

## Optical absorption of $\text{Bi}_{12}\text{SiO}_{20}:\text{Sn}$ crystals

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The results of experimental research of stationary and photoinduced optical absorption of tin-doped  $\text{Bi}_{12}\text{SiO}_{20}$  crystals are presented. Peculiarities of the tin influence on the absorption are due to its occurrence into the crystal lattice in  $\text{Sn}^{4+}$  and  $\text{Sn}^{2+}$  charge states substituting for  $\text{Si}^{4+}$  ions.

**Keywords:**  $\text{Bi}_{12}\text{SiO}_{20}$ , crystals, doping by Sn ions, stationary and photoinduced optical absorption, charge state of Sn ions.

Представлены результаты экспериментального исследования стационарного и фотоиндуцированного оптического поглощения кристаллов  $\text{Bi}_{12}\text{SiO}_{20}$ , легированных оловом. Особенности влияния олова на поглощение связываются с его вхождением в зарядовых состояниях  $\text{Sn}^{4+}$  и  $\text{Sn}^{2+}$  в кристаллическую решетку вместо ионов  $\text{Si}^{4+}$ .

**Оптичне поглинання кристалів  $\text{Bi}_{12}\text{SiO}_{20}:\text{Sn}$ .** *Т.В.Панченко, А.О.Дяченко.*

Представлено результати експериментального дослідження стаціонарного та фотоіндукованого оптичного поглинання кристалів  $\text{Bi}_{12}\text{SiO}_{20}$ , легованих оловом. Особливості впливу олова на поглинання пов'язані з його входженням у зарядових станах  $\text{Sn}^{4+}$  і  $\text{Sn}^{2+}$  в кристалічну решітку замість іонів  $\text{Si}^{4+}$ .

### 1. Introduction

Single crystals of sillenites  $\text{Bi}_{12}\text{MO}_{20}$  (BMO, where  $M = \text{Si}, \text{Ge}, \text{Ti}$ , respectively) are effectively used in optoelectronics devices and dynamic holography for recording, processing and storage of optical information. One of the most essential problem is modification the properties of a number of BMO (optical absorption, photoconductivity, photochromism) by doping. To date it is accumulated a considerable amount of experimental data on the role of impurity elements in *d*-sillenites [1–3]. By the example of  $\text{Bi}_{12}\text{TiO}_{20}$  a number of functional characteristics of patterns of change depending on the type 3*d*-ions (Cr, Mn, Fe, Cu, Ni, Co) and the nature of these transitions in intracenter were identified [2].

However, BMO as wide band gap semiconductors are also important to study the

possibility of changing the structure of the local levels of the band gap (BG) and the transition scheme of the "impurity level — zone" in order to optimize the ratio between the impurity optical absorption and photoconductivity. It is known that some admixture of *p*-elements (transition metals Al, Ga) leads to the effect of "enlightenment" — a sharp decrease in optical absorption and photosensitivity in the spectral range of the optical recording media, i.e., in the blue-green spectral region (region "shoulder absorption" due to intrinsic defects of BMO) [4–6]. To compile information on the impact on the structure of BG other studies of antireflective *p*-elements are of interest. These may be tin ions, the electron configuration of which ( $5s^2 5p^2$ ) is similar to the configuration of Al ( $3s^2 3p^2$ ) and Ga ( $4s^2 4p^2$ ). However, the effect of ions on the proper-

ties of Sn crystals BMO has not previously been studied.

The paper presents the results of study of stationary and photoinduced optical absorption (photochromic effect (PCE)) of crystals  $B_{12}SiO_{20}$  (BSO), tin-doped (BSO:Sn).

## 2. Experimental

Crystals BSO and BSO:Sn were grown by the Czochralski method along the crystallographic direction [001]. Content of Sn dopant in the crystals of BSO:Sn was 0.12 mass.% of the mass according to the spectral emission analysis. Samples were prepared in the form of a set of polished plates of thickness  $d = 0.3 \div 5$  mm with large faces (001). Before examining the PCE sample was led to an equilibrium state by heating to 800 K and subsequent slow ( $\sim$  days) cooled in the dark to  $T_0 = 85$  K.

With a spectrophotometer "Cary-4E" at  $T_0$  in the range of photon energy  $h\nu = 0.5-3.4$  eV, which covered the entire area of the optical transparency of the crystal BSO, spectra of stationary and photoinduced optical transmission were recorded. Photoinduced state of the crystal is excited and wash light with a photon energy  $h\nu_1 = 2-2.8$  and  $h\nu_2 = 0.5-2.3$  eV, respectively, from the halogen lamp 600 W power HPLA with interference filters. The procedure was as follows. On the samples provided in the equilibrium state, the transmission spectra were measured stationary  $t_0(h\nu)$ . After photoactivation patterns by light with  $h\nu_1$  (10 min), which is removing the electronic subsystem of the balance, spectra of photoinduced transmission  $t^{pi}(h\nu)$  were recorded. The samples were then illuminated with light of  $h\nu_2 \leq h\nu_1$  when the return to equilibrium of the electron subsystem, and the spectra were recorded  $t^{pd}(h\nu)$ , characterizing the optical erasure (OE) photoinduced transmission. To eliminate the influence of the backlight all manipulations (warm, placing a sample in the cryostat) were carried out with the weak red illumination, which does not cause PCE.

We investigated the transmission spectra corresponding to steady-state absorption spectra of  $\alpha_0(h\nu)$ , absorption after photoactivation  $\alpha^{pi}(h\nu)$  and the optical erasure PCE  $\alpha^{pd}(h\nu)$ , and the difference spectra characterizing PCE and optical blurring:  $\Delta\alpha^{PCE}(h\nu) = \alpha^{pi}(h\nu) - \alpha_0(h\nu)$  and  $\Delta\alpha^{pd}(h\nu) = \alpha^{pi,max}(h\nu) - \alpha^{pd}(h\nu)$ , respectively, where

$\alpha^{pi,max}$  — photoinduced absorption maximum (saturated PCE). The absorption spectra were calculated by the method of [7].

## 3. Results and discussion

The results obtained are as the follows.

Admixture of tin ions discolor crystals BSO:Sn, changing their color from yellow-brown, typical for BSO, to slightly greenish.

Stationary optical absorption spectra  $\alpha_0(h\nu)$  of the crystals BSO:Sn poorly structured, in contrast to the BSO crystals they do not have the "shoulder" of the optical absorption (Fig. 1a). However, in the near-IR and visible region absorption is increased (Fig. 1b, c). The difference spectrum of stationary absorption  $\Delta\alpha_0(h\nu) = \alpha_{0BSO:Sn}(h\nu) - \alpha_{0BSO}(h\nu)$ , where  $\alpha_{0BSO}(h\nu)$  and  $\alpha_{0BSO:Sn}(h\nu)$  — absorption of the BSO crystals and BSO:Sn, can be divided into A- and B-ranges with  $h\nu \approx 2-3.3$  and  $0.5-2$  eV, respectively. A-range contains bands of enlightenment, B-range — additional absorption. They show how the partial compensation of the intrinsic defects of BSO by Sn ions is realized, and demonstrate occurrence of the additional color centers (Fig. 2).

Photoinduced absorption spectra  $\alpha^{pi}(h\nu)$  of the crystals BSO:Sn and BSO significantly different in character of the spectral intensity distribution. In the area A Sn causes a decrease in the photoinduced absorption, whereas the B-field is increased (Fig. 1).

Spectra PCE  $\Delta\alpha^{PCE}(h\nu)$  complex structured (Fig. 3) point out the new absorption bands in the BSO:Sn crystals in the IR-range. Using the procedure described in [8] we divided these spectra for the crystals BSO ( $\Delta\alpha^{PCE}_{BSO}(h\nu)$ ) and BSO:Sn ( $\Delta\alpha^{PCE}_{BSO:Sn}(h\nu)$ ) for the individual components of the Gaussian shape. The technique allows to determine the number of components, their spectral position and half-breadth without a priori set these parameters. It have been found that most of the PCE bands of the BSO crystals and BSO:Sn have the same spectral position ( $h\nu_{max}$ ) and close the half-width values, differing mainly in the intensity (Fig. 3, Table 1). In all likelihood, these bands are associated with the intrinsic defects of BSO. Only in the IR-range the new band with  $h\nu = 0.58; 0.8$  eV was introduced by ions Sn.

In order to determine the contribution of Sn ions in the emergence or disappearance

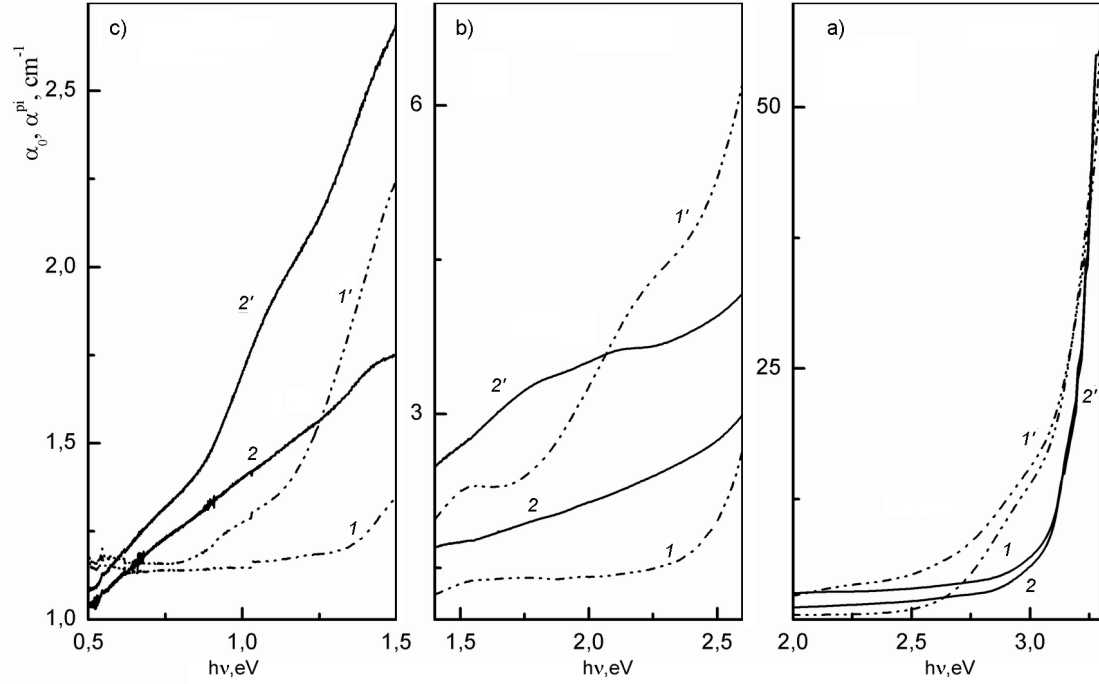


Fig. 1. Spectra of stationary optical absorption  $\alpha_0(h\nu)$  (1, 2) and optical absorption  $\alpha^{pi}(h\nu)$  after photoactivation (1', 2') for BSO (1, 1') and BSO:Sn (2, 2') crystals.

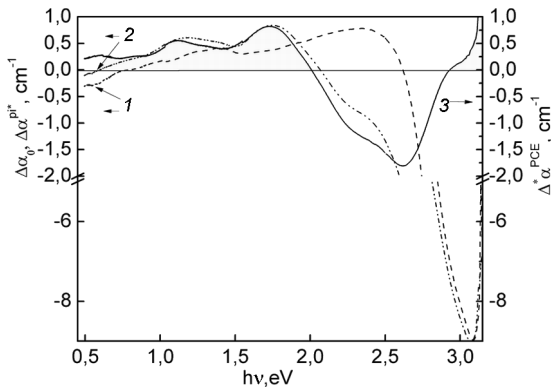


Fig. 2. Spectra of optional stationary absorption  $\Delta\alpha_0(h\nu)$  (1), optional photoinduced absorption  $\Delta\alpha^{pi}(h\nu)$  (2) and optional PHE  $\Delta^*\alpha^{PCE}(h\nu)$  (3).

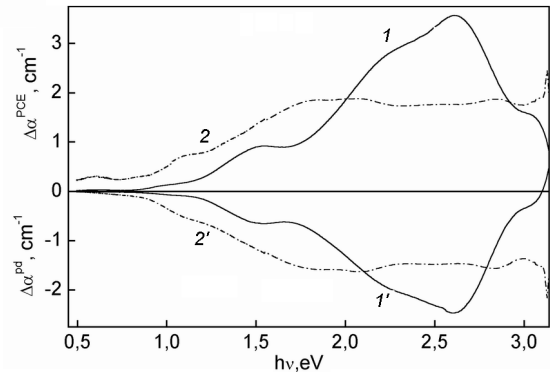


Fig. 3. Spectra of PCE  $\Delta\alpha^{PCE}(h\nu)$  (1, 2) and optical destruction of PCE  $\Delta\alpha^{pd}(h\nu)$  (1', 2') for BSO (1, 1') and BSO:Sn (2, 2') crystals.

of the optically active color centers of BSO there were calculated the spectra of optional photoinduced absorption  $\Delta\alpha^{pi}(h\nu) = \Delta\alpha^{pi,max}_{BSO:Sn}(h\nu) - \Delta\alpha^{pi,max}_{BSO}(h\nu)$  and optional PCE  $\Delta^*\alpha^{PCE}(h\nu) = \Delta\alpha^{PCE}_{BSO:Sn}(h\nu) - \Delta\alpha^{PCE}_{BSO}$ . They were identical by the structure to the range of additional steady-state absorption  $\Delta\alpha_0(h\nu)$  (Fig. 2), with the difference that the ratio of the integrated absorp-

$$\frac{\int_{h\nu_1}^{h\nu_2} \Delta\alpha^{pi}(h\nu) dh\nu}{\int_{h\nu_1}^{h\nu_2} \Delta\alpha_0(h\nu) dh\nu}$$

B- and A-bands increases from 0.3 to 1.3 in favor of the B bands PCE.

When illuminated by light with a photon energy of the B-range the almost complete optical erasure of PCE of BSO crystals can be achieved, ensuring that the spectra OE  $\Delta\alpha^{pd}(h\nu)$  and PCE  $\Delta\alpha^{PCE}(h\nu)$  are mirror symmetric. For crystals BSO:Sn the complete optical erasure cannot be reached, they are not erased the new band of the B-range, introduced by Sn ions (Fig. 2).

For discussion of the results it is of interest to consider the location and charge state of Sn ions in the crystals of BSO

Table 1. Estimated the Gaussian band parameters

№	Bi <sub>12</sub> SiO <sub>20</sub> :Sn			Bi <sub>12</sub> SiO <sub>20</sub>		
	Band (eV)	Half width (eV)	Strength (cm <sup>-1</sup> )	Band (eV)	Half width (eV)	Strength (cm <sup>-1</sup> )
1.	0.58	0.02	0.27	–	–	–
2.	0.8	0.018	0.16	–	–	–
3.	1.07	0.037	0.58	1.05	0.04	0.1
4.	1.35	0.04	0.63	1.36	0.039	0.35
5.	1.57	0.04	1.0	1.55	0.04	0.63
6.	1.83	0.04	1.39	1.85	0.038	0.9
7.	2.1	0.039	1.45	2.12	0.04	1.75
8.	2.36	0.04	1.25	2.37	0.041	2.2
9.	2.62	0.04	1.38	2.65	0.041	3.05
10.	2.87	0.025	1.35	2.9	0.022	0.95
11.	3.09	0.024	1.64	3.08	0.019	1.15

Table 2. Probabilities of substitution of structure-forming ions Si<sup>4+</sup> and Bi<sup>3+</sup> by dopant ions in BSO:Sn crystals

Ion	<i>r</i> , Å [10]	c.n. [10]	χ [11]	Substitution of Si <sup>4+</sup> ions		Substitution of Bi <sup>3+</sup> ions	
				<i>Q</i> , kJ/mol	<i>W</i> , arbitrary units	<i>Q</i> , kJ/mol	<i>W</i> , arbitrary units
Si <sup>4+</sup>	0.4	4	1.9	–	–	–	–
Bi <sup>3+</sup>	1.1	1.17	5	2.01	5.1	0.2	–
Bi <sup>5+</sup>	0.9	6	2.01	3.4	0.3	–	–
Sn <sup>4+</sup>	0.4	4	1.8	0.46	2.2	0.52	1.92
Sn <sup>2+</sup>	1.36	8	1.8	4.5	0.22	0.2	5.1
O <sup>2-</sup>	–	–	3.27	–	–	–	–

given that Sn ions can have two degrees of oxidation of Sn<sup>2+</sup> and Sn<sup>4+</sup>.

To this end, the model isomorphism mixing energy "matrix — the impurity ion" can be estimated:

$$Q = a(\Delta r/R_{avg})^2 + b(\Delta s)^2, \quad (1)$$

where *a* and *b* — the constants for given matrix values, Δ*r* — the difference between the ionic radii of replacing each other cations, *R*<sup>\*</sup> — the average length of bonds in the oxygen polyhedron (Si–O, Bi–O), Δ*s* — difference of ionicity *s*<sub>1</sub> and *s*<sub>2</sub> of ties "cation — oxygen ion" [9]. The value of Δ*r* was on the "physical" ionic radii with the coordination number (c. n.) [10]. The ionicity determined according to [9], as *s*<sub>1</sub> = (χ<sub>*k,1*</sub> – χ<sub>0</sub>)/(χ<sub>*k,1*</sub> + χ<sub>0</sub>) and *s*<sub>2</sub> = (χ<sub>*k,2*</sub> – χ<sub>0</sub>)/(χ<sub>*k,2*</sub> + χ<sub>0</sub>), where χ<sub>*k,1*</sub>, χ<sub>0</sub> and χ<sub>*k,2*</sub> — structure-forming electronegativity atoms (Si, Bi), O and Sn atoms, respectively. We used values χ<sub>*k,1*</sub>, χ<sub>0</sub> and

χ<sub>*k,2*</sub> [11] and found Δ*s*<sub>1</sub>, Δ*s*<sub>2</sub> to replace the ions Sn<sup>2+</sup> ions Si<sup>4+</sup> or Bi<sup>3+</sup>, Δ*s*<sub>3</sub>, Δ*s*<sub>4</sub> — ions to replace Sn<sup>4+</sup> ions Si<sup>4+</sup> or Bi<sup>3+</sup>, Δ*s*<sub>5</sub>, Δ*s*<sub>6</sub> — for replacement or Bi<sup>3+</sup> ions Bi<sup>5+</sup> ions Si<sup>4+</sup>, respectively (Table 2).

The *a* and *b* values were estimated using the ratio for the impurity distribution coefficient *K*<sub>*d*</sub> [12]:

$$\ln K_d \approx \approx R^{-1}[(\Delta H(T_{cr}^{-1} - T_f^{-1}) - Q(1.2T_{cr}^{-1} - t^{-1})], \quad (2)$$

where Δ*H*<sub>*f*</sub> is the melting heat; *T*<sub>*cr*</sub>, the crystallization temperature; *T*<sub>*f*</sub>, the melting temperature of dopant; *t* = 1092 K, the empirical constant, *R* = 8.314 J·(mol·K)<sup>-1</sup>. The known thermodynamical Δ*H*, *T*<sub>*cr*</sub>, *T*<sub>*f*</sub> values and distribution coefficient *K*<sub>*d*</sub> = 0.2 and 0.13 for impurity ions Al<sup>3+</sup> and Ga<sup>3+</sup> [4] were used to calculate, from the ratio 2, *Q*<sub>Al</sub> and *Q*<sub>Ga</sub> energies for the crystals BSO:Al

and BSO:Ga, correspondingly. Taking into account the data from [10, 11] and the values  $Q_{Al}$ ,  $Q_{Ga}$ ,  $(\Delta r/R_{avg})$ ,  $\Delta s$  for the cases of  $Si^{4+}$  substitution by the impurity ions  $Al^{3+}$  and  $Ga^{3+}$  [4], we found the coefficient  $a = 1.36 \cdot 10^4$  and  $b = 4.6 \cdot 10^4 \text{ J} \cdot (\text{mol})^{-1}$  from the ratio 1.

Using obtained  $a$  and  $b$  values we estimated energies  $Q$  and the probability evaluation  $W \sim Q^{-1}$  for the inclusion of  $Sn^{4+}$ ,  $Sn^{2+}$  ions into  $Si^{4+}$ ,  $Bi^{3+}$ -sites and  $Si^{4+}$  substitution by  $Bi^{3+}$ ,  $Bi^{5+}$  ions (Table 2).

We found that the most likely replacement of ions  $Si^{4+}$  by ions  $Sn^{4+}$  is in oxygen tetrahedra, a further embodiment is a substituted ions  $Bi^{3+}$  by ions  $Sn^{2+}$  in oxygen distorted octahedra.

To discuss the results we shall take into account that in undoped BSO the PCE may be associated with "antistructural" bismuth ions ( $Bi_{Si}^{3+}$  and  $Bi_{Si}^{5+}$ ) occupied positions of ions  $Si^{4+}$  in oxygen tetrahedra. Model with 3 and 5-valent bismuth positions Si or Ge was proposed in [13]. It was successfully used for prediction and synthesis of the new sillenites in which  $M$ -positions were occupied by different pairs of the 3 and 5-valent ions [14], it was used to explain the physical properties of sillenites, for example, in [15]. Moreover, the presence of ions of  $Bi_{Si}^{3+}$  established with the help of neutron-structural analysis, although the presence of ions  $Bi_{Si}^{5+}$  excluded [16]. However, considering that in [16] the photoactivated centers have not been studied, it is possible to prevent appearance of ions  $Bi_{Si}^{5+}$  as a result of photoionization of  $Bi_{Si}^{3+}$ . For example, formation of the ions  $Bi_{Si}^{4+}$  was detected by magnetic circular dichroism and optical detection of magnetic resonance in  $Bi_{12}GeO_{20}$  crystals illuminated by blue light [17].

Antistructural bismuth ions are responsible mainly for the yellow-brown color of BSO, and deep donor levels in the band gap associated with them shoulder the optical absorption and photoconductivity of the impurity in the shoulder area. PCE is due to the formation centers  $[BiSiO_4]$  and intracenter optical transitions in them [17].

If  $Sn^{4+}$  ions enter to the crystal BSO replacing the holes  $Si^{4+}$  the concentration of antistructural bismuth ions decreases and the crystals BSO:Sn discolor, while PCE weakens. It confirms the identity of the structure of the spectra of additional stationary and photoinduced absorption of crystals BSO and BSO:Sn in the A-region (Fig. 2). For appearance of the new absorp-

tion bands in the B-region the ions  $Sn^{2+}$  may be responsible whose charge is compensated by oxygen vacancies  $V_O^{2+}$ .

Intensification of these bands under the influence of photoactivation, in all probability, is due to the restoration of  $Sn^{4+}$  ions due to photochemical reaction:  $Sn^{4+} + 2e \rightarrow Sn^{2+}$ , accompanied by appearance of the hole centers  $O^-$  at the vertices of oxygen tetrahedra ( $e^-$  — electron charge). Due to interaction of  $O^-$  with the nearest cations the excess (relative to  $O^{2-}$ ) of positive charge (hole) does not belong to centers  $O^-$ , but it is localized on the set of ion-stabilizers  $Sn^{4+}$ , which compensate this charge.

#### 4. Conclusions

The first time stationary and photoinduced optical absorption of the crystals  $Bi_{12}SiO_{20}$  doped with tin have been investigated.

It was found that the impurity Sn causes: a) discoloration of BSO crystals, which exhibits as decreasing of the absorption "shoulder"; b) intensification of the PCE in the spectral region of  $h\nu = 0.5-2.0 \text{ eV}$  and its weakening in the "absorption shoulder" — region of  $h\nu = 2.0-2.8 \text{ eV}$ ; c) stability to optical erasure of the PCE spectral bounds in  $h\nu = 0.5-1.0 \text{ eV}$  range.

It was defined the preferential occurrence of  $Sn^{4+}$  ions in tetrahedral positions  $Si^{4+}$  ions in the presence of a certain amount of ions  $Sn^{2+}$ , whose charge is compensated by oxygen vacancies  $V_O^{2+}$ .

It is proposed the scheme of electronic transitions  $Sn^{4+} + 2e \rightarrow Sn^{2+}$  responsible for the PCE.

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