Explanation of the Apparent Sublinear Photoconductivity of Photorefractive Barium Titanate

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We explain the apparent sublinear intensity dependence of photoconductivity in barium titanate. In our model shallow acceptors act as a reservoir for charges optically excited from the donors. As this reservoir fills, the fraction of occupied donors changes appreciably, changing the lifetime of the free carriers. We identify two types of barium-titanate crystals having quite different photorefractive characteristics depending on their relative density of donors and acceptors, and we find that the depth of the shallow acceptor level is $\sim 0.4 \pm 0.1$ eV in both types of crystals.

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The photoconductivity of $BaTiO_3$ does not scale linearly with light intensity. In 1977, Fridkin and Popov measured an $I^{0.5}$ dependence using electrodes attached to the crystal.[1] In 1984, Ducharme and Feinberg[2] found an $I^{0.68}$ dependence of the speed-of-light–induced charge migration (which is proportional to the photoconductivity). In most photorefractive materials doubling the incident optical intensity doubles the charge migration rate, but not so in $BaTiO_3$. Here we show that the apparent sublinear photoconductivity of $BaTiO_3$ is caused by shallow acceptors, and that the empirical I^x functional dependence, while producing a reasonable fit to the data, is not the fundamentally correct functional dependence.

We identify two types of barium-titanate crystals which we call type *A* and type *B*. A type-*A* crystal has an erasure speed that increases almost linearly with light intensity (and can be approximated as speed $\propto I^{x\sim 0.9}$), a steady-state photorefractive grating strength that varies very little with intensity, and a small dark conductivity. A type-*B* crystal has an erasure speed that increases decidedly less than linearly with light intensity (and can be approximated as speed $\propto I^{x\sim 0.6}$), a steady-state photorefractive grating strength with a marked intensity dependence, and a large dark conductivity. We show below that a simple two-level model of deep donors and shallow acceptors explains the very different behaviors of these two types of $BaTiO_3$ crystals.

We postulate that in type-*A* crystals the density of donors greatly exceeds that of acceptors ($N_D \gg N_A$), while in type-*B* crystals the density of donors is comparable or slightly less than the density of acceptors ($N_D \leq N_A$). Previous models of the photorefractive effect assumed that either the donors or the acceptors (but *not* both) took part in charge transport,[3,4] or neglected thermal excitations,[5] or invoked additional levels.[6,7] In our model charges (assumed to be holes) in *both* the donors and the acceptors can be excited by light, and we also permit thermal excitation of holes from the acceptors into the valence band. We position the donors near the middle of the band gap of the crystal (which is ~ 3.1 eV for $BaTiO_3$) and the acceptors close to the top of the valence band, so that at room temperature the only likely thermal excitation is from the acceptors. The Fermi level is located on the donor levels for $N_D > N_A$ and on the acceptor level for $N_D < N_A$. A key feature of this model is that holes optically excited from the donors can accumulate in the shallow acceptors, where they can be thermally reexcited. The equations describing the change in the populations of these levels are a two-level adaptation of those found in Ref. 7:

$$\frac{\partial N_D^+}{\partial t} = -s_D I N_D^+ + \gamma_D n (N_D - N_D^+) , \tag{1}$$

$$\frac{\partial N_A^-}{\partial t} = (s_A I + \beta)(N_A - N_A^-) - \gamma_A n N_A^- , \tag{2}$$

$$\frac{\partial n}{\partial t} + \frac{\partial N_D^+}{\partial t} - \frac{\partial N_A^-}{\partial t} + \frac{1}{e}\nabla \cdot \mathbf{J} = 0 , \tag{3}$$

$$\mathbf{J} = e\mu n \mathbf{E} - \mu k_B T \nabla n , \tag{4}$$

$$\nabla \cdot \mathbf{E} = (e/\epsilon)(n + N_D^+ - N_A^-) , \tag{5}$$

where I is the total optical intensity, N_D^+ is the density of ionized donors, N_A^- is the density of full acceptors, n is the density of free holes, s_D and s_A are the light excitation cross sections from the donors and acceptors, γ_D and γ_A are the free-carrier recombination constants for donors and acceptors, β is the thermal excitation rate from the shallow acceptors, $\mathbf{J}$ is the current density, $\mathbf{E}$ is the total static electric field, μ and ϵ are the carrier mobility and dielectric constant of the crystal, respectively, along the direction of charge migration, e is the electric charge, and $k_B T$ is the thermal energy.

We solve these equations for light intensities $I < 10^7$ W/cm^2, where the generation rate of free carriers is small compared with the fast (10^{10} Hz) recombination rate to the traps.[8] For this case, the density of free holes is small compared to the light-induced change in either the density of ionized donors or full acceptors,

$$n \ll |N_D^+ - (N_D^+)_{I=0}| , \quad n \ll |N_A^- - (N_A^-)_{I=0}| . \tag{6}$$

Note that because holes optically excited from the donors can accumulate in the acceptors, both N_D^+ and N_A^- can be appreciably changed by light, even though n

remains small.

Consider a photorefractive grating with wave vector $k=4\pi(\sin\theta)/\lambda$ along the z direction. This grating is formed by two coherent writing beams with intensities I_1 and I_2 and wavelength λ in the crystal crossing at a full angle 2θ inside the crystal. Let an intense erasing beam (not coherent with the writing beams) simultaneously flood the crystal with a uniform intensity I_0. This makes the total light intensity $I=(I_1+I_2+I_0)\mathrm{Re}(1+me^{-ikz})$, and the modulation of the grating $m\equiv 2(I_1I_2)^{1/2}/(I_1+I_2+I_0)$ much less than 1. If the writing beams are suddenly removed, the grating will begin to decay. We find that the energy density Φ needed to erase the grating to $1/e$ of its initial value is

$$\Phi=\frac{\epsilon}{e\mu f(k)}\frac{\gamma_D(N_D-N_{D0}^+)}{s_D N_{D0}^+}, \tag{7}$$

where N_{D0}^+ is the spatially uniform density of ionized donors. Solving Eqs. (1)–(3) to eliminate the intensity-dependent quantity N_{D0}^+ yields

$$\Phi=\frac{\Phi_0}{1+\beta/s_AI_0}\left[\mathrm{sgn}(N_A-N_D)+\left[1+\frac{4s_D\gamma_AN_AN_D}{s_A\gamma_D(N_A-N_D)^2(1+\beta/s_AI_0)}\right]^{1/2}\right]^{-1}, \tag{8}$$

where

$$\Phi_0\equiv\frac{2\epsilon}{e\mu f(k)}\frac{\gamma_AN_D}{s_A|N_A-N_D|}, \tag{9}$$

and $\mathrm{sgn}(N_A-N_D)\equiv-1$ for type-A crystals, and $\mathrm{sgn}(N_A-N_D)\equiv+1$ for type-B crystals.

For all type-B crystals that we studied the approximation

$$\frac{4s_D\gamma_AN_AN_D}{s_A\gamma_D(N_A-N_D)^2}\gg 1+\frac{\beta}{s_AI_0} \tag{10}$$

holds, as long as the light-induced conductivity of the crystal exceeds its dark conductivity. In this case, Eq. (8) for a type-B crystal simplifies to

$$\Phi_B=\frac{\Phi_{0B}}{(1+\beta/s_AI_0)^{1/2}}, \tag{11}$$

where

$$\Phi_{0B}\equiv\frac{\epsilon}{e\mu f(k)}\left(\frac{\gamma_A\gamma_DN_D}{s_As_DN_A}\right)^{1/2}. \tag{12}$$

Figure 1 shows the calculated intensity dependence of Φ, the energy density needed to erase a previously written grating to $1/e$ of its initial value. Note that at high intensity Φ becomes constant in both type-A and type-B crystals, which implies that the photoconductivity becomes linear at these high intensities. Also, at low intensities in type-A crystals the photoconductivity is linear with intensity I, while in type-B crystals it is proportional to $\sqrt{I}$. These features of the photoconductivity can be easily missed if the same information is displayed in the traditional log-log plot of speed versus intensity (as shown in the inset), where the curves appear to be straight lines of constant slope x ($0.5<x<1$), implying an oversimplistic I^x functional dependence for the photoconductivity.

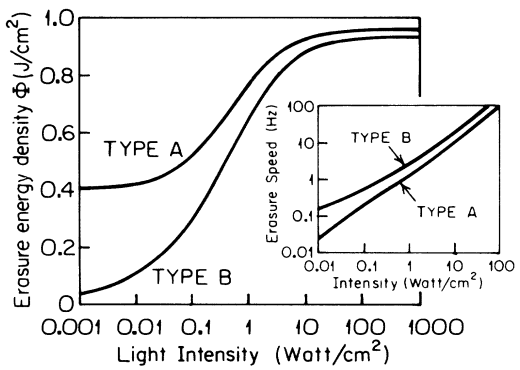

FIG. 1. Predicted dependence of Φ (the energy density required to erase a photorefractive grating to $1/e$ of its initial value) on light intensity for the two types of $BaTiO_3$ crystals. Inset: A log-log plot of the calculated erasure speed vs intensity showing the apparent I^x behavior.

To verify our two-level model we measured the light-induced erasure rate of photorefractive gratings as a function of the incident light intensity. Three as-grown $BaTiO_3$ samples (named Cat, Free, and Rob) were selected for their different characteristics. The Rob crystal is type A with a long dark storage time ($T_{\mathrm{dark}}>10^4$ sec at room temperature). Both the Cat and Free crystals are type B and have short dark storage times ($T_{\mathrm{dark}}\sim 1$ sec at room temperature). The same Cat crystal was previously studied in Ref. 2; we repeated the measurements over a wider range of crystal temperature and light intensity. Two optical writing beams, of comparable intensity, intersected in the crystal at a full internal angle of $2\theta=25°$. After the writing beams had written a photorefractive grating to steady state, both writing beams were blocked and the grating was allowed to decay. An intense erasing beam flooded the crystal at all times, and thereby avoided large changes in the shallow trap population when the writing beams were turned off. The erasing intensity was 10 times the total writing intensity. All these optical beams were at 514.5 nm and polarized perpendicular to the c axis of the crystal. The crystal temperature was stabilized to $\pm 1°$. The relative grating strength was measured by a weak, extraordinary polarized 632.8-nm laser beam incident at the Bragg angle.

Figure 2 is the plot of Φ vs I_0 in the Rob crystal (a

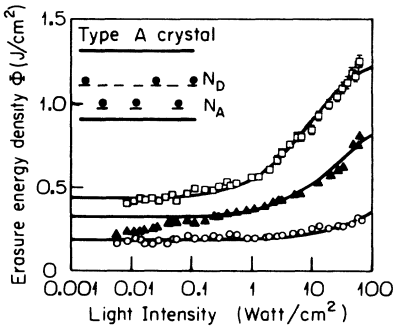

FIG. 2. Φ vs I_0 at various temperatures of the Rob crystal of $BaTiO_3$, a type-A crystal: $T=25\,^{\circ}C$ (□), $T=47\,^{\circ}C$ (▲), $T=90\,^{\circ}C$ (○). Solid curves are simultaneous best fits by Eq. (8).

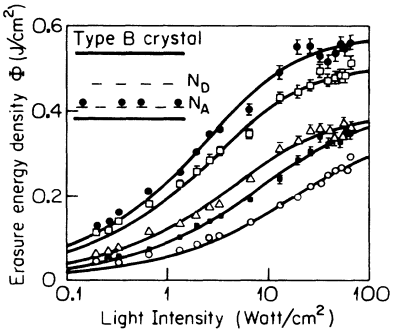

FIG. 3. Φ vs I_0 at various temperatures of the Cat crystal of $BaTiO_3$, a type-B crystal: $T=17\,^{\circ}C$ (●), $T=25\,^{\circ}C$ (□), $T=35\,^{\circ}C$ (△), $T=43\,^{\circ}C$ (■), $T=52\,^{\circ}C$ (○). Solid curves are best fits by Eq. (11).

type-A crystal) for three temperatures. The solid curves are simultaneous least-squares fits of the data by Eq. (8) which contains three parameters: Φ_0 (which sets the amplitude), β/s_A (which determines the point of inflection), and $p_2 \equiv 4s_D\gamma_A N_A N_D/\gamma_D s_A (N_D - N_A)^2$. (From a simultaneous least-squares fit of all of the data we obtain $p_2=23$.) According to theory, β (the thermal excitation rate out of the shallow traps) increases with temperature T according to

$$\beta = \beta_0 e^{-E_T/k_B T}, \tag{13}$$

where E_T is the energy separation of the shallow trap level from the valence band, and β_0 is a constant. Fitting the values of β/s_A at the various temperatures by Eq. (13) we estimate the depth of the shallow trap levels in the Rob crystal to be $E_T \sim 0.36$ eV.

Figure 3 shows a semilogarithmic plot of Φ vs I_0 for the Cat crystal. Note that the function Φ increases with light intensity even at low intensities; this is caused by the light-induced change in the density of un-ionized donors. Comparison with Fig. 1 shows that the Cat crystal is a type-B sample with $N_D \leq N_A$. At high intensity Φ flattens, because the density of holes in the shallow acceptors (and the corresponding density of un-ionized donors) is beginning to saturate. Note that the data at higher crystal temperatures flatten at higher intensities, because it requires more light to saturate an acceptor that has a larger thermal excitation rate. The solid curves are least-squares fits by Eq. (11) using Φ_{0B} and β/s_A as the two fitting parameters.

Figure 4 shows a semilogarithmic plot of the parameter β/s_A as a function of the inverse thermal energy $1/k_B T$ for both the Cat and Free crystals (both type B). From the slope of these graphs and using Eq. (13), we obtain the depth of the shallow traps in the Cat crystal to be $E_{T\,\mathrm{Cat}} = 0.5 \pm 0.15$ eV, and $E_{T\,\mathrm{Free}} = 0.3 \pm 0.1$ eV in the Free crystal.

The depth of the shallow traps in type-B crystals can also be determined by measuring the rate of decay of photorefractive gratings in the dark as a function of the crystal temperature. If the total intensity is sufficiently low ($I \ll \beta/s_A$), the grating forms only on the shallow acceptors in type-B crystals, and will decay in the dark exponentially at a rate

$$\Gamma_{\mathrm{dark}} = \frac{e\mu f(k)}{\epsilon} \frac{\beta_0}{\gamma_A N_D} e^{-E_T/k_B T}.$$

In order to obtain E_T, we first correct for the strong temperature dependence of the mobility μ by multiplying the dark-decay rate by Φ_{0B} at each temperature. A semilogarithmic plot of $\Gamma_{\mathrm{dark}}\Phi_{0B}$ vs $1/k_B T$ yielded a straight line for the Cat and Free crystals with $E_T \sim 0.4$ eV in both cases, in good agreement with the values of E_T determined above.

We now understand why the dark conductivity is much smaller for a type-A crystal than for a type-B crystal. In a type-A crystal in the dark and in thermal equilibrium, the acceptors will be empty of holes and there will be negligible conduction in the dark. In contrast, in a type-B crystal there are always some holes in the acceptors available for thermal excitation, so the dark conductivity is relatively large.

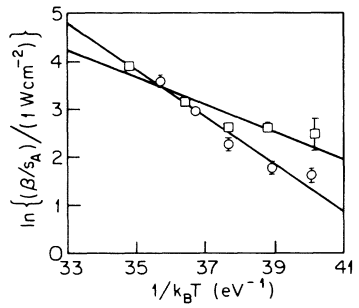

FIG. 4. Plot of the measured intensity needed to saturate the shallow traps (normalized to 1 W/cm²) vs the inverse thermal energy for two type-B crystals. (a) Circles, Cat crystal. The slope of the line yields $E_T \sim 0.5 \pm 0.15$ eV. (b) Squares, Free crystal. The slope of the line yields $E_T \sim 0.3 \pm 0.1$ eV.

We also predict the intensity dependence of the space-charge field. In general, photorefractive gratings will form on both the donors and the acceptors. Equations (1)–(5) predict that the amplitude E_{sc} of the steady-state space-charge field $E_{sc}e^{-ikz}$ will vary strongly with intensity in type-B crystals but only weakly in type-A crystals. We obtain

$$E_{sc} = +im\frac{k_BT}{e}\eta(I)\frac{k}{1+k^2/(k_{0,\text{donor}}^2+k_{0,\text{acceptor}}^2)}, \quad (14)$$

where

$$\eta(I)\equiv\frac{k_{0,\text{donor}}^2+k_{0,\text{acceptor}}^2/(1+\beta/s_AI)}{k_{0,\text{donor}}^2+k_{0,\text{acceptor}}^2}. \quad (15)$$

The function $\eta(I)\leq 1$ approaches unity at high intensity. The Debye screening wave vectors for the donors and acceptors are defined by

$$k_{0,\text{donor}}^2\equiv\frac{e^2}{\epsilon k_BT}\frac{N_{D0}^+(N_D-N_{D0}^+)}{N_D}, \quad (16)$$

and

$$k_{0,\text{acceptor}}^2\equiv\frac{e^2}{\epsilon k_BT}\frac{N_{A0}^-(N_A-N_{A0}^-)}{N_A}. \quad (17)$$

Here N_{D0}^+ and N_{A0}^- are the spatially uniform densities of ionized donors and filled acceptors, respectively, both of which vary with light intensity.

For a type-B crystal operated in a regime where the light-induced photoconductivity exceeds the dark conductivity, Eq. (10) holds, and the function η in Eq. (15) becomes $\eta(I)=\frac{1}{2}[1+1/(1+\beta/s_AI)]$. This causes E_{sc} to increase by a factor of 2 as the light intensity is increased from low intensities $I\ll\beta/s_A$ to high intensities $I\gg\beta/s_A$. For a type-A crystal, $\eta\sim 1$ for all intensities, so that E_{sc} should vary only weakly with intensity.

We confirmed the above by measuring the magnitude of the photorefractive space-charge field and found that, as predicted by theory, E_{sc} varied appreciably with optical intensity in type-B crystals but not in type-A crystals. For the Cat and Free crystals the space-charge field increased with increasing light intensity by a factor of more than 2.3 over the intensity range $I=0.1$–70 W/cm^2, consistent with their assignment as type-B crystals. In contrast, for the Rob crystal (a type-A crystal) the grating strength changed by only $\sim 20\%$ over the same intensity range for all temperatures studied.

Equation (8) also explains our cw and pulsed erasure data of Ref. 9. In those experiments we erased gratings with pulsed light beams of high peak intensity but low average intensity in two additional type-A crystals of $BaTiO_3$ (Swiss and Hop). Our theory predicts that in this case it takes the same amount of energy to erase a photorefractive grating by continuous illumination as by a train of light pulses having the same average intensity.

The critical parameter controlling whether a crystal is type A or type B is $\chi\equiv N_AN_D/(N_A-N_D)^2$, which varies rapidly near the compensation point $N_A=N_D$. This suggests that our as-grown $BaTiO_3$ crystals are nearly compensated, which explains why their photorefractive characteristics vary so much from one sample to the next.

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