

Changes in the optical absorption induced in the $\text{Bi}_{12}\text{TiO}_{20}:\text{Al}$ crystal by exposition to short- and long-wavelength radiation

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Abstract. The impurity absorption model is used to describe the experimentally observed reversible changes in the optical absorption spectrum induced in the $\text{Bi}_{12}\text{TiO}_{20}:\text{Al}$ crystal by subsequent exposition to short-wavelength radiation with $\lambda_i = 532$ nm and longer-wavelength radiation with λ_n changing from 588 to 1064 nm. The model takes into account the photoinduced transitions between two metastable states of a deep defect center leading to the change of its position in the crystal lattice under conditions of strong lattice relaxation.

1. Introduction

$\text{Bi}_{12}\text{TiO}_{20}$ (BTO) crystals belonging to the sillenite family are promising for application in dynamic holography based on counter interaction of light waves in reflective geometry [1 – 4]. This is due to high values of the space charge field of reflective holograms formed in the BTO crystals due to considerable concentration of photoactive defect centers inherent in the crystals through which the photoinduced redistribution of the electric charge occurs [5, 6]. The special feature of the BTO crystals is the strong photochromic effect also observed at room temperatures; it consists in reversible changes of the optical absorption induced by exposition to visible radiation [7, 8]. The main reason for the increase in the optical absorption in the BTO crystals is considered to be the capture of photoexcited charge carriers (electrons) from deep donor centers to less deep traps characterized by the photoionization cross section larger than in the initial state [9 – 11]. Such process in which the nonequilibrium charge carriers participate can lead to an increase in the photorefractive sensitivity of the BTO crystals in the near-IR range of the spectrum [12, 13]. Another reason for the increased absorption in the BTO crystals that is not associated with electron photoexcitation to the conduction band can be generation of defects for which intracenter transitions occur as a result of exposition to light [11]. In [14] the intracenter character of transitions in the BTO:Al crystal in the wavelength range from 500 to 900 nm characterized by a resonant dependence of the photo- and thermoinduced changes in the light absorption was suggested.

Detailed experimental investigations performed in [15, 16] demonstrated that exposition to short-wavelength radiation with the wavelength $\lambda_i = 532$ nm caused an increase in the optical absorption in the BTO:Al crystal and resulted in the spectrum whose shape in the wavelength range 470–1000 nm was independent of the initial crystal state. The subsequent exposition to a longer-wavelength



radiation with λ_n changing from 588 to 1064 nm led to the enhanced transmittance of the BTO:Al crystal in the entire examined spectral range. In this case it was established that the enhanced transmittance fixed in the saturation region depended nonmonotonically on the wavelength and reached a maximum at $\lambda_n \sim 670$ nm. It should be noted that the observed changes in the optical absorption spectra for the BTO:Al crystal during enhanced-diminished transmittance cycles were reversible and well reproduced experimentally.

In the present work, to describe the experimentally observed reversible changes in the optical absorption spectrum induced in the BTO:Al crystal by subsequent exposition to short- and long-wavelength radiation, the model is considered that takes into account strong relaxation of the lattice during photoinduced transitions between two metastable states of a deep defect center. The redistribution of center concentrations over the states that differ by the photoabsorption cross sections arising during such transitions leads to changes in the optical absorption additional to changes caused by the photoinduced electron redistribution over the deep donors via the conduction band and by generation and decay of defects for which intracenter transitions occurred.

2. Theoretical model

As is well known [17 – 19], localized optically induced changes in the electronic configuration of the deep defect centers of some types in semiconductor and dielectric materials are accompanied by considerable reconstruction of such centers manifested via changes in their positions in the lattice. This effect called the photoinduced lattice relaxation [17] leads to the possibility of photocontrollable change of the properties of crystals comprising such centers and of their application as recording media [18]. The configuration coordinate diagram [17, 19] best described the change in the geometry of the defect caused by the change in its electronic state.

Let us consider the deep defect center that can be in two metastable states A and C with the potential energy minima shifted along the configuration coordinate Q (Fig. 1). The parabolas $E_{d1}(Q)$ and $E_{d2}(Q)$, described by the well-known relations [20]

$$E_{d1}(Q) = a_1(Q - Q_1)^2, \quad (1)$$

$$E_{d2}(Q) = E_{02} + b_2(Q - Q_2)^2, \quad (2)$$

characterize the energies of the ground (1) and excited (2) states of the centers with the parameters a_1 and b_2 of the parabolic functions that differ from each other taking into account the thermal excitation energy E_{02} .

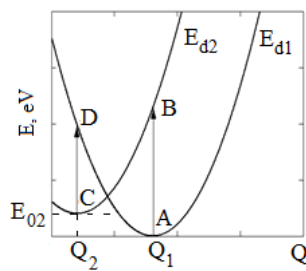


Figure 1. Configuration coordinate diagram of a defect center.

For vertical transitions that can be induced only by light radiation, the configuration coordinates Q_{v1} and Q_{v2} corresponding to the quantum energy $\hbar\omega_{12}$ causing optical transitions from the ground to the excited state

$$\hbar\omega_{12} = E_{d2}(Q_{v1}) - E_{d1}(Q_{v1}), \quad (3)$$

and to the energy $\hbar\omega_{21}$ of optical transitions back to the ground state

$$\hbar\omega_{21} = E_{d1}(Q_{v2}) - E_{d2}(Q_{v2}), \quad (4)$$

can be obtained from Eqs. (1)–(4) in the following form:

$$Q_{v1}(\hbar\omega) = \frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2} - \sqrt{\left(\frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2}\right)^2 - \frac{E_{02} - \hbar\omega + a_1 Q_1 - b_2 Q_2}{a_1 - b_2}}, \quad (5)$$

$$Q_{v2}(\hbar\omega) = \frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2} - \sqrt{\left(\frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2}\right)^2 - \frac{E_{02} + \hbar\omega + a_1 Q_1 - b_2 Q_2}{a_1 - b_2}}. \quad (6)$$

Assuming that the energy distributions for the defect center concentrations in the ground state, $N_{d1}(E_{d1})$, and in the excited state, $N_{d2}(E_{d2})$, are described by the Boltzman distributions and considering relations (1) and (2), we find their dependences on the corresponding configuration coordinates

$$N_{d1}(Q) = N_{d10} \exp\left(-\frac{a_1 (Q - Q_1)^2}{k_B T}\right), \quad (7)$$

$$N_{d2}(Q) = N_{d20} \exp\left(-\frac{b_1 (Q - Q_2)^2}{k_B T}\right), \quad (8)$$

where N_{d10} and N_{d20} are particle concentrations in the ground state for $Q = Q_1$ and in the excited metastable state for $Q = Q_2$, respectively; k_B is the Boltzmann constant, and T is the absolute temperature.

Taking into account Eqs. (7) and (8), the expressions determining the spectral dependence of the absorption coefficient $k_{d1}(\omega)$ caused by the optical transitions from the ground state to the excited state, and of the absorption coefficient $k_{d2}(\omega)$ caused by the reverse transitions can be written in the form

$$k_{d1}(\omega) = \hbar\omega S_{d1} N_{d10} \exp\left(-\frac{a_1 (Q_{v1} - Q_1)^2}{k_B T}\right), \quad (9)$$

$$k_{d2}(\omega) = \hbar\omega S_{d2} N_{d20} \exp\left(-\frac{b_1 (Q_{v2} - Q_2)^2}{k_B T}\right), \quad (10)$$

where S_{d1} and S_{d2} are the photoabsorption cross sections for the ground state and excited state, respectively.

Thus, the optical absorption in the crystal caused by the examined deep defect center is spectrally dependent, and its absorption coefficient $k_d(\omega)$ is determined by the sum

$$k_d(\omega) = k_{d1}(\omega) + k_{d2}(\omega), \quad (11)$$

depending, according to Eqs. (9), (10) and (5), (6), on the concentrations of the centers in the ground and excited states, the thermal excitation energy E_{02} , differences between their photoabsorption cross sections and the energy parameters a_1 and b_2 , and the shift between the ground and excited states on the configuration coordinate $Q_1 - Q_2$. The optical transitions induced by exposition of the crystal to radiation with a certain frequency ω_n lead to redistribution of the center concentration between these states. An analysis demonstrates that the equilibrium condition defined by equality of the numbers of direct and reverse transitions is established when the condition

$$k_{d1}(\omega_n) = k_{d2}(\omega_n) \quad (12)$$

is satisfied.

3. Approximation of the spectral dependences of the optical absorption

The spectral dependences of the optical absorption in the BTO:Al crystal observed experimentally in [15] can be approximated by the impurity absorption model that takes into account the contribution of electrons photoexcited from deep donor centers to the conduction band and the intracenter transitions [11] supplemented by the model of the defect center interacting with the lattice that is based on the application of the configuration coordinate diagram considered above. Below we restrict ourselves by an analysis of the approximation of three experimental dependences from [15] shown by open circles in Fig. 2.

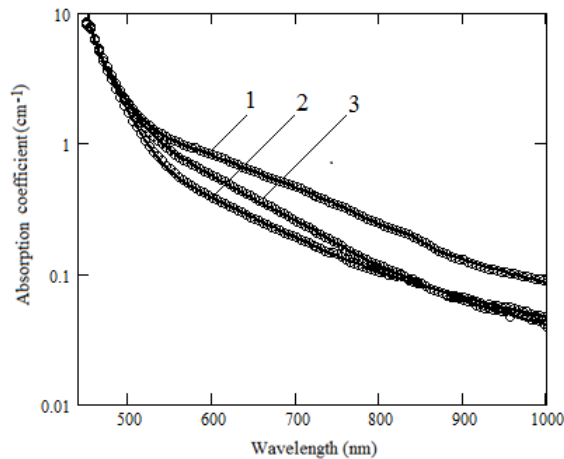


Figure 2. Experimental and calculated spectral dependences of the optical absorption coefficient for the $\text{Bi}_{12}\text{TiO}_{20}\text{:Al}$ crystal exposed first to laser radiation with a wavelength of 532 nm (1) and then to radiation with wavelengths of 663 (2) and 780 nm (3), respectively, until saturation. The open circles are for the experimental data, and the solid curves are for the calculated dependences

Dependence 1 in this figure shows the absorption spectrum for the BTO:Al crystal exposed in the initial stage of each experiment to laser radiation with the wavelength $\lambda_i = 532$ nm and the intensity $I_i = 15.4$ mW/cm² for 1930 s. This dependence was reproduced well irrespective of the initial state of the BTO:Al sample [15]. Spectral dependences 2 and 3 shown in Fig. 2 illustrate the subsequent exposition of the crystal to continuous laser radiation with the wavelength $\lambda_n = 663$ nm ($I_n = 270$ mW/cm² and the exposure time until saturation $t_n = 960$ s) and $\lambda_n = 780$ nm ($I_n = 4$ mW/cm² and $t_n = 6420$ s), respectively, in the second stage of the experiments leading to the enhanced transmittance of the crystal.

The approximation of the experimental spectral dependences of the optical absorption in the BTO:Al crystal yielded the following values of the model parameters for the absorption coefficient caused by deep defect centers and described by Eqs. (9) and (10): $a_1 = 5.426$ eV, $b_2 = 6.480$ eV, $E_{02} = 0.103$ eV; $Q_1 = 0.8$, $Q_2 = 0.2$; $S_{d1} = 3.94 \cdot 10^{-5}$ cm²·eV⁻¹ and $S_{d2} = 1.0 \cdot 10^{-4}$ cm²·eV⁻¹. The parameters N_{d10} and N_{d20} , depending on the illuminating radiation wavelength ensuring the fulfillment of balance condition (12) for transitions between the deep center states, are presented in Table 1 for laser radiation with three wavelengths used in experiments by Dyu et al. [15] and for nonmonochromatic radiation of a semiconductor light-emitting diode with the average wavelength $\lambda_n = 588$ nm. For nonmonochromatic radiation, the experimental technique was analogous to that used in [15]. In the first stage, the BTO:Al sample was irradiated by laser radiation with the wavelength $\lambda_i = 532$ nm that caused the diminished transmittance of the crystal; the subsequent sample exposition to incoherent radiation with $\lambda_n = 588$ nm and intensity $I_n = 0.3$ mW/cm² in the second stage caused the enhanced transmittance of the crystal with saturation at $t_n = 2760$ s.

Table 1. Parameters of the deep defect center model depending on the irradiated wavelength

λ , nm	N_{d10} , m ⁻³	N_{d20} , m ⁻³
532	$4.68 \cdot 10^{23}$	$7.33 \cdot 10^{23}$
588	$8.55 \cdot 10^{23}$	$3.45 \cdot 10^{23}$
663	$10.7 \cdot 10^{23}$	$1.33 \cdot 10^{23}$
780	$11.5 \cdot 10^{24}$	$0.50 \cdot 10^{23}$

To approximate satisfactorily the spectral dependences, three intracenter transitions with the Gaussian spectral characteristics and maxima at quantum energies of 1.49, 1.62, and 1.77 eV must be taken into account together with the electron photoexcitation to the conduction band from four donor centers with average ionization energies of 1.08, 1.56, 1.96, and 2.75 eV. The energy parameters of the defect centers that characterized these processes in the BTO:Al crystal were close to those used in [11]. The approximated spectral dependences shown in Fig. 2 by solid curves demonstrate good agreement with the available experimental data.

An analysis of the model parameters used to approximate the experimental spectral dependences of the optical absorption in the BTO:Al crystal demonstrated the following. The increased optical absorption induced in the BTO:Al crystal by exposition to short-wavelength radiation with the wavelength $\lambda_i = 532$ nm was due to the increased contribution of the intracenter transitions to the radiation absorption, photoinduced increase in the degree of occupation by electrons of the centers with ionization energies of 1.08 and 1.96 eV, and photoexcitation of deep defect centers and their transition from the ground state to the excited metastable state (see Fig. 1). The subsequent exposition to long-wavelength radiation led to the reduced contribution of intracenter transitions to the absorption during occupation by electrons of the centers with ionization energies of 1.08 and 1.96 eV. In this case, the degree of occupation by electrons of the center with ionization energy of 1.56 eV increased, and the concentration of the deep defect centers in the excited state decreased due to their photoinduced transitions to the ground state.

Thus, the observed nonmonotonic dependence of the enhanced transmittance for the Bi₁₂TiO₂₀:Al crystal, having the diminished transmittance, on the wavelength λ_n of radiation leading to the enhanced transmittance can be caused not only by quantitative changes of contributions to the impurity absorption described in [11], but also by photoinduced transitions of the deep defect center between the ground and excited states, accompanied by strong electron-phonon interaction with distortion of the crystal lattice. For energy of the radiation quantum with $\lambda_i = 532$ nm corresponding to the vertical transition from the state A (Fig. 1) with maximum concentration of the centers to the ground state, they are effectively translated to the excited state (AB transition), leading to the diminished transmittance of the crystal. The enhanced transmittance of the crystal will be maximum for radiation with energy of the quantum at which the CD transition occurs (in the examined case, at the wavelength $\lambda_n \approx 670$ nm).

4. Conclusions

Thus, the reversible changes in the optical absorption spectrum for the BTO:Al crystal observed experimentally in [15] and induced by the subsequent exposition to short- and long-wavelength radiation are well described by the impurity absorption model, considering the photoexcitation of electrons from the deep centers to the conduction band and the intracenter transitions [11], complemented by the model of deep defect centers with two metastable states interacting with the lattice. The photoinduced transitions between these states are accompanied by changes in the configuration coordinates. The observed photoinduced changes in the optical absorption in the BTO:Al crystal can be caused not only by the photoinduced electron redistribution over the deep donors via the conduction band and by generation and decay of defects for which the intracenter transitions occur, but also by redistribution of the deep center concentration between two metastable states with different photoabsorption cross sections.

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