Thermochromic Effect in Doped Bi$_{12}$SiO$_{20}$ Crystals

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Optical-temperature investigations of stationary and photo-induced absorption in undoped and Al (or Ga) doped Bi$_{12}$SiO$_{20}$ crystals are discussed. In the wave-number range 22000–4000 cm^{-1} under temperatures from 80 to 650 K, peculiarities of thermochromic effect have been revealed and temperature dependences of intensity of bands forming photo- and thermochromic effects have been found. A correlation between these dependences and spectra of thermostimulated current is explained.

1. Introduction

Thermochromic and photochromic effects (TCE and PCE, respectively) often accompany each other. In photorefractive crystals with general formula Bi$_{12}$MO$_{20}$ (BMO, M = Si, Ge, Ti, and some other elements), PCE has been studied in detail (mainly spectral distribution of photoinduced absorption in BMO both undoped and doped by various dopants as well as PCE kinetics under its pulse excitation [1–4]), while little attention was given to TCE. However, interesting temperature dependences have been revealed for both impurity optical absorption and absorption caused by intrinsic point defects in BMO. These dependences may be stepwise and/or have extremes in different temperature ranges depending on the doping impurity type and on the preliminary processing of the crystal [5–7].

BMO crystals are important basic elements in devices for recording, treatment and storage of optical information in optoelectronics and dynamical holography. So it is interesting, on the one hand, to study in more detail the temperature influence on some optical characteristics of BMO, and on the other hand, to reveal the role of defects and impurities in occurring peculiarities of both absorption temperature dependences and TCE.

In the present work, the thermochromic effect and temperature dependences for stationary and photoinduced optical absorption were studied for pure Bi$_{12}$SiO$_{20}$ (BSO) and BSO crystals doped by aluminum and gallium dopants (BSO:Al and BSO:Ga), respectively.

2. Experimental

The BSO, BSO:Al, and BSO:Ga crystals were grown along [001] crystallographic direction by the Czochralski method. The content of Al and Ga dopants was 0.01 and 0.02 wt.%, respectively, according to data of spectral-emission analysis.

Samples were (001) polished plates with thickness $d = 5.05$ mm (BSO), 2.55 mm (BSO:Al), and 4.8 mm (BSO:Ga).

Spectral-temperature measurements were carried out for stationary $\alpha^{st}(\nu, T)$ and photoinduced $\alpha^{ph}(\nu, T)$ optical absorption modes as well as for PCE in BSO, BSO:Al, and BSO:Ga crystals. For this aim, two double beam spectrophotometers Specord M40 and Cary-5E controlled by a micro-computer were used for registration of optical transmission spectra $t^{st}(\nu, T)$, and $t^{ph}(\nu, T)$ in the frequency range from 22000 to 4000 cm^{-1} ($\nu = 1/\lambda$, λ is wavelength, T is absolute temperature). The PCE was excited by the light with energy $h\nu = 3.3$ eV using a mercury quartz lamp with 400 W power. A liquid nitrogen cryostat with a sample was embedded into the measuring chamber of the spectrophotometer.

A small electric furnace with resistance 6.5 Ω and power 15 W was used for heating. Temperature was varied with time t according to relation $T = T_0 + \beta t$, with $\beta = 0.16$ K s^{-1}. Measurement accuracy was $\approx 1\,°$C. Temperature investigations were carried out both in the high temperature ($\Delta T_1 = 293-650$ K) and the low temperature ($\Delta T_2 = 85$–291 K) ranges.

In the first range, ΔT_1, the influence of temperature (under its cycling variation) on the stationary absorption was studied because here PCE was either weakened (as in BSO) or not observed (as in BSO:Al and BSO:Ga [8]).

For a set of fixed temperatures T_i (with $T_0 = 293$ K), optical transmission spectra were registered under heating $t^{st}(\nu, T_i)$ and under cooling $t^{st*}(\nu, T_i')$.

In the second range, ΔT_2, the temperature influence (in the regime of its linearly increase with time from $T_0^* = 85$ K) on the intensity of photoinduced absorption in the PCE bands was studied, i.e. under fixed frequencies ν_1. Heating velocity was $V_1 = 0.03$ K/s and $V_2 = 0.1$ K/s. As a result, the dependences $t^{ph}(\nu_i, T)$ were obtained.

According to the technique [6], all the obtained transmission spectra and dependences were translated into proper spectra and temperature dependences of optical absorption: $\alpha^{st}(h\nu, T_i)$, $\alpha^{st*}(h\nu, T_i)$, $\alpha^{ph}(h\nu, T_0^*)$, $\alpha^{st}(h\nu, T_0^*)$, and $\alpha^{ph}(h\nu_i, T)$. PCE spectra were calculated as $\Delta\alpha^{PCE}(h\nu, T_0^*) = \alpha^{ph}(h\nu, T_0^*) - \alpha^{st}(h\nu,$

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T_0^*); TCE spectra — as $\Delta\alpha^{TCE}(h\nu, T_0^*) = \alpha^{st*}(h\nu, T_0) - \alpha^{st}(h\nu, T_0)$.

The thermoinduced absorption was determined as $\Delta\alpha^{TI}(h\nu, T) = \alpha^{st*}(h\nu, T_1') - \alpha^{st*}(h\nu, T_1)$, where T_1' and T_1 are the same temperature values achieved under heating and cooling, respectively. PCE spectra were calculated as $\Delta\alpha^{PCE}(h\nu, T_0^*) = \alpha^{ph}(h\nu, T_0^*) - \alpha^{st}(h\nu, T_0^*)$; TCE spectra — as $\Delta\alpha^{TCE}(h\nu, T_0^*) = \alpha^{st*}(h\nu, T_0) - \alpha^{st}(h\nu, T_0)$.

3. Results and discussion

3.1. Photochromic effect

The $\alpha^{st}(h\nu, T)$ and $\alpha^{ph}(h\nu, T)$ spectra of undoped BSO crystals at temperatures, which not exceeding the room one ($T_0 = 293$ K) show characteristic bands of stationary and photoinduced optical absorption [8]. These are caused by presence of point defects of high concentration ($\approx 10^{18}$ cm^{-3}) in the BSO crystals. Doping the BSO by Al, Ga ions decreases intensity of these bands and shifts the short wavelength edge of $\alpha^{st}(h\nu, T)$ and $\alpha^{ph}(h\nu, T)$ spectra towards $h\nu$ close to the band gap width ($\Delta E_g \approx 3.3$ eV at $T = 80$ K) [8]. Our investigations have shown how these ions changed PCE spectra when all these crystals were grown under equal technology conditions: in BSO:Al and BSO:Ga the intense PCE bands appear in the range $h\nu = 0.5-1.5$ eV, whereas in BSO crystals these occur near the "shoulder" of absorption ($h\nu = 2.3-2.8$ eV), Fig. 1.
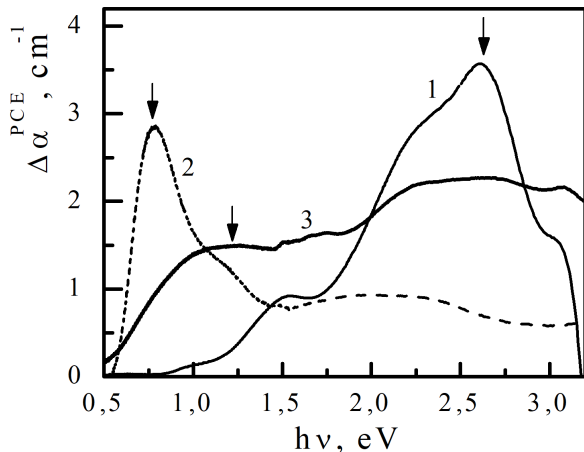

Fig. 1. PCE spectra of BSO (1), BSO:Al (2), and BSO:Ga (3) crystals at $T_0^* = 80$ K. Arrows indicate some characteristic absorption bands.

Influence of temperature is found to be different as well. Temperature increase from $T_0^* \approx 80$ K to $T_0 \approx 290$ K weakens PCE in BSO crystals, whereas in doped BSO:Al and BSO:Ga crystals, the PCE practically completely disappears.

3.2. High temperature range

Optical-temperature investigations in the range $\Delta T_1 = 290-650$ K have revealed a long wavelength shift of "impurity tail" of the edge absorption; this shift was caused by narrowing the gap band with temperature, however it was different for undoped and doped crystals (Fig. 2). Absorption spectra obtained under "heating-cooling" cycles showed a "negative hysteresis", i.e. the absorption before heating was significantly higher than after heating (Fig. 2a).
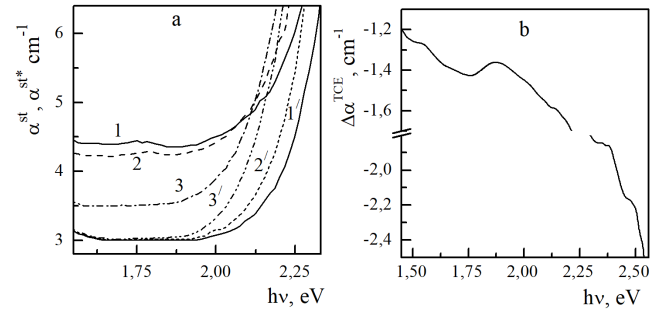

Fig. 2. (a) BSO crystal absorption spectra $\alpha^{st}(h\nu, T_0)$ and $\alpha^{st*}(h\nu, T_1)$ obtained at $T_0 = 290$ and $T_1 = 370$, 470 K under heating to $T_i = 650$ K (curves 1, 2, and 3) and cooling to 290 K (curves $1', 2', 3'$); (b) BSO crystal TCE spectrum $\Delta\alpha^{TCE}(h\nu, T_0) = \alpha^{st*}(h\nu, T_0') - \alpha^{st}(h\nu, T_0)$ obtained after the "heating-cooling" cycle.

In BSO crystals after heating to $T_1 \leq 620$ K, the absorption drops in all the observed spectral range (the crystal is "decolorized"). The intensity decrease of individual bands with $h\nu_{max}$ forming the structure of spectra of the crystal decolorizing, i.e. the "negative" TCE: $\Delta\alpha^{TCE}(h\nu, T_0) = \alpha^{st*}(h\nu, T_0) - \alpha^{st}(h\nu, T_0')$, indicates the thermal destruction of BSO intrinsic defects with optical activation energies $E^{opt} = h\nu_{max} = 1.55$, 1.85, 2.1, 2.2, 2.3, and 2.5 eV; new absorption centers are not generated (Fig. 2b). The bands with similar $h\nu_{max}$ values are observed also in PCE spectra (Fig. 1). However, under heating to 650 K, the absorption begins to increase in the spectral band $E^{opt} = 1.7$ eV (Fig. 3, curve 1); then under cooling to the room temperature, the absorption drops again (Fig. 3a, curve 1').

In the work by Khudyakova and Grebenchukov [9], influence of annealing on BSO in the temperature range $\Delta T_{an} = 890-1050$ K was studied. Increasing T_{an} resulted in intensification of the absorption band with a maximum at $\lambda = 450$ nm. The authors [9] have connected this with increase of the concentration of intrinsic defects in BSO. Thus, we can assume in our case that $T_1 = 620$ K is the limiting temperature when the process of absorption centers destruction changes into their thermoinduced generation.

Temperature dependences of thermoinduced absorption intensity $\Delta\alpha^{TI}(h\nu, T) = \alpha^{st*}(h\nu, T) - \alpha^{st}(h\nu, T_0)$ at $T \geq T_0$ are found to be dropping stepwise and/or having extremes in the bands mentioned above; the temperature ranges of the steps and extremes are the same both for heating and cooling regimes (Fig. 3a).

Differentiation of $\Delta\alpha^{TI}(h\nu, T)$ curves by temperature provides insight into extreme temperatures $T_{max} = 375$
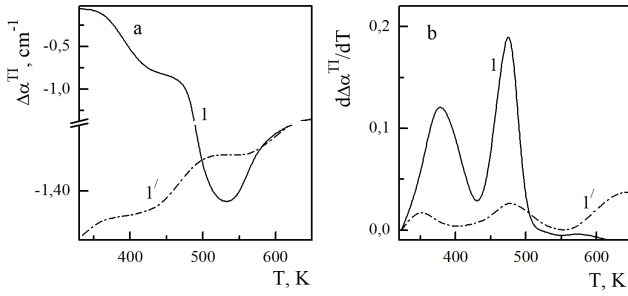
Fig. 3. (a) Temperature dependences of a thermoinduced decolorizing $\Delta\alpha^{TI}(h\nu, T)$ of the absorption band with $h\nu_{\max} = 1.7$ eV under heating (1) and cooling (1') of a BSO crystal; (b) appropriate derivatives $d\Delta\alpha^{TI}(h\nu, T)/dT$ on $\Delta\alpha^{TI}(h\nu, T)$ (curves 1, 1').

and 475 K, when the rate of absorption center concentration variation is maximal (Fig. 3b). It is interesting that these temperatures are close to values corresponding to maxima in thermostimulated current curves [10].

For alloyed crystals, generally analogous results have been obtained. Influence of alloying of BSO on TCE appears only at $T_1 \geq 630$ K near the absorption edge with $h\nu \geq 3.0$ eV (Fig. 4a). Here, the intense "positive" TCE indicates occurrence of thermoinduced absorption centers connected with an alloying dopant. Temperature dependences $\Delta\alpha^{TI}(h\nu, T)$ of the thermoinduced absorption differ from ones for temperature ranges including steps and extremes (Fig. 4b). Differentiation of $\Delta\alpha^{TI}(h\nu, T)$ curves in the band with $h\nu_{\max} = 1.7$ eV gives broad bands of different intensity for heating (1) and cooling (1') curves with its small temperature shift (Fig. 4b). Temperature positions of maxima of these bands $T_{\max} = 400$ and 525 K, as also for the undoped BSO, correlate with data obtained for thermostimulated current curves [10].

3.3. Low temperature range

In the range $\Delta T_2 = 85-291$ K, temperature dependences of absorption band intensities with $h\nu_{\max} = 1.7$ and 2.6 eV in PCE spectra have been studied for pure and doped BSO crystals. A stepwise decline of $\Delta\alpha^{PCE}(h\nu, T)$ curves is observed for BSO crystals (Fig. 5a). For BSO:Al and BSO:Ga crystals, additionally to the "steps" a peak at $T_{\max} = 200$ K is observed (Fig. 5b). Nature of this peak needs further investigation. Differentiation of $\Delta\alpha^{PCE}(h\nu, T)$ curves gives bands $T = 106, 155, 230$ K (BSO:Al) and 150, 210, 275 K (BSO) of different intensity (Fig. 5c,d). These data also correlate with data obtained for thermostimulated current curves [11, 12]. Temperature positions of maxima of these bands shift to the high temperature region with increasing heating velocity from 0.03 to 0.1 K/s. Due to the method of "the first slope" the energy of thermal activation was estimated (Table I). The ratio of the optical and thermal activation energy $E_a^{opt}/E_a^{th} = 1.6-4.3$ indicate electron–phonon interaction typical for semiconductors.
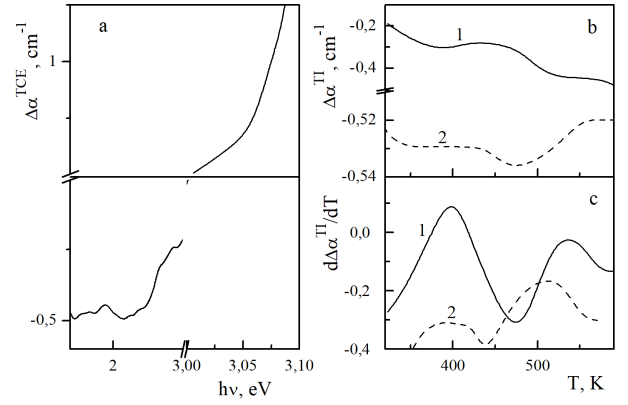

Fig. 4. (a) TCE spectrum $\Delta\alpha^{TCE}(h\nu, T_0)$ after a "heating-cooling" cycle for a BSO:Ga crystal; (b) dependence of thermoinduced absorption $\Delta\alpha^{TI}(h\nu_{\max}, T)$ in the band with $h\nu_{\max} = 1.7$ eV under heating and cooling (curves 1 and 1', respectively); (c) appropriate derivates $d\Delta\alpha^{TI}(h\nu_{1max}, T)/dT$ (curves 1 and 1') for the BSO:Ga crystal.

TABLE I

Parameters of absorption centers in BSO:Al crystal

Peak	$V_1 = 0.03$ K/s			$V_2 = 0.1$ K/s		
	$T_{\max}$ [K]	E_a^{th} [eV]	E_a^{opt}/E_a^{th}	$T_{\max}$ [K]	E_a^{th} [eV]	E_a^{opt}/E_a^{th}
1	106.6	0.22	$3.87 - 4.26$	115	0.26	$3.28 - 3.61$
2	155.1	0.44	$1.69 - 1.74$	206.3	0.42	$1.77 - 1.82$

It should be taken into account that in the range $h\nu = 0.5-2.6$ eV, absorption is controlled by BSO intrinsic defects and impurity ions forming donor and accepter local levels in the band gap. Under optical or thermal excitation, redistribution of electrons over these levels occurs in crystals. This changes intensities of absorption bands of a type of "impurity level permitted band". Absorption coefficient is determined by concentration of absorbing centers N, $\alpha \approx \sigma N(T)$, where σ — capture cross-section of photons (assumed be weakly dependent on temperature). Then $dQ(T)/dT \approx \sigma\, dN(T)/dT$. If the centers are charged (ionized donors and/or accepters), variation of their concentration, i.e. total charge Q, with temperature $dQ(T)/dT \approx de N(T)/dT$, where e is electron charge, is equivalent to occurrence of a thermostimulated current in the electric circuit with a crystal sample. Discharging of a certain type local level from the current carriers causes a step in the temperature dependence of PCE or TCE spectral band intensity and appearance of maxima in $d\Delta\alpha^{PCE}(h\nu, T)/dT$ and $d\Delta\alpha^{TCE}(h\nu, T)/dT$ curves. Thus, the correlation between temperature positions of maxima on the curves and the maxima of thermostimulated currents are explained. In the case when absorption centers are deep and electrically neutral and the absorption is caused by intra-center transitions, no correlation would be. Such deep centers have been revealed in BSO:Al crystals [13].
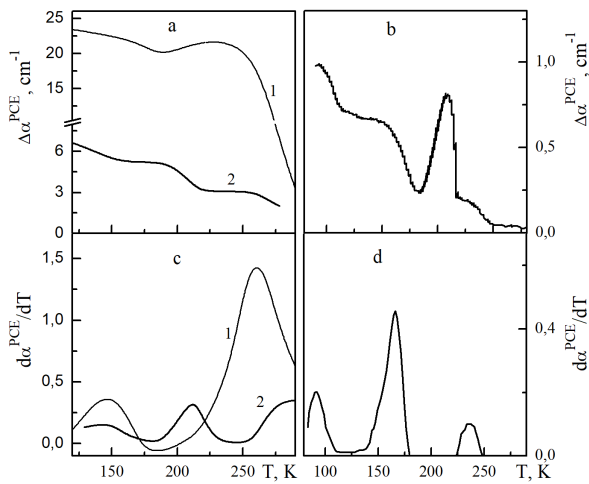
Fig. 5. (a, b) Temperature dependences of PCE intensity $\Delta\alpha^{PCE}(h\nu, T)$ in absorption bands with $h\nu_{\max} = 2.6$ eV (a, 1) and 1.7 (a, 2, and b) for BSO (a) and BSO:Al (b) crystals; (c, d) appropriate derivatives $d\Delta\alpha^{PCE}(h\nu, T)/dT$ (curves 1 and 2).

Thus, a complex of current and luminescence methods of thermoactivation spectroscopy may be completed by the method of "optical thermoactivation spectroscopy". It gives a possibility to reveal electrically neutral centers of optical absorption and find a relation between thermal and optical activation energies of charged absorption centers.

4. Conclusions

— As a rule, the thermochromic effect in undoped and doped by Al and Ga BSO crystals under heating from 80 to 630 K is determined by destroying of intrinsic and photoinduced absorption centers in the range $\nu = 22000-4000$ cm^{-1}. Thermoinduced centers occur at $T \geq 620$ K with $\nu \geq 22000$ cm^{-1}. Their concentration is higher for doped crystals. — The correlation has been revealed between temperature positions of peaks in the curves of thermostimulated currents and $d\Delta\alpha^{PCE}(h\nu, T)/dT$ and $d\Delta\alpha^{TI}(h\nu, T)/dT$ plots. This result indicates the similarity of mechanisms for thermoexcitation of charge carriers.

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