

RECOMBINATION OF PHOTOEXCITED CARRIERS IN $\text{Bi}_{12}\text{TiO}_{20}$ MONOCRYSTALS

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The temperature dependences of the photocurrent have been measured in $\text{Bi}_{12}\text{TiO}_{20}$ monocrystals. Various intensities of monochromatic green and white exciting light were applied. Thermal quenching of the photocurrent, related to two types of recombination centre, has been observed. One of them has been found to be located 1.65 eV above the valence band. Thermally stimulated currents have been measured and the influence on the photocurrent has been discussed. The temperature dependences of the carrier mobility-lifetime product have been obtained at various light intensities. They show a strong rise, from 10^{-11} to $10^{-4} \text{ cm}^2/\text{V}$, in the 77-400 K range.

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1. Introduction

Monocrystalline photorefractive $\text{Bi}_{12}\text{TiO}_{20}$ (BTO) is an attractive material for many applications such as dynamic holography and wave-front phase conjugation [1,2]. Recombination significantly affects the concentration and distribution of the photoexcited carriers, and for this reason it is of great importance for the quality of optical recording. Photoconductivity investigations are among the main sources of information on the recombination processes. Two types of recombination centre ("slow" and "fast") are usually assumed [3] to describe carrier recombination. However, in fact, several kinds of centre can exist, with different capture cross sections. The parameters of the recombination centres, such as their concentrations, carrier cross sections, energy depths etc., can be determined from temperature and light intensity photocurrent measurements.

In this article, the temperature dependences of the photocurrent have been measured in BTO monocrystals, at various intensities of monochromatic green and white exciting light. Two "slow" defect centres dominating recombination in different temperature ranges have been distinguished, and the energy position of deeper one has been determined. The temperature dependence of the carrier mobility-lifetime product has also been obtained.

2. Experimental details

BTO crystals were grown in air, using a standard Czochralski set-up, from the high-temperature solution of Bi_2O_3 and TiO_2 ("Suprapur"), mixed in the ratio 11:1, at a pulling rate of 0.1 mm/h. More details of the growth process have been described elsewhere [4]. Optically clean plates (0.7-1 mm thick) were cut perpendicularly to the grown axis {001}, and were polished to optical grade.

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Electrical and photoelectrical measurements were performed by Keithley 610 Electrometer. Contacts of sputtered gold (about 0.5-0.7 cm long and spaced 0.15 cm apart) on the top of the plates were used. The linear current-voltage characteristics were measured at applied voltages up to 100 V. Steady state photocurrent measurements were carried out using monochromatic light from a LED (normal incidence to the plate surface, $\lambda = 525$ nm i.e. 2.36 eV, fluxes $F = 5.10^{13}$ - 4.10^{15} cm⁻².s⁻¹). This light was used for two reasons: (i) in order to determine the mobility-lifetime, $\mu\tau$, product monochromatic light was necessary and (ii) the green line of Ar lasers is usually used for holographic storage. Since the optical band gap of BTO crystals is 3.25 eV, white light from a halogen lamp ($P_{max} = 20$ mW/cm² and neutral density filters) was also applied, for comparison.

3. Results and discussion

The temperature dependences of the photocurrent I_p at various F are presented in Fig. 1a. A photocurrent rise was observed when the sample was heated up to 230 K. At relatively low light intensities, two maxima (at 235 K and 265 K) are well resolved in the curves, followed by a photocurrent increase in the high-temperature range (starting at about 310 K). The position of the first (low-temperature) maximum did not depend on the light intensity. However, the second one shifted to higher temperatures when the intensity increased. The current minimum following the second maximum also moved to higher temperatures. Similar temperature dependences have been obtained when using white light (Fig. 1b). However, surprisingly, in this case the minimum moved to lower temperatures with increasing light intensity.

The photocurrent decrease that follows the maximum values at 235 K and 265 K may be considered as thermal quenching. It is known [3] that, in n-type photoconductors, thermal quenching of the photocurrent results from the motion of the demarcation level for holes towards the middle of the gap with rising temperature. The quenching starts when the demarcation level crosses the level of a certain recombination centre. This centre turns into a trap, and the recombination flow is redirected to a deeper recombination centre (or centres), decreasing the carrier lifetime and hence the photocurrent. Similarly, the demarcation level moves to the gap center with decreasing light intensity. Therefore, one can expect that the beginning of the thermal quenching will shift to higher temperatures with increasing light intensity. The condition for the break from maximum sensitivity to less sensitivity, both at a fixed light intensity with increasing temperature and at a fixed temperature with decreasing light intensity, is given by $\ln(n) = \text{const}_1 - E_1/kT$, where n is the concentration of photoexcited electrons, E_1 is the energy of the “slow” recombination center, and k is Boltzmann's constant. If one plots the maximum photocurrent values, obtained at different light intensities, as a function of $1/T$, a straight line is expected, with a slope of $-E_1/k$. Similarly, the condition for the break from decreasing sensitivity to the lowest sensitivity is given by $\ln(n) = \text{const}_2 - E_1/kT$. Consequently, the dependence of the photocurrent values at the minima as a function of $1/T$ has to be a straight line with the same slope.

In Fig. 1a, two parallel straight (dotted) lines are shown connecting the photocurrent values in the second maximum and the minimum at ~ 310 K. A value of 1.65 eV has been determined from both lines. The same value has been obtained from the position of the second maximum, when excited with white light (Fig. 1b). Furthermore, a photocurrent intensity dependence has been measured in the range of the second thermal quenching (Fig. 1a-inset). Two slopes have been observed: super-linear ($I_p \sim F^{2.04}$) at lower intensities and sub-linear ($I_p \sim F^{0.92}$) at high ones. The observation of two such slopes is expected [3] and indicates that transformation of the recombination centers into traps takes place at a certain light intensity. Hence, keeping in mind that “pure” BTO is an n-type semiconductor [5], one can assume that a recombination center exists at about 1.65 eV above the valence band.

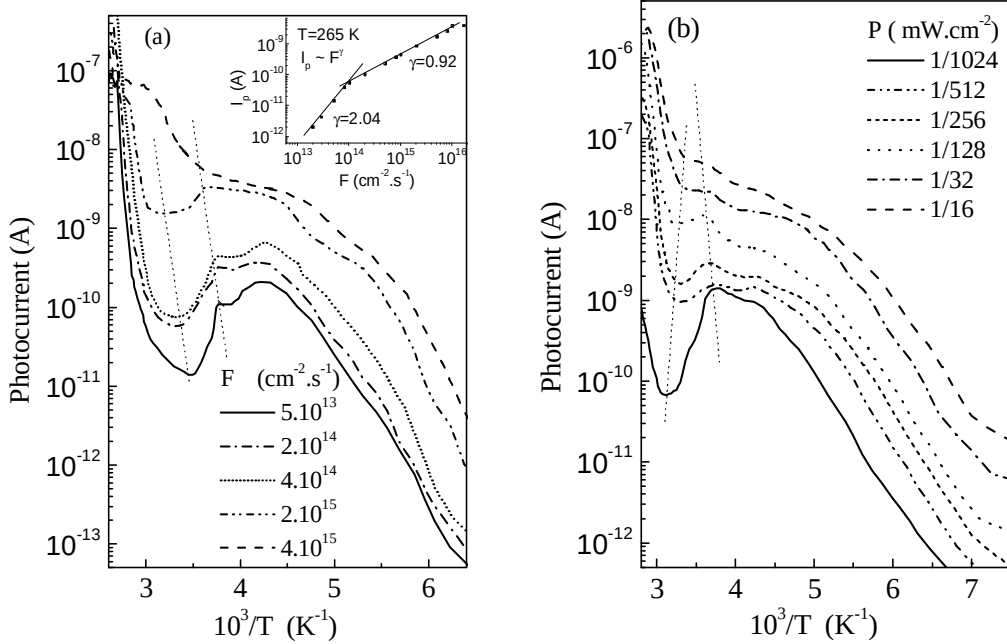


Fig. 1. Temperature dependences of the photocurrent I_p of a BTO monocrystal at various intensities of: (a) green ($\lambda=525$ nm) and (b) white light. The inset shows the I_p intensity dependence measured at 265 K.

In order to understand the unusual temperature behavior of the photocurrent minimum observed with white light illumination (Fig. 1b), both thermally stimulated currents (TSC) and the temperature dependence of the photocurrent have been measured (Fig. 2). It is seen that in the range 77 - 260 K, the TSC values are about two orders of magnitude lower than the photocurrent. They strongly increase at higher temperatures and approximate the photocurrent at around 320 K, indicating the existence of deep traps of a high concentration. The carrier release from these traps can significantly affect the shape of the photocurrent, and probably causes the shift in the position with increasing light intensity. As for the fixed position of the first photocurrent maximum, it seems that it is not due to carrier release from a trap. Most likely, it is also related to some recombination center whose thermal behavior is not well expressed. This could be related to the reverse effect of the intensity and temperature increase on the demarcation level shift, as well as to the influence of the second center.

The knowledge of the mobility-lifetime product of photoexcited carriers is important for high quality optical storage. It has been determined from the temperature dependences of the photocurrent when excited with monochromatic light ($\lambda=525$ nm). Generally, for predominantly electron conductivity, the photocurrent is expressed as $I_p(T) = K\mu_n(T)n(T)$, where K is a geometrical factor, $K=eAE$ (here e is the electron charge, A is the current cross section, E is the applied electric field), and μ_n is the electron mobility. On the other hand, the concentration of photoexcited electrons is connected with free electron lifetime τ_n , as $n = \Phi\tau_n$, where Φ denotes the free electron generation rate defined as: $\Phi = F_{eff}\alpha$. The effective monochromatic light flux F_{eff} is defined as $F_{eff} = F(1 - e^{-\alpha d})/\alpha d$. It can be estimated using the absorption coefficient α and the sample thickness d . Then, we obtain $\mu(T)\tau(T) = I_p h\nu / eUl(F(1 - e^{-\alpha d}))$, where U is the applied voltage, and l and r are the length and distance between the electrodes, respectively. The $\mu\tau$ temperature dependences obtained at various intensities of the incident flux F are shown in Fig. 3. A strong rise of about 5 orders of magnitude is observed up to 230 K, followed by a not so strong decrease between 230 and 300 K and another increase in the high temperature range. It has to be pointed out that the intensity increase causes a decrease in $\mu\tau$, which could be related to the intensity induced shift of the quasi-Fermi levels towards the conduction and valence bands. It is then possible for new “fast” recombination centers to be involved in the recombination process, thus decreasing the lifetime of the photoexcited carriers. Values between 1.5×10^{-7} and 3×10^{-7} cm²/V have been determined for the room temperature

mobility lifetime product. They are close to the value obtained by other authors [6] using a different technique.

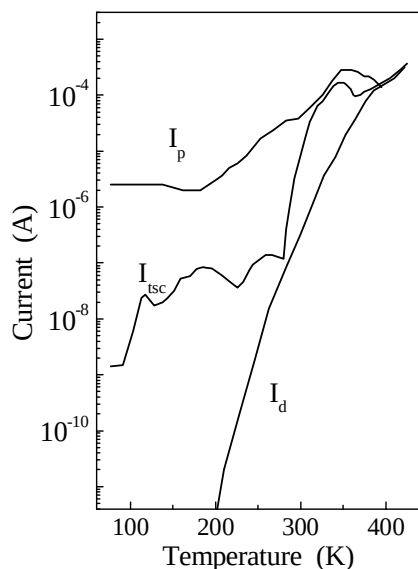


Fig. 2. Temperature dependences of the dark- (I_d), photo- (I_p) and thermally stimulated (I_{tsc}) currents of a BTO monocrystal. All curves were measured at $U=100V$; $P=20 \text{ mW/cm}^2$.

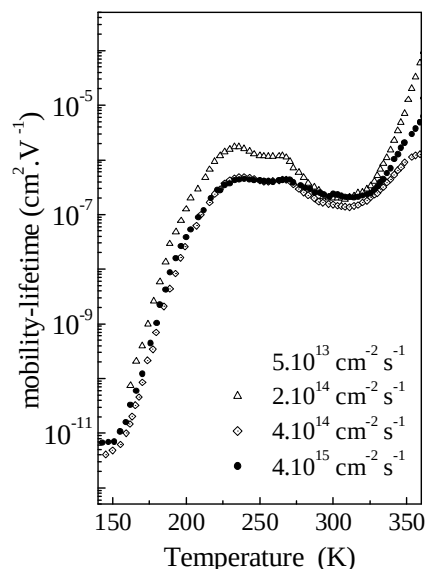


Fig. 3. Temperature dependences of the mobility-lifetime product of a BTO monocrystal, excited with monochromatic weakly absorbed light ($\lambda = 525 \text{ nm}$), at various intensities as shown in the figure.

4. Conclusions

The study of the temperature dependences of the photocurrent, performed under illumination with green and white light, has shown that below room temperature the recombination of photoexcited carriers in BTO monocrystals is mainly governed by two types of slow recombination centre. It has been found that one of them is situated at 1.65 eV above the valence band. The photocurrent shape above room temperature is significantly affected by carrier release from deep traps. It has also been observed that the mobility-lifetime product changes by over seven orders of magnitude in the temperature range 77-400 K.

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