

# Impedance Spectra of Doped Bismuth Silicate $\text{Bi}_{12}\text{SiO}_{20} : \text{Ge}$ Crystals

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**Abstract**—The specific features of the behavior of the impedance spectra of germanium-doped  $\text{Bi}_{12}\text{SiO}_{20}$  single crystals with the sillenite structure have been studied. It has been found that the obtained dependences exhibit a dispersion corresponding to the distribution of the relaxation times. An analysis of the experimental data performed by the graphical-analytic method has made it possible to separate the contributions to the conductivity due to the crystal bulk and the sample–electrode interface. The role played by the impurity factor and lone electron pairs of trivalent bismuth ions in the formation of the defect structure of the crystal has been demonstrated.

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## 1. INTRODUCTION

Crystals with the sillenite structure have been widely used due to a unique combination of electrical, nonlinear-optical, and magnetic properties in modern piezoelectric engineering, acoustoelectronics, and optoelectronics [1]. Oxygen-containing compounds such as bismuth sillenites exhibiting wide energy gaps, high resistivity, and low charge mobility have been extensively studied in recent years [2]. In particular, bismuth silicate  $\text{Bi}_{12}\text{SiO}_{20}$  (BSO) exhibits photochromic properties, good photoconductivity, and also high rate of the photorefractive response; these properties make it possible to use this material as a media for recording information and in devices of space–time modulation of light as an active element.

The attention paid to bismuth compounds, in particular, sillenites, in modern materials science is due to the existence of  $\text{Bi}^{3+}$  ions with an active lone electron pair in the structure, which provides the formation of oxide polar compounds with unique optical, pyroelectric, and other properties [3]. In spite of a wide area of practical applications, a detailed concept of electronic processes proceeding in materials of the Bi–Si–O system in alternating electric fields and characterizing the drift mechanism of the charge transfer is absent up to now.

This work is devoted to the experimental study of the electrophysical characteristics of bismuth sillenite  $\text{Bi}_{12}\text{SiO}_{20}$  single crystals doped with germanium (BSO : Ge). The study was performed by the method of measuring the complex impedance in an alternating electric field.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The homogeneous BSO : Ge single crystals were grown by the Czochralski method along crystallographic direction [001] in air using platinum crucibles. The samples were prepared as polished  $1 \times 3 \times 5$ -mm bars, and electrodes were made of a conducting paste (aquadag). The frequency dependences of the impedance modulus  $|Z|$  and the phase shift angle  $\varphi$  between the current and the voltage were measured with step-by-step change in frequency in the range  $f = 5 \times 10^2$ – $10^6$  Hz at measuring voltage amplitude of 1 V using an E7-20 precision immittance meter. Then, we calculated the spectra of real  $Z'(f) = |Z|\cos\varphi$  and imaginary  $Z''(f) = |Z|\sin\varphi$  impedance components.

To estimate the single-crystal perfection and to obtain information on the structural features of the sample surface, we studied the surface morphology on a Solver 47 Pro atomic-force microscope (AFM) operating in the tapping mode under atmospheric conditions at room temperature. The studies were performed using a silicon cantilever with topographic scanning. The obtained image (Fig. 1) is characterized by a quasi-periodic wave relief with scattering of heights and lateral sizes of the formations in the base.

## 3. RESULTS AND DISCUSSION

Figures 2 and 3 show dependences  $Z'(f)$  and  $Z''(f)$  for the  $\text{Bi}_{12}\text{SiO}_{20}$  single crystal in the absence of constant bias. These dependences demonstrate a dispersion that is observed as the decrease in the values of the complex impedance components as the measuring electric field frequency increases. At low frequencies

in the range of  $10^2$ – $10^4$  Hz, the studied functions sharply go down and, from a frequency  $f > 10^4$  Hz, the spectra of the imaginary and real components of the complex impedance correspond to a constant minimum level.

The impedance dispersion is characterized by the time of electrical relaxation that is usually determined by the graphical–analytic method using a hodograph, namely, by constructing the dependence of the impedance imaginary component  $Z''$  on its real component  $Z'$ . According to the available information [4], the shape of the obtained curves (Fig. 4) suggests the existence of two relaxation mechanisms: one of them describes the contribution due to the diffusion mechanism expressing the gradient of the carrier concentration at the interface (Fig. 4a), and another mechanism expresses the bulk properties of the single crystal related to the material microstructure (Fig. 4b). The highest imaginary component of the impedance corresponds to the maximum of the hodograph curve observed at the characteristic frequency  $f_{\max}$ . The electrical relaxation time calculated using relationship  $\tau_0 = 1/2\pi f_{\max}$  is determined as the average relaxation time of the impedance of the sample with electrodes, and it is  $\tau_0 = 6.3 \times 10^{-6}$  s in our case. The electronic state of the contact to the electrode is determined by the influence of the charge formed at local surface levels, the existence of a potential barrier at the interface, and also the energy structure of trapping levels in the material bulk.

The physical processes in the studied sample can be described using an approximation of the experimental dispersion characteristics of the complex impedance components by corresponding equivalent electrical circuit. The obtained experimental data allow us to propose the equivalent circuit (insert in Fig. 4a), consisting of elements  $Z_b$  and  $Z_{\text{int}}$  connected in series, expressing the contributions in the impedance of the charge transfer processes in the crystal bulk and at the interface, respectively.

An analysis of the experimental data on studying the temperature–frequency dependences of the electrical conductivity [5, 6] allowed the conclusions in favors of the hopping character of the electrical transport in BSO [7, 8] over local states whose origin is due to the nonstoichiometry defects and the existence of impurity atoms. It was also found that the charge transfer over these energy states (trapping centers) is related to the only carrier type, namely, electrons. An analysis of the structural features of the studied semiconductor indicates a significant role played by a lone electron pair of  $\text{Bi}^{3+}$  cations in the formation of defect centers and corresponding local states in the energy gap. In this case, the concentration of charge centers is determined by the content of bismuth ions in the crystal.

The structural changes in the studied compound can also be related to substituting of germanium for

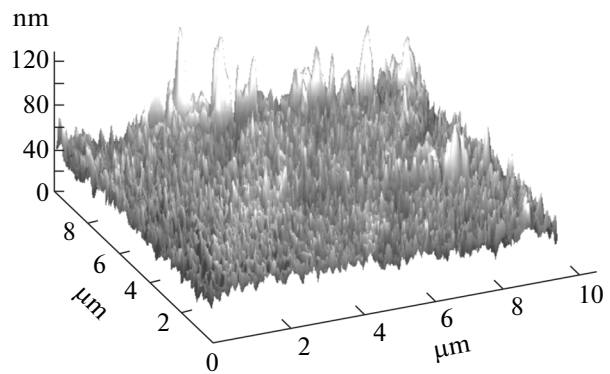


Fig. 1. AFM image of the  $\text{Bi}_{12}\text{SiO}_{20} : \text{Ge}$  sample surface.

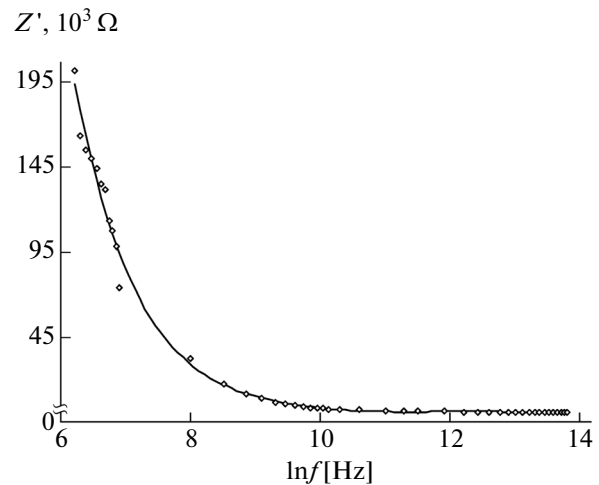


Fig. 2. Spectral dependence of the active part of the impedance of the  $\text{Bi}_{12}\text{SiO}_{20} : \text{Ge}$  single crystal.

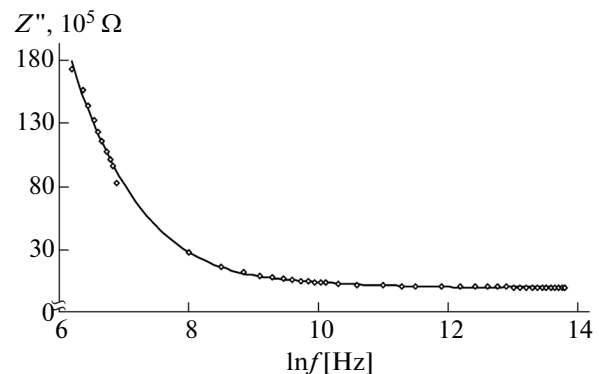


Fig. 3. Spectral dependence of the reactive part of the impedance of the  $\text{Bi}_{12}\text{SiO}_{20} : \text{Ge}$  single crystal.

bismuth in the distorted octahedral [9]. The incomplete impurity substitution of  $\text{Bi}^{3+}$  ions with a lone electron pair in the sillenite composition can favor the change in the physical properties of the material by

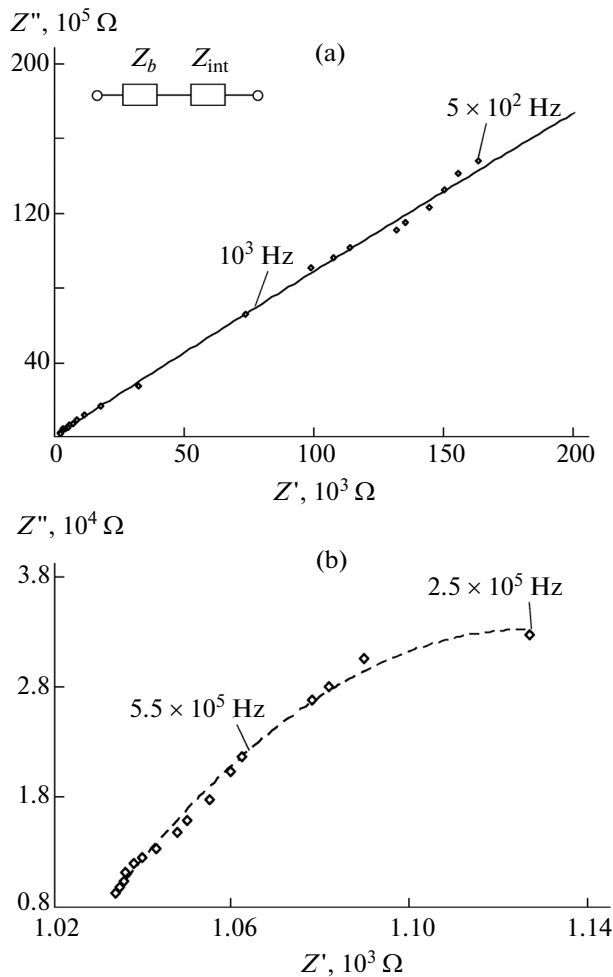


Fig. 4. (a) Low-frequency and (b) high-frequency parts of impedance hodograph  $Z''(Z')$  of the  $\text{Bi}_{12}\text{SiO}_{20}:\text{Ge}$  sample.

means of the formation of more symmetric structural coordination. In particular, during doping the BSO single crystals, the structural oxygen tetrahedra are probable to be distorted with the formation of oxygen vacancies which are capable to capture an electron, according to the condition of compensation. Because the BSO crystal lattice is high-polarized, the existence of defects in the sillenite bulk leads to active relaxation processes which can be due to a quasi-dipole polarization [10].

#### 4. CONCLUSIONS

Thus, the specific features of the impedance spectra were studied for the first time on the germanium-doped bismuth silicate single crystal in the measuring frequency range of  $5 \times 10^2 - 10^6 \text{ Hz}$ . It was shown that, in the studied range of the measuring frequencies, the curves of the active and reactive components of impedance undergo the dispersion that is characterized by the decrease in  $Z'$  and  $Z''$  as the electric field frequency increases. At low frequencies ( $f < 10^4 \text{ Hz}$ ), the impedance hodograph is substantially changed, and it demonstrates the influence of the sample-electrode interface on the charge transfer.

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