Light-Induced Absorption of Ru-Doped $Bi_{12}TiO_{20}$ Crystals

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ABSTRACT

The effect of ruthenium doping on optical properties of $Bi_{12}TiO_{20}$ (BTO) single crystals is studied. A low concentration of ruthenium do not change absorption behavior of BTO, however higher ruthenium addition significantly shifts the optical absorption to the near infrared spectral region with an absorption shoulder appearing around 1.8 eV. The absorption coefficient increases with increasing the Ru concentration. Light-induced absorption changes are observed and the dynamics of build-up and dark decay processes are investigated. Results show that concentration of shallow levels increase with Ru content. Evolution of the build -up and dark decay of light induced absorption consists of fast and slow components: the first process occurs within few seconds, while the second one needs several hours (or days). It is established that light-induced absorption can be modified by preliminary illumination and thermal treatments thus multi-level lead to the transient and persistent parts of light-induced absorption. A model, assuming one deep and two shallow levels is proposed to explain the bi-exponential behavior of the build-up and the dark decay of light- induced absorption when the crystals are preliminary annealed in oxygen atmosphere.

Keywords: doped crystals, photorefractive materials, optical properties, absorption, light-induced absorption

1. INTRODUCTION

Photorefractive crystals are promising materials for various non-linear applications[1-2]. In the crystals illumination with inhomogeneous laser light created by the interference of the reference and signal beam excites charge carriers from impurity levels into the conduction or valence bands, the charge carriers migrate (by diffusion or drift) and finally are trapped by empty impurities. The resulting space charge field modulates the refractive index via the electro-optic effect. Since the photorefractive effect is due to the trapping dynamics of the photogenerated charge carriers, detailed knowledge of the photoactive centers nature and their spatial distribution is essential in order to tailoring the crystal properties for special applications. Light-induced absorption spectroscopy is a useful technique to investigate the photorefractive traps properties.

BTO single crystals are promising photorefractive materials with high photosensitivity and high carrier mobility, which permit achievement of fast response time. They found a wide application in real-time holography, optical information processing, optical interconnection and communications, etc[3]. Moreover BTO crystals can be easily doped and thus the crystal properties can be changed in a desired direction. Introduction of appropriate defects or trap centers can be achieved by doping with different elements during the crystal growth[4-8].

BTO crystals exhibit light-induced absorption, which usually is explained using the so-called "two-center model"[9]. The two-center charge transport model is based on the assumption that two different impurity centers are present and each of them occurs in two different valence states. For electron conductivity the first center is deep and the second more shallow with respect to the conduction band edge. Illumination excites electrons from the deep center into the conduction band, they migrate and captured by the deep center. For high light intensity the electron concentration in the conduction band become large enough than large amount of electrons is possible to be captured by shallow tarps. Thus redistribution of electrons from the deep into the shallow centers leads to different absorption cross sections and finally to the light-induced absorption changes in the crystals. This model was confirmed to explain the non-linear intensity dependence of photoconductivity, temperature dependence of photoconductivity and light-induced absorption, sensitization of the crystals for infrared recording by green illumination also in $KNbO_3$, $BaTiO_3$ and among other crystals[10-12].

Strong light-induced absorption effect with two-step decay on a time scale of few seconds and days were observed in undoped BTO[4]. Large light-induced absorption changes were detected in BTO crystals, doped with Ga, Ce, V and P[5].

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Recently, a new charge transport model that includes deep donors in three valence states and shallow traps has been proposed to explain the slow increase of a light-induced absorption over a long period of time in undoped BTO[13]. Despite of the success of the two-center model, the photorefractive centers have not yet clearly identified in doped BTO crystals.

In this paper we study the influence on Ru-doping on the light-induced absorption properties in BTO crystals for the first time to our knowledge.

2. EXPERIMENT

BTO crystals doped with two different concentrations of ruthenium were grown in Czochralski apparatus using the Top Seeded Solution Growth method (TSSG). The purity of the starting products Bi_2O_3 and TiO_2 were 99.999% and their proportion was 11:1 in weight. Ruthenium was introduced into the melt solution in the form of RuO_2. The concentrations of Ru in the grown crystals determined by Atomic Absorption Spectroscopy were 1×10^{18} cm^{-3} and 1×10^{19} cm^{-3}. For simplicity, hereinafter we will denote crystals with low and high ruthenium content as BTO:Ru(1) and BTO:Ru(2), respectively.

Transmission spectra were measured on double polished crystal plates with a thickness approximately 1 mm in the wavelength range 400-850 nm using Cary 5I spectrophotometer. Reflection spectra were measured on plates with one polished and one grinded side in a visible spectrum using Perkin-Elmer 330 spectrophotometer with special references for calibrations at 488; 514.5; 576; 633 and 672 nm. The bulk absorption coefficient α (cm^{-1}) was calculated by taking into account the crystal's transmission, reflection and thickness using the formula:

$$T = \frac{(1 - R^2)\exp(-\alpha d)}{1 + R^2 \exp(-2\alpha d)}$$

(1)

In order to characterize absorption changes due to shallow centers induced by light illumination we performed the measurements of light-induced absorption under laser illumination of 532 nm as a pump beam. The probe beam wavelength is 633 nm. The experimental set-up for the light-induced absorption measurements is shown in Fig.1. The crystals were illuminated with pump light with a fixed wavelength of $\lambda = 532$ nm (Verdi solid-state laser). Simultaneously weak probe light emitted by 250 W QTH lamp of a grating monochromator (Oriel MS 257) illuminated the samples. The probe beam intensity I_{probe} was kept small (several $\mu W/cm^2$) to avoid any additional absorption changes. The probe beam transmitted through the crystal was collected by computer-controlled photomultiplier tube (PMT). Holographic notch filter for 532 nm was placed before the PMT in order to eliminate the influence of the pump beam scattering light.
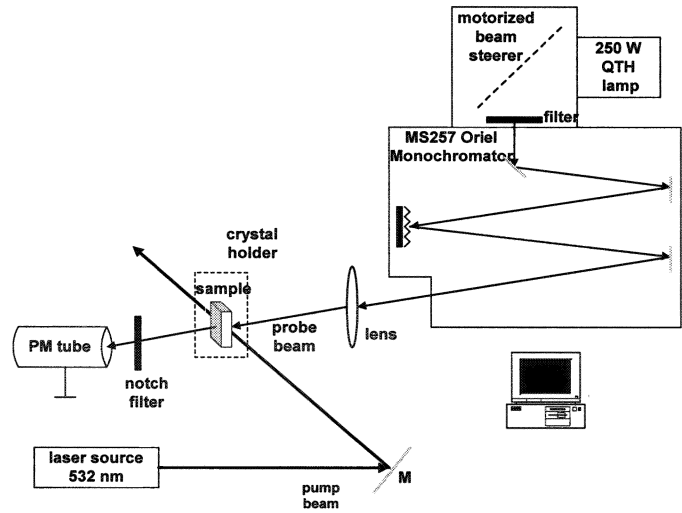

Fig. 1: Experimental set-up for light-induced measurements.

We measured the transmitted beam intensity before and after light illumination by pump beam. The light-induced absorption change α_{li} (cm^{-1}) was calculated from the change of the transmitted probe light intensity, using the following formula[12]:

$$\alpha_{li} = \frac{1}{d} \ln \left[\frac{I_{pump_{off}}}{I_{pump_{on}}} \right]$$

(2)

where d is the crystal thickness and $I_{pump\ on}$ and $I_{pump\ off}$ are the values of the intensities of transmitted probe light when pump light is on and off, respectively.

We measured the light-induced absorption changes on two different initial states of the crystals: annealed (after heating in oven at 200°C) and colored state (after preliminary illumination with green light). The thermal annealing leads to a maximum level of transmission and we consider this state as "oxidized" state. Green illumination durations were from several seconds to hours in order to obtain the saturation value of the coloration effect. We called this saturated state as the "colored" state.

3. RESULTS AND DISCUSSIONS

3.1. Bulk absorption

The absorption coefficient dependence on photon energy for two different concentration of Ru in comparison with undoped BTO is shown in Fig. 2. As it is seen a low concentration of ruthenium do not change absorption shoulder of BTO. A typical well-defined broad absorption shoulder is observed in BTO:Ru(1) and undoped BTO, reaching from the band edge (3.2 eV) up to 2.3 eV. It was established that this absorption shoulder is due to the contribution of an intrinsic antisite defect ($Bi^{3+} + h$) formed by occupation of tetrahedraly coordinated Ti^{4+} - site by a Bi^{3+}, coupled with a hole, mainly localized at the oxygen neighbors[14]. However doping with higher ruthenium concentration significantly shifts the region of optical absorption to the near IR spectral region with an absorption shoulder appearing around 1.8 eV. Obviously the bulk absorption coefficient increases with increasing the Ru content.
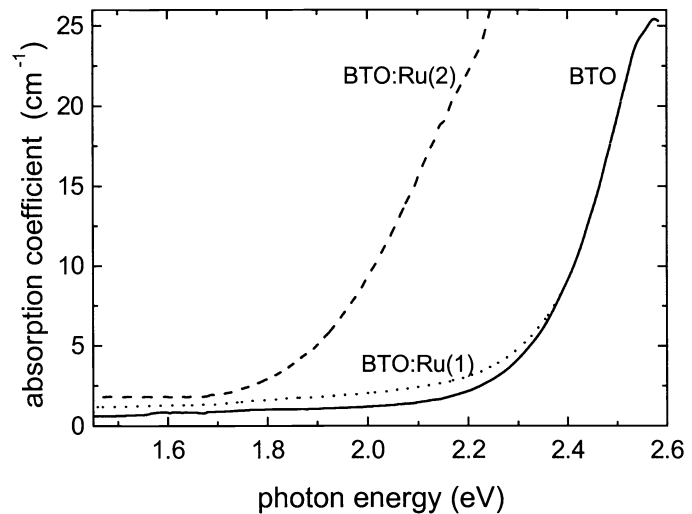

Fig.2: Absorption coefficient dependence on photon energy of BTO crystals doped with different concentration of Ru.

3.2. Light-induced absorption

Homogeneous illumination with a pump light at 532 nm generates light-induced absorption changes. All investigated samples exhibit light-induced absorption changes suggest the existence of both deep and shallow centers. Figure 3 shows the light-induced absorption change under illumination with 0.3 W/cm^2 pump light intensity depending on the probe wavelength. The results show that the light induced absorption value for the low Ru concentration is a little higher than undoped BTO sample. Since the absorption cross section generally varies with the probe wavelength, the light-induced absorption varies also with the probe wavelength and for undoped and BTO:Ru(1) becomes transparent when the probe wavelength is larger than 700 nm. However, even at the same pump intensity, the light-induced absorption in highly Ru doped BTO
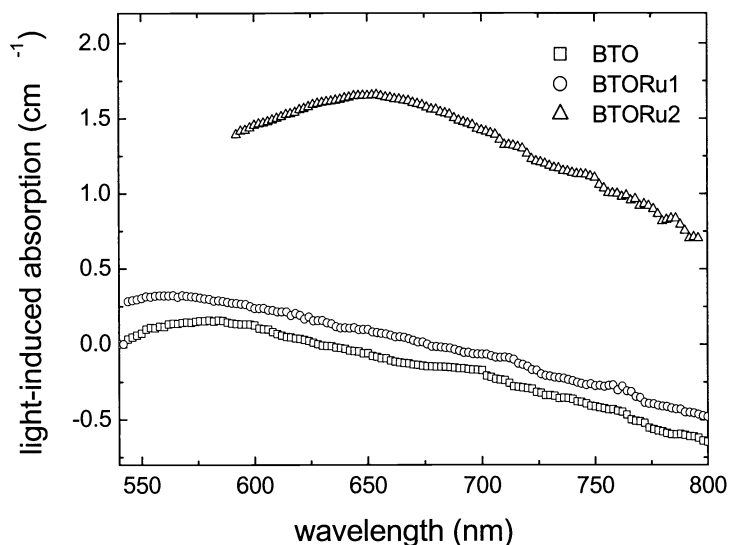

Fig.3: Light-induced absorption changes depending on the probe light. The pump light is $\lambda = 532$ nm with intensity I = 0.3 W/cm^2.

crystal is much higher for whole visible spectral range. This indicates that the concentration of shallow traps increases linearly with increasing the Ru concentration.

The light-induced absorption dynamics was measured during green pump light illumination and after the pump light is switched off. A decrease of the probe beam intensity was observed after the pump beam was switched on. After illumination with a pump light, redistribution of electrons from the deep into the shallow centers occurs and as a result absorption is changed, because the absorption cross-sections for the deep and the shallow traps are different. Figure 4 shows an example of a typical build-up and dark decay process of the light-induced absorption in BTO:Ru(1). The pump light intensity is $I = 2$ W/cm^2 and it is switched on at the moment $t = 65$ s and switched off at $t = 670$ s. As can be seen from Fig. 4 the light-induced absorption change takes place for several seconds, suggesting that shallow traps are populated during the pump light illumination. Similar dynamic process was

Fig.4: Time evolution of the transmitted probe beam power in BTO:Ru(1). The pump light is switched on at $t = 65$ s and switched off at $t = 670$ s.

observed also for non-doped BTO and BTO:Ru(2) crystals. By use of 633 nm as probe beam, the maximum vales of light-induced absorption changes depending on pump beam intensity is shown in Fig. 5. As it seen the changes of light-induced absorption increases with increasing the Ru concentration and consequently the concentration of shallow levels increases with increasing the Ru content.

We found that the dynamic of light-induced absorption depends on the preliminary treatment of the crystal. Light-induced absorption values can be modified either by illumination with green light or thermal annealing. This leads to the transient and persistent parts of the light-induced absorption effect. Figure 6 (a) shows an example of a typical build-up process of the light-induced absorption (after the pump light is switched on at the time $t = 0$) for BTO:Ru(2) sample at "bleached" and "colored" states. As it can be seen the build-up process of the "bleached" crystal consists of two slow components. However, when the initial state is "colored" response time of build-up process is much faster than that in a "bleached" state.

The dark-decay dynamics of the light-induced absorption for both "bleached" and "colored" states of BTO:Ru(2) are shown in Fig. 6 (b). The dark relaxation at "bleached" state could be described as a two-step process: the first decay process is much faster than the second one. The first process occurs within few seconds, while the second one needs more time. The second part of the dark decay process indicates that the relaxation time for the light-induced absorption can be longer as several hours or days. This points out that the secondary (shallow) traps are relatively deep in the Ru-doped BTO band gap structure.
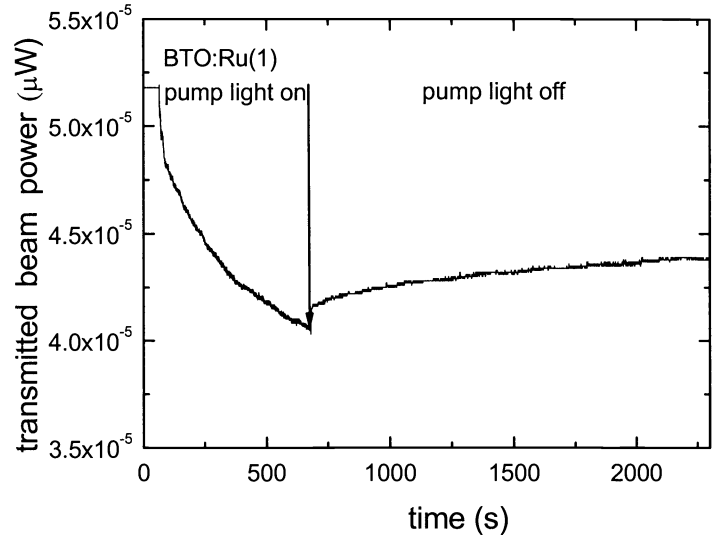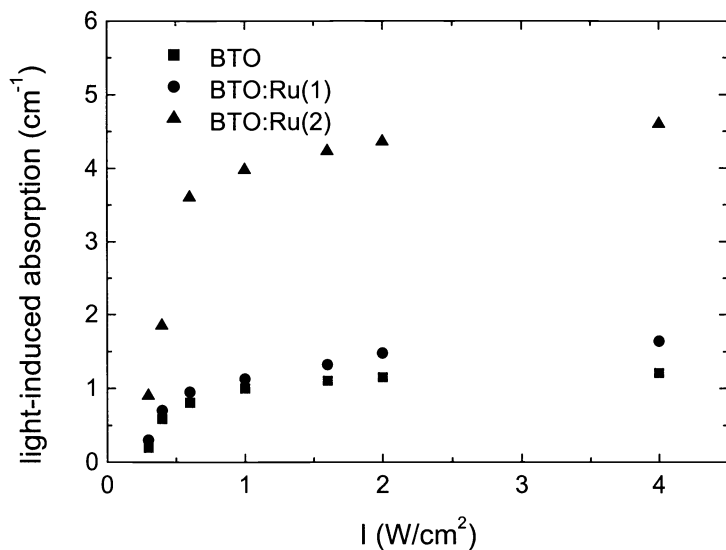

Fig.5: Light-induced absorption dependence on the pump light intensity, the probe beam is 633 nm.
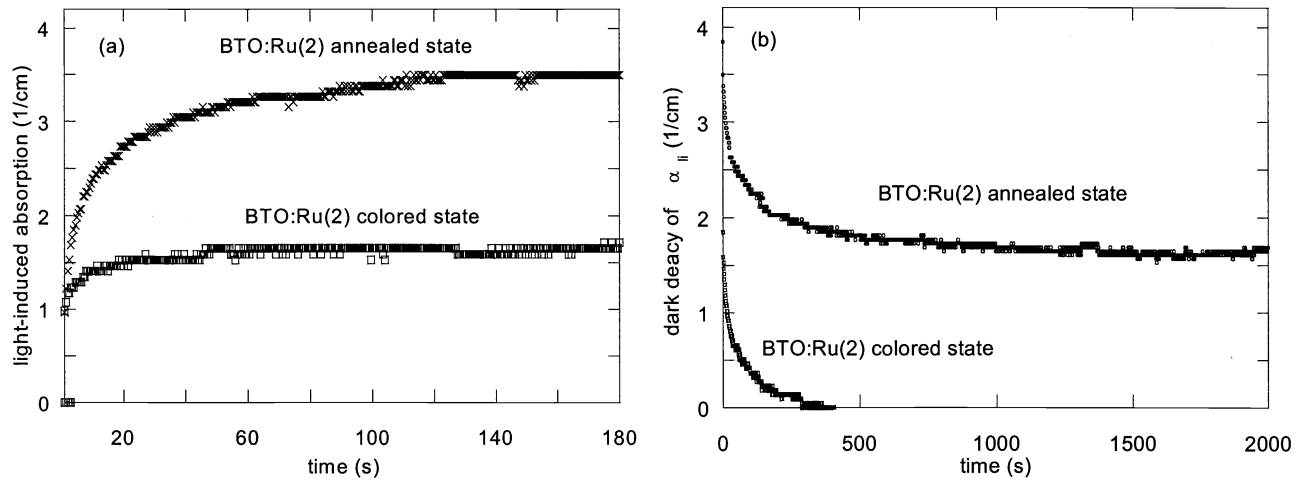
Fig.6: Evolution of light-induced absorption build-up (a) and dark decay (b) process during the time for BTO:Ru(2) at "annealed" and "colored" states. Pump light is 532 nm I = 2 W/cm^2, probe light is 633 nm.

In the framework of the two-center model we assume the presence of one deep photorefractive center N_1 and two shallow photorefractive centers N_{2a} and N_{2b}. One of these shallow levels is very closed to the conduction band (level 2a) and the second one is between the deep level and the shallowest level (level 2b). Band diagram is shown in Fig.7. At room temperature level (2a) is shallow enough to be empty, while level (2b) needs an external source of light energy and/or higher temperature annealing to ionize its impurity centres. Thus, if these two centers are initially empty, photogenerated electrons from the deep level will stay trapped in the deeper shallow level, while the shallowest will decay quickly by thermal energy as soon as the light is turned off, returning to its original empty state. To be ionized, the deeper shallow centers (2b) need to receive sufficient energy, either optically or thermally. Assuming this situation, the rate equations, the charge conservation and the constant trap density can be expressed by well known equations[12]:
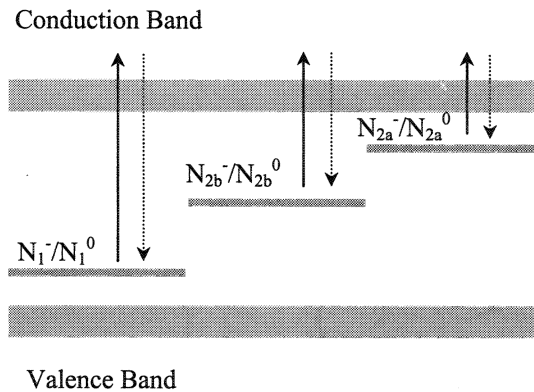

Fig.7: Band diagram of one deep (1) and two shallow levels (2a) and (2b).

$$\frac{dN_1^-}{dt} = -\left(\beta_1 + q_1 S_1 I + r_1 N_e\right)N_1^- + r_1 N_1^{\ 0} N_e \qquad (3a)$$

$$\frac{dN_{2a}^-}{dt} = -\left(\beta_{2a} + q_{2a}S_{2a}I + r_{2a}N_e\right)N_{2a}^- + r_{2a}N_{2a}^{\ 0}N_e \tag{3b}$$

$$\frac{dN_{2b}^-}{dt} = -\left(\beta_{2b} + q_{2b}S_{2b}I + r_{2b}N_e\right)N_{2b}^- + r_{2b}N_{2b}^{\ 0}N_e \tag{3c}$$

$$N_1 = N_1^- + N_1^{\ 0} \tag{4a}$$

$$N_{2a} = N_{2a}^- + N_{2a}^{\ 0} \tag{4b}$$

$$N_{2b} = N_{2b}^- + N_{2b}^{\ 0} \tag{4c}$$

$$N = N_1 + N_{2a} + N_{2b} \tag{5}$$

where: N_i^- - density of sources; N_i^0 - density of traps; N_e - density of electrons in conduction band; s_i - photon absorption cross sections, β_i - thermal generation rates, r_i - recombination coefficients, I - light intensity, N - whole impurity concentration. The sub indexes i = 1, 2a, 2b correspond to the species N_1, N_{2a} and N_{2b}. Thus the rate equations for level (i) can be derived as follow:

$$N_i^-(t) = r_i N_i N_e \tau_i [1 - \exp(-t/\tau_i)] \tag{6}$$

where: $\quad \tau_i = \dfrac{1}{\beta_i + q_i S_i I + r_i N_e}$ is a time constant. $\tag{7}$

Case (a): if the initial state is oxidized, we assume that both the relatively shallow levels are essentially empty ($N_{2a\ (I=0)}^- = N_{2b\ (I=0)}^- = 0$). The conservation of charge can be expressed by:

$$N_{2a}^-{}_{(I\neq0)} + N_{2b}^-{}_{(I\neq0)} = N_1^-{}_{(I=0)} - N_1^-{}_{(I\neq0)} \tag{8}$$

$$\frac{dN_1^-}{dt} + \frac{dN_{2a}^-}{dt} + \frac{dN_{2b}^-}{dt} = 0 \tag{9}$$

Thus the build-up of absorption induced by illumination is:

$$\alpha_{li} = S_{2a}N_{2a(I\neq0)}^- + S_{2b}N_{2b(I\neq0)}^- - S_1(N_{1(I=0)}^- + N_{1(I\neq0)}^-) = C_a[1 - \exp(-t/\tau_{2a})^{-t/\tau_a}] + C_b[1 - \exp(-t/\tau_{2b})] \tag{10}$$

where: $C_a + C_b = \alpha_{li,0}$ is a steady-state light-induced absorption.

It can be seen that the build-up of light induced absorption will display exponential behavior with two time constants: τ_a and τ_b.

Case (b): if the initial state is "colored" (means level (2b) filled with electrons but level (2a) empty due to its high thermal generation rate), the resulting charge transfer process for absorption build-up would be:

$$N_{2a}^-{}_{(I\neq0)} = N_1^-{}_{(I=0)} - N_1^-{}_{(I\neq0)} \tag{11}$$

$$\alpha_{li} = (S_{2a} - S_1)r_{2a}N_{2a}N_e\tau_{2a}[1 - \exp(-t/\tau_{2a})] = \alpha_{li,C}[1 - \exp(-t/\tau_{2a})] \tag{12}$$

where $\alpha_{li,C}$ is the maximum change of absorption when starting with a fully colored sample.

In a dark (I=0) approximately all mobile electrons are captured by the deep traps and probably any electrons could present in the shallow traps because of the high thermal generation rate. Thus the number of charge carriers in level (i) is possible to express by:

$$N_i^- = r_i N_i N_e \tau_{di} e^{-t/\tau_{di}} \tag{13}$$

where: $\tau_{di} = (\beta_i + r_i N_e)^{-1}$ is a decay time-constant $\tag{14}$

Electrons, moving from level (2b) to level (2a) can be neglected. Combining with the above derived equation for light induced absorption in the one deep, two shallow level system gives:

$$\alpha_{li} = -(S_{2a} - S_1)r_{2a} N_{2a} N_e \tau_{d2a} \exp(-t/\tau_{d2a}) - (S_{2b} - S_1)r_{2b} N_{2b} N_e \tau_{d2b} \exp(-t/\tau_{d2b}) \tag{15}$$

This formula indicates the change in absorption during the dark decay process.

Using above presented approximations, for preliminary annealed BTO:Ru(2) crystal (data presented in Fig.6a and 6b) we get values for the time constants during the build-up and dark decay process as follows: $\tau_{2a} = 26$ s; $\tau_{2b} = 85$s; $\tau_{d2av} = 123$ s and $\tau_{d2b} = 4.6$ hours.

It is well known that BTO crystals have a complex structure that allows a number of charge trapping sites. Usually, the deep level is related to the intrinsic defects due to the Ti^{4+} or replaced by $(Bi^{3+} + h)$ vacancies in tetrahedral positions[14]. In case of Ru-doping the band gap becomes more complicated due to the assumption based on Electron Paramagnetic Resonance (EPR) studies[15], that Ru-ions can exist simultaneously in three different valence states: Ru^{3+}, Ru^{4+} and Ru^{5+}. In general Ru^{4+} can occupy Bi^{3+} sites in tetrahedral positions, however it also can substitute some Ti^{4+} atoms due to the high distribution coefficient, i.e. the ruthenium concentration in the melt and in the crystal are nearly the same. We expect that Ru ions occur in BTO:Ru crystals in the valence state 3^+ and 4^+ and the Ru ions in the third valence state 5^+ are created under annealing in oxygen atmosphere. Further investigation can clarify this assumption. It should be noted that in our highly doped BTO crystal Ru presents in a large amount concentration and probably it will have a substantial contribution for the photorefractive properties at the near infrared region

4. CONCLUSIONS

Effect of different concentrations of ruthenium on the absorption and light-induced absorption process in BTO crystals was investigated. A low concentration of ruthenium does not change absorption shoulder of BTO, however a higher concentration (10^{19} cm^{-3}) increases the absorption significant and shifts the absorption shoulder to the NIR wavelengths. The addition of ruthenium results to stronger light induced absorption effect and consequently to increase the concentration of shallow centers. It was established that light-induced phenomena depend on preliminary treatment of the samples and thermal annealing could influence concentration of shallow levels. Modification of two-center model with one deep and two shallow levels is hypothesized as the mechanism responsible for the light induced absorption changes. We hope large concentrations of shallow levels should be useful for infrared sensitization. Furthermore, with appropriate Ru concentration we believe to improve the photorefractive performance at 1.06 μm.

ACKNOWLEDGEMENTS

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