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Photoinduced charge effects in $K_{0.984}Li_{0.016}TaO_3$

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Abstract. Photoinduced effects were studied in $K_{0.984}Li_{0.016}TaO_3$, making use of birefringence and second-harmonic generation as probes of structural modifications induced by illumination at 2.4 eV. It is shown that photoinduced charges have no direct influence on the size and orientational freedom of polar microregions. Quenching of the polar order by illumination is only observed in the presence of an external field and it is consistent with the build-up of a depoling field, owing to space-charge formation. Light of energy below 2 eV is not effective by itself, but it can be if the sample is pre-sensitized with photons of higher energy.

1. Introduction

The presence of photoinduced charges in materials possessing a spontaneous polarization is known to produce electrical and optical effects connected with charge trapping and localization [1]. These phenomena, although extensively studied in the traditional framework of photorefractivity [2], are often not well understood from the standpoint of microscopic mechanisms.

New insight has recently been gained into the interaction of light with a polar structure. For example, photoinduced charge has been shown to produce a decrease in switchable polarization and to change the hysteresis cycle of lead–lanthanum zirconate titanate (PLZT) ceramics [3] and of multi-domain $BaTiO_3$ crystals [4]. In the latter case, enhancement of light- induced refraction gratings was obtained by suitable alternation of poling–depoling treatments and optical recording [5]. The effects seem consistent with a locking of the polar pattern, owing to the trapping of free carriers at domain walls.

Interesting effects have also been reported for strontium–barium niobate (SBN), a relaxor ferroelectric, where by suitable light treatment it is possible to produce a spatial modulation of depoling fields or a biasing of the coercive field [6, 7]. In this case, space-charge processes seem to be the controlling feature.

Knowledge of photoinduced effects is less developed for polar glasses. These materials are characterized by mesoscale structure of the spontaneous polarization, with a frustrated cooperative behaviour which is ascribed to the inherent disorder of dipolar interactions [8], or to the presence of random fields [9]. For example, the structure of $K_{1-x}Li_xTaO_3$ (KLT), for small concentrations of Li, is described as an ensemble of polar nanoregions (correlation length, about 8 nm, for $x = 0.016$), whose size does not increase appreciably on cooling from the paraelectric to the glassy phase [10]. This pattern nucleates well above T_f and constitutes an imprint for polarization.

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KLT is known to possess appreciable photoconductive properties [11, 12], whose relationship to the polar structure has not yet been clarified. Photoexcited charges might interfere with this system, either screening the dipole interactions [13] or modifying the random fields. In addition, charge trapping might block the orientational freedom of microdomains, similar to what happens in barium titanate. As a result, the photocurrent should be accompanied by specific alterations in the polar properties. In order to investigate such phenomena, we have undertaken a series of experiments, using linear birefringence (LB) and second-harmonic generation (SHG) to detect light-induced modifications in the polar structure of KLT. The experiments were performed in particular around the freezing temperature, where polar alignment is still sensitive to external or internal fields.

We show in the present paper that the poling properties are not modified by mere irradiation with ionizing light prior to the application of a field. On the contrary, the response of the system is quenched if the same light is applied simultaneously with the field. This is consistent with the formation of space charge, which one can relate to the photoconductivity of KLT. Quenching phenomena are found even with non-ionizing light below 2 eV, when the crystal is pre-sensitized by illumination at higher energies. This particular memory effect allows one to control the amount of space charge through the dose of ionizing radiation.

2. Experimental details

The experiments were performed on a single crystal of KLT with $x = 0.016$. Its freezing temperature $T_f \approx 36$ K is known from previous measurements of LB and SHG in zero field [10]. This value agrees with data on samples of similar concentration [14]. The crystal was cut into a parallelepiped (5 mm $\times$ 10 mm $\times$ 5 mm) with sides parallel to the cubic axes of the paraelectric phase. Pt electrodes were sputtered on two 5 mm $\times$ 10 mm parallel faces and the poling field applied along a direction, hereafter denoted z. Typical values of the poling field were 40 kV m^{-1}. The sample was mounted in a closed-cycle cryostat and cooling runs were performed at a controlled rate of 0.017 K s^{-1}.

The excitation of free carriers, which is revealed by the photocurrent, is the basis for light-induced modifications. Large photocurrents were found when illuminating the sample with 514.5 nm light, i.e. well below the energy of the optical gap. The carriers necessary for this are thought to come from the photoionization of accidental impurities, whose identification continues to be debated [15]. In agreement with earlier work [12], the magnitude of photocurrents was largest in the low-temperature phase. We measured the relative yield at a series of irradiating wavelengths, and the results are shown in table 1.

Table 1. Dependence of the photocurrent on the excitation wavelength. Measurements were made at 20 K, after field cooling in the dark at 40 kV m^{-1}. The observed currents are normalized to the flux of incident photons.

λ (nm)	Photocurrent per unit photon flux (10^{-27} A m^2 s)
488	1.2×10^3
514.5	5.8×10^2
580	2.2
610	2.0

The photocurrents, measured with a Keithley electrometer model 602, were typically in the range 10^{-7}–10^{-4} A, comfortably larger than the noise limit (about 5×10^{-11} A). The quoted data refer to measurements at 20 K on a pre-poled sample. Nevertheless the trend is qualitatively the same at higher temperatures, up to several kelvins above T_f. As it appears, the yield of photocurrent drops radically in magnitude on increasing the wavelength from the blue to the red region of the spectrum. With our present sensitivity, photocurrents were no longer detectable at 633 nm or higher wavelengths. Therefore we think that red and infrared (IR) radiations are not able to excite carriers directly in the crystal as cooled.

The experimental set-ups for LB and SHG were reported in [10]. In both cases, the probe beam impinged on the sample at normal incidence, perpendicular to z. For SHG, we employed a Q-switched Nd-YAG laser (wavelength, 1.06 μm; pulse duration, 20 ns; 2 mJ/pulse) operated at 2 Hz. The emitted 532 nm light was observed in forward (zz) geometry. Its intensity was measured by fast analogue pulse detection and averaging. The exciting beam was focused on a spot of 0.5 mm diameter.

For LB, the sample was placed between crossed polarizers, the probe beam being polarized at 45° from the z axis. Variations in birefringence were monitored by measuring the intensity transmitted by the analyser. The standard probe was 1.06 μm light from the free-running Nd-YAG laser. In some cases the 633 nm line of an He–Ne laser was employed. The measuring beam could be expanded to cover the whole sample for qualitative inspection (imaging the LB pattern on a screen, and making use of an IR visualizer in the case of 1.06 μm) or focused to a waist of 30 μm for quantitative measurements.

The He–Ne beam and the Nd-YAG beam were arranged to be collinear, so as to monitor LB and SHG in the same region of the crystal; the LB probe was maintained inside the larger spot of the SHG probe. To induce photoeffects we employed primarily the 514.5 nm line of the Argon-ion laser.

2.1. Birefringence

Denoting by angular brackets the average over the probed volume, the refractive index anisotropy observed in our experiments is given by

$$\Delta n = \langle n_z \rangle - \langle n_y \rangle = C\big(f_z - f_y\big)P^2.$$

The last equality is derived under the assumption that the local values of P^2 do not depend on the direction of the spontaneous polarization $\boldsymbol{P}$ [10]. The quantities f_i are the volume fractions of microdomains with polar directions $i = \pm x, \pm y, \pm z$, and $\sum f_i = 1$. C is a material constant, depending on the electro-optic coefficients. The appearance of LB requires $f_z - f_y \neq 0$. The fact that a small birefringence occurs in unpoled KLT above T_f is accidental and is attributed to the presence of built-in stresses. Variations in Δn observed on poling at fixed temperature (or across a given range of T) reveal essentially a net change in the relative number of microdomains oriented along the z and y directions. In this way, birefringence is a probe of poling effects induced by on–off cycles of an applied field.

2.2. Second-harmonic generation

The emission of second harmonics (SH) is associated with the presence of a finite second-order optical susceptibility $\chi^{(2)}$. In KLT in the presence of a local polarization, one can assume that $\boldsymbol{\chi}^{(2)}(\boldsymbol{r}) = \mathbf{b} : \boldsymbol{P}(\boldsymbol{r})$, with $\mathbf{b}$ a known material constant [10, 16]. Simplifying to a scalar notation, and assuming a pump beam of wavevector $\boldsymbol{k}_\omega$, the intensity of the emitted second harmonic field of wavevector $\boldsymbol{k}_{2\omega}$ is proportional to the $\boldsymbol{K}$th Fourier transform of the correlation function of local polarization, with $\boldsymbol{K} = \boldsymbol{k}_{2\omega} - 2\boldsymbol{k}_\omega$.

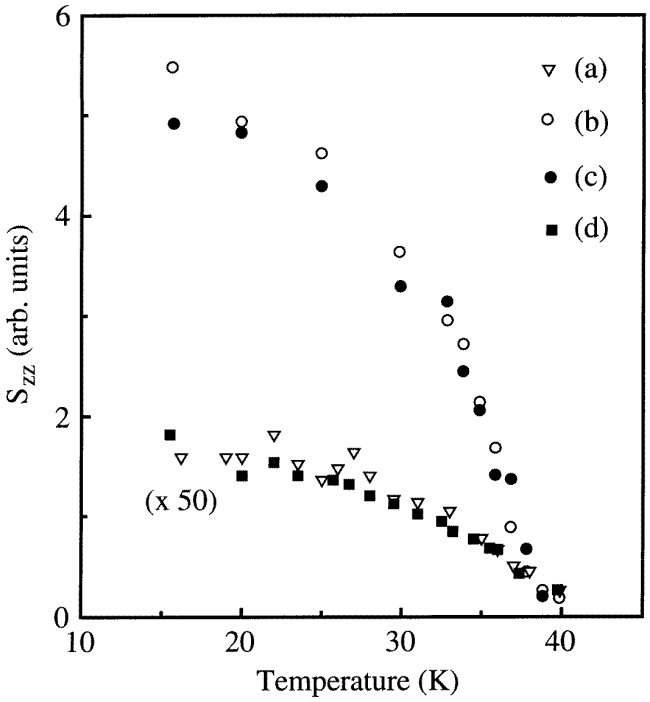

Figure 1. Second harmonic signal versus temperature in different poling conditions: (▽) zero-field cooling (multiplied by a factor of 50); (○) field cooling (40 kV m^{-1}); (●) field cooling after illumination at 40 K in a zero field with 514.5 nm light (fluence $\Phi = 60$ J cm^{-2}); (■) field cooling during illumination with 514.5 nm light (100 mW cm^{-2}) (multiplied by a factor of 50).

With a sufficiently small correlation length ξ and a simple geometry, with pump light and emitted light polarized along the z axis, the forward-emitted intensity can be shown to scale as [17]

$$S_{zz} \propto f_z P^2 \xi^3.$$

From this equation we notice that SH monitors changes in the polar structure with great sensitivity, owing to the cubic dependence on ξ. For a detailed application of these concepts, see [10, 17].

3. Results and discussion

Light-induced effects on the polar structure are expected to be most prominent around the freezing temperature. In fact there is no possibility of polar clustering far above T_f, whereas the high viscosity of the glassy system [18, 19] would slow down any observable modification of the polar pattern at low temperatures. In view of this, the effects of illumination were investigated starting the cooling cycles from above the freezing point.

Figure 1 shows the evolution of second harmonic intensity emitted from the crystal, during a series of similar cooling runs from 40 K, in various conditions of illumination. The open symbols represent the standard behaviour prior to any light treatment. The open triangles refer to zero-field cooling and correspond to the known freezing of spontaneous polarization below T_f; the open circles illustrate the large increment of polar order induced

by field cooling at 40 kV m^{-1}. Both features have been commented on in previous work [10].

The full symbols illustrate the modifications of the basic behaviour when the sample is subjected to different light treatments. The full circles show the effect of field cooling, after uniform illumination with 514.5 nm light (60 J cm^{-2}) in zero field; in this case, the increment of SHG is similar to that observed on poling the untreated crystal (open circles). By contrast, the full squares show the effect of field cooling during illumination with the same light. Here the increment was completely suppressed, the poling curve coinciding with that obtained in zero field.

The different situations depicted by the full symbols indicate that the polar alignment is affected by the light treatment only if an electric field is present. Experiments were also performed at fixed temperatures between 40 and 60 K, looking for the instantaneous response of SHG to on–off cycles of the applied field, in various combinations with 514.5 nm light. Again, a net suppression of poling occurred only when light and field were applied together, confirming the previous results. All these observations suggest that charges excited into the crystal are unable to block a realignment of the polar structure, unless they drift as a result of the poling field.

The above experiments were repeated, measuring the growth of LB at 1.06 μm during field cooling, as an alternative probe of polar ordering. The results were entirely similar to those found with SHG.

In order to investigate the spatial structure of photoinduced effects, visual checks were made on the birefringence of the entire crystal, after intense irradiation of a small spot (100 μm) by means of focused 514.5 nm light. The observations were performed at 40 K, passing an expanded beam of 1.06 μm light through the crystal between crossed polarizers and projecting the pattern on an IR-sensitive screen.

Upon application of the electric field the pattern was seen to change over the entire sample, except in the local spot where the 514.5 nm light had been concentrated. From this we deduce that photoexcited carriers are able to influence only the restricted region in which they were generated. This localization of the effects was reported for highly Nb-doped potassium tantalate in earlier work [20]. Presumably, the drift of the carriers is trapping limited and gives rise to a space-charge field; this locally counteracts the applied field, thus inhibiting the alignment of polar microdomains which is the cause of LB and SHG increments.

The above arguments are in principle insufficient to exclude an alternative mechanism, namely locking of microdomains by charge trapping, regardless of local fields. More insight was obtained by a sequence of SHG experiments, starting with the crystal in a zero field at 40 K. As shown in figure 2(a), one has initially a low yield of SH which is indicative of the disordered state of the unpoled sample at this temperature. Upon application of the poling field (40 kV m^{-1}) the second-harmonic signal rises to an appreciable level, as expected. Removal (short-circuiting) of the field causes a quick decrease in the signal, followed by a slowly decaying tail. In figure 2(b), a narrow beam of ionizing light is passed through the spot being monitored. This has no influence on the second-harmonic signal in zero field but strongly modifies the poling response; following the application of the field, the signal develops a momentary increase but quickly relaxes to the zero-field value. This state is not modified by removal of the ionizing light. However, if the sample is short-circuited, a finite second-harmonic signal reappears. The latter demonstrates that the suppression of poling is not irreversible: this excludes a permanent reduction in switchable polarization.

This behaviour appears to confirm the formation of a permanent space charge, owing to the drift of photocarriers from the interior to the edge of the illuminated region. From

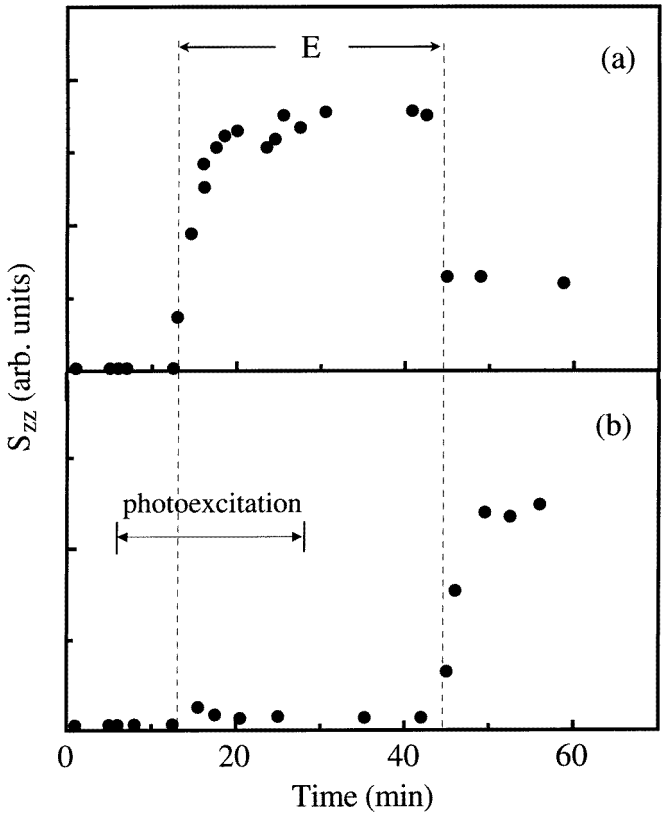

Figure 2. Second-harmonic signal response to an external field (40 kV m^{-1}), observed at $T = 40$ K (a) in the absence and (b) in the presence of ionizing light.

this viewpoint the suppression of poling is explained by the build-up of a local field, which counteracts the applied field. When the latter is turned off, the polarization realigns in the reverse sense as dictated by space charge alone.

After the experiments of figure 2(b), the picture was corroborated by the following observations:

(i) the application of a field of opposite polarity, i.e. of the same sign as the assumed space-charge field, causes a further enhancement of the second-harmonic signal;

(ii) if the short-circuited crystal is re-illuminated, the second-harmonic signal returns quickly to values typical of zero field, while a photodepolarization current appears.

This means that newly generated carriers neutralize the existing space charge.

From the spectral dependence of photocurrent (table 1), red and IR light are expected to induce negligible ionization in the sample. In fact, radiation at these wavelengths was unable to interfere with the poling response of the untreated sample. This no longer holds if the sample is pre-irradiated with ionizing light of higher energy; in this case the growth of birefringence in a field-cooled cycle is suppressed when measurements are effected with a 633 nm probe light. Such quenching of the poling response is more or less complete, depending on the total fluence of pre-illumination. Observations in this sense are illustrated in figure 3. No suppression, on the contrary, was observed when 1.06 μm light was used

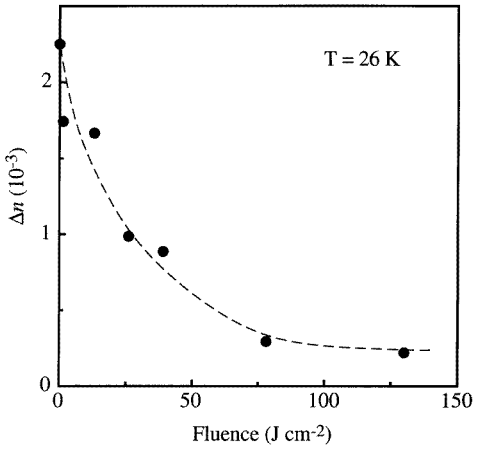

Figure 3. Birefringence Δn at $T = 26$ K versus the fluence of 514.5 nm light in the pre-irradiated sample. Data refer to field cooling from 40 K, after illumination in zero field. The probe is 633 nm light. The line is a guide to the eye.

as a probe.

This memory of previous illumination is interpreted as follows. The 514.5 nm light ionizes some unknown centre within the gap, producing free carriers which are quickly trapped in shallow impurity levels. Subsequent irradiation at 633 nm, although not ionizing *per se* is able to re-excite the trapped charges. The picture is consistent with the appearance of photocurrents, generated by 633 nm light in the pre-illuminated crystal. Evidence of a similar photoconductive memory was recently reported for $Sr_{1-x}Ca_xTiO_3$ [21].

Memory effects become less efficient as the wavelength increases; at 830 nm a photon fluence 100 times higher was necessary to observe a reduction comparable with that of figure 3. Radiation at 1.06 μm was found to be ineffective in all experiments.

4. Conclusions

From the present work, the following conclusions are drawn concerning photo-induced effects in polarized KLT with $x = 0.016$.

(i) At temperatures in the vicinity of T_f, where the polar pattern possesses orientational freedom, poling can be suppressed or inverted locally with appropriate combinations of light and fields. This is a pre-requisite for optical write–erase procedures.

(ii) Poling modifications are connected with the formation of space charge, i.e. with the drift of photoexcited carriers. They are not observed in the absence of drift; this excludes a direct influence of trapped charge as such on the speed or the amount of polar alignment.

(iii) In the temperature range examined, the limiting mechanism for local poling–depoling processes is the build-up of space charge, which is controlled by the dose of light excitation.

These features make a distinction with respect to the case of typical ferroelectrics, such as $BaTiO_3$ and PLZT where the pinning of domain walls by trapped carriers is responsible for the decrease in switchable polarization [3, 4]. Conversely, they are reminiscent of phenomena observed in the relaxor SBN [6, 7].

The present results emphasize the special caution needed when interpreting optical experiments, e.g. Raman data [22], in the presence of possible artefacts due to an ionizing light probe.

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