

# Optical and thermal reducing of photochromic effect in Al doped $\text{Bi}_{12}\text{SiO}_{20}$ crystals

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Results of experimental studying the processes of reversible optical and thermal reducing of the photochromic effect in  $\text{Bi}_{12}\text{SiO}_{20}:\text{Al}$  crystals are presented. It is shown that the optical reducing is the most effective in the region  $h\nu = 0.5 - 2$  eV and at  $h\nu > 1.4$  eV the reducing process passes to excitation of the photochromic effect. The thermal reducing is held in two steps with the ultimate bleaching at  $T^h = 152$  and 208 K. It is suggested the model of electron transitions such as "impurity level — band", where nonstoichiometric ions  $\text{Bi}^{5+}_{\text{Si}}$  (donors) and ions  $\text{Al}^{3+}_{\text{Si}}$  (acceptors) are responsible for impurity levels. Besides intracenter transitions in complexes  $[\text{Al}_{\text{Si}}\text{O}_4]$  make a contribution to the processes of exiting and reducing of the photochromic effect.

**Keywords:**  $\text{Bi}_{12}\text{SiO}_{20}$  crystals, doping, photochromic effect, optical erasure of photochromic effect, thermal erasure of photochromic effect.

Представлены результаты экспериментального исследования процессов обратимого оптического и термического ослабления фотохромного эффекта в кристаллах  $\text{Bi}_{12}\text{SiO}_{20}:\text{Al}$ . Показано, что оптическое гашение наиболее эффективно в диапазоне  $h\nu = 0.5 - 2$  eV, а при  $h\nu > 1.4$  eV процесс ослабления переходит в процесс восстановления фотохромного эффекта. Термическое гашение происходит в два этапа с максимальным обесцвечиванием при  $T^h = 152$  и 208 K. Предложена модель электронных переходов типа "примесной уровень — зона", где за примесные уровни отвечают нестехиометричные ионы  $\text{Bi}^{5+}_{\text{Si}}$  (доноры) и ионы  $\text{Al}^{3+}_{\text{Si}}$  (акцепторы). Кроме того, в процессы возбуждения и гашения фотохромного эффекта вносят вклад внутрицентровые переходы в комплексах  $[\text{Al}_{\text{Si}}\text{O}_4]$ .

**Оптичне і термічне ослаблення фотохромного ефекту у кристалах  $\text{Bi}_{12}\text{SiO}_{20}$ , легованих Al.** А.А.Дяченко, Т.В.Панченко.

Подано результати експериментального дослідження процесів зворотного оптичного і термічного послаблення фотохромного ефекту у кристалах  $\text{Bi}_{12}\text{SiO}_{20}:\text{Al}$ . Показано, що оптичне гасіння найбільш ефективно у діапазоні  $h\nu = 0.5 - 2$  eV, а при  $h\nu > 1.4$  eV процес ослаблення переходить у процес відновлення фотохромного ефекту. Термічне гасіння проходить у два етапи з максимальним знебарвленням при  $T^h = 152$  и 208 K. Запропоновано модель електронних переходів типу "домішковий рівень — зона", де за домішкові рівні відповідають нестехіометричні іони  $\text{Bi}^{5+}_{\text{Si}}$  (донори) та іони  $\text{Al}^{3+}_{\text{Si}}$  (акцептори). Крім того, у процеси збудження та гасіння фотохромного ефекту вносять вклад внутрішньоцентрові переходи у комплексах  $[\text{Al}_{\text{Si}}\text{O}_4]$ .

## 1. Introduction

Photochromic effect (PCE) accompanies processes of recording, treatment and storage

of optical information in photorefractive crystals of sillenite family with general formula  $\text{Bi}_{12}\text{MO}_{20}$  (BMO where M = Si, Ge, Ti,

and some other elements). It is interesting is to study the possibilities of optimization of the PCE characteristics and understand its physical nature.

By now, some information has been accumulated about wide range of the possibilities for modification of photoinduced absorption intensity spectral distribution (PCE spectra) due to doping [1–5]. Investigations on kinetics of changing the parameters of recording information were carried out [6–8], but the questions related with "erasing" (reducing) the PCE were practically not discussed. It is only known that in both pure and doped crystals the PCE may be reduced by either light illuminating from nearby infrared range or by heating to relatively moderate temperatures ( $T = 300 - 500$  K). Taking into consideration a complex spectrum of local electron levels in the forbidden band (width  $\Delta E_g \approx 3.3$  eV) of non-doped sillenites [5], for explanation of the PCE, this or that models for photoinduced redistribution of electrons over these levels have been proposed [1–8]. At this time, it was established that PCE is related with formation of  $F$ -centers  $[\text{Bi}_{\text{Si}}\text{O}_4]$  [5] and intra-center transitions within [5]. In BSO and BGO crystals doped by transition metal ions (Cr, Mn, Cu, Ag, etc.), the PCE is connected with photoinduced changing the charge state of these ions [10, 11]; but the question about induced by them modification of the forbidden band local level structure remains open.

It is known that ions of nontransition metals with stable valence ( $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ) substituting M-cations ( $\text{Si}^{4+}$ ,  $\text{Ge}^{4+}$  or  $\text{Ti}^{4+}$ ) play the role of acceptors compensating donor centers which are caused by intrinsic defects of the nondoped BMO crystals [4]. At that, stationary optical absorption is abruptly drops in whole spectral range of BMO transmittance. It can be assumed that PCE would increase due to photoinduced transfer into empty donor levels however it becomes weaker than in nondoped BMO. Additionally, magneto-optical investigations have shown that PCE in BMO:Al crystals is related with formation of the  $F$ -centers  $[\text{Al}_{\text{Si}}\text{O}_4]$  where ions  $\text{Al}^{3+}$  substitute  $\text{Si}^{4+}$  ions, and charge compensation is realized due to hole centers  $\text{O}^-$ . It is assumed that the PCE spectra are formed at the expense of intra-center transitions [9]. Thus, the question about mechanism of the processes of electrons redistribution over local levels in the forbidden band by photoinduced absorption remains open. Useful information about this

might give study of the processes of optical and thermal erasing PCE in  $\text{Bi}_{12}\text{SiO}_{20}$  (BSO) crystals doped by Al (BSO:Al).

## 2. Experimental

Crystals BSO:Al were grown by the Czochralski method along the crystallographic direction [001]. Al content in the crystals BSO:Al according to data of spectral-emission analysis was 0.5 mass.%. The samples were prepared as a set of plates with thickness  $d = 0.3 \div 5$  mm with large polished planes (001). Because of impact of sillenite previous history on results of their optical and electrophysical measurements according [12], the samples were got into electronic system equilibrium state by heating to 800 K and subsequent low (about a day) cooling in darkness to  $T_0 = 85$  K.

Using spectrophotometer "Cary-4E" at  $T_0$  in the light quantum energy  $h\nu = 0.5 - 3.4$  eV overlapping the band of BSO crystal optical transparency, and spectra of stationary and photoinduced optical transparency were recorded. The crystal photoinduced state was excited by light with quantum energy  $h\nu_1 = 3.3$  eV. Optical erasing of the PCE was carried out by light with quantum energy from the range  $h\nu_2 = 0.5 \div 2.6$  eV. The light source was a halogen lamp HPLA of 600 W power with interference light filters. Thermal erasing of the PCE was realized by fractional heating in the temperature range from 85 to 300 K. To exclude the influence of background lighting, all manipulations were fulfilled under low red lighting which does not excite the PCE.

The procedure was as follows. On the samples brought into equilibrium state, spectra of stationary transmission  $t_0(h\nu)$  were measured. After photoactivation (20 min) of the samples by light with  $h\nu_1$  resulting in unbalancing the electron subsystem, and attaining PCE saturation, the spectra of photoinduced transmission were recorded  $t^{pi}(h\nu)$ . Then step-by-step optical erasing PCE (OE PCE) was carried out using light with  $h\nu_{2,i} = 0.5, 0.6, 0.8, 1, 1.4, 1.8,$  and  $2.6$  eV. The duration of illumination was similar at every stage (10 min). After each stage, the spectra OE PCE  $t^{pd}_i(h\nu)$  were recorded. Thermal erasing PCE (TE PCE) was carried out by heating to temperatures  $T^h_i = 128, 152, 171, 189, 208, 229, 258$  and  $286$  K. The heating temperature was varied linearly with rate  $0.1 \text{ K}\cdot\text{c}^{-1}$ ; after attaining given value  $T^h_i$ , the sample was cooled to

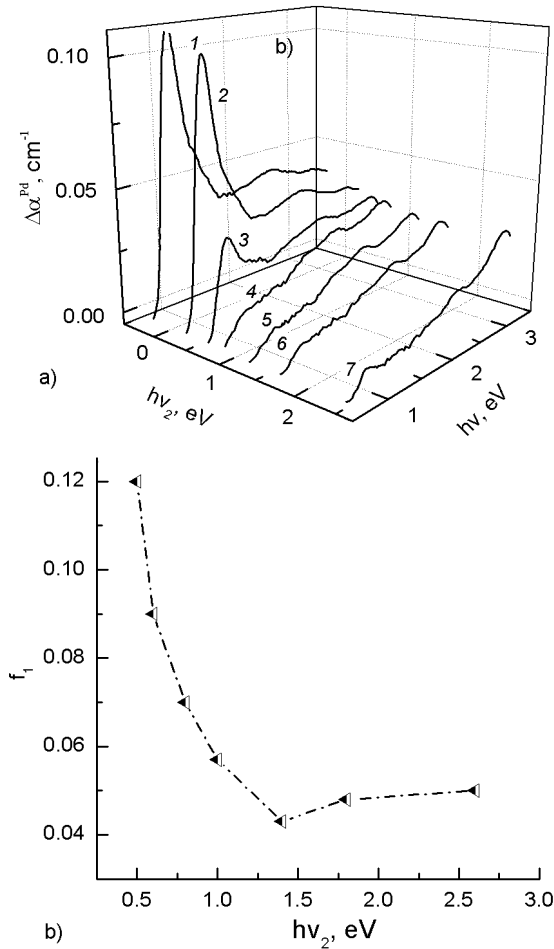


Fig. 1. a) PCE spectra after light illumination with  $h\nu_1 = 3.3$  eV (1) and OE PCE spectra, which was carried out using light with  $h\nu_{2,i} = 0.5$  (2), 0.8 (3), 1.0 (4), 1.4 (5), 1.8 (6) and 2.6 (7) eV; b) function of OE PCE  $f_1(h\nu_2)$ . Dependence of integral photoinduced absorption on light quantum energy  $h\nu_2$ .

initial temperature  $T_0$  and TE PCE transmission spectra  $t^{Td_i}(h\nu)$  were recorded.

There were studied the spectra of stationary absorption  $\alpha_0(h\nu)$  corresponding to transmission spectra, and difference spectra characterizing saturated PCE  $\alpha^{PCE}(h\nu) = \alpha^{Pi}(h\nu) - \alpha_0(h\nu)$ , where  $\alpha^{Pi}(h\nu)$  — absorption after light photoactivation with  $h\nu_1$ , as well as spectra OE PCE  $\Delta\alpha^{Pd_i}(h\nu)$  and TE PCE  $\Delta\alpha^{Td_i}(h\nu)$ :  $\Delta\alpha^{Pd_i}(h\nu) = \alpha^{PCE}(h\nu) - \alpha^{Pd_i}(h\nu)$  and  $\Delta\alpha^{Td_i}(h\nu) = \Delta\alpha^{PCE}(h\nu) - \alpha^{Td_i}(h\nu)$ , where  $\alpha^{Pd_i}(h\nu)$  — absorption after reducing PCE using light with  $h\nu_{2,i}$ ,  $\alpha^{Td_i}(h\nu)$  — absorption after heating to  $T^h_i$ , respectively. Additionally, there were determined dependences of integral absorption on the light quantum energy  $h\nu_{2,i}$  and tem-

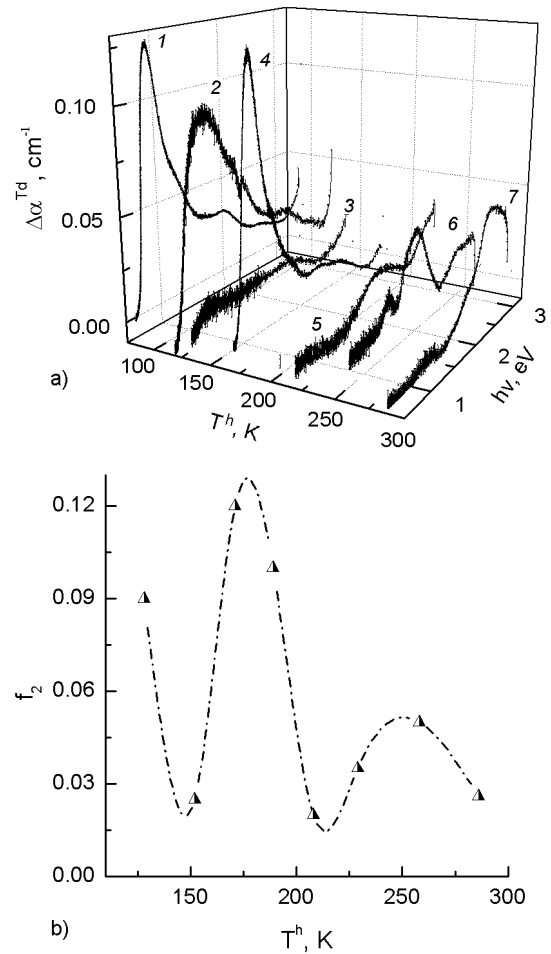


Fig. 2. a) PCE spectra after light illumination with  $h\nu_1 = 3.3$  eV (1) and TE PCE spectra, which was carried out by heating to temperatures  $T^h_i = 128$  (2), 158 (3), 171(4), 229 (5), 258 (6) and 286 (7) K; b) function of TE PCE  $f_2(T^h)$ . Dependence of integral photoinduced absorption on temperature  $T^h_i$ .

perature  $T^h_i$ , characterizing the OE PCE and TE PCE.

The absorption spectra  $\alpha(h\nu)$  were calculated from the ratio:

$$t = (1 - R)^2 \exp(-\alpha d) / (1 - R^2 \exp(-2\lambda d)) \quad [13].$$

### 3. Results and discussion

Results obtained are the following. The procedure of the PCE optical erasing give a family set of spectra  $\Delta\alpha^{Pd}(h\nu, h\nu_2)$ , where  $h\nu_2$  is the parameter determining quantum energy of the erasing light (Fig. 1a). The OE PCE function  $f_1(h\nu_2)$ , characterizing the variation of integral photoinduced absorption passes through a minimum at  $h\nu_2 = 1.4$  eV (Fig. 1b). Using the technique from [14], the spectra  $\Delta\alpha^{Pd}(h\nu)$  were resolved into

Table. Intensity ratio of the individual Gaussian components in OE PCE and TE PCE spectra

Method of erasing PCE	Region	Spectral positions $h\nu_{max}$ , eV	Intensity ratio of the Gaussian components		
Optical	A	2.71	0.89	0.97	1.04
		2.95	0.92	1.03	1.1
		3.3	0.97	1.0	1.15
	B	0.8	0.57	0.59	0.58
		1.17	0.71	0.72	0.7
		1.74	0.86	0.84	0.85
Thermal	A	2.71	0.11	0.4	2.3
		2.95	0.3	0.9	2
		3.3	0.4	0.95	2.5
	B	0.8	0.13	1.5	0.16
		1.17	0.1	1.3	0.12
		1.74	0.3	1.45	0.33

individual Gaussian components, spectral positions  $h\nu_{max}$  being a series: 0.8, 1.17, 1.52, 2.16, 2.71, 3.16 and 3.3 eV. It is interesting that intensity dependences of  $\Delta\alpha^{Pd}(h\nu, h\nu_2)$  spectra components on the  $h\nu_2$  value are found to be different for the high- and low-energy spectral ranges (A, where  $h\nu \approx 2 - 3.3$  eV, and B, where  $h\nu = 0.5 - 2$  eV). The intensities of components forming the dominant band of the PCE spectra in B-range decrease monotonically with  $h\nu_2$  increasing, their ratio being constant (Table). The intensities of the components from A-range, as  $h\nu_2$  increases, pass through the minimum at  $h\nu_2 \approx 1.4$  eV that is the PCE spectrum is completely restorable under specified condition. It indicates the reversibility of the process "excitation — optical reducing PCE".

The procedure of thermal erasing PCE gives a family set of spectra  $\Delta\alpha^{Td}(h\nu, T^h)$ , where  $T^h$  is temperature as the parameter determining the erasing thermal energy (Fig. 2a). The TE PCE function  $f_2(T^h)$ , characterizing variation of integral photoinduced absorption passes through maxima at  $T^h = 171$  and 258 K (Fig. 2b). Under thermal erasing PCE, the dependences of  $\Delta\alpha^{Td}(h\nu, T^h)$  spectra component intensities versus  $T^h$  are found to be also different for A- and B-ranges, their intensity ratio does not remain for both (A and B) ranges (Table). The intensities of components from A-range pass through minima at  $T^h = 152$  and 208 K that indicates changing the process of thermal erasing the PCE by the process of exciting the thermochromic effect. Consequently,

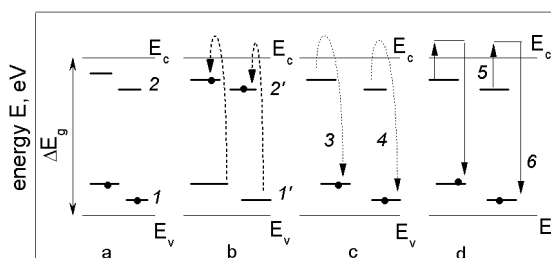


Fig. 3. a) Initial stationary state (1 — acceptor levels, 2 — donor levels); b — photoionization with appearing PCE (emptying acceptors 1', filling donors 2'); c — optical erasure of PCE; d — temperature erasure of PCE.

the TE PCE don't exclude the ability of the material to PCE.

The results obtained unambiguously indicate the existence of at least three types of centers responsible for the PCE. For explaining the peculiarities of the OE PCE and TE PCE processes we apply the band model of BSO:Al crystals (Fig. 3).

It is known that  $Al^{3+}$  ions substituting in BSO:Al crystals  $Si^{4+}$  ions in the centers of oxygen tetrahedral form  $Al^{3+}_{Si}$  centers playing the role of acceptors [4, 5]. Decolorization of the BSO:Al crystals indicates partial compensating by these acceptors those donor centers created by intrinsic BSO defects. Such donors may be antistructural ions  $Bi^{5+}_{Si}$  under substituting  $Si^{4+}$  ions ( $Bi^{5+}_{Si}$ ) [15]. Then, in initial stationary state, BSO:Al crystals contain ionized acceptors and donors (Fig. 3a). Under photoionization, with appearing the PCE, elec-

trons leaving acceptor levels return onto small donors (Fig. 3b). Besides, oxygen ions can supply electrons in oxygenic crystals. Under illumination electrons transition from valence band with the next capture to the electron traps is possible. Herewith, the hole  $p$  in the valence band is captured by oxygen ion  $O^{2-} + p \rightarrow O^-$ . Interacting with  $Al^{3+}_{Si}$  they form  $[Al_{Si}O_4]$  centers which were found by magneto-optical methods [9]. The OE PCE means, under action of light quanta with energy less than need for excitation PCE, returning the electrons from the low donor levels onto acceptor ones (transitions 3 and 4, Fig. 3c). The TE PCE provides thermal ionization of the deep donors by electrons from valence band (Fig. 3d). This mechanism is confirmed by the fact that temperature position of the peaks of the curve  $f_2(T^h)$  for TC PCE  $T_{max1} = 189$  K and  $T_{max2} = 258$  K (Fig. 2b) correlate with the position of the thermally stimulated conductivity peaks (transitions 5, Fig. 3d) and the thermoluminescence peaks (transition 6, Fig. 3d) [12, 16].

#### 4. Conclusions

The question about nature of the processes which are responsible for PCE, as well as reversible OE PCE and TE PCE in  $Bi_{12}SiO_{20}:Al$  crystals were investigated.

It was suggested the model of electron transitions under exiting and reducing PCE which is based on existence of three types of defects: acceptor centers  $Al^{3+}_{Si}$ , donor centers  $Bi^{5+}_{Si}$  and complexes  $[Al_{Si}O_4]$ .

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