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Photochromic effect and photoconductivity in undoped and doped $Bi_{12}SiO_{20}$ crystals

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Stationary and photoinduced spectra of optical absorption and photoconductivity of undoped and doped (by Cu-, Ag- and Mo-ions) $Bi_{12}SiO_{20}$ crystals have been investigated in a spectral range of 0.5–3.5 eV. The action of doping on photochromic effect and induced photoconductivity is determined. The temperature dependence of photoinduced optical absorption and photoconductivity is observed. The absence of the correlation is shown between spectral distributions and temperature dependencies of these effects.

Key words: *photochromic effect, optical absorption, photoconductivity, sillenite crystals*

PACS: *78.20.-e, 78.40.-q*

1. Introduction

Photoinduced phenomena in the sillenite family crystals $Bi_{12}MO_{20}$ (BMO, with M = Si, Ti, Ge) are studied intensively because these crystals are widely used as functional media in different types of light-modulating devices. So, the study of photoinduced processes and their modification by doping is very important in these applications.

At present, the effect of different doping ions on optical and photoelectric properties has been studied on $Bi_{12}TiO_{20}$ (BTO) crystals only [1–5]. It is shown, in particular, that Cu – ions considerably increase the photochromic effect (PCE) in the visible range of spectra and decrease PCE in IR [1,6,7]. Mo-ions reduce the relaxation time of photoinduced optical absorption [5,7]. Nevertheless, the PCE mechanisms have not been studied well enough. It seems that unified investigations of PCE and photoconductivity (PC) can provide useful information in solving this problem. In the present paper, the results of investigations of PC and PCE in $Bi_{12}SiO_{20}$ (BSO) crystals doped by Cu-, Ag- and Mo-ions are presented.

2. Experiments

Nominally undoped and doped BSO crystals were grown using the Czochralski method. Dopants (Cu-, Ag- and Mo- ions) were introduced in the starting materials in an oxide form. The content of Ag, Mo and Cu in BSO crystals constitutes 0.1, 0.1 and 0.3 mass %, respectively. Optical absorption ($\alpha_0(h\nu)$, $\alpha^{\mathrm{PI}}(h\nu)$) and photoconductivity ($\Delta\sigma_0^{\mathrm{P}}(h\nu) = \sigma_0^{\mathrm{P}}(h\nu) - \sigma_0^{\mathrm{T}}, \Delta\sigma^{\mathrm{PI}}(h\nu) = \sigma^{\mathrm{PI}}(h\nu) - \sigma^{\mathrm{T}}$) spectra have been studied where $\sigma_0^{\mathrm{T}}(\nu)$ – dark conductivity, $(\alpha_0(h\nu), \sigma_0^{\mathrm{P}}(h\nu))$ and $(\alpha^{\mathrm{PI}}(h\nu), \sigma^{\mathrm{PI}}(h\nu))$ – optical absorption and photoconductivity spectra before and after the blue light illumination corresponding to stationary and excited state of the crystals. Induced absorption $\Delta\alpha^{\mathrm{PI}}(h\nu) = \alpha^{\mathrm{PI}}(h\nu) - \alpha_0(h\nu)$ and induced (additional) photoconductivity (IPC) spectra $\Delta^*\sigma^{\mathrm{PI}}(h\nu) = \Delta\sigma^{\mathrm{PI}}(h\nu) - \Delta\sigma_0^{\mathrm{P}}(h\nu)$ characterizing PCE and IPC have been analyzed.

Optical transmission spectra $t(h\nu)$ were obtained using Specord M 40, Specord NIR 61 and Cary – 5E spectrophotometers. Measurements were carried out on polished plane-parallel (001)-cuts with 0.03–5 mm thickness. Absorption spectra $\alpha(h\nu)$ were calculated according to [6]. Photoconductivity spectra were measured by means of the monochromator SPM-2 using the techniques of synchronous detection. Ag-electrodes were obtained by Ag-paste firing. All measurements were carried out at

$T = 80$ K. PCE and IPC were excited using 600 W halogen lamp. To return from the excited to the initial stationary state, the samples were slowly heated up to 800 K and then cooled down to 80 K during 24 hours.

3. Results and discussion

The common picture of the effect of Ag-, Cu-, Mo- ions on the absorption and photoconductivity spectra is given in (figure 1). Stationary spectra $\alpha_0(h\nu)$ show new structural bands of absorption (with respect to undoped BSO) in near IR (BSO:Ag, BSO:Cu) and blue-green range (BSO:Mo) (figure 1a). But stationary photoconductivity spectra $\Delta\sigma_0^{\mathrm{PI}}(h\nu)$ show small changes. There should be noted a substantial decrease of photosensitivity (with respect to BSO) in the BSO:Cu crystals in the whole spectral range (figure 1b).

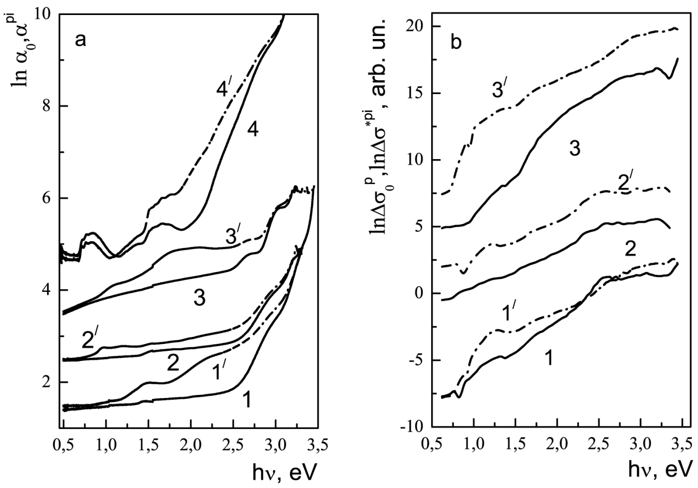

Figure 1. Spectra of optical absorption $ln\alpha_0(h\nu)$; $ln\alpha^{\mathrm{PI}}(h\nu)$ (a) for BSO (a, 1, 1′), BSO:Ag (a, 2, 2′), BSO:Mo (a, 3, 3′) and BSO:Cu (a, 4, 4′) crystals and spectra of photoconductivity $ln\Delta\sigma_0^{\mathrm{P}}$, $ln\Delta\sigma^{*\mathrm{PI}}$(b) for BSO (b, 1, 1′),BSO:Ag (b, 2, 2′), BSO:Cu (b, 3, 3′) crystals after illumination by dark blue light. T = 80 K. Curves $ln\alpha_0(h\nu)$ and $ln\alpha^{\mathrm{PI}}(h\nu)$ are displaced on a vertical line on 3 (a, 1, 1′), 0.5 (a, 2, 2′), 2 (a, 3, 3′) and 6 (a, 4, 4′) units. Spectra of photoconductivity BSO:Cu and BSO:Ag are displaced on a vertical in relation to spectra BSO on 14 and 9 units, accordingly.

The spectra of photoexcited state $\Delta\alpha^{\mathrm{PI}}(h\nu)$ and $\Delta\sigma^{*\mathrm{PI}}(h\nu)$ are characterized by an increase of absorption and photoconductivity with the change of the absorption band structure, while the photoconductivity spectra become more diffusive (figure 1).

There is no correlation between the spectral distribution of absorption and photoconductivity. There are no absorption peaks related to a doped photosensitivity threshold within the IR and the absorption shoulder is considerably shifted with respect to the band of the increased photosensitivity in a visible spectral range (figure 1a, b). It seems that intra-center absorption creates a background that veils the absorption peaks of the “doping level – allowed band” types.

The impurity effect on PCE and IPC is as follows. Cu ions considerably increase PCE in a visible range of spectra and decrease in IR. There are additional absorption bands in near IR due to Ag-ions. Mo-ions provide the PCE in a visible range higher than in the undoped BSO crystals (figure 2a).

The IPC is observed in the overall investigated spectral range. In the long-wave range the effect is weak and is typical of semiconductors, i.e. it is conditioned by filling the impurity levels. In a short-wave range (adjacent to absorption edge) IPC is too strong and $\Delta^*\sigma^{\mathrm{PI}}(h\nu)$ spectra are rather complicated. In BSO crystals the illumination causes a reduction of photosensitivity in a band near 2.5 eV. Near the fundamental absorption edge, intensive bands of IPC with $h\nu_{max} \approx$

3 eV and 3.03 eV are observed and PCE decreases. In BSO:Cu crystals, IPC takes place only in narrow boundary bands. (figure 2b). PCE and IPC spectra are essentially different. IPC spectra distribution have a form of a band adjacent to the UV - edge of investigated range (figure 2a), whereas PCE bands are shifted to its middle part (figure 2b).

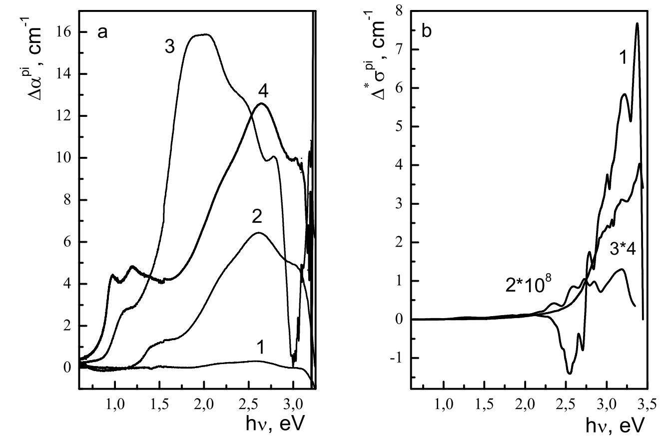

Figure 2. Spectra of PCE $\Delta\alpha^{\mathrm{PI}}(h\nu)$ (a) and IPC $\Delta\sigma^{*\mathrm{PI}}(h\nu)$ (b) for BSO (a, 1, b, 1), BSO:Cu (a, 2, b, 2), BSO:Mo (a,3), BSO:Ag (a, 4, b, 3) crystals. T = 80 K.

The $\Delta\alpha^{\mathrm{PI}}(h\nu)$, $\alpha_0(h\nu)$ and $\alpha^{\mathrm{PI}}(h\nu)$ spectra analysis within the framework of the ligand crystalline field theory shows that photochemical reactions are responsible for the following changes of the doping ion charge: $Cu^{3+} \longrightarrow Cu^{2+}$; $Ag^{+} \longrightarrow Ag^{2+}$; $Mo^{5+} \longrightarrow Mo^{4+}$, during transition to the metastable photoinduced state. Cu- and Ag-ions replace Bi^{3+}-ions in octahedral and Mo-ions replace Si^{4+}-ions in tetrahedral positions of BSO lattice. Distinctions between the temperature dependences of photoinduced absorption and induced photoconductivity turn out to be another confirmation of distinctions of the PCE and IPC nature (figure 3). They contain the regions of in-

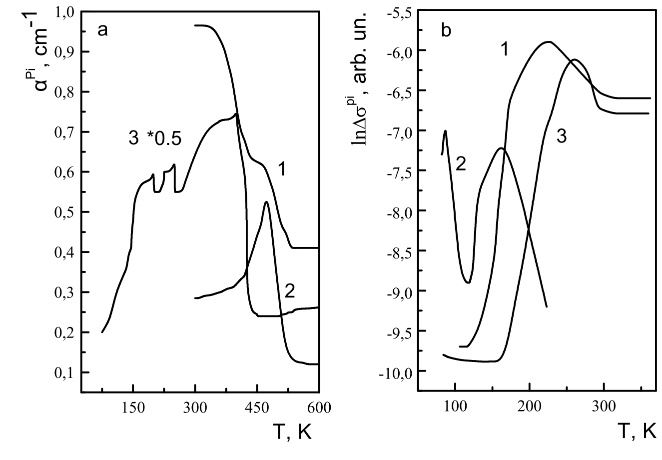

Figure 3. The temperature dependences of photoinduced optical absorption by light (a) and photoinduced photoconductivity (b) with $h\nu = 1.65$ eV for BSO crystals (a, 1, b, 1), BSO:Cu (a, 2, b, 2), BSO:Ag (a, 3, b, 3).

creasing and decreasing of $\Delta\alpha^{\mathrm{PI}}(h\nu)$ and $\Delta^{*}\sigma^{\mathrm{PI}}(h\nu)$ dependences in different temperature intervals. Moreover, the $\Delta\sigma^{\mathrm{PI}}(T)$ dependences show the effects of thermoactivation and thermal extinction of photoconductivity which may be described using a model of the two-center recombination [8].

We assume that a distinction between PCE and IPC consists in the following. PCE is mainly due to intra-central optical transitions in doping centers. The charge state of these centers changes due to photochemical reactions. IPC is due to the photoinduced redistribution of the charge carries between local levels in a forbidden gap which are responsible for photoconductivity in a spectral range adjoining the absorption edge or due to the charge transitions from the valance band on the shallow levels forming the tails of states near the valence and conductivity bands. The commonness of PCE and IPC excitement spectra can be explained by the fact that the transport of photo-excited charge carries is a common link in the mechanisms of both effects. The drift and diffusion components provide a photocurrent under IPC excitement and only the diffusion component provides PCE. If the carrier transport takes place under recombination on slow-centers, then PCE and IPC intensification is observed. If recombination is realized by means of fast centers, then IPC and PCE decrease. High degree of the shallow level filling near the band conductivity bottom is a necessary condition for PCE. Apparently it assists the electron localization and the charge state change of deep centers responsible for PCE.

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Фотохромізм та індукована фотопровідність чистих і легованих кристалів силікосиленіта

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У спектральному діапазоні 0.5–3.5 eV досліджені стаціонарні і фотоіндуковані спектри оптичного поглинання і фотопровідності, чистих і легованих іонами Cu, Ag і Mo кристалів $Bi_{12}SiO_{20}$. Спостерігали вплив легування на фотохромний ефект і індуковану фотопровідність, отримали температурні залежності фотоіндукованого оптичного поглинання і фотопровідності. Показана відсутність кореляції у спектральному розподілі і у температурній залежності обох ефектів.

Ключові слова: *фотохромний ефект, оптична абсорбція, фотопровідність, кристали силеніту*

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