New Photorefractive Mechanism in Centrosymmetric Crystals: A Strain-Coordinated Jahn-Teller Relaxation

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We present observations and an explanation of a photorefractive effect in strained centrosymmetric KTN and KLTN crystals in the absence of an externally applied electric field. Centrosymmetric crystals are forbidden to display the classical photorefractive effect without application of an applied field. Nevertheless, in diffraction experiments, centrosymmetric KTN:Cu and KLTN:Cu crystals show index changes of up to 1.7×10^{-5} and photorefractive response at more than 120 °C above the phase transition. Experiments described here allow us to conclude that a Jahn-Teller relaxation of the spatially modulated Cu^{2+} dopant concentration is responsible.

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The photorefractive properties of potassium tantalate niobate (KTN) were identified more than fifteen years ago [1] but the difficulty of growing high-quality crystals hindered their study until recently. When the crystals are illuminated by a spatially periodic intensity pattern the resulting charge redistribution results in a spatially periodic electric field $E_{sc}(x)$ which leads, via the electro-optic effect, to an index grating $\delta n(x)$. We have succeeded in growing optical quality KTNs and potassium lithium tantalate niobates (KLTNs) with high dopant concentrations and wide ranges of lithium and niobium concentrations [2]. Recent investigations of these crystals have revealed a photorefractive response which cannot be explained by the conventional electro-optic theory. This new effect is expected to occur in most transition metal doped perovskites especially when a strain is present. In the KTNs and KLTNs reported on here, the strain is due to the growth process.

Perovskite oxide photorefractives operated above the phase-transition temperature (paraelectric and centrosymmetric phase) lack a linear electro-optic coefficient. Instead, the photorefractive mechanism in these symmetric materials arises through the quadratic electro-optic effect. Here the Bragg matched term of the index grating due to a spatially periodic field $E_{sc}(x)$ in the presence of an applied electric field E_0 can be written [3] as $\delta n = n_0^3 g(\varepsilon\varepsilon_0)^2 E_0 E_{sc}(x)$, where g is the relevant quadratic electro-optic coefficient, and n_0 the index of refraction. We assume that the polarization is linear ($P=\varepsilon E$) and that the dielectric constant $\varepsilon \gg 1$. Thus the conventional photorefractive effect is zero in the absence of a spatially uniform electric field.

Nevertheless, our experiments reveal the existence of a zero electric field photorefractive (ZEFPR) effect in KTN and KLTN at temperatures at least 120 °C above the phase transition where the crystal is nominally symmetric. No effect is seen with undoped crystals or with thermally reduced samples. The diffraction expected from absorption gratings is 3 orders of magnitude too weak to explain the effect. The studies of the phenomena which are described here reveal a new photorefractive mechanism. In this paper we describe the effect and present what we believe is the most plausible explanation. The experimental results supporting the explanation follow and, finally, we give results of a theory of Jahn-Teller relaxation.

The zero external field photorefractive (ZEFPR) effect was first noticed by us [3,4] in KTN and KLTN crystals. This photorefractive effect was attributed to the presence of a growth induced strain [5]. In addition, Yang *et al.* [6] have cited an "extremely small" effect in KTN in the absence of an applied field, but without explanation. Recently, we have developed a method of producing KTNs and KLTNs with high niobium concentrations of high optical quality, and in these crystals, the effect is greatly enhanced. Under certain conditions of crystal preparation we have been able to produce zero field index gratings with $\Delta n = 1.7\times10^{-5}$, and diffraction efficiencies of over 20% in a 4.15-mm-thick sample using 488-nm argon laser beams.

In the crystals which displayed a strong ZEFPR effect, the photorefractive dopant was copper, which is stable as either Cu^{1+} or Cu^{2+}. The Cu^{2+} ion is known to cause large Jahn-Teller (J-T) distortions, especially in octahedral symmetry. The Cu^{1+} ion by contrast, has no tendency to distort. The illumination of the crystal by the periodic intensity pattern of the optical field leads to a mimicking spatially periodic Cu^{2+}/Cu^{1+} ratio due to excitation of electrons (from Cu^{1+}) and trapping by Cu^{2+}. This, as explained above, gives rise to a spatially periodic distortion [7]. Since the copper concentration is relatively small in the KLTNs we do not expect a cooperative ordering of the distortions; rather, their orientation should be random. But when a macroscopic (growth induced) strain is present, as is the case in the crystals studied, the distortions will orient preferentially in order to minimize that strain. The result is a spatial modulation of the strain field in phase with the intensity which leads to a corresponding modulation of the index of refraction (index grating) via the photoelastic effect. We expect this phenomenon to be quite general, although only noticeable when the conventional photorefractive effect is forbidden.

The strain in the crystals is due to the particulars of the growth process; we describe it only briefly here since it is discussed in detail elsewhere [2]. The crystal grows as a series of cubical shells, expanding from the seed. During the growth the composition of the crystal changes which is attendant by an increase in the lattice constant. Thus each face of the cubical shell of the growing crystal must be compressed slightly to mesh with the previous cubical shell. In this way there arises a compressive strain in the plane of each face of the cube which increases with distance from the seed crystal. Similarly, there is also a tensile strain perpendicular to each face of the cube which also increases with distance from the seed. These strains induce a linear birefringence which is readily apparent when the crystal is viewed through crossed polarizers. When a small sample is cut from the grown crystal near the center of one of the cube faces, the strain in the sample will be homogeneous: uniformly compressive in two directions and uniformly tensile in the third.

To test the validity of the theory of J-T relaxation we investigated the dependence of the index grating on the strain present in the crystal. The experimental setup for performing diffraction experiments is illustrated in the inset of Fig. 3. Two extraordinary beams at 488 nm symmetrically incident, created an optical intensity standing wave inside the sample. After several minutes, one of the beams was blocked with an electronic shutter for 50 msec. While the shutter was closed we measured the optical power which was diffracted by the grating into the direction of the blocked beam. The diffraction efficiency, η, is defined as the ratio of the diffracted power to the power incident on the crystal. We corrected for losses from facet reflections.

Unless otherwise indicated, all measurements were performed at room temperature on several KTNs and KLTNs. We determined that in homogeneously strained samples the diffraction efficiency increased as the square of the interaction length and was independent of total intensity. We constructed a two-dimensional vise to be able to compensate the growth induced strain with external pressure applied in two dimensions. The diffraction efficiency in a 2.85-mm-thick sample was reduced by 40% when the internal strain was minimized. Additionally, the effect is reduced when the sample is exposed to heat treatments which reduce the internal strain but which leave the conventional photorefractive properties unchanged [8].

Although this evidence shows that the ZEFPR effect relies partially on the macroscopic strain, it remains to be shown that the strain does not induce a morphic lowering of the crystal symmetry, allowing a linear electro-optic coefficient. We tested for the existence of a linear electro-optic effect in a sample of $K_{0.994}L_{0.0006}T_{0.700}N_{0.299}$ by measuring the birefringence induced under application of electric fields in various directions. A Soleil-Babinet compensator between crossed polarizers oriented at 45° to the crystal axes was used to measure the birefringence at 633 nm. The results were fitted to a third-order polynomial but the best fit was purely quadratic to the resolution of the experiment. Measurements were repeatable to $\delta(\Delta n) < 5\times10^{-7}$. This indicates an almost perfect quadratic electro-optic effect with $g_{11}-g_{12}=0.123$ m^4C^{-2}, which agrees with previously published values for KTN [9]. It should be noted that the absence of a third-order term indicates little or no polarization nonlinearity. We conclude that the strain does not induce a linear electro-optic coefficient.

Next, a series of experiments were performed to verify anticipated characteristics of the ZEFPR effect. For these experiments a $K_{0.990}L_{0.0019}T_{0.730}N_{0.27}$:Cu sample was used, where $[Cu^{2+}]=3.1\times10^{18}$ cm^{-3}, determined from optical absorption data [10]. The crystal was centrosymmetric above its phase transition at $T_c \sim -23\,°C$.

First, since the ZEFPR effect is due to a strain "grating" which modulates the refractive index via the photoelastic effect, we expect at most weak dependence on the dc/low-frequency dielectric constant ε. We confirmed this by measuring the dependence of the ZEFPR effect on temperature near the phase transition (here ε obeys the Curie-Weiss law). Using the setup as in Fig. 3, two interfering 488-nm beams with equal intensities of ~ 500 $mW\,cm^{-2}$ uniformly illuminated the crystal. No field was applied during writing of the diffraction grating. After a writing time of 60 s, one beam was blocked and the other beam attenuated to minimize erasure, and the resultant diffraction was measured. After the diffraction due to the ZEFPR effect was determined, a field was applied to determine the index change due to the quadratic electro-optic effect. Finally, after each measurement, the gratings were completely erased by flooding the crystal with uniform illumination and raising the temperature, if necessary. The results for various temperatures are illustrated in Fig. 1. The quadratic effect increases dramatically as the phase-transition temperature ($-23\,°C$) is approached because of the concomitant increase in dielectric constant. The extremely high diffraction efficiencies with a $\sin^2$ rollover at high fields are characteristic of the quadratic effect in centrosymmetric KLTN [3,4]. The $\sim 1\%$ diffraction efficiency observed at zero electric field is caused by the ZEFPR effect. It is independent of the dielectric constant since it is nearly a constant for the seven temperatures investigated which range through the ferroelectric transition at $-23\,°C$. Although the ZEFPR effect diffraction is weak in the configuration used for this

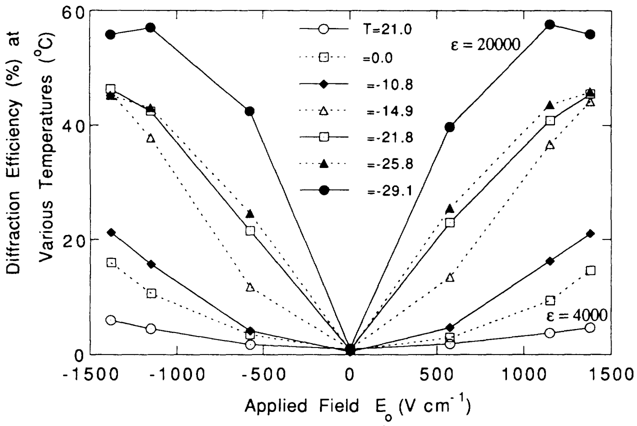

FIG. 1. The diffraction efficiency vs applied field and temperature for an index grating written with zero applied field. The small zero-field value is independent of temperature, whereas the quadratic electro-optic contribution increases by more than an order of magnitude.

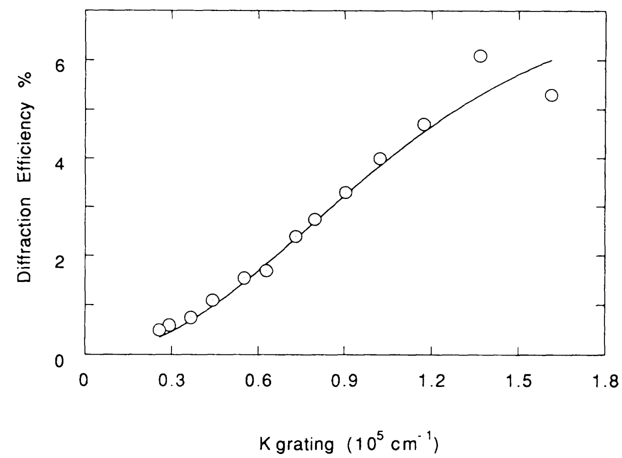

FIG. 2. Diffraction efficiency vs the grating **K** vector for a 4.15-mm KLTN crystal. The curve shows the best fit to Eq. (1) with $N_a = 2.8\times10^{18}$ cm^{-3}, in agreement with results from optical absorption data.

experiment, the same sample yielded over 20% diffraction efficiency at a higher angle of beam incidence. The fact that the ZEFPR index grating has no noticeable dependence on the dielectric constant proves that the effect is distinct from the quadratic electro-optic effect. The ZEFPR effect is a new phenomenon which has nothing to do with the polarization caused by a space charge field ($P=\varepsilon E$).

Our model stipulates that the magnitude of the ZEFPR index grating depends linearly on the spatial modulation of the Cu^{2+} ions. Since the Cu^{2+} modulation is equal to the modulation of the photoexcitable charge carriers, we expect the ZEFPR index grating to have the same functional dependence as the light-induced space-charge electric field caused by the charge modulation. From the basic Kukhtarev model for the space charge field induced by the interfering beams we have [11]

$$E_{sc} = i\frac{(2I_1I_2)^{1/2}}{I_1+I_2}\,\frac{KTk/e}{1+K^2kT\varepsilon/e^2N_A}\cos2\theta\,, \qquad (1)$$

where θ is the angle of beam incidence in the crystal, I_1 and I_2 are the beam intensities, and K is the index grating wave vector. The dependence on E_{sc} was tested by monitoring the diffraction efficiency as a function of the grating wave vector and the beam intensity ratios. We determined a relation between the index change and the space charge field for the ZEFPR effect from the $E_0=0$ data of Fig. 1 to be $\Delta n_{ZEFPR} = 5\times10^{-9}E_{sc}$ in cgs units. Figure 2 shows the diffraction efficiency versus K. Peak diffraction efficiency of 6.1% was observed, corresponding to $\Delta n = 9.1\times10^{-6}$. The best fit of the data to Eq. (1) occurs for $N_a = 2.8\times10^{18}$ cm^{-3}, which is near the value (3.1×10^{18} cm^{-3}) obtained from absorption data. Figure 3 plots the diffraction versus beam intensity ratios, along with the theoretical curve from Eq. (1). The good correspondence of the data in Figs. 2 and 3 with Eq. (1) allows us to conclude that the index change of the ZEFPR effect varies as the space charge field.

Our final test of the ZEFPR effect was to measure the phase of the ZEFPR index grating relative to the intensity grating of the writing beams. Since the index grating is modulated by the local Cu^{2+} concentration, we expect it to be in phase with the intensity, so that no two-beam coupling (power exchange between the two writing beams) will occur. This condition was verified by testing for two beam coupling with the setup of Fig. 3. No power transfer was observed even though strong diffraction occurred when either beam was blocked. Two-

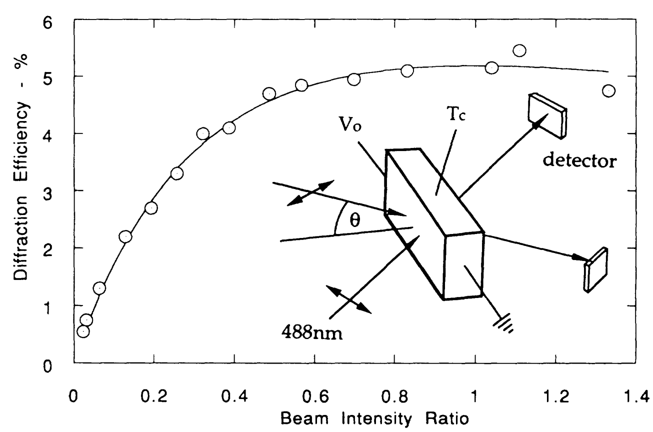

FIG. 3. The diffraction efficiency of a KLTN crystal vs the beam intensity ratios. The curve is the theoretical dependence of the space charge field on the modulation depth. Inset: The experimental geometry. V_0 is the applied voltage (=0 when measuring the ZEFPR effect), and Tc is the temperature control.

beam coupling was observed, however, when an electric field was applied. The zero phase of the ZEFPR gratings further confirms the distinction of the ZEFPR effect from electro-optic mediated photorefractive effects where the phase must be nonzero because it is due to the intrinsically nonlocal space charge field.

The tests described above form the basis for our conclusion that the ZEFPR effect is caused by a Jahn-Teller relaxation in conjunction with the photoelastic effect. In what follows we present a simple theory of the interaction between the local J-T distortions and a macroscopic strain field. We consider a crystal with a growth induced tensile strain along the **x** axis ($u_1>0$). The energy of the strained crystal per unit volume is given by $E=(u_1^2/2)[c_{11}-2c_{12}\sigma]$, where the usual index contraction is used, σ is Poisson's ratio, and c_{ij} are the elastic constants.

The J-T distorting centers distributed randomly throughout the volume of the crystal will alter the strain so that $u_i'=u_i+\Delta u_i$ where Δu_i is the change in macroscopic strain due to the summation of the individual J-T distortions. The individual distortions are elongations of the oxygen octahedra in one of three orthogonal directions. We denote y as the fraction of distorting centers oriented along the **x** axis, and $(1-y)$ as the remaining fraction distributed along either the **y** or the **z** axes. We readily determine $\Delta u_1[y]=\Delta u_1[1][(1+\sigma)y-\sigma]$, where $\Delta u_1[1]$ is the strain change when $y=1$ (complete ordering).

The decrease in elastic energy per unit volume resulting from the reduction in strain $\Delta u_i[y]$ is obtained as $\Delta E[y]=-u_1\Delta u_1[y][c_{11}-2c_{12}\sigma]$. The entropy change of the ordering follows readily by counting the number of configurations of the distortions. There are (ny) distorting centers oriented along the **x** axis per unit volume, and $n(1-y)$ oriented along either the **y** or **z** axes. The entropy change ($\Delta S=k\ln W$) is found to be $\Delta S[y]=-nk\{y\ln[y]+(1-y)\ln[(1-y)/2]\}$. Minimizing the free energy yields the temperature dependence of the ordering parameter. We calculate that

$$y[\beta]=e^{\beta U}/(e^{\beta U}+2)\,, \qquad (2)$$

where the "strain alignment energy" per distorting center $U=\Delta E[1](1+\sigma)/n$ and $\beta=1/kT$. From this we conclude that large macroscopic strains lead to ordering of distortions; our preliminary results indicate that $\beta U\sim 0.4$ so that the partial ordering occurs.

Finally, the index grating results from the periodic change in the optical impermeability tensor, $\delta\beta_{ij}=p_{ij}\delta(\Delta u_j[y])$, where $\delta(\Delta u_j[y])$ is the periodic strain variation calculated above and p_{ij} are the photoelastic constants. We note that even in the absence of macroscopic strain $\delta\beta_{ij}\neq 0$ unless $\sigma=0.5$. The determination of the parameters of this theory, particularly $\Delta u_i[y]$, is ongoing

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