Excitation and erasure of photochromic effect in the $Bi_{12}SiO_{20}$ (BSO) crystals doped with Al, Ga and Sn

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Abstract. We present the results of experimental investigations of the processes of excitation and erasure of photochromic effect (PCE) in undoped $Bi_{12}SiO_{20}$ (BSO) crystals and the BSO crystals doped with Al, Ga and Sn ions (BSO:Al, BSO:Ga and BSO:Sn, respectively). The PCE spectra, the spectra of optical erasure of the PCE (OE PCE), as well as the PCE excitation and PCE erasure functions are obtained. It is demonstrated that the sets of individual components of the PCE spectra for the doped crystals are very similar for different impurity ions, though the intensities of those components are different. Doping of BSO manifests itself in weakening PCE in the blue-green region of the spectrum and its strengthening in the spectral region given by $hv = 0.5 \div 2.0$ eV. The OE PCE is almost complete and the components that cannot be erased are observed only for the BSO:Sn crystals. We have evidenced that a limiting photon energy ($hv^* \approx 2$ eV) exists, for which the photoexcitation leads to the PCE for the crystals staying in their initial stationary state, but erases the PCE if the crystals passed into the state with the maximal saturated PCE.

1. Introduction

Sillenite crystals $Bi_{12}MO_{20}$ with M = Si, Ge, and Ti (abbreviated hereafter as BMO) are efficiently applied in different optoelectronic devices [1]. Recording, processing and storage of optical information are often based on the photorefractivity and the photochromic effect (PCE) in those crystals, as well as on their high photosensivity in the blue-green spectral region. A large number of those applications imply a demand for optimized optical and photoelectric properties of BMO, e.g., using their doping. It is well-known that Al, Ga, Ca and B impurity ions decrease the photoconductivity and the optical absorption, weaken the PCE, improve the electro-optics [2–5], and have a significant influence on the operational characteristics of spatial light modulators [6, 7]. Cu, Al, Mn and Ni ions impose a number of non-stationary effects such as differentiation of excitation intensity for the holographic gratings, erasure of their diffraction efficiency, non-smoothness of recording and destruction (readout) kinetics for 3D holograms [8], and instability of photoinduced absorption in the BMO crystals.

The influence of the impurity ions is determined by the changes they introduce in the structure of local energy states of the band gap and/or in the dominating mechanism of electronic transitions. Up to date, some regularities of the changes in the functional characteristics of BMO depending on the character of intra-centre electronic transitions for 3d ions (Cr, Mn, Fe, Cu, Ni

and Co) have been unveiled [9–12]. New results concerning the trap levels, deep centres and the quasi-dipoles available in the BMO crystals doped with non-transition metal ions have been obtained, using the methods of thermo-activation and optical spectroscopy [5]. However, these results are partly inconsistent and still not sufficient for deep generalizations (for instance, for unravelling a role of the impurity level-to-gap transitions). Here useful information can be expected from the studies of the PCE occurring in BMO doped with different *p*-elements.

In the present work we report the results concerned with the features of excitation and erasure of the PCE in $Bi_{12}SiO_{20}$ (BSO) doped with the *p*-elements having $3sp$, $4sp$ and $5sp$ electronic configurations, BSO:Al ($3s^2 3p^1$), BSO:Ga ($4s^2 4p^1$), and BSO:Sn ($5s^2 5p^2$) crystals.

2. Experimental

BSO, BSO:Al, BSO:Ga and BSO:Sn crystals were grown with a Czochralski method along the crystallographic direction [001]. According to the spectral emission analyses, the contents of the impurity ions in our crystals were equal to 0.046 (BSO:Al), 0.05 (BSO:Ga) and 0.12 (BSO:Sn) mass %. Samples for investigations were prepared in the shape of polished plates, with the thicknesses 0.3÷5.0 mm and large (001) faces. Prior to the PCE analysis, all the samples were brought to equilibrium by heating them up to 800 K and then slowly (for several days) cooling down to $T_0 = 85$ K in darkness.

The spectra of steady-state and photo-induced optical transmissions were detected with a Cary-4E spectrophotometer at $T = T_0$. This was done at the photon energies $hv = 0.5÷3.4$ eV that cover the entire region of optical transparency of the BSO crystals. Photo-induced states of the samples were excited and erased using the light with the photon energies $hv_1 = 2÷2.8$ eV and $hv_2 = 0.5÷2.3$ eV, respectively. A 600 W HLPA halogen lamp equipped with interference filters was utilized for that aim.

The experimental procedures were as follows. At first, steady-state optical transmission spectra $t_0(hv)$ were measured for the samples brought to the equilibrium state. After that the samples were photo-activated for 10 min by the photons hv_1, so that the electronic subsystem leaved the equilibrium state. Then the spectra of photo-induced transmission $t^{pi}(hv, hv_1)$ were recorded, with hv_1 being a parameter. Finally, the samples were illuminated by the light with $hv_2 \leq hv_1$, thus returning the electronic subsystem to the equilibrium state. The $t^{pd}(hv, hv_2)$ spectra (with hv_2 being a parameter) that characterize the optical erasure (OE) of the photo-induced transmission were measured. For eliminating any backlight influences, all the manipulations (heating a sample or placing it into a cryostat) were carried out using a weak red illumination, which did not cause the PCE.

We measured the steady-state absorption spectra $\alpha_0(hv)$, the absorption spectra $\alpha^{pi}(hv)$ after photo-activation, the spectra $\alpha^{pd}(hv)$ of optical erasure of the PCE (OE PCE) corresponding to the transmission spectra, and then calculated the difference spectra characterizing respectively the PCE and its optical erasure:

$$\Delta\alpha^{pi}(hv) = \alpha^{pi}(hv) - \alpha_0(hv),$$

$$\Delta\alpha^{pd}(hv) = \alpha^{pi,max}(hv) - \alpha^{pd}(hv),$$

where $\alpha^{pi,max}$ represents the maximal photo-induced absorption (i.e., the saturated PCE).

Besides, we calculated the function of PCE excitation $f_1(hv_1) = \int_{0.5}^{3.5} \Delta\alpha^{pi} dhv(hv_1)$ (the integral absorption that characterizes the PCE depending on the energy of exciting photons) and

the function of OE PCE $f_2\left(hv_2\right) = \int\limits_{0.5}^{3.5} \Delta\alpha^{pd}\,dhv\left(hv_2\right)$ (the integral absorption that characterizes the dependence of OE PCE on the energy of photons erasing the PCE). The absorption spectra were obtained following the technique described in Ref. [13].

3. Results and discussion

The results derived in our experiments are as follows. Doping of the BSO crystals with Al, Ga and Sn ions changes their tint from yellowish-brown to almost colourless. The effect depends on the exact contents and types of the impurities and the colour can change from pale-pinkish (BSO:Al) to smoky (BSO:Ga) or greenish (BSO:Sn).

As it has already been mentioned for the BSO:Al and BSO:Ga crystals [2, 3], the steady-state optical absorption spectra of all the doped crystals are weakly structured. Contrary to the BSO crystals, they do not manifest a well-known optical absorption shoulder correlated in its spectral position with the maximal impurity-induced photoconductivity in BSO, which is located in the blue-green spectral region. The Al, Ga and Sn ions induce one more common effect, a strong fall in the absorption observed in the overall spectral range under test and a short-wavelength shift of the fundamental absorption edge (by $0.1 \div 0.2$ eV, as compared with BSO). However, the absorption of the BSO:Sn crystals increases in the near-infrared, unlike the case of BSO [14]. It is well-known that a yellow-brown colour of undoped BSO mainly stems from its intrinsic nonstoichiometric defects, in particular antistructural defects and ions substituting Si^{4+} in the centres of oxygen tetrahedra. The presence of those ions has been revealed by means of neutron structural investigations [15], and they have been identified using the methods of magnetic circular dichroism and optical detection of the magnetic resonance [16]. Notice that discoloration of the BSO crystals points to partial compensation of Al^{3+}, Ga^{3+} and Sn^{4+} ions by the intrinsic defects in BSO and the fact that these ions substitute Si^{4+}. Furthermore, some additional colour centres can be imposed by the Sn^{2+} ions.

The spectra of photo-induced absorption $\alpha^{pi}(hv)$ for the pure and doped BSO crystals are sufficiently different with respect to the character of their intensity distributions. However, these crystals have the two spectral regions, A and B, in common, which are defined respectively by the photon energies $hv \approx 2 \div 3.3$ and $0.5 \div 2$ eV. The Al, Ga and Sn ions decrease the photo-induced absorption in the region A and increase it in the region B.

As seen from Fig. 1, the PCE spectra $\Delta\alpha^{pi}(hv)$ have a complex structure. Using the procedures suggested in Ref. [17], we have decomposed the spectra into their individual Gaussian constituents i. This technique allows for determining the number of the components, and their spectral positions and half-widths, with no a priori knowledge on those parameters. Similar spectral positions $(hv_{max,i})$ and close half-widths for the components i of the PCE observed in BSO, BSO:Al, BSO:Ga and BSO:Sn have been obtained for the region A, with only slight differences among the intensities. Most probably, these bands are associated with the intrinsic defects occurring in BSO. On the other hand, new PCE bands appear inside the region B after Al, Ga and Sn ions are incorporated (see Table 1).

Under illumination of the BSO crystals by the photons with the energy hv_2, we obtain almost complete optical erasure of all the PCE bands, and both the OE PCE spectra $\Delta\alpha^{pd}(hv)$ and the PCE spectra manifest a 'mirror' symmetry (see Fig. 1). In case of the BSO:Sn crystals, the erasure of all of the PCE bands cannot be achieved. As seen from Fig. 1b, the bands located in the region B, which are formed by the Sn ions, are not erased.
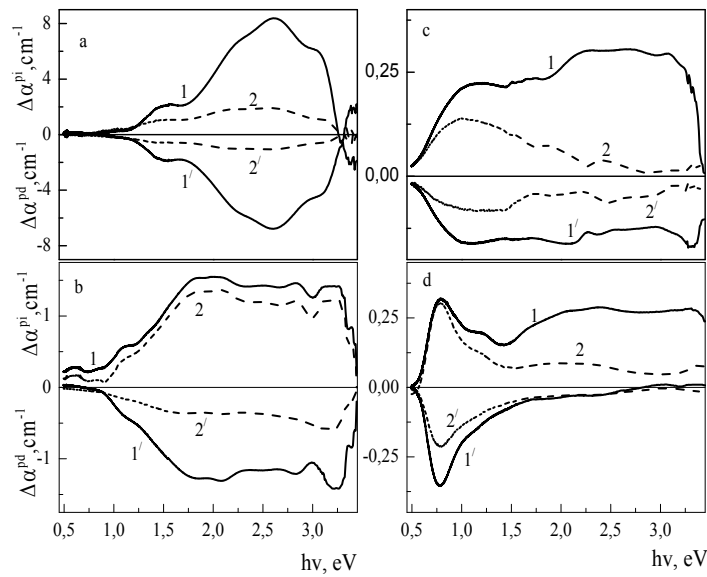
Fig. 1. PCE spectra $\Delta\alpha^{pi}(hv)$ (1, 2) detected under light illumination with hv_1 = 3.35 (1) and 2.27 eV (2), and OE PCE spectra $\alpha^{pd}(hv)$ (1′, 2′) detected under light illumination with hv_2 = 1 (1′) and 2.2 eV (2′). Panels (a), (b), (c) and (d) correspond respectively to BSO, BSO:Sn, BSO:Ga and BSO:Al.

Table 1. Estimated parameters of individual Gaussian bands identified in our experimental spectra (see the text).

Crystal	$Bi_{12}SiO_{20}$:Sn			$Bi_{12}SiO_{20}$:Al			$Bi_{12}SiO_{20}$:Ga		
Para-meter	Band (eV)	Halfwidth (eV)	Strength (cm^{-1})	Band (eV)	Halfwidth (eV)	Strength (cm^{-1})	Band (eV)	Halfwidth (eV)	Strength (cm^{-1})
1	0.58	0.02	0.27	–	–	–	–	–	–
2	0.8	0.018	0.16	0.8	0.04	0.31	0.8	0.041	0.11
3	1.07	0.037	0.58	1.17	0.038	0.17	1.09	0.045	0.17
4	1.35	0.04	0.63	1.52	0.037	0.12	1.45	0.045	0.14
5	1.57	0.04	1.0	1.74	0.038	0.14	1.6	0.045	0.16
6	1.83	0.04	1.39	1.95	0.037	0.16	1.86	0.042	0.16
7	2.1	0.039	1.45	2.16	0.04	0.18	2.12	0.04	0.19
8	2.36	0.04	1.25	2.42	0.041	0.23	2.37	0.041	0.23
9	2.62	0.04	1.38	2.71	0.041	0.22	2.66	0.041	0.25
10	2.87	0.025	1.35	2.95	0.018	0.26	2.88	0.026	0.19
11	3.09	0.024	1.64	3.16	0.026	0.21	3.1	0.026	0.19
12	3.2	0.023	1.4	3.37	0.026	0.23	3.26	0.026	0.17

The analysis of the functions $f_1(hv_1) = \int_{0.5}^{3.5} \Delta\alpha^{pi} dhv(hv_1)$ and $f_2(hv_2) = \int_{0.5}^{3.5} \Delta\alpha^{pd} dhv(hv_2)$ has shown an interesting feature in the PCE excitation and erasure. For all of our crystals, there is a

threshold photon energy $hv^* \approx 2$ eV. This light excites the PCE if the crystal remains in its stationary state and erases the PCE if it has passed to the photo-excited state (see Fig. 1).

For further discussion of the feature mentioned above one must take into account that the PCE in undoped BSO is associated with formation of the photochromic centres [16]. Similarly, $[Al_{Si}O_4]$, $[Ga_{Si}O_4]$ and $[Sn_{Si}O_4]$ centres are formed in the BSO:Al, BSO:Ga and BSO:Sn crystals, in which Al^{3+}, Ga^{3+} and Sn^{4+} ions substitute Si^{4+}, whereas the charge compensation for Al^{3+} and Ga^{3+} is provided by the hole centres O^- [14, 18, 19]. It is important that, in all the cases, the absorption spectra are formed by the intra-centre transitions. Then the availability of the threshold photon energy hv^* can be explained using a configuration coordinate model shown in Fig. 2.
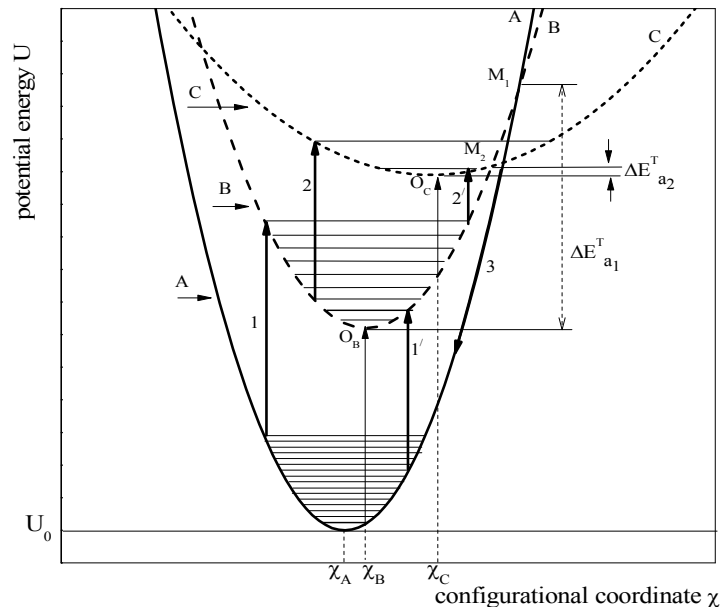

Fig. 2. Configuration coordinate diagram explaining excitation and erasure of the PCE in our crystals: dependences of potential energy U of photochromic $[Al_{Si}O_4]$ centres on the configuration coordinate χ for a stationary state (A), a photo-induced PCE-determining state (B) and a state causing PCE erasure (C).

In Fig. 2, the transitions $1–1'$ correspond to the photon energy ranges and the coordinates χ for which the PCE is excited. The energy difference between the crossing point (M_1) and the minimum energy (O_B) in the curve B determines the energy $\Delta E_{a_1}^T$ of thermal PCE erasure, which is required for thermally activating the B→A transitions. This idea agrees with the experimental data which testifies that the PCE disappears whenever BSO:Al, BSO:Ga and BSO:Sn are heated up to the room temperature. The transitions $2–2'$ indicate filling of the electronic levels of the excited state C, which is a final state for the photochromic centres irradiated from the hv_2 region. The $1–1'$ and $2–2'$ regions have the same limiting energies hv^* corresponding to the $1'$ and 2 transitions, a minimum for the PCE excitation and a maximum that limits the B→C transitions. The energy difference between the crossing point M_2 of the C and A curves and the minimum energy (O_C) in the curve C determines the energy $\Delta E_{a_2}^T$ of thermal PCE erasure for the C→A transitions. Finally, the case $\Delta E_{a_2}^T \ll \Delta E_{a_1}^T$ means a possibility for the C→A transitions with the activation energy close to zero, i.e. the OE PCE (and the three transitions) occurring at the temperatures lower than the room one.

4. Conclusions

Summing up our results, we have shown that the main features of the excitation and erasure of the PCE observed in the BSO:Al, BSO:Ga and BSO:Sn crystals, in which the Si^{4+} ions are isomorphically substituted with Al^{3+}, Ga^{3+} and Sn^{4+}, are governed by the intra-centre electronic transitions occurring in the photochromic centres $[Al_{Si}O_4]$, $[Ga_{Si}O_4]$ and $[Sn_{Si}O_4]$.

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Анотація. *У роботі представлено результати експериментального дослідження процесів збудження і стирання фотохромного ефекту (ФХЕ) в нелегованих кристалах $Bi_{12}SiO_{20}$ (BSO) і кристалах BSO, легованих іонами Al, Ga та Sn (BSO:Al, BSO:Ga, BSO:Sn, відповідно). Отримано спектри ФХЕ і оптичні спектри стирання ФХЕ (ОС ФХЕ), а також функції збудження і стирання ФХЕ. Показано, що набір спектральних компонент ФХЕ для всіх легованих кристалів майже незмінний, а різні домішкові йони відрізняються лише за співвідношеннями відповідних інтенсивностей. Легування кристалів BSO виявляється в послабленні ФХЕ в зелено-голубій області спектру і його посиленні в області hv = 0.5÷2.0 еВ. ОС ФХЕ практично довершений – лише для кристалів BSO:Sn спостерігаються компоненти, які не вдається стерти. Встановлено існування граничної енергії фотонів hv* ≈ 2 еВ, для якої фотозбудження приводить до появи ФХЕ в кристалах зі стаціонарними вихідними станами, але до стирання ФХЕ в кристалах, які перебувають у стані максимального насичення ФХЕ.*