Changes in the optical absorption induced by sequential exposition to short- and long-wavelength radiation in the BTO:Al crystal

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Abstract. Modifications of the spectral dependences of the optical absorption induced in the Bi₁₂TiO₂₀:Al crystal as a result of sequential exposition to cw laser radiation first with the wavelength λ₉ = 532 nm and then with the longer wavelength λ₋,ₙ = 588, 633, 655, 658, 663, 700, 780, 871, or 1064 nm are investigated. We revealed that after the short-wavelength exposition to radiation with λ₉ = 532 nm, the optical absorption in the crystal increases, and in the range 470–1000 nm, yields the spectrum whose form is independent of a prehistory. The subsequent exposition to longer-wavelength radiation leads to bleaching of the crystal in the examined spectral range. A maximum diminishing of the optical absorption in the crystal is observed upon exposure to radiation with the wavelength λ₋₅ = 663 nm. To describe the experimentally observed reversible changes in the optical absorption spectrum in the Bi₁₂TiO₂₀:Al we use the impurity absorption model that 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

Bi₁₂TiO₂₀ (BTO) crystals belonging to the sillenite family are promising for application in dynamic holography based on contradirectional interaction of light waves in reflection geometry [1-4]. This is due to high values of the space charge field of reflection 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 sillenite 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]. 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 in [14]. In addition, third reason for changes in absorption may be the optically induced transitions between two metastable states of the deep defect centers in the crystal, which are accompanied by considerable reconstruction of such centers manifested via changes in their positions in the lattice [15].

In this paper we experimentally investigate the changes in spectral dependences of the optical absorption in the Bi$_{12}$TiO$_{20}$:Al crystal caused by sequential exposition to cw laser radiation to the shortest wavelength $\lambda_g = 532$ nm in the first stage followed by exposition to the longer wavelength $\lambda_{l,n}$ taking in different experiments value of 588, 633, 658, 663, 780, 871, or 1064 nm, respectively. To describe the observed reversible changes the model taking into account strong relaxation of the lattice during photoinduced transitions between two metastable states of a deep defect center, in addition to the impurity absorption model included both the photoexcitation of electron from deep centers to the conduction band and the intracenter transitions [11], is considered.

2. Experimental method and results

The examined Bi$_{12}$TiO$_{20}$:Al sample was grown by the TSSG method and had the thickness $d = 6.6$ mm along the [100] crystallographic direction. Its transmission spectra were registered for the initial crystal state and after each exposition. All experiments were performed at room temperature.

The experimental investigations performed previously in [16] demonstrated that exposition to short-wavelength radiation with the wavelength $\lambda_g = 532$ nm caused an increase in the optical absorption coefficient $k_g(\lambda)$ 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. We established that the subsequent exposition to a longer-wavelength radiation with $\lambda_{l,n}$ changing from 588 to 1064 nm led to the enhanced transmittance of the BTO:Al crystal in the entire examined spectral range with absorption coefficients $k_{l,n}(\lambda)$, which reaches saturation depending on the employed wavelength $\lambda_{l,n}$.

Even though the dependences $k_g(\lambda)$ and $k_{l,n}(\lambda)$ were monotonic [16], the spectral dependences of the changes in absorption $\Delta k_n = k_g(\lambda) - k_{l,n}(\lambda)$ demonstrated a resonant character. Figure 1 shows the spectral dependences characterising the maximum changes in the optical absorption for the Bi$_{12}$TiO$_{20}$:Al crystal with enhanced transmittance, preliminary illuminated by green light ($\lambda_g = 532$ nm), reached by its subsequent illumination with longer-wavelength radiation at $\lambda_{l,n} = 663$ (curve 1), 655 (curve 2), 633 (curve 3), 780 (curve 4), 871 (curve 5), or 1064 nm (curve 6).

![Figure 1](image.png)

**Figure 1.** Experimental spectral dependences $\Delta k_n(\lambda)$ of the BTO:Al crystal preliminary illuminated with laser radiation $\lambda_g = 532$ nm observed after subsequent illumination with $\lambda_{l,n} = 663$ (1), 655 (2), 633 (3), 780 (4), 871 (5), or 1064 nm (6) until saturation.

It should be noted that the maximum decrease of the optical absorption in the Bi$_{12}$TiO$_{20}$:Al crystal was observed after exposition at the wavelength $\lambda_{l,5} = 663$ nm. The changes in the optical absorption during enhanced-diminished transmittance cycles were reversible and well reproduced experimentally.
3. Theoretical model

As is known [15, 17], 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 [15]. The configuration coordinate diagram [17] 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 \( Q \) (figure 2). The parabolas \( E_{d1}(Q) \) and \( E_{d2}(Q) \), described by the well-known relations [18]

\[
E_{d1}(Q) = a_1(Q - Q_1)^2, \quad (1)
\]
\[
E_{d2}(Q) = E_{02} + b_2(Q - Q_2)^2, \quad (2)
\]

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 2. Configuration coordinate diagram of a defect center.](image)

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

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

and to the energy \( \hbar \omega_{v2} \) of optical transitions back to the ground state

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

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

\[
Q_{v1}(\hbar \omega) = \frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2} - \left[ \frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2} \right]^2 - \frac{E_{02} - \hbar \omega + a_1 Q_1 - b_2 Q_2}{a_1 - b_2} \right]^{1/2}, \quad (5)
\]
\[
Q_{v2}(\hbar \omega) = \frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2} - \left[ \frac{a_1 Q_1 - b_2 Q_2}{a_1 - b_2} \right]^2 - \frac{E_{02} + \hbar \omega + a_1 Q_1 - b_2 Q_2}{a_1 - b_2} \right]^{1/2}. \quad (6)
\]

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 Boltzmann distributions, we find the absorption coefficients \( k_{d1}(\omega) \) and \( k_{d2}(\omega) \) caused respectively by the optical transitions from the ground state to the excited state and by the reverse transitions, as
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; \( S_{d1} \) and \( S_{d1} \) are the photoabsorption cross sections for the ground and excited state, respectively; \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature.

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

\[
k_d(\omega) = k_{d1}(\omega) + k_{d2}(\omega),
\]

depending, according to equations (7), (8) and (5), (6), on the concentrations of the centers in the ground and excited states, the thermal excitation energy \( E_0 \), 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 \( \omega_n \) 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

\[
k_{d1}(\omega_n) = k_{d2}(\omega_n)
\]

is satisfied.

4. Approximation of the spectral dependences of the optical absorption

The spectral dependences of the optical absorption in the BTO:Al crystal 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 three experimental dependences from [16] shown by open circles in figure 3. 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 \( \lambda_g = 532 \) nm. Spectral dependences 2 and 3 shown in figure 3 illustrate the subsequent exposition of the crystal to continuous laser radiation with the wavelength \( \lambda_{l,2} = 663 \) nm and \( \lambda_{l,3} = 780 \) nm, respectively, in the second stage of the experiments.

![Figure 3](image-url)
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 caused by deep defect centers and described by equations (7) and (8): \( a_1 = 5.426 \text{ eV}, b_2 = 6.480 \text{ eV}, E_{02} = 0.103 \text{ eV}; Q_1 = 0.8, Q_5 = 0.2; S_{d1} = 3.94 \times 10^{-5} \text{ cm}^2 \text{eV}^{-1} \) and \( S_{d2} = 1.0 \times 10^{-4} \text{ cm}^2 \text{eV}^{-1} \). The parameters \( N_{d10} \) and \( N_{d20} \), depending on the illuminating radiation wavelength ensuring the fulfillment of balance condition (10) for transitions between the deep center states, are presented in table 1 for laser radiation with three wavelengths and for nonmonochromatic radiation of a light-emitting diode with the average wavelength \( \lambda_{l1} = 588 \text{ nm} \). For nonmonochromatic radiation, the experimental technique was analogous to that used in [16]. In the first stage, the BTO:Al sample was irradiated by laser radiation with the wavelength \( \lambda_d = 532 \text{ nm} \) that caused the diminished transmittance of the crystal; the subsequent sample exposition to incoherent radiation with \( \lambda_{l1} = 588 \text{ nm} \) and intensity \( I_1 = 0.3 \text{ mW/cm}^2 \) in the second stage caused the enhanced transmittance of the crystal with saturation at \( t_1 = 2760 \text{ s} \).

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 in the BTO:Al crystal were close to those used in [11]. The approximated spectral dependences shown in figure 3 by solid curves demonstrate good agreement with the available experimental data.

| \( \lambda, \text{ nm} \) | \( N_{d10}, \text{ m}^{-3} \) | \( N_{d20}, \text{ m}^{-3} \) |
|-----------------|-----------------|-----------------|
| 532             | 4.68 \times 10^{23} | 7.33 \times 10^{23} |
| 588             | 8.55 \times 10^{23} | 3.45 \times 10^{23} |
| 663             | 10.7 \times 10^{23} | 1.33 \times 10^{23} |
| 780             | 11.5 \times 10^{24} | 0.50 \times 10^{23} |

An analysis of the model parameters used to approximate the experimental data demonstrated the following. The increased optical absorption induced in the BTO:Al crystal by exposition to short-wavelength radiation with the wavelength \( \lambda_d = 532 \text{ nm} \) 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 figure 2). The subsequent exposition to long-wavelength radiation led to the reduced contributions to the absorption for intracenter transitions and as the result of the light-induced depletion of 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 Bi\(_2\)TiO\(_3\):Al crystal, having the diminished transmittance, on the wavelength \( \lambda_{l,n} \) 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 \( \lambda_d = 532 \text{ nm} \) corresponding to the vertical transition from the state A (figure 2) 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 \( \lambda_d \approx 670 \text{ nm} \)).
5. Conclusions
Thus, illumination of the BTO:Al crystal with cw laser radiation at the wavelength \( \lambda_g = 532 \text{ nm} \) yields maximum values of the optical absorption in the range 470–1000 nm and the spectral dependence \( k_g(\lambda) \) independent of the initial crystal state. Subsequent illumination of the examined sample with longer-wavelength laser radiation at the wavelength \( \lambda_{l,n} = 588, 633, 655, 658, 663, 700, 780, 871, \) or 1064 nm leads to its enhanced transmittance. The minimum values of \( k_{l,n}(\lambda) \) were observed after illumination of the BTO:Al crystal by light at \( \lambda_{l,5} = 663 \text{ nm} \). The changes in the optical absorption spectrum for the BTO:Al crystal 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.

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