AIP | Applied Physics Letters

Improvement of the photorefractive efficiency of BaTiO3 by γ irradiation

Thomas R. Moore and Robert W. Boyd

Citation: Applied Physics Letters **61**, 2015 (1992); doi: 10.1063/1.108344
View online: http://dx.doi.org/10.1063/1.108344
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/61/17?ver=pdfcov
Published by the AIP Publishing

Improvement of the photorefractive efficiency of $BaTiO_3$ by γ irradiation

Thomas R. Moore and Robert W. Boyd
The Institute of Optics, University of Rochester, Rochester, New York 14627

(Received 29 May 1992; accepted for publication 12 August 1992)

We report that the photorefractive response of as-grown $BaTiO_3$ crystals can be improved by γ irradiation from a Co^{60} source. An increase in photorefractive response was observed with irradiation doses exceeding 10^6 rad, with a maximum observed increase in two-beam coupling gain of $\sim 15\%$. We interpret our results within the context of a well-known model of photorefractivity in $BaTiO_3$ and conclude that γ irradiation increases the effective trap density and possibly also increases the normalized conductivity in samples where both holes and electrons contribute to photorefractivity.

Improving the photorefractive efficiency of $BaTiO_3$ crystals has been the subject of active research for some time. Altering the photorefractive properties after crystal growth is of particular interest, but oxidation, reduction, and poling of the crystals are the only nondestructive methods currently known that can accomplish this.[1] Published reports indicate that γ irradiation can increase the photorefractive efficiency of lithium niobate,[2-4] but to our knowledge there has been no investigation into the effects of γ irradiation on $BaTiO_3$. In this letter we present results of an investigation into the effects of γ irradiation on photorefractive $BaTiO_3$ and we report that the photorefractive efficiency of $BaTiO_3$ can be substantially improved by γ irradiation.

To investigate the effects of γ irradiation on $BaTiO_3$ we measured the two-beam coupling (TBC) gain as a function of grating period for two crystals, irradiated both crystals with γ rays from a CO^{60} source, and then repeated the TBC measurements. This sequence was repeated for irradiation doses totaling 10^5, 10^6, 10^7, and 10^8 rad (water). Irradiations were performed at the University of Massachusetts at Lowell and extreme care was taken to ensure that the crystals were not subjected to physical shock or allowed to approach the phase transition temperature of ~ 6 °C during transportation.

Beam coupling experiments were performed using a single-mode Ar^+ laser ($\lambda = 514$ nm). The alignment was such that the grating normal was parallel to the *c* axis and the light was polarized parallel to an *a* axis. This arrangement minimized the effects of stimulated photorefractive scattering (beam fanning) by utilizing the small r_{13} electro-optic coefficient. The intensity ratio of the pump to the probe was ~ 30 so that the measurements were made in the limit of small intensity modulation and the undepleted pump approximation applied.

The crystals were both single $BaTiO_3$ crystals, electrically and mechanically poled and measuring $\sim 5 \times 5 \times 2$ mm. The dominant charge carriers were holes in both crystals and remained so throughout the experiments.

The TBC gain was measured in the usual way by interfering a strong pump beam with a weak probe beam inside the crystal. We calculated the total gain G by taking the ratio of the transmitted probe intensity with the pump beam present to the transmitted probe intensity with the pump beam absent. Absorption within the crystal was significantly less than the total gain, and therefore the TBC gain coefficient may be approximated by $\Gamma = \ln(G)/L$, where L is the interaction length within the crystal.

The normalized maximum TBC gain coefficient for each crystal is plotted as a function of the γ irradiation dose in Fig. 1. One of the crystals (denoted crystal A) exhibited little change in photorefractive efficiency with γ irradiation, while the second crystal (denoted crystal B) showed a marked change in photorefractivity. We have not observed any degradation in this increased photorefractivity during experiments spanning several weeks.

To interpret our observations theoretically we may choose either of two models that are often used to describe both hole and electron transport in photorefractive crystals.[5] The first model attributes simultaneous electron and hole transport to a single set of combination centers, thought to be Fe^{2+} and Fe^{3+} in $BaTiO_3$.[6] The second model attributes two separate species of combination centers to electron and hole transport mechanisms. Our results can be described by either of the two models; however, since the former model is usually adequate in describing as-grown $BaTiO_3$ we will examine our results in this context.

The equation for the TBC gain may be derived directly from the equations of Kukhtarev *et al.*[7] Assuming our experimental geometry, negligible absorption in the crystal, negligible dark conductivity (compared to the photoconductivity), no applied electric field, negligible bulk photovoltaic effect, and short diffusion length compared with the grating period we may write the TBC gain coefficient as[8,9]

$$\Gamma = \frac{2\pi n^3 r_{13}}{\lambda} F\Sigma \left(\frac{E_d E_q}{(1/\Lambda)E_d + \Lambda E_q} \right), \tag{1}$$

where n is the index of refraction, r_{13} is the applicable electro-optic coefficient, λ is the wavelength of the light, and Λ is the grating period, F is the fractional poling factor, and Σ is the normalized conductivity given by

$$\Sigma = \frac{\mu_h p - \mu_e n}{\mu_h p + \mu_e n}, \tag{2}$$

where μ_h and μ_e are the hole and electron mobilities, and p and n are the free hole and electron concentrations. [Note that we follow the terminology of Ref. (9), and refer to Σ as the "normalized conductivity;" even though unlike a

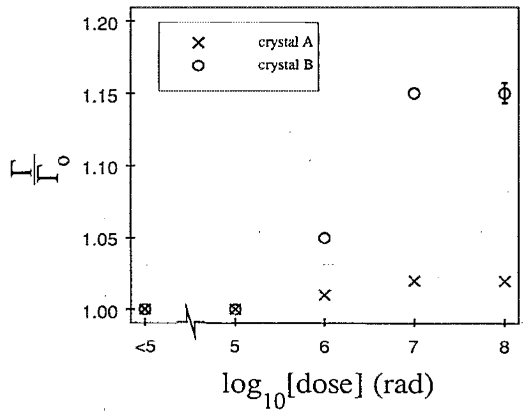

FIG. 1. Plots of the TBC gain coefficient for two crystals as a function of γ irradiation dose. The gain has been normalized to the as-grown gain (Γ_0) for each crystal to facilitate display on one graph.

conventional conductivity Σ can change sign.] Here we have defined the diffusion field (E_d/Λ) and the limiting space-charge field (ΛE_q) by

$$E_d=\frac{2\pi k_B T}{e}$$

and

$$E_q=\frac{2e}{\epsilon} N_{\text{eff}},$$

where ϵ is the dc dielectric constant. N_{eff} is the effective trap density given by

$$N_{\text{eff}}=\frac{NN^+}{N+N^+}, \tag{3}$$

where N and N^+ are the concentrations of the two photoactive centers.

As noted by Klein and Valley,[9] if we ignore any dependence of Σ on Λ, Eq. (1) can be recast in the form

$$\frac{1}{\Lambda\Gamma}=y+m\Lambda^{-2}, \tag{4}$$

which is the equation for a straight line with intercept given by

$$y=\frac{\lambda e}{4\pi^2 n^3 k_B T r_{13}}\left(\frac{1}{F\Sigma}\right) \tag{5}$$

and slope of

$$m=\frac{\lambda\epsilon}{4\pi e n^3 r_{13}}\left(\frac{1}{F\Sigma N_{\text{eff}}}\right). \tag{6}$$

The independence of Σ and Λ is maintained as long as the diffusion length for both carriers is small compared to the grating period.[10]

If both the slope and intercept change after γ irradiation we may determine the relative effect on N_{eff} and Σ without assuming any material parameters. Denoting the above defined parameters with superscripts 0 and γ indicating before and after γ irradiation, straightforward algebra reveals that

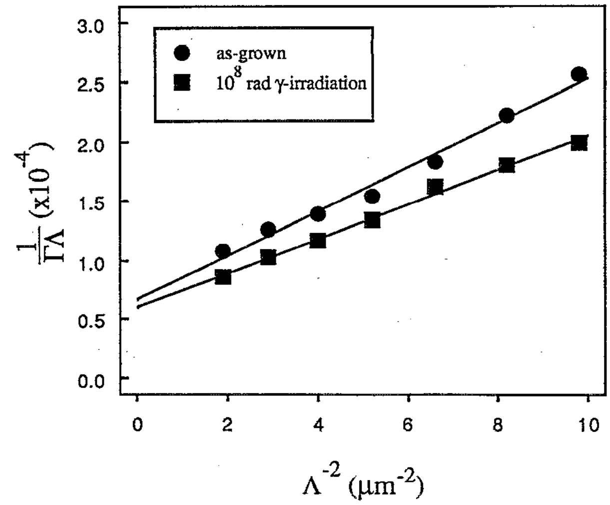

FIG. 2. Plots of the inverse of the product of the grating period and the TBC gain coefficient as a function of the inverse of the square of the grating period for crystal B before and after irradiation of 10^8 rad. The lines are the results of a linear regression of the data. Experimental errors are less than the size of the data points.

$$\frac{N_{\text{eff}}^\gamma}{N_{\text{eff}}^0}=\frac{m^0 y^\gamma}{m^\gamma y^0}, \tag{7}$$

and

$$\frac{\Sigma^\gamma}{\Sigma^0}=\frac{y^0}{y^\gamma}. \tag{8}$$

To determine other material values it is necessary to assume a value for r_{13} and ϵ. Once values for r_{13} and ϵ are assumed, values for $N_{\text{eff}}^{0,\gamma}$ and $F\Sigma^{0,\gamma}$ may be calculated; however, there is much ambiguity in the literature as to the exact values of the electro-optic coefficients for $BaTiO_3$. For example, as noted by Klein,[11] the reported values of r_{13} vary by a factor of ~ 7, and recently it has been suggested that all of the published values are inappropriate for use in a TBC experiment such as ours.[12]

Figure 2 shows a plot of $(1/\Lambda\Gamma)$ vs Λ^{-2} for the crystal that exhibited a significant change in photorefractivity with γ irradiation. The straightline fit is determined by linear regression and it is obvious that γ irradiation produced a noticeable change in the slope and a small change in the intercept of the line. The fit to the data reveals that: $m^0=1860(\pm 80)$ μm^2, $m^\gamma=1450(\pm 70)$ μm^2, $y^0=6700$ (± 300), and $y^\gamma=6400$ (± 100). Using Eqs. (7) and (8) we may calculate

$$\frac{N_{\text{eff}}^\gamma}{N_{\text{eff}}^0}=1.23\pm 0.10$$

and

$$\frac{\Sigma^\gamma}{\Sigma^0}=1.05\pm 0.05.$$

Therefore, within the context of this model, the increased photorefractivity after γ irradiation is due to an increase in the effective trap density and possibly a slight increase in the normalized conductivity.

The analysis presented above assumes that the fractional poling F did not change as the result of γ irradiation. If the fractional poling did change, one would expect it to decrease. Since we observed an increase in the TBC gain we cannot account for our observations of a change in Γ as a consequence of a possible change in fractional poling. In the event of a change in F, our theoretical analysis would be altered somewhat. We see from Eqs. (7) and (8) that if F decreases, the inferred values of Σ^{γ} would decrease whereas the inferred value of N_{eff}^{γ} would remain unchanged.

As stated earlier, the assumption of a single photoactive species present in two different ionization states usually applies to as-grown barium titanate crystals; but the physical mechanism in which γ irradiation may simultaneously increase N_{eff} and Σ is still unclear. It is clear however that the increased photorefractivity is due to an increase in the effective trap density and a reduction in the effects attributable to having both holes and electrons participate in the photorefractive process (the latter may be due entirely to the former). All of our data, including the differing response between the two crystals, may be explained by assuming that increased photorefractivity is due to an increase in the hole donor concentration (N^+) upon γ irradiation. We note that an increase in N^+ with no change in N will result in a significant increase in N_{eff} and Σ only if $N \gtrsim 20N^+$. We propose that γ irradiation increases N^+ in $BaTiO_3$, and that in crystal A the as-grown value of N/N^+ was much smaller than the value of N/N^+ in crystal B in the as-grown state.

Under the assumption that γ irradiation increases N^+, the saturation of the improvement in photorefractivity observed for doses greater than 10^7 rad may be attributed to either of two phenomena. The most likely explanation is that there is a limited number of centers within the crystal that can be turned into hole donors by γ irradiation. A second possibility is that in each case γ irradiation has increased N^+ to a value significantly greater than $\sim 0.05N$ and therefore a further increase in N^+ does not result in a significant increase in either N_{eff} or Σ.

Since the source of the charge carriers is unknown it is difficult to determine the precise physical effects that γ irradiation has on the crystal. However, estimates of the cohesion energy of ABO_3-type crystals indicate that the ~ 1.25 MeV γ rays used for irradiation will not cause dislocations of the constituent ions in $BaTiO_3$,[4] so any observed effects are probably not due to induced crystal defects (i.e., color centers).

In conclusion, we have demonstrated that γ irradiation can improve the photorefractive properties of some as-grown $BaTiO_3$ crystals. We have demonstrated that this increase in photorefractivity is due in part to an increase in the effective trap density and possibly in part to an increase in the normalized conductivity within the crystal.

We wish to thank Donald Walters of the U.S. Naval Postgraduate School for the generous loan of two $BaTiO_3$ crystals and Mary Montesalvo and David Mckee of the University of Massachusetts at Lowell for extensive and cheerful help in the irradiation of our samples. We also thank M. B. Klein for advice on determining some of the physical parameters of our crystals. This work was supported by the U.S. Army Research Office through a University Research Initiative.

[1] S. Ducharme and J. Feinberg, J. Opt. Soc. Am. B **3**, 283 (1986).
[2] R. Yu. Azimzade, A. Kh. Zeinally, L. S. Kogan, and A. L. Timofeev, Sov. Phys. Tech. Phys. **24**, 1143 (1979); E. S. Vartanyan, R. K. Ovsepyan, A. R. Pogosyan, and A. L. Timofeev, Sov. Phys. Solid State **26**, 1464 (1984).
[3] J. Rosa, K. Polak, and J. Kubatova', Phys. Status Solidi **111**, K85 (1982); T. R. Volk, M. A. Ivanov, M. L. Meil'man, and N. M. Rubinina, Sov. Phys. Solid State **29**, 497 (1987).
[4] T. R. Volk, Optoelectron. Instrum. Data Process **5**, 1 (1988).
[5] G. C. Valley, J. Appl. Phys. **59**, 3363 (1986).
[6] M. B. Klein and R. N. Schwartz, J. Opt. Soc. Am. B **3**, 293 (1986).
[7] N. Kukhtarev, V. B. Markov, S. G. Odulov, M.S. Soskin, and V. L. Vinetskii, Ferroelectrics **22**, 949 (1979).
[8] A. Marrakchi, J. P. Huignard, and P. Gunter, Appl. Phys. **24**, 131 (1981).
[9] M. B. Klein and G. C. Valley, J. Appl. Phys. **57**, 4901 (1985).
[10] F. P. Strohkendl, J. M. C. Jonathan, and R. W. Hellwarth, Opt. Lett. **11**, 312 (1986).
[11] M. B. Klein, in *Photorefractive Materials and Their Applications I*, edited by P. Gunter and J.-P. Huignard (Springer, Berlin, 1989), pp. 195–236.
[12] P. Gunter and M. Zgonik, Opt. Lett. **16**, 1826 (1991).