Light-induced relaxation dynamics in Rh-doped Bi$_{12}$TiO$_{20}$ crystals

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Abstract. The lifetime of the excited charge carriers in Rh-doped BTO crystals is characterized by measuring the time-resolved photoinduced absorption (PIA) after nanosecond pulse excitation from a frequency doubled Nd:YAG laser ($\lambda=532$ nm). It was found that the Rh-addition in the BTO structure slows down the relaxation decay in comparison with non-doped BTO, which is attributed to additional trapping centers related to the rhodium dopant. The experimental curve is well fitted by a double-exponential decay which is ascribed to the presence of two different shallow traps contributing to the charge transport and recombination mechanisms in Rh-doped BTO crystal.

1. Introduction

Sillenite type photorefractive crystals ((Bi$_{12}$SiO$_{20}$ (BSO), Bi$_{12}$TiO$_{20}$ (BTO)) are well known as one of the best inorganic materials for real-time image processing and related applications [1]. Due to the excellent photoconductivity and high charge carrier mobility, they found applications in dynamic information processing, interferometry, optical metrology, etc. [2]. Very recently the ability to combine sillenite crystals with liquid crystals (LCs) into an organic-inorganic hybrid structure (optically addressed light valve devices) became an attractive issue that opens further possibilities to design new nonlinear optical devices for real-time image processing and display technology [3,4]. For that reason special efforts have been made to further enhance photosensitivity and response time of the sillenites, especially in the near infrared (NIR) spectral range [5]. Generally, the modification of crystal properties by changing the stoichiometry during the crystal growth process, by reduction/oxidation treatments or by adding suitable dopant in a structure, is a well known approach. For instance, by varying the stoichiometry, Mokrushina et al. [6] found a correlation between the deficiency of oxygen in non-doped BSO crystals (grown in oxygen free atmosphere) and NIR sensitivity improvement, later on confirmed also by Raita et al [7]. Among the variety of elements transition metals ions are particularly interesting for the optimization of the properties via doping, because they can exist in different valence states after appropriate light illumination [8]. For example, we found [9] that ruthenium (Ru) is an excellent dopant in BSO structure which significantly improves the photosensitivity as well as the response speed during holographic recording in the NIR after green light pre-excitation (with optical energy close to the transition of the main photorefractive center of sillenites—the so-called antisite Bi defect $-$), located at 2.2 eV below the conduction

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band (CB) at room temperature \([10]\)). Recently \([11]\), we have also reported that rhodium (Rh) acts as another very effective trap center in the BTO crystal structure. A response time of 0.1 s was measured during real-time holography at the NIR wavelength of 1064 nm without any preliminary treatment. When the sample was pre-exposed with 532 nm light, the detected response time reduces becomes to 0.02 s. Also, Rh is well known as a unique dopant for BaTiO\(_3\) crystals, that makes it sensitive in the NIR due to the Rh\(^{3+}\) and Rh\(^{4+}\) coexistence \([12]\).

In the present work, we report photoinduced absorption (PIA) measurements of the relaxation dynamics of the excited charge carriers in a Rh-doped BTO crystal in comparison with non-doped BTO.

2. Experimental details

Rh-doped BTO crystals were grown by the top seeded solution growth method \([13]\). The growth process was conducted at an atmosphere of 85% air and 15% Ar. Rhodium was introduced into the melt solution as RhO\(_2\) and the Rh concentration of 5.2 \(\times\) 10\(^{18}\) cm\(^{-3}\) in the grown crystals was determined by atomic absorption spectroscopy.

For the absorption measurements an optically polished crystal plate (thickness of 0.5 mm) was prepared. The absorption spectra were measured in the visible range using a Varian Cary 5 UV spectrophotometer. To study the PIA and the relaxation dynamics a pump-probe technique (flash photolysis instrument LP 920) was used. The crystal plate was irradiated with single shot pulses from a frequency doubled Q-switched Nd:YAG laser (\(\lambda=532\) nm, pulse duration 6 ns). A weak monochromatic probe beam (at 600 nm) transmitted through the sample was used to measure the absorption changes. The signal was detected by a photomultiplier and recorded by a high bandwidth digital storage oscilloscope. The measured time scale extends from the first few nanoseconds to the several hundred seconds after pulse photoexcitation. A xenon lamp operating in a pulsed mode was used as a source for the probe beam for short time scanning (ranges below 1 ms). Alternatively, for long-time scanning (up to 100 s) a halogen lamp was used as a probe source.

![Schematic diagram of the flash photolysis set-up.](image)

The crystal sample prepared in a thin plate was placed in a holder allowing near anti-collinear geometry with an angle of 5° between the pump and probe beam (figure 1). At least 10 single-shot measurements were always averaged in order to improve the signal to noise ratio. Also, we waited several minutes between each two shots, which is considered to be sufficient to complete the relaxation process.

The monitored PIA data are presented as change in the optical density (OD):
which is calculated from the transmittance $T$, i.e., the ratio of transmitted intensity through the sample $I$ to the incident intensity $I_0$ of the probe light.

3.3. Results and discussions

Figure 2 shows the absorption spectrum of a Rh-doped BTO crystal compared to the non-doped BTO. Obviously, the absorption edge is shifted to the red and NIR range by Rh addition. Moreover, a broad peak with rather low optical density is detected in the wavelength interval from 700 nm to 825 nm, which can be attributed to the increased concentration of Rh containing defects that may act as effective trap centers. By reducing the oxygen pressure during the crystal growth process, we can expect that the concentration of oxygen vacancies increases, leading to more stoichiometric defects, consequently to more Ti$^{4+}$ vacancy defects. Such a host environment allows Rh ions to occupy energetically more suitable positions, which affects the absorption spectrum and NIR sensitivity.

Figure 2. Optical absorption spectrum of Rh-doped BTO crystal compared to non-doped BTO.

Figure 3 shows the dark decay of the induced optical density changes for a Rh-doped BTO crystal plate measured at room temperature. A long lasting component of the relaxation process is clearly observed. We found that the relaxation decay process for Rh-doped crystals is well fitted by a sum of two exponential decay functions:

$$OD(t) = OD_f \exp\left(-\frac{t}{\tau_f}\right) + OD_s \exp\left(-\frac{t}{\tau_s}\right)$$  \hspace{1cm} (2)$$

where “f” and “s” correspond to a faster and a slower component of the decay, $OD_f$ and $OD_s$ denote their amplitudes, $\tau_f$ and $\tau_s$ are their time constants, respectively. The presence of these two components in the dark decay can be attributed to the existence of two different types of traps centers. We have determined a relatively fast decay component with a time constant of $\tau_{f(BTO:Rh)} = 1.1 \text{ s}$ and a slower one with a time constant of $\tau_{s(BTO:Rh)} = 13 \text{ s}$ by fitting the BTO:Rh data using eq. (2).

Figure 4 presents the relaxation decay of a non-doped BTO crystal taken in the same experimental conditions. Again a slow exponential decay can be clearly recognized at later times in this semilog plot.
Figure 3. Time dependence of the light-induced OD change in Rh-doped BTO after ns laser pulse excitation until the full relaxation. The symbols are experimental data and the solid line is the result of the fitting procedure yielding relaxation decay time constants of $\tau_1 = 1.1$ s and $\tau_2 = 13$ s at room temperature.

Figure 4. Time dependence of the light-induced OD change in non-doped BTO after ns laser pulse excitation until the full relaxation. The symbols are experimental data and the solid line is the result of the fitting procedure yielding relaxation decay time constants of $\tau_{f1} = 0.01$ s, $\tau_{f2} = 0.15$ s and $\tau_s = 4.5$ s at room temperature.
However, for non-doped BTO the fast component is multi-exponential. Adding a single fast exponential to the slow component yields a poor fit of the data. A strong improvement was obtained with two fast components with decay times $\tau_{f1(\text{BTO})} = 0.01\text{ s}$ and $\tau_{f2(\text{BTO})} = 0.1\text{ s}$, either of them much smaller than the value for the slow decay of $\tau_{s(\text{BTO})} = 4.5\text{ s}$. In fact, the fast component of the decay is non-exponential which becomes more evident from measurements in shorter time scales (not shown here).

The relaxation process of non-doped BTO is completed faster in comparison with Rh-doped BTO, using the same pump intensity. Not only is the fast initial decay, relatively more important in the undoped crystal, also the decay time of the slow component is three times smaller. The slower relaxation process in the doped crystal can be attributed to the incorporation of rhodium.

The above results of non-doped BTO may be related to recently published PIA data of BTO crystals, irradiated with a high intensity laser pulse of 532 nm [14]. However, the authors reported about near permanent changes in the optical properties after intense irradiation, with very slow relaxation process with decay time in order of hours. This was attributed to the existence of intermediate level traps in the forbidden band gap of the BTO crystals.

At the same time, we have recently characterized non-doped BSO crystals with rather faster relaxation decay (complete decay occurs within few ms) [15] in comparison with the non-doped BTO. The difference is supposed to be due to the different intrinsic defects and trap levels in BTO and BSO crystal structure [10]. Detection of longer relaxation times in Rh-doped BTO shows that Rh-addition introduces specific traps in BTO crystal structure. The depth of these trap levels and their concentration can contribute to slower recombination of the excited electrons in comparison with non-doped BTO. In comparison, other transition metal dopants were shown to also slow down the carrier relaxation dynamics in sillenites, with a particularly strong effect demonstrated for Ru in BSO [15] and Cr in BTO [16]. For example, we have measured relaxation decay time of $\tau = 3.2\text{ s}$ and $\tau = 20\text{ s}$ for Ru-doped BSO [15] and $\tau = 10\text{ s}$ and $\tau \sim 10^3\text{ s}$, respectively for Cr-doped BTO [16]. Different doping behavior can be attributed to the different densities and activation energies of the relevant tapping centers, involved in the charge transport mechanism.

4. Conclusion
The dynamics of charge carriers generated by nanosecond pulse laser excitation in Rh-doped $\text{Bi}_{12}\text{TiO}_{20}$ is studied. Comparing to non-doped BTO, the rhodium addition slows down the recombination kinetics as observed by photo-induced absorption. This can be attributed to introduction of additional rhodium related defects introducing trap levels and to increased densities of the relevant trapping centers.

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4. References
[1] Gunter P and Huignard J P 2007 Photorefractive materials and their applications 3 (Berlin-Heidelberg: Springer)
[2] Frejlich J 2007 Photorefractive materials (New Jersey: Wiley-Interscience)
[3] Bortolozzo U, Residori S and Huignard J P 2008 J. Phys. D 41 224007
[4] Bortolozzo U, Residori S and Huignard J P 2012 Materials 5 1546
[5] Gvozdovskyy I, Shcherbin K, Evans D R and Cook G 2011 Appl. Phys. B 104 883
[6] Mokrushina E V, Bryushinin M A, Kulikov V V, Petrov A A and Sokolov I A 1999 J. Opt. Soc. 16 57
[7] Raita E, Kobozev O, Kamshilin A A and Prokofiev V V 2000 Opt. Lett. 25 1261
[8] Ramaz R, Rakitina L, Gospodinov M and Briat B 2005 Opt. Mat. 27 1547
[9] Marinova V, Liu R C, Lin S H, Chen M S, Lin Y H and Hsu K Y 2013 Opt. Lett. 38 495
[10] Obecnermid R 1985 Phys. Stat. Soli (A) 89 263
[11] Marinova V, Liu R C, Lin S H and Hsu K Y 2011 Opt. Lett. 36 1981
[12] Radoua, Delaye P, Pankrath R and Roosen G 2003 *J. Opt. A* **5** S477
[13] Sveshtarov P and Gospodinov M 1991 *J. Cryst. Growth* **113** 186
[14] Matusevich A, Tolstik A, Kisteneva M, Shandarov S, Matusevich V, Kiessling A and Kowarschik R 2008 *Appl. Phys. B* **92** 219
[15] Marinova V, Ahmad I and Goovaerts E 2010 *J Appl. Phys.* **107** 113106
[16] Marinova V and Goovaerts E 2013 *Bulg. Chem. Commun.* **45** 218