Observation of an intrinsic nonlinearity in the electro-optic response of freezing relaxors ferroelectrics

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Abstract: We demonstrate an electro-optic response that is linear in the amplitude but independent of the sign of the applied electric field. The symmetry-preserving linear electro-optic effect emerges at low applied electric fields in freezing nanodisordered KNTN above the dielectric peak temperature, deep into the nominal paraelectric phase. Strong temperature dependence allows us to attribute the phenomenon to an anomalously reduced thermal agitation in the reorientational response of the underlying polar-nanoregions.

OCIS codes: (160.2750) Glass and other amorphous materials; (190.4400) Nonlinear optics, materials.

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1. Introduction and motivation

Compositional disorder can profoundly change the response of ferroelectric crystals. Disorder on the nanoscale can introduce dispersion in the dielectric response, thermal hysteresis, and anomalous relaxation times, traits that are typical of relaxor ferroelectric behavior [1]. In many respects, the unique properties of the relaxor state can be modelled as arising from a network of randomly interacting polar-nanoregions (PNRs) embedded in a highly polarizable medium [2, 3]. The study of relaxors is attracting a growing interest, fueled by the promise of transferring these properties to the numerous and pervasive applications where standard ferroelectrics are key, examples being anomalously large capacitance and giant piezoelectricity [4].

Recent investigations are centered on the electro-optic response of relaxors. For example, in photorefractive nonlinear beam propagation, where the electro-optic effect translates an optically induced space-charge field into an index of refraction, history-dependence and increased quadratic electro-optic response has led to the demonstration of scale-free optics [5], and reprogrammable soliton nonlinearity [6, 7]. Up to a few degrees above the so-called dielectric peak temperature T_m, the quadratic electro-optic effect has been shown to be history-dependent and greatly enhanced [8, 9].

Some relaxor crystals can also manifest a so-called freezing temperature, a temperature at which the dielectric relaxation time diverges [10, 11]. When freezing intervenes, an anomalous scaling of response with temperature and a strong characteristic nonlinearity in the polarization P versus electric field E curve occurs: the $P(E)$ relation assumes a twisted nonlinear "S"-shape even for low bias electric fields and for temperatures deep into the paraelectric phase (from several to tens of degrees above T_m) [12]. Whereas optical studies have reported the measurement of the quadratic electro-optic coefficients in disordered ferroelectrics in proximity of the dielectric peak (giant electro-optic effect) [13], no previous experiments have investigated if and how this freezing-induced twisted polarization changes the nature of the electro-optic response.

We here report, for the first time, the electro-optic response for a freezing relaxor. Cross-polarizer experiments in compositionally disordered $K_{1-x}Na_xTa_{1-y}Nb_yO_3$ (KNTN) reveal the signature "S"-like distortion in the polarization versus electric field response with an anomalously strong temperature-dependence. The behavior, observed even at low electric bias fields (<0.5 kV/cm), is described by a shifted-temperature Langevin reorientation and attributed to a frustrated PNR thermal agitation. The intrinsically nonlinear $P(E)$ is deduced from the measurement of the index of refraction behavior that changes in proportion to the absolute value of the applied electric field bias. The freezing response is observed to be incompatible both with previously reported linear and quadratic electro-optic effects [14].

Our results suggest that whereas the linear effect emerges in systems with a broken inversion symmetry , i.e., poled ferroelectrics, and the quadratic effect occurs in systems with no pref-

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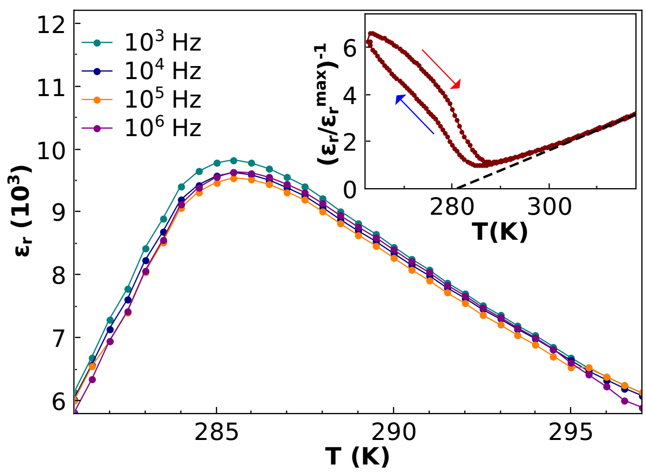

Fig. 1. Dielectric spectroscopy: Real part of the KNTN dielectric constant in the quasi-static temperature regime (cooling rate $\alpha \simeq \pm 0.1 mK/s$) manifesting dispersion. The inset shows (at 1KHz) the ergodicity breaking below T_m, signalled by marked thermal hysteresis for cooling/heating curves at the same α, and the deviation from Curie-Weiss mean-field behavior (black dashed line) in the region $T < T^* = 305K$.

erential direction, such as paraelectrics or disordered ceramics, this new type of electro-optic response occurs in a system where inversion symmetry holds globally, above the mesoscopic scale of hundreds of nanometers, but is locally broken on the nanometer scale.

2. Experimental

The KNTN, with $K_{0.89}Na_{0.11}Ta_{0.63}Nb_{0.37}O_3$, is grown through the top-seeded solution method by extracting a zero-cut $1.17^{(x)}$ x $1.90^{(y)}$ x $2.43^{(z)}$ mm optical quality specimen. In order to identify the relaxor-type behavior, i.e., where permanent dynamic PNRs affect the response, we perform dielectric spectroscopy using a standard LCR meter setup for different frequencies and a thermal chamber. The results of dielectric constant measurements are reported in Fig. 1. What emerges are i) a frequency dependent T_m (temperature at which the dielectric constant has its peak, $T_m = 285.5K$ at 1KHz) and ii) a violation of the mean-field Curie-Weiss law $\varepsilon_r = C/(T - T_C)$ for $T < T^* = 305K$ (see inset in Fig. 1), so that T^* marks the range in which the random dynamics of PNRs affect properties depending on the square of the polarization P^2 [15]. The glassy nonergodic state is flagged below T_m by giant thermal hysteresis. Optical experiments are carried out in the region $T_m < T < T^*$ where the PNRs allow an optimal optical transmission but where glassy physics effects are still observed [16, 17].

We perform cross-polarizer experiments and observe the transmission as a function of bias electric field and temperature. The optical setup is shown in Fig. 2(a). A Gaussian beam from a doubled Nd-Yagg laser ($\lambda = 532$nm) **S** is expanded to an approximate plane-wave of $10mm$ radius by the two confocal lenses **F1** and **F2**. Linearly polarized light at 45° with respect to the plane of the experiment is transmitted by the first polarizer **PL1**, passes through the sample and then through the second polarizer **PL2** orthogonal to the first. The sample, oriented parallel to the plane of the experiment with the input facet approximately orthogonal to the propagation direction z, is zero-cut along its principal $m3m$ axes and is biased by a static elecric field **E** applied onto the x-facets; the temperature is controlled by a Peltier cell. Transmitted light is collected by the exit lens **F3** and the power is detected through power meter **D**. We implement a plane-wave intensity of approximately $1.5\mu W/cm^2$, and no photorefractive effects associated with Cu impurities (~ 0.001 atoms per mole) for the duration of our experiments are detected.

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In Fig. 2 we report the cross-polarizer transmission images cooling the sample from T^* to T_m at a cooling rate of $\alpha \simeq 0.1$K/s (Fig. 2(b-d)). A homogeneous and disordered weak transmission of light is observed in the whole temperature range for zero-field-cooling. For values of T in proximity of T_m ($T - T_m < 4$K), an external field causes organized ferroelectric structures to form. For example, at $T \simeq T_m$, a field $E \simeq 1$kV/cm causes the formation of large ferroelectric domains with geometrically fixed boundaries at 45° with respect to the principal axes of the crystal (Fig. 2(d)).

We next proceed to quantify transmission properties 5-15 K above T_m. Light is transmitted because the sample changes the relative phase of the x and y polarized components of the optical field (respectively parallel and orthogonal to the external field E) through the relative electro-optic modulation of the index of refraction Δn. The output transmitted intensity I and the input intensity I_0 are connected to this field-induced relative phase-shift $\Delta\phi$ through the relationship $I/I_0 = \sin^2(\Delta\phi/2)$, where $\Delta\phi = \Delta n(2\pi/\lambda)L$, and L is the length of the crystal along the propagation direction. Analyzing the dependence of $\Delta\phi$ on E allows us to detect the macroscopic dependence of Δn on E and hence obtain the crystal P versus E response.

In Fig. 3 we report intensity transmission data at different temperatures T as a function of applied bias field E. The crystal is cooled to the operating temperature with a cooling rate of $\alpha \simeq 0.1$K/s, and, in distinction to previous experiments, during this cooling no external bias

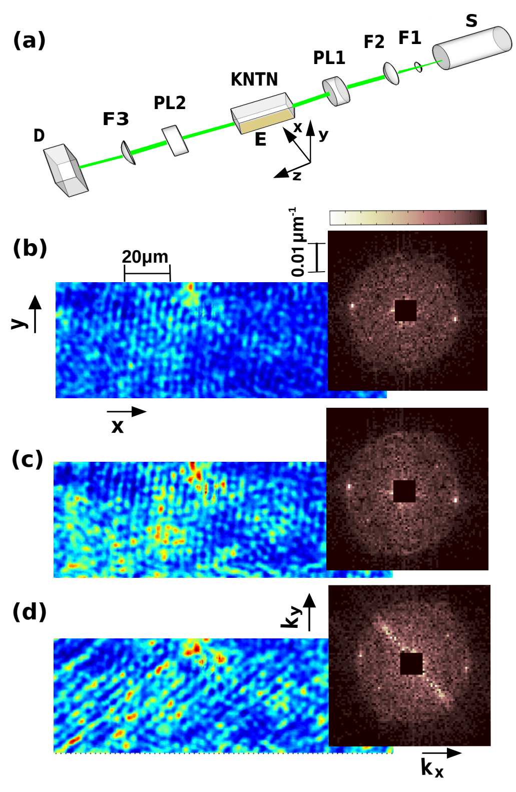

Fig. 2. (a) Cross-polarizer setup and (b) transmission microscopy images (intensity is in arbitrary units) in zero-field-cooling at $T = 287K$ and (c) at $T = T_m = 285.5K$; (d) applying a $0.85kV/cm$ dc field the glassy state at T_m turns into ferroelectric domains with geometrically fixed boundaries at 45° with respect to the principal axes of the crystal. Normalized intensity Fourier transform (insets in (b), (c) and (d)) that highlights the appearance of a diagonal feature in the spectrum associated to ferroelectric domains. The added spectrum in (d) is continuous, with no fixed periodicity, typical of a globally disordered state.

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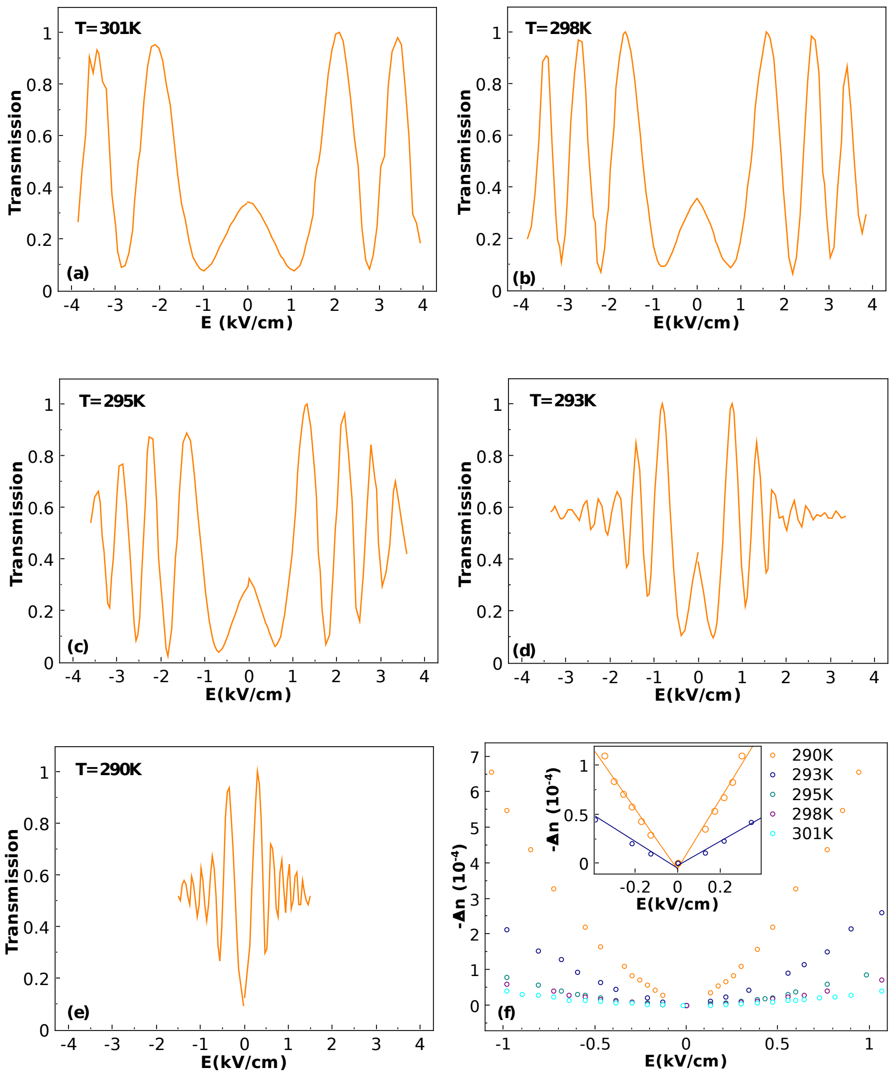

Fig. 3. Transmission I/I_0 of light through crossed polarizers as a function of E for different temperatures: (a) for $T = 301$K, (b) 298K, (c) 295K, (d) 293K, and (e) 290K. In the latter case the natural birefringence of the KNTN sample has been compensated with a $\lambda/4$ waveplate. Note the decreasing visibility in the fringe pattern for high fields and lower temperatures, as expected in PNR dominated media. (f) Summary and comparison of Δn versus E for the different temperatures signalling the spike-like distortion (highlighted in the inset for 290 and 293 K, lines are fits with $-\Delta n \propto |E|$) of the expected parabolic dependence as T_m is approached.

field is applied [13]. Data is taken for the decreasing field amplitude loop (the field amplitude is decreased during our experiments), and no residual polarization is detected at zero field. As testified by the rapid decrease in fringe period, the electro-optic response is seen to increase anomalously as T_m is approached. Moreover, fringe visibility is found to decrease for high fields and for lower temperatures, the signature that PNRs are dominating response [8, 13]. The sinusoidal fringe pattern is therefore modified by a field-dependent pre-factor M_d that depends

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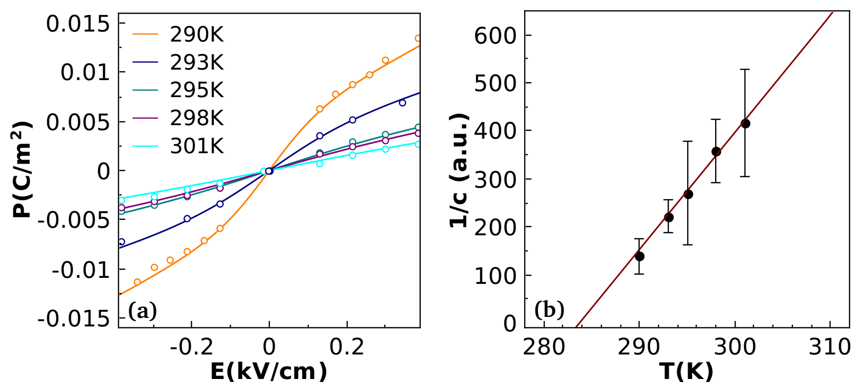

Fig. 4. (a) The P versus E relationship as a function of T from the measured values of $\Delta n(E)$ ($P = \pm(-2\Delta n/n_0^3(g_{11} - g_{12}))^{1/2}$, the sign depending on the sign of E) indicates a temperature dependent distortion of linearity towards an S-shaped behavior. Full lines represent the fit with the super-polarization model of Eq. (1). (b) Linear temperature scaling of the inverse fit parameter c (see text) that gives the shift temperature $T_0 = (283 \pm 2)K$.

on the PNR size. In Fig. 3(e) we report the fringe pattern with a $\lambda/4$ waveplate that compensates the non-zero value of transmission at $E = 0$. We are thus able to measure the natural birefringence to be $\Delta\phi_0 \simeq -0.36$ radians. In Fig. 3(f) we summarize the Δn versus E data for the different temperatures: we note that the index of refraction modulation gradually switches from the typical quadratic field dependence distinctive of a paraelectric phase at T = 301K to a low-field strongly nonlinear (spike-like) dependence at T = 290K, even though no changes in the crystal symmetry occurred.

3. Discussion

To investigate the physical underpinnings of this anomalous spike-like behavior we proceed to reconstruct the P versus E relationship from the Δn versus E data, at the different values of T. Indeed, in the paraelectric phase, the change in the inverse of the sample optical index of refraction tensor n^2 is $\Delta(1/n^2)_{ij} = g_{ijkl}P_kP_l$, where P_k (and P_l) are the components of the polarization and the g_{ijkl} those of the quadratic electro-optic 4-tensor (indices run through the three spatial axes and summation over repeated indices is implied). Considering the m3m symmetry of the KNTN sample, contracting the electro-optic effect for an input linear polarization at 45° with respect to the principal x and y axes (and a corresponding orthogonal output linear polarization), and considering the x directed bias field, $\Delta n = -(1/2)n_0^3(g_{11} - g_{12})P^2$. Here, $n = n_0 + \Delta n$, and $n_0 = 2.31$ is the unperturbed index of refraction, and $g_{eff} \equiv (g_{11} - g_{12}) = 0.14$ C^{-2}m^4 (as measured at values of $T > T^*$). The resulting P versus E curves are reported in Fig. 4(a), in the range between $T = 301K$ and $T = 290K$. We first note that, as expected for a system that has global inversion symmetry, no residual polarization or standard ferroelectric hysteresis behavior emerges. However, in distinction to a standard system with inversion symmetry, where the polarization should be predominantly linear in the electric field, here the polarization manifests a gradually increasing nonlinearity at low bias fields. Indeed, decreasing the temperature towards T_m, the polarization response passes from a linear function of the field to the peculiar S-shaped curve observed in non-optical freezing relaxor experiments [12, 18].

Negligible hysteresis and zero-field residual polarization indicate that dipoles associated to the PNRs spontaneously flip during measurements, so that our starting model is that of Langevin reorientation. Considering the predominant role of PNRs, an ensemble of uniform noninteracting clusters having uniaxial symmetry has an average polarization [12] $\mathbf{p} =$

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$\rho p_0 \tanh[p_0|E|/kT]\,\mathbf{u}$, where ρ is the density of clusters with dipole moment p_0, kT the thermal energy and $\mathbf{u}$ the field unit vector. This behavior is, however, evidently incompatible with the data in Fig. 4(a), since the large variations occur for an apparently negligible relative change in temperature $\Delta T/T \sim 0.03$. In turn, the curves are compatible with a shifted-temperature Langevin reorientation $\mathbf{p}_{PNR} = \rho p_0 \tanh[p_0|E|/k_B(T-T_0)]\mathbf{u}$, where T_0 is a phenomenological parameter. The macroscopic polarization P is now composed of a dipolar contribution and a standard linear susceptibility χ_p due to the paraelectric host. Specifically,

$$\mathbf{P} = \mathbf{p}_{PNR} + \mathbf{p}_{\chi_p} = \rho p_0 \tanh\left[\frac{p_0|E|}{k_B(T-T_0)}\right]\mathbf{u} + \varepsilon_0 \chi_p \mathbf{E} \quad , \tag{1}$$

where the first term dominates the low-field response and the second prevails at high fields where the PNR response is saturated. The full lines in Fig. 4(a) are a fit of measured P to Eq. (1) for low values of E. Best fits provide values of the parameter $c = p_0/k_B(T-T_0)$ that, as reported in Fig. 4(b), give $T_0 = (283 \pm 2)K$.

The resulting electro-optic response in the cross-polarizer configuration is hence associated with

$$\begin{aligned}\Delta n = &-(1/2)n^3 g_{eff}\varepsilon_0^2(\varepsilon_r-1)^2E^2 - n^3 g_{eff}\rho p_0 \tanh\left[\frac{p_0|E|}{k(T-T_0)}\right]\varepsilon_0(\varepsilon_r-1)|E| \\ &-(1/2)n^3 g_{eff}\rho^2 p_0^2 \tanh^2\left[\frac{p_0|E|}{k(T-T_0)}\right] \quad .\end{aligned} \tag{2}$$

For values of $T-T_0$ such that $p_0|E|/k(T-T_0) \gg 1$, the second term describes the spike-like contribution $\Delta n \propto |E|$. This term is indeed dominant over the first, which is the standard quadratic term arising from the paraelectric host, whereas the third term can be neglected.

We underline that this freezing response is intrinsically different from the standard linear $\Delta n \propto E$ and quadratic $\Delta n \propto E^2$ effects associated, respectively, to systems that are noncentrosymmetric and centrosymmetric. In a system with global inversion symmetry, spatial inversion causes $E \to -E$ but $\Delta n \to \Delta n$, and the leading response is congruently quadratic in the amplitude of E. In our freezing-PNR-dominated system, which has no globally-defined symmetry [19], spatial inversion causes $E \to -E$, $\Delta n \to \Delta n$, but the leading response is still *linear* in the amplitude of E. From an applicative perspective, the modular contribution can forward new functions, such as the ability to rectify an oscillating bias electric field with negligible distortion.

4. Conclusions

Summarizing, we have demonstrated a temperature-tunable electro-optic effect with $\Delta n \propto |E|$ for low applied fields in nanodisordered freezing KNTN. The effect arises deep into the nominal paraelectric phase, above the dielectric peak temperature, and can be modelled as arising from a temperature-shifted Langevin reorientation of the underlying PNRs.

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