Strong ultraviolet induced absorption and absorption gratings in BaTiO$_3$

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Efficient optical pumping of impurity levels in BaTiO$_3$ is achieved using low intensity ultraviolet (UV) exposure. The resulting large photoinduced absorption in the visible is assessed in the context of interband charge transfer. An induced absorption of up to 12 cm$^{-1}$ is observed at 633 nm. The effect, which takes place close to the UV-exposed crystal surface, occurs on a millisecond time scale. © 1996 American Institute of Physics

I. INTRODUCTION

It is known that the optical properties of oxide crystals, such as BaTiO$_3$, LiNbO$_3$, and KNbO$_3$, are strongly influenced by the presence of impurity levels in the band gap of the material. In terms of the photorefractive effect, the distribution and population of these levels have been the focus of much recent research into the tailoring of materials to respond to near infrared wavelengths compatible with compact solid-state laser diodes. In order to participate efficiently in the charge transfer mechanism, such an impurity level must fulfill two basic requirements. Firstly, there should exist a high number density of traps at an appropriate energy level to allow photoexcitation to occur at the desired wavelength. Secondly, these traps must have a sufficiently high occupation to provide significant absorption at that wavelength. The first of these requirements can be satisfied by impurity inclusion (either intentional or unintentional) in the crystal structure during the growth process. However, the second requirement, the filling of these traps, may be additionally influenced by optical illumination. Exposure to high-power pulsed visible wavelengths has already been shown to enhance the photorefractive response at longer wavelengths in crystals of BaTiO$_3$ (Ref. 4) and LiNbO$_3$. Rapid redistribution of charge may, however, also be achieved by illumination with low-power ultraviolet (UV) light, as demonstrated by the interband photorefractive effects recently observed in KNbO$_3$. Since the photon energy of UV light exceeds that of the material band gap, electrons and holes are excited by band-to-band transitions. Recombination of these charges into traps in the band gap offers the possibility of rapid population of any of the impurity levels. Even at moderate cw UV intensities the process is fast enough to allow photoexcitation. The absorption at longer wavelengths, arising from photoexcitation from these impurity levels, is therefore enhanced by this charge transfer process. This article describes these large UV-induced changes in the absorption characteristics of BaTiO$_3$ in the visible to near-infrared range. The experimental observations are explained in terms of a simple model involving interband charge transfer and a single effective impurity level. Fast formation of absorption gratings for the visible wavelength is also demonstrated using this effect.

II. EXPERIMENTS

In the experiments described below we used a nominally undoped, cut, polished, and poled sample of BaTiO$_3$ of dimensions 5.23×5.80×6.10 mm$^3$ with the c axis parallel to the 6.1 mm edge. UV exposure was provided by the 364 nm line of an Argon ion laser. Since the corresponding photon energy of 3.4 eV exceeds the band-gap energy of BaTiO$_3$ at 3.1 eV, band-to-band phototransitions dominate. An initial measurement using a Perkin–Elmer Lambda 9 spectrophotometer revealed an enhancement of the visible absorption characteristics of the crystal upon simultaneous illumination with UV. The range of the enhancement extended from around 450 to 800 nm. A more detailed analysis of the UV-induced changes in the absorption was then performed using a HeNe laser beam as a probe, whose wavelength of 633 nm lies near the midpoint of this enhancement range.

Due to the high UV absorption to be described below, optically induced changes are expected to occur close to the exposed crystal surface. In anticipation of this, the absorption coefficient of the UV radiation itself was first examined. This was estimated by launching the red probe beam parallel to the exposed face of the crystal at some arbitrary depth d$_1$ and noting the induced transmission change of the red beam for a given incident UV intensity I$_1$. The probe beam was then moved to a different depth d$_2$, and the UV intensity adjusted to the value I$_2$ to obtain the same change in red transmission as before. Without knowing the precise form of the relationship between induced absorption change and UV intensity, but assuming only that it is a monotonic function (in other words, that a given UV intensity uniquely identifies an induced absorption change and vice versa), the UV absorption coefficient, which is assumed to be independent of intensity, may be calculated using

$$\alpha_{UV} = \frac{1}{2} \ln \left( \frac{I_2}{I_1} \right).$$

Using this technique, the absorption at 364 nm of our sample was measured to be $\alpha_{UV} = 1.2 \pm 0.3 \times 10^3$ cm$^{-1}$ when light is polarized \( \perp \) c, and $\alpha_{UV} = 1.4 \pm 0.4 \times 10^3$ cm$^{-1}$ polarized \( \parallel \) c. These values are in good agreement with previously published UV absorption data for BaTiO$_3$. Such high values indicate that the UV absorption occurs over a depth of $\sim 2/\alpha_{UV} = 17$ μm, at which point 87% of the $\perp$-polarized UV light is absorbed. This implies that the in-

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duced red absorption change $\Delta \alpha_r$ occurs over a correspondingly short distance. In the experiments presented below attention is focused on the case where the UV light is polarized $\parallel c$, for which the light penetration depth is larger. Corresponding measurements for light polarized $\perp c$ yield qualitatively similar results.

The following experiments investigated both the magnitude and time response of the induced absorption change in the red. As a first experiment, a low-power unfocused red probe beam with intensity $I_r = 10 \text{ mW cm}^{-2}$ ($I_r = P_r/\pi w_0^2$, where $P_r$ and $w_0$ are the power and beam waist, respectively) was aligned to propagate normal to the crystal surface which was exposed to a UV intensity of 110 mW cm$^{-2}$. The fractional change in transmitted probe intensity was observed to be 2%. Assuming that such a change occurs due to enhanced absorption over a depth of only 17 $\mu$m then this would imply $\Delta \alpha_r \sim 12 \text{ cm}^{-1}$; a significant enhancement of the unmodified background red absorption measured to be $\sim 0.1 \text{ cm}^{-1}$ in this crystal. Crystal heating due to the UV illumination combined with shifting of the band edge was ruled out as a possible cause of this change when a separate analysis of the probe transmission as a function of crystal temperature revealed only very slight fluctuations of less than 0.2% between 25 and 45 °C.

The following analysis was performed using the simple experimental arrangement as presented in Fig. 1, which was based on total internal reflection of the probe beam from the UV-exposed crystal surface. Using this geometry, scattering due to imperfections of the crystal edge polish were avoided. Furthermore, interaction near the surface was ensured without the need for a waveguiding layer or special crystal preparation. Figure 2 illustrates the magnitude of the induced red absorption of red light polarized $\perp c$ as a function of the UV intensity $I_{UV}$. The transmitted red intensity $I_r'$ is related to the induced red absorption $\Delta \alpha_r$ by

$$\Delta \alpha_r l_{\text{eff}} = \ln \left( \frac{I_r'(I_{UV}=0)}{I_r'(I_{UV})} \right),$$

where $l_{\text{eff}}$ is the effective interaction length of the probe through the induced layer. Figure 2 shows the considerable enhancement of $\Delta \alpha_r$ by exposing the crystal to low UV intensities. Assuming uniform absorption in the red in a 17-$\mu$m-thick layer, we calculate from the total internal angle of $5^\circ$ an effective interaction length $l_{\text{eff}} \sim 390 \mu$m.

As strong absorption is potentially very interesting for obtaining fast response, the time dynamics of the induced effect deserve particular attention. Figure 3 illustrates the buildup of the induced red absorption. Since the time-response curves do not fit exactly a simple exponential, the time $\tau_1$ taken to reach half the saturated induced absorption value is used to characterize the speed of the effect. This is plotted in Fig. 4 as a function of $I_{UV}$. It can be seen that increasing the UV intensity not only has the effect of enhanc-

FIG. 1. Experimental arrangement used to determine the absorption changes produced by UV illumination (schematic). The incident UV intensity is $I_{UV}$ and the incident red probe intensity $I_r$. The red probe beam is focused with a 80 mm focal length lens onto the UV-exposed crystal surface and totally internally reflected with an internal angle of $5^\circ$.

FIG. 2. Magnitude of the induced absorption change at $\lambda$=633 nm as a function of the UV intensity $I_{UV}(\lambda_{UV} = 364 \text{ nm})$ with a probe beam intensity $I_r = 200 \text{ mW cm}^{-2}$. The solid curve shows the theoretical dependence predicted by Eq. (4).

FIG. 3. Build-up dynamics of the absorption change in the red upon exposure to different UV intensities. Red intensity $I_r = 65 \text{ mW cm}^{-2}$.

FIG. 4. Build-up time of the induced red absorption as a function of $I_{UV}$. The time $\tau_1$ is measured when half the saturated value is reached. The solid curve is the theoretical plot according to Eq. (5).


FIG. 5. Relaxation dynamics of the absorption change in the red upon blocking the UV illumination. The initial UV intensity is $I_{UV} = 400$ mW cm$^{-2}$.

FIG. 6. Relaxation time of the induced red absorption as a function of the red beam intensity $I_r$. The time $\tau_i$ is measured when half the initial saturated value is reached. The solid curve is the theoretical plot according to Eq. (6).

FIG. 7. Schematic band diagram showing the transitions considered in the model of Eq. (3). The trap level with total density $N_D$ is considered to be responsible for the induced absorption in the red. Photon absorption occurs in the filled traps (density $N_D$).

III. DISCUSSION

From Figs. 4 and 6, it can be seen that faster response occurs where red and UV intensities are highest. Although the process is complicated by the presence of multiple trapping levels in the band gap, the essential features of the observed behavior may be estimated by considering the following simple model. A schematic band scheme illustrating its main features is shown in Fig. 7. The dominant process is UV light excitation of electrons directly from the valence band to the conduction band. A free-electron population density is created, from where the charges may recombine either directly with the holes in the valence band (recombination constant $\gamma_{dir}$) or into acceptor levels within the band gap. In our model we do not describe the effects of interband transitions explicitly, instead we consider their combined influence on the free-electron density $n$. The concentration of electrons in the conduction band created as a result of the combination of all processes may be described by $n = \kappa (I_{UV})^x \{ 0.5 \leq x \leq 1 , \kappa : constant \}$ where the value of the exponent $x$ depends upon the extent to which direct interband charge recombination dominates the decay of the conduction band electrons. Of the many impurity levels in the band gap we consider explicitly only one. The trap number density of this level is $N_D$ of which $N_D^{-}$ are occupied. Electrons may be photoexcited from this level to the conduction band by absorption of a red photon. The trapping level is assumed to be empty in the dark (i.e., $N_D^{-} = 0$) and is populated only by recombination of electrons from the conduction band, with a recombination coefficient $\gamma$. The rate equation for the density of occupied traps $N_D^{-}$ is described by

$$\frac{dN_D^{-}}{dt} = \gamma n(N_D - N_D^{-}) - (s_r \gamma n + \beta)N_D^{-}$$

(3)

where $s_r$ is the constant for photoexcitation from a trap by absorption of a red photon and $\beta$ is the thermal excitation rate. Thus, the second term on the right-hand side of Eq. (3) describes the processes by which charge leaves the considered trapping level. The steady-state induced absorption at the red wavelength is proportional to the number density $N_D^{-}$ of occupied traps and can be expressed by solving Eq. (3) as

$$\Delta \alpha_r = \frac{s_r \gamma n N_D}{\gamma n + s_r I_r + \beta} \approx \frac{s_r \gamma N_D \kappa I_{UV}^x}{\gamma \kappa I_{UV}^x + s_r I_r + \beta}$$

(4)

The half times for the buildup and relaxation are given respectively by

$$\tau_i = \frac{\ln 2}{\gamma n + s_r I_r + \beta} \approx \frac{\ln 2}{\gamma \kappa I_{UV}^x + s_r I_r + \beta}$$

(5)

and
The solid curves in Figs. 2, 4, and 6 are obtained using the above expressions by approximating the experimental temporal response by a single exponential. In Eqs. (4) and (5) it is also assumed that the exponent $x$, which relates the electron density $n$ and $I_{UV}$, does not vary significantly over the range of UV intensity investigated. The parameters obtained from the fits are $x = 0.65$, $s_x = 7.7 \times 10^{-4}$ m$^2$J$^{-1}$, and $\beta = 0.75$ m$^{-1}$, and the curves show good agreement despite the simplifications assumed. The thermal emission rate of $0.75$ m$^{-1}$ implies that the traps (which may be populated in a few milliseconds, Fig. 4) act as an effective, long-lived ($\beta^{-1} \approx 1.3$ s) reservoir of charges. Additionally, Eq. (4) shows that the magnitude of the effect may be enhanced by deliberate impurity inclusion.

Potential applications such as optical correlation, spatial light modulation, and beam steering have led to much interest in the field of optically induced gratings. It is therefore valuable to consider the process of fast grating formation in the current context of light-induced absorption. By interfering two equal intensity coherent UV beams (again polarized $\parallel c$) impinging on an $a$ face of the crystal, a grating was arranged with its wave vector $\perp c$. Bragg matching the HeNe probe beam (polarized $\perp c$) in a transverse geometry similar to the one described in Ref. 9 allowed isotropic diffraction from the UV-induced absorption grating to be observed. The probe beam was once again launched slightly below the crystal edge and totally internally reflected from the UV exposed crystal surface. The UV writing beam was chopped mechanically and the grating response monitored by measuring the diffracted red probe signal. Figure 8 shows the diffracted red signal as a function of time after the crystal is exposed to the UV. The curves clearly show an increase in both the maximum diffracted intensity (and hence grating strength) and speed of response with increasing UV intensity. The diffraction efficiency $\eta$ of a sinusoidal absorption grating may be calculated using the formula derived by Kogelnik\(^{10}\)

$$\eta = \sinh^2\left(\frac{\Delta \alpha d}{4 \cos \theta}\right) \exp \left(-\frac{\alpha d}{\cos \theta}\right),$$

(7)

where $\alpha$ is the average absorption value, $\Delta \alpha$ the absorption modulation amplitude, $d$ the interaction length, and $\theta$ the internal Bragg angle for diffraction. For our experimental geometry the effective thickness is $\approx 900$ $\mu$m. For the maximum diffraction efficiency of $\eta = 0.04\%$ shown in Fig. 7, we calculate from Eq. (7) a modulation in the absorption constant of $\Delta \alpha = 10^{-4}$ cm$^{-1}$. The high red probe intensity $I_r$ accounts for the low saturated value of $\Delta \alpha$, as can be seen from Fig. 5 and consideration of Eq. (4), and enhances the speed of the effect as expected from Eq. (5). For $I_{UV} = 92$ mW cm$^{-2}$ the time taken to reach half the maximum diffraction efficiency is only 1.2 ms. The holographic sensitivity $S = (1/\ell_{eff})(\partial \eta/\partial (I_{UV})) \approx 2$ cm/mJ is of the same order of magnitude of what is usually measured for photorefractive gratings in BaTiO$_3$ recorded at green/blue wavelength.\(^{11}\) It is remarkable that these absorption gratings can show similar sensitivities to photorefractive phase gratings because the latter are usually a manifestation of a stronger optical nonlinearity.

In summary, exposure of BaTiO$_3$ to low UV intensities has been shown to modify significantly the charge distribution in impurity levels within the material. Efficient optical population of traps in a thin layer (of a few $\mu$m) beneath the exposed crystal surface has been demonstrated, making the effect entirely compatible with waveguide geometries. The UV optical population process, which occurs on a ms time scale, has been examined in terms of induced absorption in the visible, and analyzed in detail using an interband charge transfer model. This effect may be used to construct a saturable absorber for the visible with a controllable threshold. In addition, the charge transfer process may also find application in enhancement of holographic sensitivity and improvement of waveguide device characteristics.


