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Relaxation of light-induced absorption in Cr-doped $Bi_{12}TiO_{20}$ crystals

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The lifetime of the excited charge carriers in Cr-doped $Bi_{12}TiO_{20}$ (BTO) crystals is characterized by measuring the optical density changes after nanosecond pulse excitation. It is found that the Cr-addition in the BTO crystal structure significantly increases the relaxation decay time, which is attributed to the increased densities of trapping centers. The observed relaxation dynamics follows a double-exponential behavior, assigned to the two long-lived intermediate levels in BTO:Cr crystal structure.

Keywords: doped BTO crystal, light-induced absorption, charge carriers, trapping centers

INTRODUCTION

Sillenite crystals $Bi_{12}M(M=Si,Ge,Ti)O_{20}$ are well known as excellent photoconductors and due to their remarkable high photosensitivity and charge carrier mobility these belong among the fastest photorefractive materials for real-time image processing and related dynamic purposes [1-3]. Sillenite crystals found applications in real-time holography, coherent light amplification, optical phase conjugation, optical information processing, optical metrology, etc. Doping with transition metal ions is well known approach to enhance the response time and photosensitivity of sillenites, especially at near infrared spectral range [4-6]. For example, Ru addition in BSO structure leads to significant improvement of the response time at 1064nm and the beam-coupling enhancement, which opens further opportunities for the development of near infrared sensitive devices for bio-medical diagnostic and real-time image processing [7]. Furthermore, by using green light pre-exposure significant improvement of the operation speed has been achieved [7].

Recently, sillenites become very attractive media for combination with liquid crystals or functional molecules into so called hybrid organic/inorganic cells (light valves) for non-linear optic and photonic applications, especially at near infrared [8-10]. In such kind of devices (optically addressed spatial light modulators) the detail characterizations of the photogenerated charge carriers dynamic processes in photoconductive substrate (as doped BTO, BSO) are essentially important. In that aspect, the light-induced absorption spectroscopy is a valuable technique to study defect levels and to characterize the transport properties of the excited charge carriers.

In the present work, we report relaxation dynamics in Cr-doped BTO induced by nanosecond pulse excitation by measuring the time evolution of the photoinduced absorption.

EXPERIMENTAL DETAILS

Cr-doped BTO crystals were grown by Top Seeded Solution Growth Method [11]. Chromium was introduced into the melt solution as Cr_2O_3 and it's concentration of 6 $x10^{18}$ cm^{-3} in the grown crystals was determined by Atomic Absorption Spectroscopy.

An optically polished plate (thickness of 0.5 mm) was prepared for the absorption measurements. The absorption spectra were measured in the visible range using a Varian Cary 5 UV spectrophotometer after thermal annealing at 350°C for 2 hours.

For the relaxation dynamics study we used pump-probe technique (Flash Photolysis instrument LP 920). The time scale length covered from the first fraction of ns (after photoexcitation) to the several hundred seconds. The sample was irradiated with single shot pulses from a frequency doubled Q-switched Nd:YAG laser (λ=532 nm, pulse duration 6 ns). A weak monochromatic probe beam

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(600 nm) transmitted through the sample was used to measure the absorption changes, detected by a photomultiplier and recorded by a high bandwidth digital storage oscilloscope. For the long-time scanning (up to several hundred seconds) a halogen lamp was used as a probe light. Alternatively, a xenon lamp operating in a pulsed mode was used for a short time scanning (ranges below 1 ms). The sample was placed in a holder allowing near anti-collinear geometry with an angle of 5° between the pump and probe beam. At least 10 shots measurements are always averaged in order to improve the signal to noise ratio. Also, we wait few minutes interval between each two shots, which is considering enough for complete the relaxation process.

For the temperature dependent measurements, the sample was fixed in a helium flow cryostat with a temperature-controlled holder. The temperature was measured with a Pt-100 thermocouple, mounted just above the sample with an accuracy of ± 1K.

The monitored light-induced absorption data are presented as change in the optical density OD

$$OD = -\log_{10} T = \log_{10}(I_0/I) \qquad (1)$$

which is related to the change in transmittance *T,* or alternatively in the relative transmitted light intensity through the sample *I* to incident light intensity I_0 .

RESULTS AND DISCUSSIONS

Figure 1 shows the absorption spectrum of Cr-doped BTO compared with the non-doped BTO. At it seen, the main absorption edge is shifted from ~400 nm to the 500 nm range. The long wavelength tail together with the three characteristic peaks

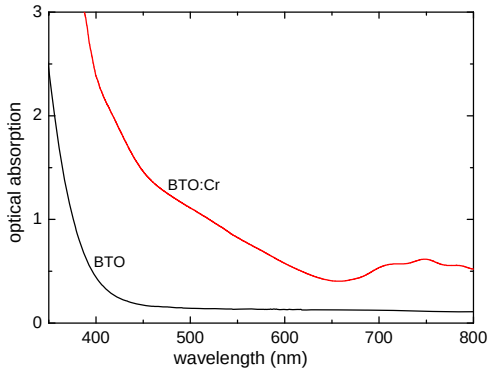

Fig.1. Optical absorption spectrum of Cr-doped BTO compared to the non-doped BTO crystal.

around 700-800 nm are typical for Cr addition into BTO structure and assigned to the strong absorption by Cr-related defects [4].

The temporal evolution of the dark decay of the light-induced absorption at different time scales (from sub-microseconds to several hundred sec range) after pulse intensity of 8 MW/cm^2 hits the sample is presented at Fig. 2 (a,b). At the beginning of the process (after the laser shot hits the sample) the signal is constant (Fig. 2a) following with long lasting component of the decay process (Fig.2b). As it seen, the relaxation process of Cr-doped BTO crystal takes very long time and 500 s time scale interval is not enough to detect the full relaxation process at room temperature. The complete relaxation of the excited charge is achieved when the sample was heated at 160°C. Further, we will focus on the tail of the decay process (at longer time range) and its temperature dependence which are supposed to reveal relevant information about the charge carrier's dynamics.

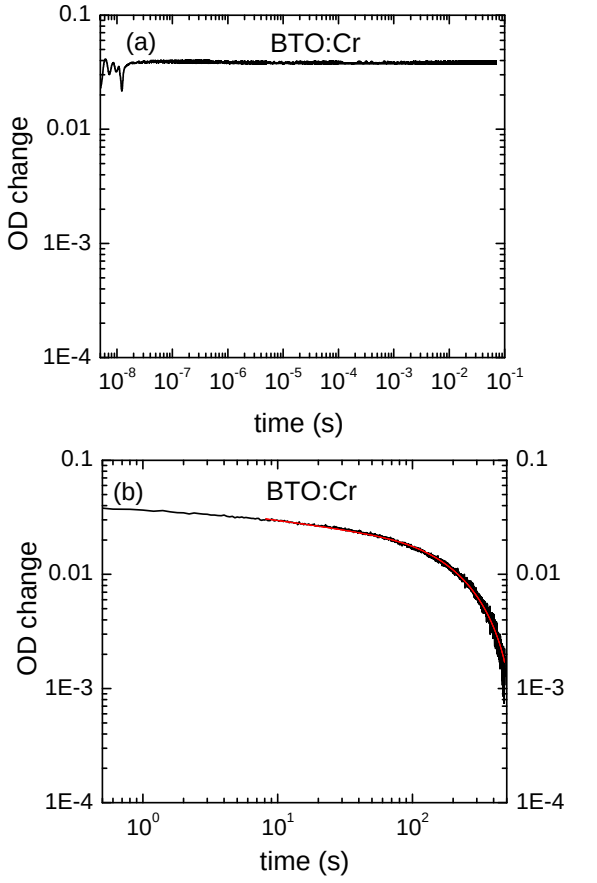

Fig. 2. Time evolution of the light-induced OD change of Cr-doped BTO after laser pulse of 532 nm hits the sample: from the beginning of the process until 500 s time scale.

It was found that in a longer time scale (Fig.2b) the OD decay is well fitted by a sum of two exponential functions:

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

where "*f*" and "*s*" correspond to a faster and a slower component of the decay, OD_f and OD_s denote their amplitudes, τ_f and τ_s are their time constants, respectively. We calculate a relatively fast component with a time constant within 10s (at room temperature) and a slower one with a long lived level ~10^3 s. After heating the sample in the cryostat (Fig.3), the complete relaxation happens with slow decay of τ_s = 253 s at 160 °C.

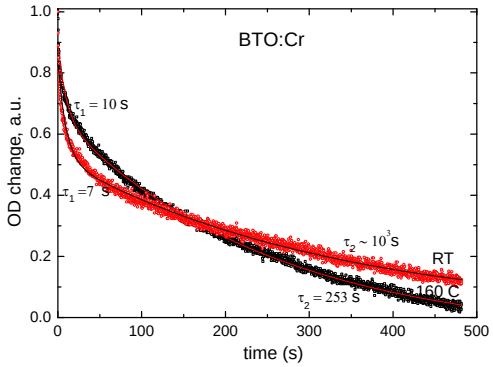

Fig. 3. Normalized OD change measured at room temperature and at 160°C. The symbols refer to the measured results, the straight lines results from the curve fitting.

The detected two time constants of Cr-doped BTO can be attributed to the existence of two different types of traps centers. The photoconductivity in sillenites is assumed as *n*-type, therefore the light-induced absorption is associated with the filling of initially empty shallow traps with the electrons released by the action of light. The measured significant slow decay gives evidence for exceptionally high concentration of Cr- related defects acting as acceptor centers with high trapping efficiency for the photoexcited electrons. Ru-addition in BSO structure also caused longer relaxation time (τ_f=3.2s and τ_s =20s) in comparison with non-doped BSO (where the decay occurs within few ms), however the relaxation process in BSO:Ru happens in much shorter time interval than in BTO:Cr [12]. The long relaxation indicates that Cr-related traps are located rather deeper in the energy gap of BTO:Cr crystal in comparison with Ru-related trap levels in BSO structure.

Light-induced absorption with a double-exponential decay on time scales ranging from seconds to even days was already observed in various sillenite crystals [5]. For example, the above presented results are in good agreement with the recently published photo-induced absorption data in BTO crystals, irradiated with a high intensity pulse laser of 532 nm [13]. The observed relaxation dynamics follows a double-exponential behavior, which the authors explained with two very long-lived (about 10^4 s to 10^5 s) intermediate levels located in the forbidden band of BTO.

Earlier, the photocurrent decay in non-doped sillenites after short pulse illumination has been studied at RT and decay curves with multiple time constants were reported. For example, the authors in [14] announced about the dark decay processes which consists of a rapid initial decay (ascribed to the filling of shallow traps below the CB) followed by a slower "coasting" decay (associated with the recombination of charges to the deep traps). Also, Okamoto et al. [15] reported the existence of several kinds of shallow acceptor levels during thermally stimulated current measurements and proposed two shallow acceptor levels to explain the transient response up to a few ms.

We suppose that in Cr-doped BTO the excited charge carriers are not directly trapped by deep centers, but they are captured and re-excited numerous times by shallow levels before they finally recombine with the deep centers.

CONCLUSION

A photo-induced absorption study of the dynamics of charge carriers generated by nanosecond pulse laser excitation in Cr-doped BTO is reported. Cr-addition significantly slows down recombination kinetics, which is attributed to the increased densities of the relevant trapping centers.

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РЕЛАКСАЦИЯ НА СВЕТЛИННО- ИНДУЦИРАНАТА АБСОРБЦИЯ В КРИСТАЛИ ОТ $BI_{12}TIO_{20}$ ДОТИРАНИ С Cr

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(Резюме)

Определено е времето на живот на възбудените зарядоносители в кристали от $Bi_{12}TiO_{20}$ (BTO) дотирани с Cr чрез проследяване на промените в светлинната абсорбция при облъчване с наносекундни лазерни импулси. Установено е че вследствие включването на Cr в кристалната структура на BTO времето на затихване на релаксацията нараства значително, което показва увеличена плътност на уловките. Наблюдаваната динамика на релаксацията следва двойно експоненциален характер, което се свързва с наличието на две междинни енергитични нива с продължително време на живот в кристалната структура на BTO: Cr.