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INVESTIGATION OF THE GYROTROPY IN THE SPECTRAL REGION OF THE ABSORPTION "SHOULDER" OF THE OXIDE CRYSTAL $Bi_{12}SiO_{20}$

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Abstract

This paper presents the research of the gyrotropy of a pure $Bi_{12}SiO_{20}$ (BSO) and doped $Bi_{12}SiO_{20}$:Al (BSO:Al) crystals in the spectral region of "absorption shoulder" using measurements of the spectra of the natural optical rotation, the magneto-optical rotation and the optical spectroscopy. It is shown that the difference in the absorption of the BSO and BSO:Al crystals is related to the presence of two types of defects in the crystals BSO:Al – impurities Al^{3+}_{Si} in $[Al^{3+}_{Si}O_4]$ and Bi^{3+}_{Si} in $[Bi^{3+}_{Si}O_4]$. A "red-shift" of the optical rotation spectrum of BSO:Al crystals has also been observed relative to the optical rotation spectrum of BSO crystals.

Key words: Faraday effect, optical activity in semiconductors, impurities in solid, absorption edges, absorption spectra of solid

Introduction. $Bi_{12}SiO_{20}$ (point group 23) are cubic crystals grown by the Czochralski technique. Their unit cell is constructed of two structural elements – tetrahedron $[Si^{4+}O^{2-}_4]$ and polyhedron $[Bi^{3+}O^{2-}_5E]$, where E is an electron pair $6s^2$ of bismuth [1]. The symmetry of the polyhedron is close to C_1 [2]. As a result, the electrical and magneto-dipole transitions in the bismuth ion Bi^{3+}in the polyhedron

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are permitted and the crystal is optically active [3]. The chromophores [BiO_5E] and [SiO_4] contribute to this activity and their contributions have a different sign [4].

A composite absorption band (from 2.4 to 3.2 eV) is observed before the absorption edge of BSO. It is called "shoulder" of absorption. The physical nature of this band is not unambiguously determined. Different models for the nature of the absorption centres that led to the appearance of the "shoulder" exist: One of the models suggests that the Bi_{Si}^{3+} ion (consisting of a xenon core and an electron pair $6s^2$) has taken the place of the ion Si^{4+} in the oxygen tetrahedron and within the complex there is a hole h^+ that provides an electrically neutral state of the complex [5,6]. The hole h^+ is located around one of the ions O^{2-} in the tetrahedral oxygen complex [7]. This model is based on the following fact: It is known that in the lattice of BSO that grows by the method of Czochralski there is an excess of bismuth and a deficiency of silicon. There are some difficulties when using this model: 1) A band with a maximum at 2.2 eV must be registered in the absorption spectrum [8]. Such absorption in the spectral region of the "shoulder" has not been observed. 2) The large difference in the ionic radii of Bi_{Si}^{3+} (120 pm) [9] and Si^{4+} (39 pm) [9] must lead to large distortions of the "correct" oxygen tetrahedron. In one other model, it is assumed that the local centres that determine light absorption in the spectral region around the 2.8 eV are silicon vacancies V_{Si} [10] or ($V_{Si} - 2V_O$) complexes, where V_O are oxygen vacancies [11]. The $Bi_{12}SiO_{20}$ crystals contain a large quantity of vacancies V_{Si} (around 10^{19} cm^{-3}) [4,12]. As a result, the intensity of the electron transitions "valence band – vacancies levels V_O" (at 2.95–3 eV) are high [13].

Experiments. The problem for the absorption of light by a crystal with optical activity can be solved without approximation by the covariant method or by the method of summation of the natural waves in the crystal. In both cases, the expressions for the intensity of the light transmitted through the crystal turn out to be very complex and are not applicable to the analysis of the experimental data. Due to that, an additional assumption is made: Since the circular dichroism (CD) is much smaller than the circular birefringence, the linear birefringence and the linear dichroism, the CD is not taken into account when measuring these quantities [13]. As a result of this assumption, two circularly polarized natural waves propagate in the absorbing optically active cubic crystals [13,14]. They have different refractive indices ($n_l \neq n_r$) and different absorptions indices ($\chi_l \neq \chi_r$). After passing through the gyrotropic absorbing BSO crystal the incident linearly polarized light becomes elliptically polarized. In the research of the gyrotropy of the BSO, two measurable quantities can be used – the dispersion of the rotation $\varphi(\omega)$ of the major axis of the polarization ellipse of the light that has passed through the crystal and the dispersion of ellipticity $\theta(\omega)$ of this ellipse. Optical rotation φ changes only the orientation of the major axis of the ellipse relative to the direction of oscillation of the electric vector of incident linearly polarized light,

and the ellipticity θ depends only on the absorption of the two normal waves in the crystal. This assertion is not strict, because the circular dichroism and the optical rotation are quantities that characterize one and the same phenomenon – the first-order spatial dispersion [13]. These two quantities can be easily measured.

The rotation $\varphi(\hbar\omega)$ and ellipticity $\theta(\hbar\omega)$ obey the equations:

$$\varphi = \frac{\pi}{\lambda}\frac{\Delta\varepsilon}{\sqrt{\varepsilon}}d, \tag{1}$$

where the light propagates along X and the permittivity tensor has the form

$$\varepsilon_{YZ}(\omega,\vec{k}) = \begin{vmatrix} \varepsilon & -i\Delta\varepsilon \\ i\Delta\varepsilon & \varepsilon \end{vmatrix}, \tag{2}$$

and [13]

$$\tan\theta = \frac{\exp(-2\pi\chi_l d/\lambda) - \exp(-2\pi\chi_r d/\lambda)}{\exp(-2\pi\chi_l d/\lambda) + \exp(-2\pi\chi_r d/\lambda)}, \tag{3}$$

where $\chi_{l,r}$ are the absorption indices of the left and right circularly polarized natural waves, and d is the thickness of the crystal. A standard system of two polarizers P, A and the crystal Cr ($P - Crystal - A$) can be used to determine the dispersion of φ. If the BSO crystal of the system is placed in an external magnetic field (in the Faraday configuration), the rotation of the major axis of the polarization ellipse of the passed light changes. Two non-diagonal components ($\Delta\varepsilon$ and $\Delta\varepsilon_{FR}$) appear in the permittivity tensor:

$$\varepsilon_{YZ}(\omega,\vec{k},\vec{H}) = \begin{vmatrix} \varepsilon & -i(\Delta\varepsilon + \Delta\varepsilon_{FR}) \\ i(\Delta\varepsilon + \Delta\varepsilon_{FR}) & \varepsilon \end{vmatrix}. \tag{2a}$$

In a first approximation, it can be expected that this will result in a rotation related to both the natural optical activity and the Faraday rotation of the BSO:

$$\varphi_{OAFR} = \frac{\pi d}{\lambda}\left(\frac{\Delta\varepsilon}{\sqrt{\varepsilon}} + \frac{\Delta\varepsilon_{FR}}{\sqrt{\varepsilon}}\right). \tag{4}$$

Then the Faraday rotation φ_{FR} is equal to the difference between equations (4) and (1)

$$\varphi_{FR} = \varphi_{OAFR} - \varphi = \frac{\pi d}{\lambda}\frac{\Delta\varepsilon_{FR}}{\sqrt{\varepsilon}}. \tag{5}$$

The ellipticity θ is determined by rotating the analyzer A about the axis of ($P - Cr - A$). The maximum I_{MAX} and the minimum I_{MIN} light transmission at a given light wavelength are measured. Then the values of the small and major axis

of the polarization ellipse are $b = \sqrt{I_{MIN}}$ and $a = \sqrt{I_{MAX}}$, respectively, and the ellipticity is

$$\theta = ATAN\left(\sqrt{\frac{I_{MIN}}{I_{MAX}}}\right).$$

If the cubic crystals are weakly absorbing and optically active, a "complex rotation" can be introduced [13]:

$$\Phi = \varphi + i\theta = \frac{\pi d}{\lambda}(\Delta n_{lr} + \Delta\chi_{lr}), \tag{6}$$

where φ characterizes the rotation of the major axis of the polarization ellipse, and the ellipticity θ characterizes the absorption indices $\chi_{l,r}$ of the left and right circularly polarized natural waves.

Therefore

$$\varphi = \frac{\pi d}{\lambda}\Delta n_{lr} \quad \text{and} \quad \theta = \frac{\pi d}{\lambda}\Delta\chi_{lr}. \tag{7}$$

Experimental results. The following experimental results have been obtained: the absorption spectrum $\alpha_{\mathrm{BSO}}(\hbar\omega)$ of BSO in the spectral region of the "shoulder" (Fig. 1A); the rotation spectrum $\varphi^{\mathrm{BSO}}(\hbar\omega)$ of the major axis of the polarization ellipse of the passed light through the crystal BSO and the spectrum $12.(\theta/d)$ (Fig. 2A); the absorption spectrum $\alpha_{\mathrm{BSO:Al}}(\hbar\omega)$ (Fig. 1B); the rotation spectrum $\varphi_{\mathrm{BSO:Al}}(\hbar\omega)$ (Fig. 3A) and the spectrum of the ellipticity $4\theta/d$ in the BSO and BSO:Al crystals (Fig. 3B).

Discussion. Models used to describe the nature of the absorption centres, which can explain all the photoinduced phenomena in the sillenites are not known. This paper describes an attempt to clarify the nature of the absorption centres in the BSO spectral region 2.4–3.2 eV.

***Absorption "shoulder" of BSO* (2.4–3.2 eV).** The computer fit shows that the measured composite absorption curve (Fig. 1A) in the spectral region of the "shoulder" consists of two Gaussian curves. The maximum of curve "1" is at 2.86 eV. This peak in the absorption spectrum of the "shoulder" is the result of "valence band – oxygen vacancies levels V_O" transitions [11, 12]. These vacancies are donors in the forbidden band (2.9 eV above top of the valence band) [12].

It is known that the absorption edge is formed by the "exciton-phonon" interaction [4]. Analysis of the band structure of the crystal shows that the bottom of the conduction band and the tops of the valence band are located at different points in the Brillouin zone [15]. The exciton transitions are indirect and exciton peaks are not observed in the absorption spectra of the crystal. Exciton effects are significant only in the spectral region of the absorption edge. At photon energies less than the band gap, these effects rapidly attenuate [2].

Our experiments showed that the spectral region of the "shoulder" can be divided into two regions - "C" and "D" (Fig. 1B). In the domain "C" $\phi_{\mathrm{BGO}}(\hbar\omega)$

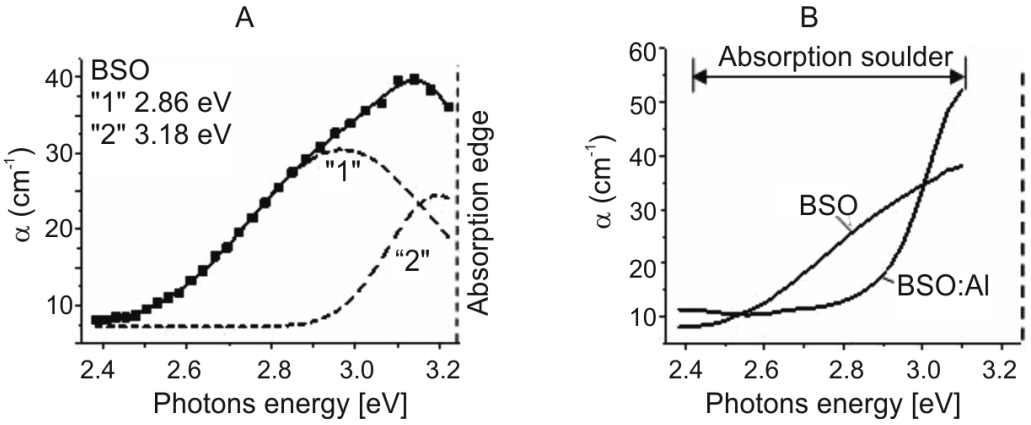

Fig. 1. A) Absorption spectrum $\alpha_{\mathrm{BSO}}(\hbar\omega)$; B) Absorption spectra $\alpha_{\mathrm{BSO:Al}}(\hbar\omega)$ and $\alpha_{\mathrm{BSO}}(\hbar\omega)$

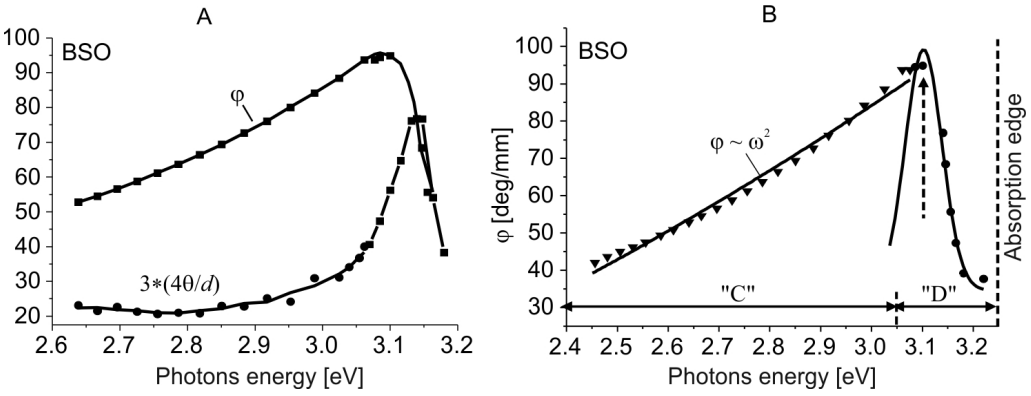

Fig. 2. A)The rotation spectra: $\varphi^{\mathrm{BSO}}(\hbar\omega)$ of the major axis of the polarization ellipse of the passed light and the circular dichroism $4\theta/d$ of natural waves; B) Correlation analysis of the curve in the spectral regions "C" and "D" within which the trend of the curve is different

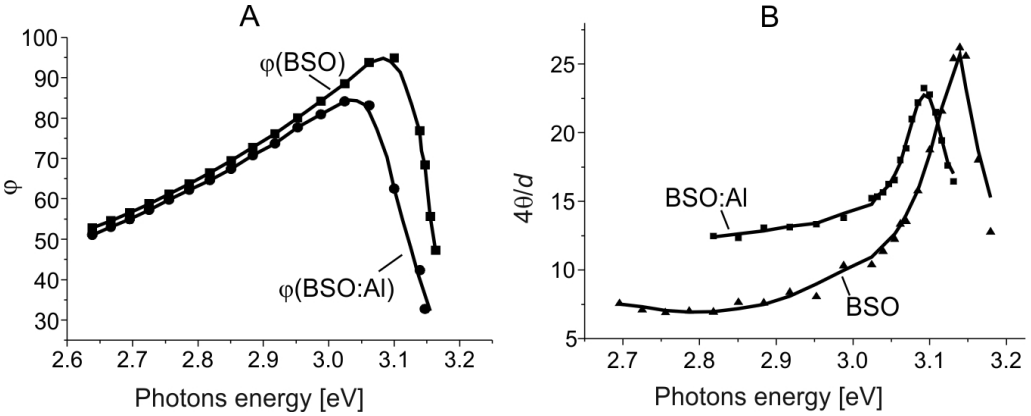

Fig. 3. A) The dispersions of the rotation $\varphi_{\mathrm{BSO:Al}}(\hbar\omega)$ and $\varphi_{\mathrm{BSO}}(\hbar\omega)$ of the major axis of the polarization ellipse of the passed light; B) The spectra $4\theta/d$ in the crystals BSO and BSO:Al

is proportional to $(\hbar\omega)^2$. In region "D" the curve is described by a peak function with the small half of the width and the maximum value $\varphi_{\rm BSO}^{MAX}(\hbar\omega) \approx 3.1$ eV. This value is close to the photon energy in the exciton spectrum of magneto-optical activity, at which the sign of the exciton rotation changes is $\varphi_{FR}^{\rm BSO} = 3.19$ eV [16,17]. This allows us to assume that the absorption peak "2" is related to the absorption of the bound exciton described in [17]. Therefore, we can assume that the absorption in the "shoulder", is formed by two types of absorption centres – oxygen vacations V_O and "defective" bismuth octahedra $[Bi_{Si}^{3+}O_4]$.

Al-*doped BSO*. Two types of defects – $[Al_{Si}^{3+}O_4^{2-}]$ and $[Bi_{Si}^{3+}O_4^{2-}]$ exist in the doped crystal $Bi_{12}SiO_{20}$:Al [6]. Due to the presence of silicon vacancies V_{Si} in the BSO crystal, aluminium takes the place of silicon in oxygen tetrahedra, forming diamagnetic centres $[Al_{Si}^{3+}O_4^{2-}]$ [17]. If the concentration the doped aluminium in the crystal increases, the ratio of the concentration of $[Bi_{Si}^{3+}O_4^{2-}]$ and $[Al_{Si}^{3+}O_4^{2-}]$ and the concentration of silicon vacancies decreases. The research described in [4,5] shows that: 1) in this case the circular dichroism CD reduced, i.e. doping of BSO with Al contributes to the gyrotropy of the impurity crystal, and 2) doping with p-elements of pure BSO practically does not change the natural optical activity if the energy of the photons in the crystal is less than 2.9 eV [4].

The measurements in [4] show that the peak in the CD spectrum (by a maximum of about 2.9 eV) decreases and disappears when the concentration of aluminium ions increases. Our experiments show that the peak "1" in the absorption "shoulder" (2.86 eV), which is associated with oxygen vacancies V_O also disappear (Fig. 1). This allows us to assume that circular dichroism in the BSO [4] is associated with transitions "valence band – oxygen vacancies levels" [12], which does not follow from the research we know so far.

The experiments showed that the aluminium impurities produced a "red-shift" of the spectrum $\varphi_{\rm BSO:Al}(\hbar\omega)$ relative to $\varphi_{\rm BSO}(\hbar\omega)$ (Fig. 3A). Such a shift is also observed in the spectra $\theta_{\rm BSO}(\hbar\omega)$ and $\theta_{\rm BSO:Al}(\hbar\omega)$ (Fig. 3B). The difference of the two rotation spectra $\varphi_{\rm BSO:Al}(\hbar\omega) - \varphi_{\rm BSO}(\hbar\omega)$ forms a "negative" Gaussian peak if the energy of the photons is $\hbar\omega > 3$ eV (Fig. 4A). If $\hbar\omega < 3$ eV, this difference is less than 5 (deg/mm) and the absorption (described by peak "1" (Fig. 1A)) has little effect on the angle of rotation φ of the major axis of the polarization ellipse, as follows from (1).

The question arises: At what energies of the photons propagating in the BSO:Al crystal does the absorption begin to affect the dispersion of the Faraday rotation $\varphi_{FR}(\hbar\omega)$. It is known [18–20] that if we neglect the absorption and energy of the photons in the semiconductor crystal is less than the band gap, the angle of Faraday rotation $\varphi_{FR}(\hbar\omega)$ is proportional to ω^2. If $\hbar\omega < 3$ eV, correlation analysis shows that the dependence $\varphi_{FR}^{\rm BSO:Al} = A(\hbar\omega)^2 + B$ describes well the experimentally measured Faraday rotation (Fig. 4B). At such photon energies $\hbar\omega$ the model of the classical oscillator can be used for BSO:Al. If $\hbar\omega > 3.1$ eV, $\varphi_{FR}(\hbar\omega)$ begins to decrease with increasing $(\hbar\omega)^2$ (Fig. 4B), the oscillator model cannot be

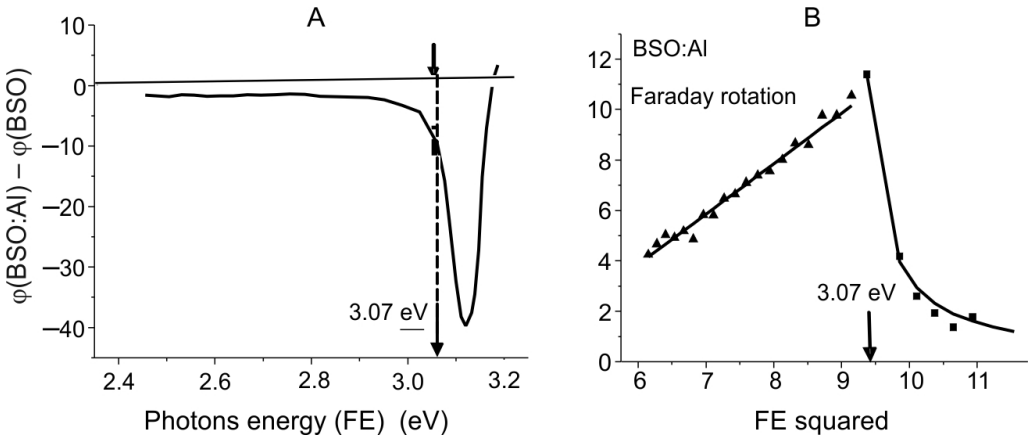

Fig. 4. A) Difference of the rotational spectra $\varphi_{\mathrm{BSO:Al}}(\hbar\omega) - \varphi_{\mathrm{BSO}}(\hbar\omega)$; B) The photons energy at which absorption begins to affect the dispersion of Faraday rotation

used and the Zeeman splitting of the exciton levels and the band structure of the crystal must be taken into account [19].

Conclusions. It has been shown that the optical absorption centres in the spectral region of the "absorption shoulder" of the BSO and BSO:Al crystals are oxygen vacancies and bound excitons in the oxygen tetrahedra of these oxide crystals.

In the spectral region of the absorption "shoulder", the difference in the absorption of the pure BSO crystal and the doped BSO:Al crystal is related to $\mathrm{Al}_{\mathrm{Si}}^{3+}$ impurities in $[\mathrm{Al}_{\mathrm{Si}}^{3+}\mathrm{O}_4]$ and $\mathrm{Bi}_{\mathrm{Si}}^{3+}$ in the defects $[\mathrm{Bi}_{\mathrm{Si}}^{3+}\mathrm{O}_4]$. $\mathrm{Al}_{\mathrm{Si}}^{3+}$ and $\mathrm{Bi}_{\mathrm{Si}}^{3+}$ have very different ionic radii. It is shown that when the concentration of $\mathrm{Al}_{\mathrm{Si}}^{3+}$ in $[\mathrm{Al}_{\mathrm{Si}}^{3+}\mathrm{O}_4]$ becomes high enough, the absorption in the "shoulder" binds mainly to the bound excitons.

The aluminium impurities in BSO:Al lead to a "red-shift" of the spectrum $\varphi_{\mathrm{BSO:Al}}(\hbar\omega)$ relative to $\varphi_{\mathrm{BSO:Al}}(\hbar\omega)$. A "negative" Gaussian peak with a maximum of about 3.12 eV and a small half-width is formed (Fig. 4A). In the region of this maximum, the rotation $\varphi_{\mathrm{BSO:Al}}(\hbar\omega)$ of the major axis of the ellipse of the transmitted light decreases almost twice compared to this rotation $\varphi_{\mathrm{BSO}}(\hbar\omega)$ in the undoped BSO crystal.

Through the experimentally measured dispersion of $\varphi_{FR}(\hbar\omega)$ (Fig. 4B) one can find the frequency regions in which the classical oscillator model is applicable and the ranges in which the band structure of the BSO:Al crystal should be taken into account. The boundary between these two regions is determined by the change in the trend of the dispersion of the Faraday rotation curve (Fig. 4B). If the model of the classical oscillator is applicable, this dispersion is determined by the linear dependence $I \sim (\hbar\omega)^2$ [18–20]. For BSO:Al this limit is about 3 eV.

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