optics. – 2015. – Vol. 16, No. 3. – P. 127 – 133.

4. **Lardhi, Sh.** Determination of the electrical, dielectrical and optical properties of sillenite $Bi_{12}TiO_{20}$ and perovskite $Bi_4Ti_3O_{12}$ / Sh. Lardhi, D. Nourekine, M. Harb, A. Ziani, L. Cavallo, K. Takanabe // The Journal of Chemical Physics – 2016. – Vol. 144. – P. 134702-1 – 8.

5. **Filipic**, **C.** Dielectric relaxation in pure and Co-doped $Bi_{12}GeO_{20}$ single crystals / C. Filipic, A. Rlos, M. Gajc, D.A. Pawlac, J. Dolinsek, A. Levstic // Journal of Advanced Dielectrics. – 2015. – Vol. 5, No 3. – P.15500223-1 – 5.

6**. Avramenko, V.P.** Electrical conductivity of doped silicosillenite crystals / V.P Avramenko, A.Yu. Kudzin, T.V. Panchenko**,** G.Kh. Sokolyanski // In the book: Semiconductors are Ferroelectrics. – Rostov-on-Don: RGU, 1984. – P. 139 – 145 (in Russian).

7. **Shen, Ch.** Orientation and Temperature Dependence of Piezoelectric Properties for Sillenite-Type $Bi_{12}TiO_{20}$ and $Bi_{12}SiO_{20}$ Single Crystals / Ch. Shen, Hu. Zhang, Ya. Zhang, H. Xu, H. Yu, J. Wang, Sh. Zhang // Crystals. – 2014. – Vol. 4. – P. 141 – 151.

8. **Panchenko, T.V.** Thermodepolarization analysis of polarization mechanisms in $Bi_{12}SiO_{20}$ crystals doped with Al and Ga ions / T.V. Panchenko, G.V. Snezhnoy // Phys. Stat. Sol. – 1993. – Vol. 35, No. 12. – P. 3248 – 3257.