Holographic gratings by spatial modulation of the Curie-Weiss temperature in photorefractive $K_{1-x}Li_xTa_{1-y}Nb_yO_3$:Cu,V

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We present experimental evidence indicating the formation of metastable dipolar gratings in potassium lithium tantalate niobate at the *paraelectric phase*. These dipolar gratings result from the formation of local metastable changes in the Curie-Weiss temperature, which, in the presence of an external electric field, induce changes in the low-frequency polarization. The polarization changes create spatially correlated birefringence gratings due to the electro-optic effect. The dipolar gratings are formed in a slow spontaneous process, to compensate for regular photorefractive gratings immediately after the creation of the latter. [S0163-1829(97)10116-3]

We present experimental evidence indicating that at the *paraelectric phase*, close to the phase transition temperature, the regular (space charge originated) photorefractive (PR) gratings are compensated for by a slow spontaneous formation of dipolar gratings. These dipolar gratings result from local metastable changes in the Curie-Weiss temperature, which, in the presence of an external uniform electric field, induce changes in the low frequency polarization. The polarization changes create spatially correlated birefringence gratings through the electrooptic effect which compensate for the PR gratings.

Usually, the PR effect is attributed to the formation of a spatially modulated space charge, which causes a correlated modulation in the birefringence through the electrooptic effect (see Ref. 1). At the paraelectric phase, the electro-optic effect is quadratic and is given by

$$\Delta n = \tfrac{1}{2} n_0^3 g P^2, \tag{1}$$

where Δn is the induced birefringence, n_0 is the refractive index, g is the effective quadratic electro-optic coefficient, and P is the low-frequency polarization (see Ref. 2). Therefore, a spatial modulation in the birefringence induced by a modulation of the polarization δP is given by

$$\delta[(\Delta n)(\mathbf{r})] = n_0^3 g P \delta P(\mathbf{r}). \tag{2}$$

If an external electric field is applied to the crystal, then the spatial modulation of the birefringence is given by

$$\delta[(\Delta n)(\mathbf{r})]_{\mathrm{sc}} = n_0^3 g \varepsilon^2 E_0 E_{\mathrm{sc}}(\mathbf{r}), \tag{3}$$

where E_0 is the applied electric field, $E_{\mathrm{sc}}(\mathbf{r})$ is the space charge field formed by the PR process, and ε is the dielectric constant. [Note that it is assumed in Eq. (3) that the crystal is slightly above the transition temperature so that $\varepsilon_r \gg 1$ where $\varepsilon = \varepsilon_0 \varepsilon_r$, and that the electric field in the crystal is below the saturation level so that $P = \varepsilon E$, where $E = E_0 + E_{\mathrm{sc}}$.] This is the so-called voltage-controlled PR effect (see Refs. 3 and 4).

The diffraction efficiency of light diffracted from a planar PR grating is given by (cf. Ref. 5)

$$\eta = e^{-\alpha d} \sin^2\left(\frac{\pi \delta(\Delta n) d}{\lambda_R \cos\vartheta} \right), \tag{4}$$

where λ_R is the wavelength of the reading beam, α is the absorption coefficient at λ_R, θ is the angle between the wave vector of the reading beam and the normal to the grating vector (assuming the reading beam matches the Bragg condition), $\delta(\Delta n)$ is the amplitude of the modulation in the birefringence created by the PR process, and d is the thickness of the material. If Eq. (3) is plugged into Eq. (4), assuming $\eta \ll 1$, so that we can set $\sin\phi \approx \phi$ and obtain

$$\eta = e^{-\alpha d} \left(\frac{\pi n_0^3 g \varepsilon^2 E_{\mathrm{sc}}(\mathbf{r}) d}{\lambda_R \cos\vartheta} \right)^2 E_0^2. \tag{5}$$

Thus it is expected that the dependence of the diffraction efficiency on the externally applied electric field will be quadratic.

The validity of the latter prediction was tested by measurements of the light intensity diffracted from a photorefractive grating written in a potassium lithium tantalate niobate (KLTN) crystal doped with Cu and V. The crystal was grown by us using the top-seeded solution growth method. Its composition was $K_{0.99}Li_{0.005}Ta_{0.857}Nb_{0.144}O_3$ (the Cu and V concentrations were below the level of detection). The phase transition temperature was determined from the dc dielectric coefficient curve (Fig. 1), and was found to be $T_c = 136.3$ K.

The crystal was put in the experimental setup described schematically in Fig. 2. The normal to the surface of the crystal coincided with the z direction. The light beams are in the (x,z) plane. The crystal principal axes were aligned with the x, y, and z directions of the system. The external electric field was applied in the x direction.

Prior to the holographic measurements, the crystal was cooled from 170 to 125 K at 0.5 K/min, while an electric field of 2.8 kV/cm was applied parallel to the x direction. We henceforth refer to this process as ''poling.''

The PR grating was written at 140 K under the following conditions: The writing beams source was an Ar^+ laser operating at a wavelength of $\lambda_W = 514$ nm. The wave vectors of the writing beams lie in the (z,x) plane directed at 9.5° and

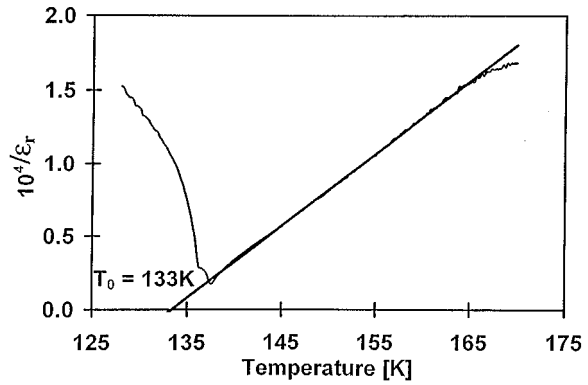

FIG. 1. Inverse of the dielectric constant $(1/\varepsilon)$ as a function of the temperature.

$-9.5°$ with respect to z. The writing beams are polarized in the y direction, and their intensity was 25 mW, with an exposure lasting 3 s, under a dc field of 2.8 kV/cm. The diffraction efficiency was monitored using a He-Ne beam operating at $\lambda_R = 633$ nm. The wave vector of the reading beam lies in the (z,x) plane, and is incident on the crystal at an angle θ with respect to z, so that the reading beam is Bragg matched to the grating formed by the writing beams. The reading beam is polarized in the (z,x) plane.

It was observed that immediately after the exposure the diffraction efficiency η depended quadratically on the applied electric field. However, the minimum of η was not obtained at $E_0 = 0$, but was shifted to $E_0 = 500$ V/cm. These results are in accord with Eq. (5); that is, we can assume that a space-charge PR grating was formed in the crystal. The fact that the minimum point of η was shifted from zero can be accounted for by assuming that during the exposure a dc space charge was formed due to the nonuniformity of the illumination, and that the poling process induced a metastable polarization in the crystal (see below).

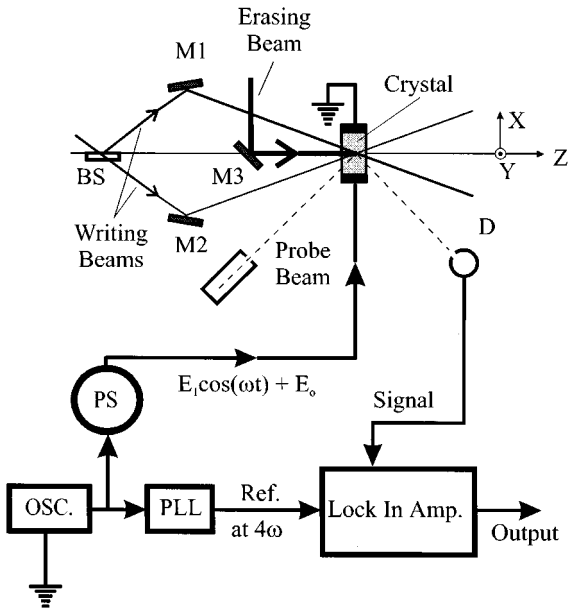

FIG. 2. Experimental setup. BS, beam splitter; $M1$, $M2$, and $M3$, mirrors; D, detector; PS, a dc voltage source; OSC, low-frequency oscillator; PLL, phase-locked loop circuit.

The crystal was then let to dwell in the dark for one hour (at 140 K), under the same dc field that was applied during the writing. During the dwell period the diffraction efficiency, which was monitored by the probe beam, continuously decreased. At the end of the dwell period the dependence of the diffraction efficiency was measured as function of the applied electric field. Here it was observed that the curve was not symmetrical around the minimum point; that is, the dependence of η on E_0 was not quadratic. Therefore, the process which caused the diffraction to decrease cannot be based on the formation of some ionic space charge (cf. Ref. 6), since the latter would not affect the quadratic dependence of η on E_0. This process can, however, be explained by the following hypothesis: If it is assumed that during the dwell period a spatial modulation of the low-frequency dielectric constant is formed, then the applied dc field E_0 will induce a modulation in the birefringence given by

$$\delta[(\Delta n)(\mathbf{r})]_D = n_0^3 g P_0 \delta P(\mathbf{r}) = n_0^3 g \varepsilon\, \delta\varepsilon(\mathbf{r}) E_0^2, \qquad (6)$$

where $P_0 = \varepsilon E_0$ and $\delta P = (\delta\varepsilon)E_0$. The total modulation of the birefringence will be the sum of the space charge and dielectric contributions [Eqs. (3) and (6), respectively]. The diffraction efficiency will accordingly be given by

$$\eta = e^{-\alpha d}\left(\frac{\pi n_0^3 g d}{\lambda_R \cos\vartheta}\right)^2 \{\varepsilon^4 E_{sc}^2(\mathbf{r}) E_0^2 + 2\varepsilon^3[\delta\varepsilon(\mathbf{r})] E_{sc}(\mathbf{r}) E_0^3 + \varepsilon^2[\delta\varepsilon(\mathbf{r})]^2 E_0^4\}. \qquad (7)$$

It can immediately be seen that the cross term in the last parentheses can account for the deviation from symmetry that was observed.

The validity of this hypothesis was investigated further by the following method: If a low-frequency ac field is applied to the crystal in addition to the dc field E_0, so that the total applied field is given by $E_0 + E_1\cos(\omega t)$, then the diffraction efficiency is of the form

$$\eta = \eta^{(4)}\cos(4\omega t) + \eta^{(3)}\cos(3\omega t) + \eta^{(2)}\cos(2\omega t) + \eta^{(1)}\cos(\omega t) + \eta^{(0)}. \qquad (8)$$

Specifically, the fourth-harmonic component $\eta^{(4)}$ is given by

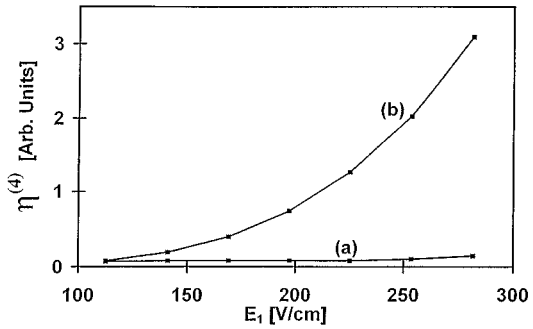

FIG. 3. $\eta^{(4)}$ vs the applied ac electric-field amplitude E_1 (a) before dwell and (b) after dwell.

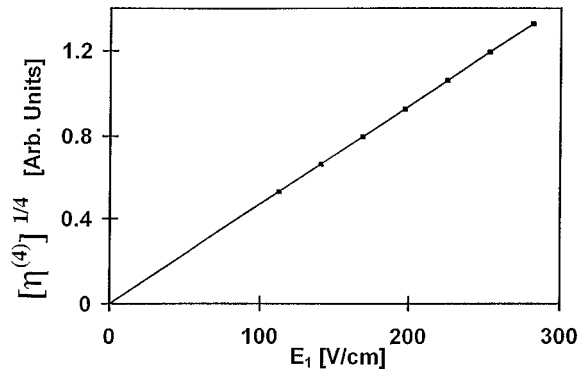

FIG. 4. The fourth root of $\eta^{(4)}$ is plotted as a function of E_1.

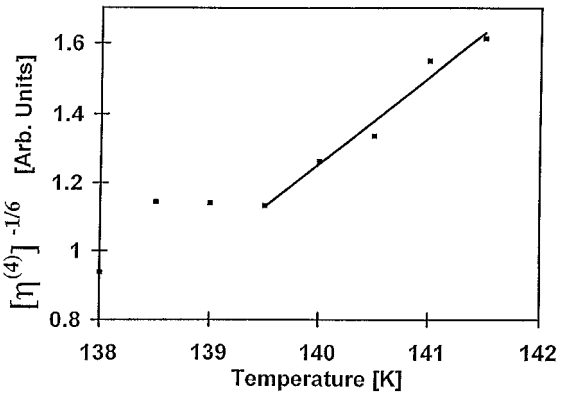

FIG. 5. The sixth root of $(1/\eta^{(4)})$ is presented as a function of the temperature.

$$\eta^{(4)}=\frac{e^{-\alpha d}}{8}\left(\frac{\pi n_0^3 g d}{\lambda_R \cos\vartheta}\right)^2 E_1^4 \varepsilon^2[\delta\varepsilon(\mathbf{r})]^2. \tag{9}$$

Note that $\eta^{(4)}$ is expected to be zero unless $\delta\varepsilon\neq 0$, and furthermore it is independent of E_{sc}. Thus measurements of $\eta^{(4)}$ can be used to isolate contributions to the diffraction which are exclusively the result of the formation of the $\delta\varepsilon$ gratings.

$\eta^{(4)}$ was measured using the setup described in Fig. 2. The oscillator was operated at 27 Hz and the phase locked loop unit supplied a reference voltage at 108 Hz in phase with the oscillator as required. The various assumptions leading to Eq. (9) were verified experimentally. (i) E_0 was set to a level for which the total diffraction efficiency is minimized to justify the assumption $\sin\phi=\phi$ made in Eq. (5). (ii) It was verified that the distortion level in the sinusoidal signal produced by the oscillator is low, so that $\eta^{(4)}$ does not contain contributions of the form $(E_2\cos 2\omega t)^2$. (iii) It was verified by Fourier analysis of the polarization current that deviations from linearity in $P=\varepsilon E$ are negligible.

Measurements of $\eta^{(4)}$ vs the applied ac electric field amplitude E_1 are shown in Fig. 3. Immediately after the writing of the PR grating, $\eta^{(4)}$ is zero [Fig. 3(a)]. As expected, at this stage, the $\delta\varepsilon$ grating has not yet been formed, and the diffraction is due exclusively to the space-charge PR grating. During the dwell period the $\eta^{(4)}$ signal increased monotonically until it saturated after about 1 h [Fig. 3(b)]. In Fig. 4 the fourth root of $\eta^{(4)}$ is plotted as function of E_1. As predicted in Eq. (9), $\eta^{(4)}$ is directly proportional to the fourth power of E_1.

The origin of the $\delta\varepsilon$ grating was investigated further by measurements of the temperature dependence of $\eta^{(4)}$. When the crystal is in the mean-field approximation region, the dependence of the dielectric constant on the temperature is given by the Curie-Weiss law

$$\varepsilon=\frac{C}{T-T_0}, \tag{10}$$

where C is the Curie constant, and T_0 is the Curie-Weiss temperature (see Ref. 7). It is therefore expected that if the $\delta\varepsilon$ grating originates from the creation of local changes in T_0, then the temperature dependence of $\eta^{(4)}$ will be given by

$$\eta^{(4)}=\frac{e^{-\alpha d}}{8}\left(\frac{\pi n_0^3 g d}{\lambda_R \cos\vartheta}\right)^2 E_1^4 \frac{C^4[\delta T_0(\mathbf{r})]^2}{(T-T_0)^6}, \tag{11}$$

where $\delta T_0(\mathbf{r})$ are the created changes in T_0. [It should be noted that the dependence of n_0 and g on the temperature is very weak (see Ref. 2)]. Consider Fig. 5, in which the sixth root of $(1/\eta^{(4)})$ is presented as function of the temperature. It can be seen that, for temperatures above 139.5 K, the sixth root of $(1/\eta^{(4)})$ has a linear dependence on the temperature. The Curie-Weiss temperature derived from this dependence is $T_0=133.5$ K. For comparison, consider Fig. 1, in which a measurement of the inverse of the dielectric constant $(1/\varepsilon)$ of this KLTN crystal as function of the temperature is presented. It can be seen that the crystal is in the mean-field approximation region for temperatures above 138 K, so that Eq. (11) is not expected to be obeyed below this temperature. Furthermore, the Curie-Weiss temperature, as derived from the dielectric measurement, is 133 K.

Finally, the Gibbs free energy was computed from a series of measurements of the dielectric constant as a function of the temperature under different electric fields. It was found that the T_0 gratings were formed only in the small temperature range above T_c, where metastable nonzero polarization can be formed [i.e., for the temperature range $T_0<T<T_2$ (as defined in Ref. 7).]

The results presented above clearly indicate that the compensation process which spontaneously follows the formation of PR gratings in KLTN originates from the creation of local metastable changes in T_0. It is known that changes in the concentration of impurities, and in particular temperature changes in the concentration of oxygen vacancies, strongly affect the phase transition (Perry[8] and Bauerle *et al.*[9]). The fact that the compensation process is very slow suggests that its microscopic origin may be attributed to the migration of vacancies which follows the formation of the PR space charge.

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