THERMALLY INDUCED EFFECTS ON OPTICAL ABSORPTION IN Ag-DOPED $Bi_{12}SiO_{20}$ SINGLE CRYSTALS

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The spectral-temperature dependences of optical absorption of $Bi_{12}SiO_{20}$ crystals doped with Ag ions were measured in the visible range of photon energy $h\nu$. The temperature of the samples was varied in heating-cooling cycles in the interval $T = 280 – 680$ K. It was shown that the spectra fulfilled Urbach rule for $h\nu > 2.1$ eV at the forbidden zone width of 3.3 eV. The Urbach rule parameters, calculated within the frame of the electron-phonon interaction model, showed anomalous behavior in the interval $T = 389 – 500$ K. The observed peaks in the temperature dependences of optical absorption were attributed to the competition of thermally induced processes of color centers formation and destruction. The color centers were assumed in the form of $Ag^{2+} – 2O^-$ and $Ag^+ – O^-$ complexes that are created due to thermal activation energy $E_{a1} = 0.1$ eV and $E_{a2} = 0.145$ eV, respectively. The spectrum of thermochromic effect characterizing non-reversible thermally induced weakening of optical absorption was detected and analyzed.

Keywords: $Bi_{12}SiO_{20}$ crystals, Ag dopant, optical absorption, thermally induced effects.

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1. Introduction

$Bi_{12}SiO_{20}$ (BSO) crystals of the sillenite family are used in devices of holographic interferometry, dynamic holography, and space-time modulation of light [1]. Optimization of optical, electro-optical, photorefractive and photochromic properties of BSO is an actual task. Doping is one of the most effective approaches allowing to control the practically valuable characteristics of crystalline materials. Earlier it was shown that doping BSO with Cr, Mn and Ag ions significantly enhanced photochromic effect (PCE), while Al and Ga impurities weakened it [2-4].

Currently, the effect of temperature on the properties of sillenites is intensively studied. Necessity to create the materials with thermostable properties causes the interest to thermally induced effects. For example, temperature dependences of photorefractive effect, steady-state and photoinduced optical absorption in BSO and other sillenite crystal were reported in [5, 6]. It is known that PCE is often intrinsically related to the thermochromic effect (TChE), but for the certain cases the relationship can be mutually exclusive. For example, doping BSO crystals with Al and Ga notably enhances TCE but vice versa weakens PCE [3].It is obvious that the physical mechanisms of thermally induced effects should be studied in more details.

The aim of this work is to study the effect of temperature on optical absorption in BSO crystals doped with Ag ions (BSO:Ag).The crystal and the dopant have been chosen with accounting that Ag impurity causes PCE in red and near-IR region of a spectrum in contrast to PCE in blue-green region observed in undoped BSO [4].Therefore, the effect is of practical interest.

2. Experiment

BSO:Ag crystals were grown by Czochralskii method along the direction [001]. Spectral emission analysis showed that concentration of Ag impurity was 0.01 mol. %. The samples were prepared as the polished plates with $8 \times 8 \times 4.7\ mm^3$ dimensions, the main surfaces were parallel to (001) crystal plane.

The spectra of steady-state optical transmittance $t_0(h\nu, T_0)$, where $T_0 = 300$ K, and transmittance after temperature action during heating $t^+(h\nu, T)$ and cooling $t^-(h\nu, T)$ were recorded in the range of light quantum energies $h\nu = 1.3 \div 2.8$ eV by using Specord M40 spectrophotometer. The temperature was varied in heating-cooling cycles in the range of

300 ÷ 680 K, the rate of temperature changing was 0.625 K/min. At T_1 = 650 K the samples were kept for 10 min and then cooled.The steady-state absorption spectra $\alpha_0(h\nu, T_0)$ as well as the heating absorption$\alpha^+(h\nu, T)$ and cooling absorption $\alpha^-(h\nu, T)$, corresponding to the transmission spectra, were determined in the experiment. These data were used to calculate the difference $\Delta\alpha^{\mathrm{TChE}}(h\nu, T_0) = \alpha^-(h\nu, T_0) - \alpha_0(h\nu, T_0)$, which characterized TChE, i.e. change of absorption after the heating-cooling cycle. The temperature dependences of the impurity optical absorption bands $a^+(T)$ and $a^-(T)$ were obtained from the parametric dependences $\alpha^+(h\nu, T)$ and $\alpha^-(h\nu, T)$. The optical absorption spectra were calculated as $\alpha(\nu, T) = (1/d)\ \ln(1/(t(h\nu, T))$, where d is the sample thickness.

3. Results and discussion

The band of intracenter absorption in Ag ions can be seen in the spectral interval $h\nu = 1.4 \div 2.1$ eV. The structure of this band was analyzed in [4] forBSO:Ag crystals with high Ag content. The influence of temperature on optical absorption in the regions below and above $h\nu \approx 2.1$ eV is slightly different. Near the fundamental absorption band ($h\nu > 2.1$ eV), heating or cooling leads to a nearly monotonic change in absorption. Accordingly, the spectra of $\alpha^+(h\nu, T)$ and $\alpha^-(h\nu, T)$ show a long-wavelength or short-wavelength shift of the Urbach edge. On the contrary, upon heating or cooling in the region of intracenter absorption ($h\nu < 2.1$ eV), the changes in absorption α and the shift of the spectra become non-monotonic (Fig. 1).In the region $h\nu > 2.1$ eV, the dependences $\ln\alpha^+(h\nu, T)$ and $\ln\alpha^-(h\nu, T)$ are close to linear, and their slope increases with decreasing temperature. This behavior indicates the fulfillment of Urbach's rule of thumb:

$$\alpha^{\pm}\left(h\nu, T\right) = \alpha_0 \exp\frac{\sigma(T)(h\nu - E_g^U)}{kT}, \qquad (1)$$

$$S = \frac{\partial(\ln\alpha)}{\partial(h\nu)}. \qquad (2)$$

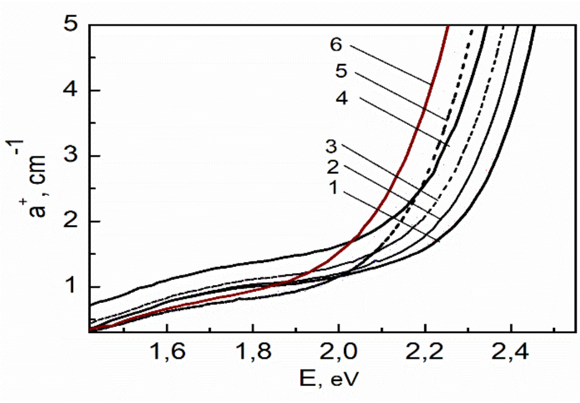


Fig. 1. Absorption spectra ofα^+($h\nu$, T) inBSO:Ag crystalsat T = 300 (1), 370 (2), 420 (3), 480 (4), 580

In (1) and (2) $\alpha_0 = 1003$ cm^{-1} and E_g^U = 3.3 eV are the coordinates of the intersection point of the dependences $\ln\alpha^{\pm} = F(h\nu, T)$ extrapolated to the high values of $h\nu$;k is the Boltzmann constant; S and σ determine the slopes of the lines $\ln\alpha^{\pm}(h\nu)$ to the $h\nu$ axis (Fig. 2, a, b).

Expressions (1) and (2) describe the electronic transitions to the impurity zone in a heavily doped semiconductor. The impurity zone is described by the distribution function of the density of electronic states as a function of energy. E_g^U determines the width of the energy gap separating the maximum of the distribution function from the valence band.

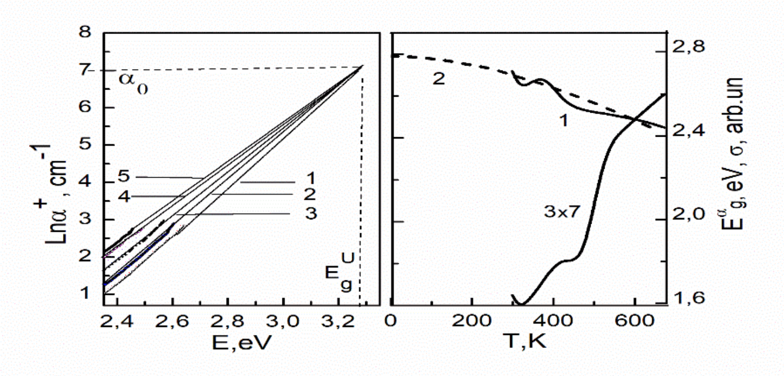
However, the found value E_g^U = 3.3 eV corresponds to the known width of the forbidden zone in undoped BSO crystals $E_g^{\alpha}(T)$.It means that Ag ions do not create the impurity zone adjacent to the bottom of the conduction band. The temperature shift of the $\ln\alpha^+(h\nu, T)$ and $\ln\alpha^-(h\nu, T)$ spectra is due to the temperature dependence of the forbidden zone width. On the other hand, expressions (1) and (2) can be explained by accounting the electron-phonon interaction. In this case, the dependences $E_g^{\alpha}(T)$ and $\sigma(T) = kT\dfrac{d\ln\alpha^{\pm}}{dh\nu}$ can be rewritten as

$$E_g^{\alpha}(T) = E_g^{\alpha}(0) - \frac{AT^2}{(\theta+T)^2}, \tag{3}$$

$$\sigma(T) = 2\sigma_0\frac{kT}{h\nu_0}\tanh\left(\frac{h\nu_0}{2kT}\right), \tag{4}$$

where $E_g^{\alpha}(T)$ and $E_g^{\alpha}(0)$ are the values of the so-called isoabsorption width of the forbidden zone at the current temperature and at $T = 0$ K, respectively. The isoabsorption bandwidth is defined as the coordinate on the $h\nu$ axis at constant value of α. In (3) and (4) A, θ and σ_0 are the empirical constants, σ_0 is inversely proportional to the strength of electron-phonon interaction, $h\nu_0$ is the energy of effective phonons interacting with photons.

A fragment of the $E_g^{\alpha}(T)$ dependence can be approximately described by expression (3) with the parameters α = 10 cm^{-1}, A = 5.3, $E_g^{\alpha}(0)$ = 2.8 eV and θ = 1006 K. The anomaly of the $E_g^{\alpha}(T)$ function is observed in the temperature range 350 ÷ 500 K (Fig. 2,b). In the same interval, there is the anomaly of the function $\sigma(T)$. The obtained values of $\sigma(T)$ are less than 1, that is typical for ionic crystals (Fig. 2,b). Additional experiments are required to determine values of σ_0 and $h\nu_0$.



(a) (b)

Fig. 2. Absorption spectra of $\alpha^+(h\nu)$ inBSO:Ag crystals at T=300 (1), 380 (2), 480 (3), 525 (4), and 680 K (5) (a). Temperature dependences of Urbach's rule parameters: $E_g^{\alpha}(T)$ (1), calculated dependences of$E_g^{\alpha}(T)$ (2) and $\sigma(T)$ (3) (b).

The heating-cooling cycle of BSO:Ag crystals causes TChE in the same spectral region $h\nu$ = 1.4 ÷ 2.6 eV, where PCE is observed [4]. In the spectrum of TChE, similarly to the changes in the spectrum of PCE, small absorption variation in the interval $h\nu_1$ = 1.4 ÷ 2.4 eV is followed by a much stronger one in the interval with $h\nu_2 \geq 2.4$ eV [4].However, TChE, unlike PCE, is characterized by a drop in absorption rather than an increase (Fig. 3, a). The temperature dependences of absorption in the intervals $h\nu_1$ and $h\nu_2$ measured on heating pass through the maximum, which disappears on cooling (Fig. 3, b). It indicates the competition between the processes of formation and destruction of color centers under temperature influence of.

Earlier it was shown that from the point of view of crystal chemistry, BSO structure is most favorable for the localization of mono- Ag^{+} and bi-valent Ag^{2+} ions in the sites of Bi^{3+} hosts with nearly octahedral ligands coordination. Charge neutrality is ensured by O^{-} hole centers. The photochemical reaction responsible for PCE is realized in accord with the scheme $\mathrm{Ag}_{\mathrm{Bi}}^{+} - e \rightarrow \mathrm{Ag}_{\mathrm{Bi}}^{2+}$ [4].

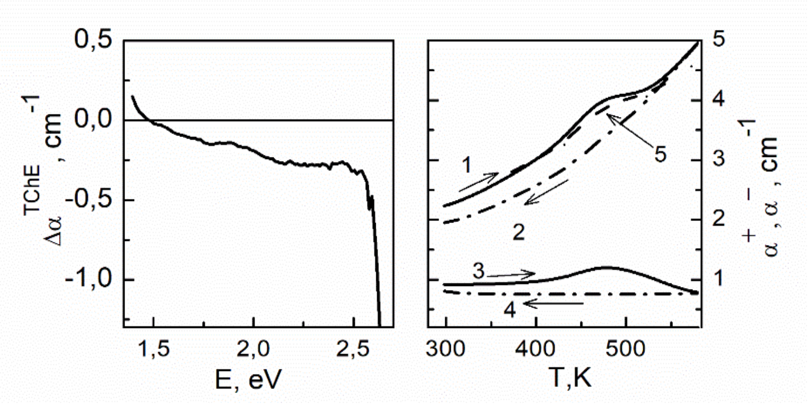
Since the changes in the absorption spectra corresponding to TChE and PCE are opposite to each other, we assume that TChE occurs due to the change in the charge state of Ag ions according to the scheme $\mathrm{Ag}_{\mathrm{Bi}}^{2+} + e \rightarrow \mathrm{Ag}_{\mathrm{Bi}}^{+}$. The maximum of $\alpha^{+}(T)$ dependence is associated with a change in the concentration N_1(T) ofAg^{2+}– $2\mathrm{O}^{-}$ centers, which can be described by

$$\frac{dN_1(T)}{dT} = -a_1 N_1(T) + a_2 N_{01} \exp\left(-\frac{E_{\mathrm{a1}}}{kT}\right), \tag{5}$$

where a_1 and a_2 are the coefficients characterizing loss and recovery of the concentration N_1 relative to the initial value N_{01}, E_a – thermal activation energy of this process. Solving (5), we obtain the equation for the concentration $N_2(T) = N_{01} - N_1(T)$ of $\mathrm{Ag}^{+} - \mathrm{O}^{-}$ centers:

$$N_2(T) = N_{01}\left\{1 - \left[a_3 \exp\left(-\frac{E_{\mathrm{a1}}}{kT}\right) + a_4 \exp\left(\frac{E_{\mathrm{a2}}}{kT}\right)\right]\right\}, \tag{6}$$

where a_3, a_4, E_{a1} and E_{a2} are the parameters characterizing the process of changing $N_2(T)$.



(a) (b)

Fig. 3. Spectrum of TChE (a). Dependences $\alpha^{+}(T)$ and $\alpha^{-}(T)$,obtained on heating (1, 3) and on cooling (2, 4) at $h\nu_1$ = 2.305 (1, 2) and $h\nu_2$ = 1.705 eV (3, 4), respectively; calculated dependence $\alpha^{+}(T)$ at $h\nu_2$ = 2.305 eV (5) (b).

One can assume that optical absorption is determined by the product of electron capture cross section σ* and the concentration of capturing centers $N_2(T)$ as $\alpha^{+}(T) = \sigma^{*} N_2(T)$. Taking the typical for deep centers value $\sigma^{*} = 6\cdot10^{-18}$ cm^{-2}, the concentration of silver ions $N_{01} = 1.2\cdot10^{16}$ cm^{-3} and the values $a_3 = 0.2$, $a_4 = 0.002$, $E_{\mathrm{a1}} = 0.1$ eV, and $E_{\mathrm{a2}} = 0.145$ eV, we calculate the curve, which corresponds to the dependence $\alpha^{+}(T)$ at $h\nu = 2.306$ eV with good accuracy (Fig. 3, b, curve 5). This confirms the proposed model of the thermally induced absorption change in BSO:Ag crystals.

4. Conclusions

1. It was shown that theedge optical absorption in BSO:Ag crystals satisfied Urbach's rule. The Urbachian width of the forbidden zone was determined as 3.3 eV.

2. Urbach's rule parameters and optical absorption showed anomalous temperature behavior in the interval $T = 350 – 500$ K.

3. TChE, giving rise to a non-reversible absorption decrease, was observed as the result of heating-cooling cycle. The spectrum of TChE was similar to that of PCE mirrored with respect to the photon energy axis.

4. The optical absorption dependences $\alpha^{\pm}(T)$ passed through the maximum. Such behavior related to competing processes of formation and destruction of color centers. The latter were assumed in the form of $Ag^{2+} – 2O^{-}$ and $Ag^{+} – O^{-}$ complexes.

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