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THE FEATURES OF EXCITATION AND ERASURE OF PHOTOCHROMIC EFFECT IN $Bi_{12}SiO_{20}$ CRYSTALS DOPED BY Al, Ga AND Sn

The results of experimental investigations of the processes of excitation and erasure of photochromic effect (PCE) in $Bi_{12}SiO_{20}$ crystals, undoped and doped by Al, Ga and Sn ions (BSO, BSO:Al, BSO:Ga, BSO:Sn, respectively) are presented. Complex PCE spectra and PCE optical erasure spectra (OE PCE) as well as PCE excitation and PCE erasure functions were obtained. It was shown that the set of individual components for PCE spectra of doped crystals is almost similar for different impurity ions with a different ratio between intensities of these components. The BSO doping is observed in weakening of PCE within the blue-green range of the spectrum and its rise within the spectral range of $h\nu$ = 0.5 - 2.0 eV. OE PCE is almost complete, only for BSO:Sn crystals the components that cannot be erased can be observed. An existence of the limiting photon energies ($h\nu^* \approx 2$ eV) which are the reason of PCE for the crystals in a stationary initial state is determined. However, it leads to the PCE erasure if the crystals are in the state with maximum saturated PCE.

Keywords: $Bi_{12}SiO_{20}$ crystals, doping by Al, Ga and Sn ions, photochromic effect, optical erasure of photochromic effect.

Подано результати експериментальних досліджень процесів збудження та гасіння фотохромного ефекту (ФХЕ) у кристалах $Bi_{12}SiO_{20}$, нелегованих і легованих іонами Al, Ga і Sn (BSO, BSO:Al, BSO:Ga,.BSO:Sn, відповідно). Отримано складно-структуровані спектри ФХЕ, спектри його оптичного гасіння (ОГ ФХЕ), а також функції збудження та гасіння ФХЕ. Показано, що набір індивідуальних компонент спектрів ФХЕ легованих кристалів практично однаковий, відмінним для різних домішок є лише співвідношення інтенсивностей цих компонент. Вплив легування на фотохромізм кристалів BSO полягає в ослабленні ФХЕ у синьо-зеленій області спектра та його підсиленні в спектральному діапазоні з $h\nu$ = 0.5 - 2.0 еВ. ОГ ФХЕ виявляється практично повним, лише для кристалів BSO:Sn присутні необоротні компоненти в ближній інфрачервоній області спектру. Встановлено, що існує граничне значення енергії квантів світла ($h\nu^* \approx 2$ еВ), фотозбудження яке зумовлює ФХЕ, якщо досліджувані кристали знаходяться в стаціонарному вихідному стані. Однак, це приводить до гасіння ФХЕ, якщо кристали приведені у стан з максимальним, насиченим ФХЕ.

Ключові слова: кристали $Bi_{12}SiO_{20}$, легування іонами Al, Ga і Sn, фотохромний ефект, оптичне гасіння фотохромного ефекту.

Представлены результаты экспериментальных исследований процессов возбуждения и гашения фотохромного эффекта (ФХЭ) в кристаллах $Bi_{12}SiO_{20}$, нелегированных и легированных ионами Al, Ga и Sn (BSO, BSO:Al, BSO:Ga, BSO:Sn, соответственно). Получены сложно-структурированные спектры ФХЭ и его оптического гашения (ОГ ФХЭ), а также функции возбуждения и гашения ФХЭ. Показано, что набор индивидуальных компонент спектров ФХЭ легированных кристаллов практически одинаков, отличительным для разных примесей оказывается лишь соотношение интенсивностей этих компонент. Влияние легирования на фотохромизм кристаллов BSO состоит в ослаблении ФХЭ в сине-зеленой области спектра и его усилении в спектральной диапазоне с $h\nu$ = 0.5 - 2.0 эВ. ОГ ФХЭ является практически полным, только для кристаллов BSO:Sn можно выделить необратимые компоненты в ближней инфракрасной области спектра. Установлено, что существует граничное значение энергии квантов света ($h\nu^* \approx 2$ эВ), фотовозбуждение которыми обусловливает ФХЭ, если исследуемые кристаллы находятся в стационарном исходном состоянии. Однако, это приводит к гашению ФХЭ, если кристаллы переведены в состояние с максимальным, насыщенным ФХЭ.

Ключевые слова: кристаллы $Bi_{12}SiO_{20}$, легирование ионами Al, Ga и Sn, фотохромный эффект, оптическое гашение фотохромного эффекта.

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1. Introduction

Sillenite $Bi_{12}MO_{20}$ (BMO, where M = Si, Ge, Ti) crystals are effectively applied in different optoelectronic devices [1]. Recording, processing and storage of optical information are based on the photorefractive and photochromic effects as well as on the high photosensitivity of these crystals in the blue-green region of the spectrum. A large number of practical applications determine the demand for optimization of optical and photoelectric properties of BMO (for instance, by doping). It is well-known that Al, Ga, Ca, and B impurity ions result in decreasing the photoconductivity and optical absorption, in weakening the photochromic effect (PCE), and in improving the electro-optical properties [2-5], They sufficiently influence on the characteristics of spatial light modulators, too [6,7]. Cu, Al, Mn and Ni ions lead to the number of non-stationary effects (a differentiation of excitation intensity for holographic gratings, an erasure of their diffraction efficiency, a non-smoothness of recording and destruction (at the readout) kinetics for 3D holograms [8], and an instability of the photo-induced absorption in BMO crystals).

An influence of impurity ions is determined by the changes which they cause in the structure of the local energy states of the band gap (BG) and/or in the dominate mechanism of electronic transitions.

The number of regularities in the changes of BMO functional characteristics, depending on the character of intracenter electronic transitions for 3d ions (Cr, Mn, Fe, Cu, Ni, Co) has been revealed by now [9-12]. New data, concerning trap levels, deep centers and quasidipoles in BMO crystals doped by ions of non-transition metals were obtained by using the methods of thermo-activation and optical spectroscopy [5]. However these data are scattered, partly inconsistent and not sufficient for generalizations, for instance, for determination of the role of impurity level – gap transitions. Useful information can be obtained from investigation of PCE in BMO crystals doped by different *p*-elements.

The results of investigation of the features of excitation and erasure of PCE in $Bi_{12}SiO_{20}$ (BSO) crystals doped by *p*-elements with 3, 4 and 5 sp-electronic configurations BSO:Al ($3s^2 3p^1$), BSO:Ga ($4s^2 4p^1$) and BSO:Sn ($5s^2 5p^2$) are presented in the paper.

2. Experiment

BSO, BSO:Al, BSO:Ga and BSO:Sn crystals were grown by Czochralski method along [001] crystallographic direction. The content of impurity ions in the crystals according to the spectral emission analysis was equal to 0.046 (BSO:Al), 0.05 (BSO:Ga) and 0.12 (BSO:Sn) mass.%. Samples were prepared in the form of the set of polished plates of 0.3 ÷ 5 mm thickness with large (001) planes. Before PCE analysis all samples were brought to equilibrium by heating up to 800 K and subsequent slow (few days) cooling in darkness down to T_0 = 85 K.

The spectra of steady-state and photo-induced optical transmission were registered by Cary-4E spectrophotometer at T=T0 in the range of photon energies hν = 0.5 - 3.4 eV, covering the entire optical transparent region of BSO crystal. Photo-induced states of the samples were excited and erased by the light with photon energies $h\nu_1 = 2 \div 2.8$ eV and $h\nu_2 = 0.5 \div 2.3$ eV, respectively, using 600 W HLPA halogen lamp equipped with interference filters. The procedure was as follows. At first, for the samples brought to equilibrium state the steady-state transmission spectra $t_0(h\nu)$ were measured. After photo-activation of the samples by the light with $h\nu_1$ (10 min) leading to transition of electronic subsystem out of the equilibrium state, the spectra of photo-induced transmission $t^{pi}(h\nu, h\nu_1)$ with $h\nu_1$ as a parameter were taken.

After that the samples were illuminated by the light with $h\nu_2 \leq h\nu_1$ providing the return of the electronic subsystem to an equilibrium state and $t^{pd}(h\nu, h\nu_2)$ spectra (with $h\nu_2$

as a parameter) characterizing the optical erasure (OE) of photo-induced transmission were registered. For elimination of the backlight influence all manipulations (warming, placing a sample in the cryostat) were carried out using a weak red illumination, which does not cause PCE.

The steady-state absorption spectra $\alpha_0(h\nu)$, the absorption spectra after photo-activation $\alpha^{pi}(h\nu)$ and the PCE optical erasure spectra $\alpha^{pd}(h\nu)$ corresponding to transmission spectra, also the difference spectra characterizing PCE and its optical erasure were taken: $\Delta\alpha^{pi}(h\nu) = \alpha^{pi}(h\nu) - \alpha_0(h\nu)$ and $\Delta\alpha^{pd}(h\nu) = \alpha^{pi,max}(h\nu) - \alpha^{pd}(h\nu)$, respectively, where $\alpha^{pi,max}$ presents maximum photoinduced absorption (saturated PCE).

Besides the function of PCE excitation $f_1(h\nu_1) = \int_{0.5}^{3.5} \Delta\alpha^{pi} dh\nu(h\nu_1)$ - integral absorption characterizing PCE in dependence on the energy of excitation photons and function of optical PCE erasure $f_2(h\nu_2) = \int_{0.5}^{3.5} \Delta\alpha^{pd} dh\nu(h\nu_2)$ – integral absorption characterizing OE PCE dependence on the energy of photons erasing PCE were investigated. The absorption spectra were calculated by the method [13].

3. Results and discussion

The obtained results are as follows. Doping of BSO crystals by Al, Ga and Sn ions leads to the change of their tint from yellowish-brown to almost colorless ones. Their tone depends on the content and type of impurities changing from pale-pinkish (BSO:Al) to smoky (BSO:Ga) or greenish one (BSO:Sn).

The steady-state optical absorption spectra of all investigated doped crystals are weakly structured as was mentioned before for BSO:Al and BSO:Ga [2, 3]. Contrary to BSO crystals, they do not have the well-known shoulder of optical absorption correlating with the spectral position of maximum impurity photoconductivity of BSO in the blue-green spectral range. The similarity between influences of Al, Ga and Sn ions is also in the strong fall of absorption in all investigated region and short-wavelength shift of the edge of fundamental absorption for 0.1 ÷ 0.2 eV (relative to BSO).

However, an increase of BSO:Sn crystal absorption compared with the BSO crystal one is revealed within the near infrared spectral region [19]. It is well-known that yellow-brown color of undoped BSO is mainly determined by its own non-stoichiometrical defects: antistructural and ions substituting Si^{4+} ions in the centers of oxygen tetrahedra. The presence of ions was proved by neutron structural investigations [14]; the ions were revealed by the methods of magnetic circular dichroism and optical detected magnetic resonance [15]. A discoloration of BSO crystals is observed at the partial compensation of Al^{3+}, Ga^{3+} and Sn^{4+} ions by intrinsic BSO defects at their substitution of Si^{4+} ions. An additional color centers can be determined by Sn^{2+} ions.

Spectra of photoinduced absorption $\alpha^{pi}(h\nu)$ of pure and doped BSO crystals are sufficiently different in the character of spectral intensity distribution. However, for both these crystals two spectral ranges, A and B, with $h\nu \approx 2 - 3.3$ and $0.5 - 2$ eV, respectively, can be separated. In the A-range Al, Ga and Sn ions lead to decrease to photoinduced absorption, while in the B-range it increases.

PCE spectra $\Delta\alpha^{pi}(h\nu)$ have complex structure (Fig. 1). We decomposed the spectra into individual Gaussian components by using the procedure presented in [16]. This technique allows determining the number of components, their spectral positions and half-widths without a priori setting of these parameters. Similar spectral positions ($h\nu_{max,i}$) and close values of half-widths for *i*-components of PCE of BSO, BSO:Al, BSO:Ga and BSO:Sn crystals (with slight difference in intensity) were determined for A-range. Most probably, these bands are associated with intrinsic BSO defects. New bands of PCE spectra observed at incorporation of Al, Ga and Sn ions are formed in the B-range (Table 1).

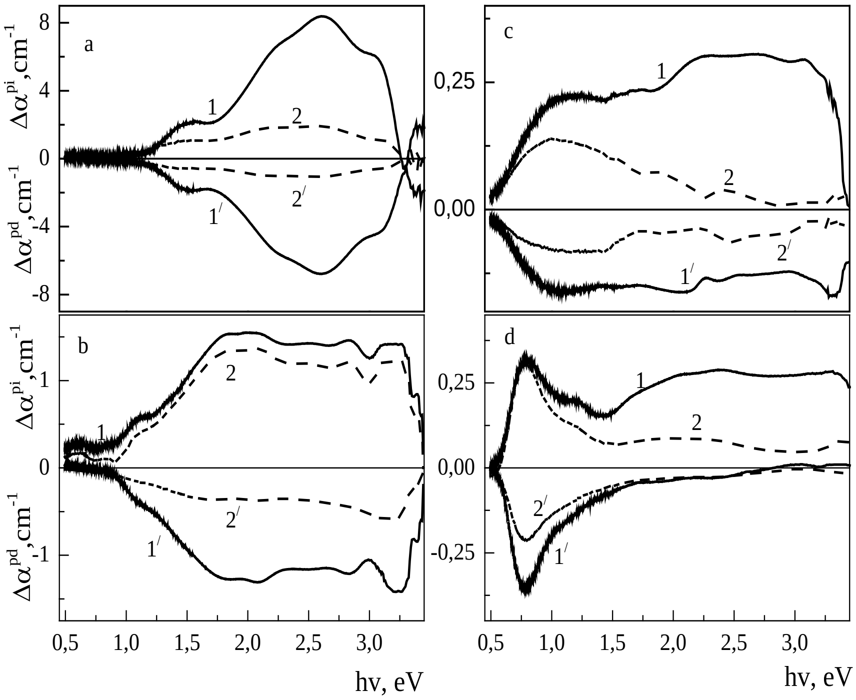

Fig. 1. Spectra of PCE $\Delta\alpha^{pi}$(hv) (1, 2) under light illumination with $h\nu_1$ = 3.35 (1), 2.27 eV (2) and optical destruction of PCE α^{pd}(hv) (1′, 2′) under light illumination with $h\nu_2$ = 1 (1′), 2.2 eV (2′) for BSO (a), BSO:Sn (b), BSO:Ga (c), BSO:Al (d)crystals.

Table 1

Estimated Gaussian band parameters

Crystal	$Bi_{12}SiO_{20}$:Sn			$Bi_{12}SiO_{20}$:Al			$Bi_{12}SiO_{20}$:Ga		
Parameters	Band (eV)	Half width (eV)	Strength (cm^{-1})	Band (eV)	Half width (eV)	Strength (cm^{-1})	Band (eV)	Half width (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

By illuminating BSO crystals with the photons of $h\nu_2$ energy, practically complete optical erasure of all PCE bands can be obtained, and the mirror symmetry of OE PCE spectra $\Delta\alpha^{pd}$(hv) and PCE spectra is observed (Fig. 1). The erasure of all PCE bands cannot be obtained for BSO:Sn crystals, namely, the bands from the B-range formed by Sn ions are not possible to be erased (Fig.1, b).

An analysis of the functions determined as $f_1(h\nu_1) = \int_{0.5}^{3.5} \Delta\alpha^{pi} dh\nu(h\nu_1)$ and $f_2(h\nu_2) = \int_{0.5}^{3.5} \Delta\alpha^{pd} dh\nu(h\nu_2)$ has shown an interesting feature in PCE excitation and PCE erasure. There is a threshold value of photon energy hν* ≈ 2 eV for all investigated crystals. Such photons excite PCE if the crystal is in the stationary state, and erase PCE if the crystal is in photo-excited state (Fig. 1).

For the further discussion of this feature one must take into account that PCE in undoped BSO is determined by formation of photochromic centers [15], in BSO:Al, BSO:Ga and BSO:Sn crystals the situation is similar. The $[Al_{Si}O_4]$, $[Ga_{Si}O_4]$, and $[Sn_{Si}O_4]$ centers are formed in this case. Al^{3+}, Ga^{3+} and Sn^{4+} ions substitute Si^{4+} ones, and a charge compensation for Al^{3+} and Ga^{3+} is provided by a hole centers O^- [17-19]. It is important that absorption spectra are formed by intracenter transitions in all cases.

In this case the presence of threshold photon energy hν* can be explained by means of the model of configuration coordinates (Fig. 2).

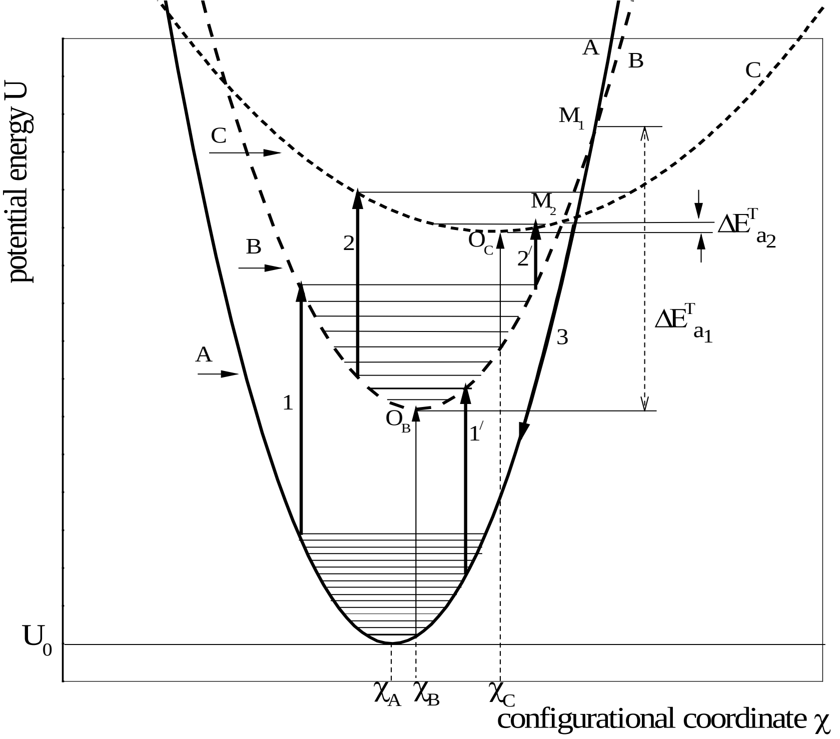

Fig. 2. Diagram of configuration coordinate. Dependencies of potential energy U of photochromic $[Al_{Si}O_4]$- centers on the configuration coordinate χ for stationary state (A), photo-induced PCE-determining state (B) and the one which cause PCE erasure (C).

The $1 - 1'$ transitions correspond to the ranges of photon energy and coordinates χ for which PCE is excited. Energy difference between cross point (M_1) and minimum energy (O_B) in the curve B determines the energy of thermal PCE erasure $\Delta E^T_{a_1}$ required for thermal activation of B → A transitions. This concept corresponds with experimental data showing that at heating up to room temperature PCE in BSO:Al, BSO:Ga and BSO:Sn crystals disappears. $2 - 2'$ transitions point to the filling of electronic levels of excited C state which is the final state for photochromic centers irradiated by the light from hν_2 range. 1 – $1^{/}$ and 2 – $2^{/}$ ranges have the same limiting values of hν* energy (which corresponds to $1^{/}$ and 2 transitions): minimum for PCE excitation and maximum one which limits B → C transitions. Energy difference between cross point M_2 for C and A curves and minimum energy (O_C) in the curve C determines the energy of thermal PCE erasure $\Delta E_{a_2}^{T}$ for C → A transitions. The case of $\Delta E_{a_2}^{T} \langle\langle \Delta E_{a_1}^{T}$ means the possibility of C → A transitions with activation energy close to zero, i.e. OE PCE (3 transitions) at low temperatures (less then RT).

4. Conclusions

So, we can conclude that in BSO:Al, BSO:Ga and BSO:Sn crystals with isomorphic substitution by Al^{3+}, Ga^{3+} and Sn^{4+} ions of Si^{4+} ones, the features of excitation and erasure of PCE are determined by intracenter character of electronic transitions in photochromic $[Al_{Si}O_4]$, $[Ga_{Si}O_4]$, and $[Sn_{Si}O_4]$ centers.

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