

## DIELECTRIC PROPERTIES OF SILICOSILLENITE CRYSTALS DOPED WITH CHROMIUM AND MANGANESE IONS

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**The effect of chromium and manganese ions on the dielectric properties of Bi<sub>12</sub>SiO<sub>20</sub> crystals is studied by the dielectric spectroscopy methods in the sound frequency range in the temperature range 280 – 800 K.**

**Keywords:** dielectric permittivity, dielectric loss, polarization, temperature-frequency characteristics, Bi<sub>12</sub>SiO<sub>20</sub> crystals, Cr, Mn impurity.

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### 1. Introduction

Crystals of silicosillenites Bi<sub>12</sub>SiO<sub>20</sub> (BSO) have a unique set of practically useful properties (piezoelectric, photorefractive, photoelectric, electro- and magneto-optical). They are successfully used in various fields of functional electronics [1]. It is of interest to extend the range of BSO applications and optimize the characteristics of existing devices. In this regard, the doping of these crystals is investigated. To date, the effect of many mono- and polyvalent impurities on optical absorption, photoconductivity, and the photorefractive effect has been studied, but insufficient attention has been paid to the dielectric properties of doped BSO crystals. It is known that BSO crystals have a high dielectric permittivity ( $\epsilon_0 \sim 40 - 50$ ), which is characterized by thermal stability up to temperatures of  $\sim 700$  K. The dielectric characteristics of BSO depend on the presence of Al and Ga impurities [2]. It was shown that doping of Bi<sub>12</sub>GeO<sub>20</sub> (BGO) crystals, which are isostructural and similar in properties to BSO, with Co ions causes a significant change in the dielectric constant and its temperature dependences in the frequency range  $f < 10^4$  Hz [3]. However, the mechanism of effects of certain impurities remains unclear. It is of interest to study the dielectric properties of doped BSO crystals further.

In this paper, we studied the effect of doping with Cr and Mn ions on the dielectric properties of BSO crystals.

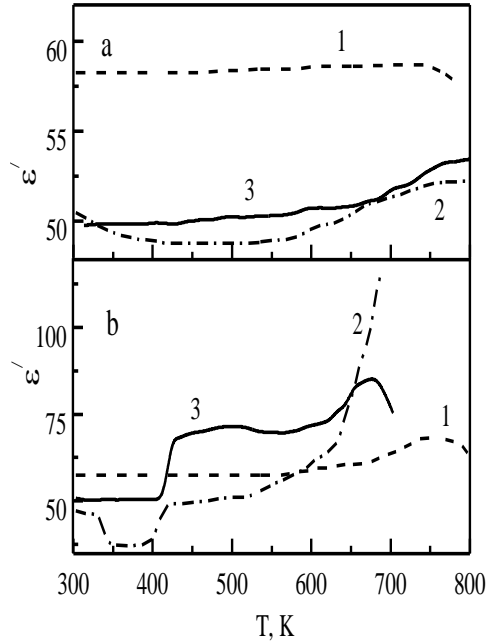
### 2. Experiment

Undoped BSO crystals and ones doped with Cr and Mn ions Bi<sub>12</sub>SiO<sub>20</sub>:Cr (BSO:Cr) и Bi<sub>12</sub>SiO<sub>20</sub>:Mn (BSO:Mn) were grown by the Czochralski method. The impurity content was 0.05 (Cr) and 0.1 mass. % (Mn). Samples were prepared in the form of polished bars in sizes  $(1 \div 1.5) \times 3 \times 9$  mm<sup>3</sup>. Pt electrodes were deposited by cathode sputtering in a vacuum. Dielectric measurements were carried out at frequencies  $f = 102 \div 105$  Hz in the temperature range 300 – 700 K. The temperature-frequency dependences of the real part of the complex dielectric permittivity  $\epsilon'(f, T)$  and the dielectric loss tangent  $tg\delta(f, T)$  were studied. The effect of preliminary polarization of samples in a constant electric field on these dependences as considered. The polarization was carried out under a voltage of  $U_p = 100 \div 285$  V at a temperature of  $T_p = 300 \div 523$  K.

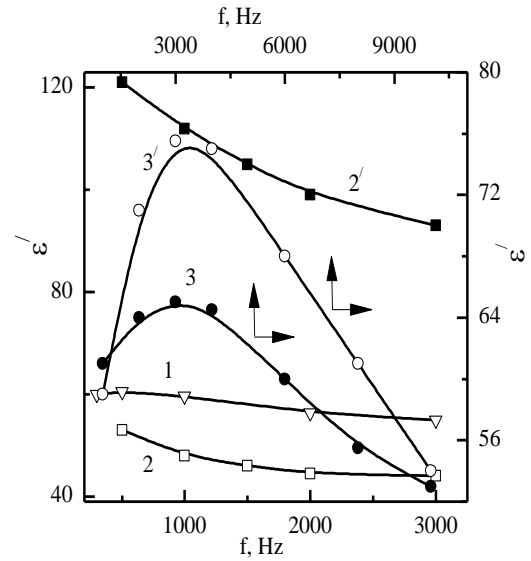
### 3. Experimental results and discussion

The numerical values of  $\epsilon'$  and the practically independence of  $\epsilon'(T)$  for BSO:Cr and BSO: Mn crystals in the initial non-polarized state at  $f \geq 10^3$  Hz differ slightly from those

obtained by us (Fig. 1a) and previously known for BSO [2–5]. We only note that both impurities (Cr and Mn ions) cause a decrease in  $\varepsilon'$  by 5–8 units. However, the situation changes significantly for polarized samples. In undoped BSO, a weak peak of the  $\varepsilon'(T)$  dependence is recorded in the range  $\Delta T_1 = 700 - 800$  K. In BSO:Mn crystals there are two peaks, but with a higher intensity in the intervals  $\Delta T_2 = 420 - 550$  K and  $\Delta T_3 = 650 - 700$  K. In BSO:Cr crystals, Cr ions provide a sharp exponential increase in  $\varepsilon'(T)$  with an increase in temperature from  $T \geq 400$  K. In the low temperature range  $\Delta T_5 = 300 - 400$  K, the  $\varepsilon'(T)$  dependence for BSO:Cr and BSO:Mn pass through a gentle minimum (Fig. 1, b).



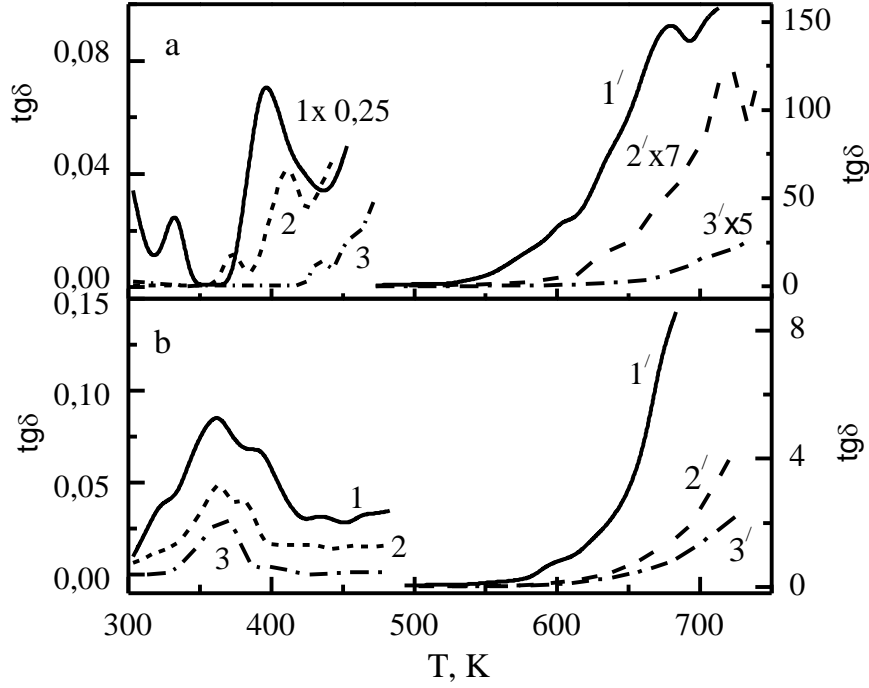
**Fig. 1. Temperature dependences of the dielectric permittivity at a frequency  $f = 103$  Hz for non-polarized (a) and polarized (b) BSO (a, 1; b, 1), BSO:Cr (a, 2; b, 2) and BSO:Mn (a, 3; b, 3) crystals.**



**Fig. 2. Frequency dependences of the dielectric permittivity of polarized BSO (1), BSO:Cr (2, 2') and BSO:Mn (3, 3') crystals for peaks with  $T_{max} = 740$  (1), 400 (2), 645 (2'), 500 (3), 675 (3') K.**

Frequency  $\varepsilon'(f)$  dependences are also significantly different. For BSO crystals in the  $\Delta T_1$  interval and for BSO:Cr crystals in the region  $T \geq 400$  K, a decrease in  $\varepsilon'(f)$  observed with an increase in the measuring frequency that is characteristic for the relaxation dispersion (Fig. 2, curves 1, 2, 3). In BSO:Mn crystals, the intensities of  $\varepsilon'(T)$  peaks in the intervals  $\Delta T_2$  and  $\Delta T_3$  pass through a maximum with increasing frequency (Fig. 2, curves 4, 5). The dispersion  $\varepsilon'$  is close to quasi-resonant with a frequency of  $\sim 10^3$  Hz. The change in the dispersion behaviour of BSO:Mn crystals relative to BSO:Cr can be associated with an increase in their electrical conductivity to  $\sigma \approx 9.7 \cdot 10^{-13} \Omega^{-1} \text{cm}^{-1}$  relative to  $\sigma \approx 9.9 \cdot 10^{-14} \Omega^{-1} \text{cm}^{-1}$  ( $T = 300$  K).

Both BSO:Cr and BSO:Mn crystals have pronounced peaks of the temperature-frequency dependences of the dielectric loss  $tg\delta(f,T)$  (Fig. 3 a, b).



**Fig. 3.** Temperature-frequency dependences of the dielectric loss  $tg\delta(f,T)$  in BSO:Cr (a) and BSO:Mn (b) crystals at frequencies  $f = 500$  (a, 1, 1'), 103 (a, 2, 2'), 3·103 (a, 3, 3'), 700 (b, 1, 1'), 5·103 (b, 2, 2'), 10·103 (b, 3, 3') Hz. Curves (1', 2', 3', a) and (1', 2', 3', b) belong to the right  $tg\delta$  axis.

In BSO:Cr crystals, a decrease in the intensity and a high-temperature shift of the peaks of the  $tg\delta(f,T)$  curves with an increase in the measuring frequency are observed (Fig. 3, a), which is characteristic for the relaxation dispersion. This made it possible to calculate the thermal activation barriers  $E_a$  and the frequencies of the relaxators  $\nu_0$  from the known relation:

$$E_a = \left[ kT_{\max 1} T_{\max 2} / (T_{\max 2} - T_{\max 1}) \right] \ln(f_1 / f_2) \quad (1)$$

where  $k$  is the Boltzmann constant,  $T_{\max 1}$ ,  $T_{\max 2}$  are the temperatures of the maxima of the  $tg\delta(f,T)$  curves,  $f_1$  and  $f_2$  are the frequencies corresponding to them. Using the temperature dependences of times of relaxation

$$\tau = \tau_0 \exp(E_a / kT), \quad (2)$$

the limit frequencies of oscillation of the relaxers  $\nu_0 = 1/\tau_0$  were found. The obtained values of  $E_a$  and  $\nu_0$  are shown in Table 1. In BSO:Mn crystals, there are no high temperature shift peaks of the  $tg\delta(f,T)$  curves. This confirms the quasi-resonant nature of the dispersion  $\varepsilon'$  with the frequency of  $\sim 103$  Hz (Fig. 3, b).

Table 1

Parameters of relaxators in BSO:Cr crystals

N	T <sub>max</sub> , K	E <sub>a</sub> , eV	ν <sub>0</sub> , s <sup>-1</sup>
1	395	0.69	10 <sup>11</sup>
2	480	0.72	2·10 <sup>10</sup>
3	550	0.78	10 <sup>10</sup>
4	595	0.81	3.2·10 <sup>9</sup>
5	635	0.84	10 <sup>9</sup>

The new peaks in the  $\varepsilon'(T)$  and  $\operatorname{tg}\delta(f,T)$  dependences for BSO:Cr and BSO:Mn crystals, compared with BSO, indicate the presence of electrically active defects such as quasi-dipoles with different parameters. Their appearance is due to the multiply charged ions of Cr and Mn and their replacement of both Bi<sup>3+</sup> and Si<sup>4+</sup> ions at the lattice sites. Based on the study of the photochromic effect [6], we assume that quasi-dipoles are of the “impurity – compensator” type where the impurity is Cr<sup>2+</sup><sub>Bi</sub> and Mn<sup>4+</sup><sub>Bi</sub> ions, which replace Bi<sup>3+</sup> in oxygen pseudo-octahedrons and the O<sup>-</sup> hole centers for Cr<sup>2+</sup><sub>Bi</sub>, and the vacancy V<sub>Bi</sub> of Bi<sup>3+</sup> ions for Mn<sup>4+</sup><sub>Bi</sub> are compensators. The quasi-dipoles Cr<sup>2+</sup><sub>Bi</sub> – O<sup>-</sup> are oriented under the action of the voltage  $U_p$  due to the jumps of hole centers between the oxygen sites of the pseudo-octahedron. Polarization is carried out as relaxation thermal. The dipole moment of the Mn<sup>4+</sup><sub>Bi</sub> – V<sub>Bi</sub> quasi-dipole can increase under the influence of  $U_p$  due to the jump of Mn<sup>4+</sup><sub>Bi</sub> to a new non-equivalent position, that is accompanied by the appearance of a returning quasielastic force of Coulomb nature. The polarization will be a quasielastic dipole, but the “mass” of the quasi-dipoles is large, that leads to a low quasi-resonant frequency (~10<sup>3</sup> Hz).

#### 4. Conclusions

1. The doping of BSO crystals with Cr and Mn ions and their polarization can significantly modify the temperature-frequency behaviour of the dielectric characteristics of BSO:Cr and BSO:Mn crystals in the sound frequency range in the temperature range 280 – 800 K.
2. The obtained characteristics of the dielectric and electret properties of BSO:Cr and BSO:Mn crystals are of interest for functional electronics.

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