Fixing of a photorefractive grating in $KTa_{1-x}Nb_xO_3$ by cooling through the ferroelectric phase transition

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We report the fixing of a photorefractive grating in $KTa_{1-x}Nb_xO_3$. The procedure involves the writing of a photorefractive grating in the cubic phase and the cooling of the sample under an applied field into the rhombohedral phase. We discuss possible mechanisms responsible for the effect.

Photorefractive materials have found use as a volume holographic storage medium. Several fixing procedures have been developed to create diffraction gratings that are not erased under readout illumination. Fixed gratings in $LiNbO_3$ were formed by heating the sample to a temperature that permitted a compensating ionic space-charge grating to form.[1] After illumination at room temperature, the electronic space-charge grating is erased, leaving only the fixed ionic grating. Micheron and co-workers have demonstrated fixing procedures in strontium barium niobate that create ferroelectric domains correlated with a photorefractive space-charge field. One procedure makes use of an applied electric field of magnitude slightly less than the coercive field to switch domains locally.[2] The other creates locally switched ferroelectric domains by cooling the sample through the ferroelectric phase transition.[3] Fixing has also been demonstrated in $Bi_{12}TiO_{20}$ (BTO) with a combination of thermal cycling and the application of an ac electric field.[4] In this Letter we describe a procedure used to fix photorefractive gratings in $KTa_{1-x}Nb_xO_3$ (KTN). It involves writing a grating in the cubic phase and cooling the sample, under an applied electric field, through the tetragonal and orthorhombic phases to the rhombohedral phase. The fixed grating can be restored to its erasable state by heating the sample back to the cubic phase. The mechanism differs from those previously described in that no compensating ionic charge or alternating ferroelectric domains are formed.

The KTN crystal was grown with the top-seeded solution growth method from a melt doped with Cu and V.[5] A thorough characterization of the photorefractive properties of KTN:Cu,V appears elsewhere.[6] Cu has been identified as the photorefractive active species, with charge transport due to electron photoexcitation from the Cu^+ ion and subsequent retrapping by a Cu^{2+} ion. A sample measuring 0.44 cm × 0.46 cm × 0.69 cm was cut and polished along the [001] crystallographic direction. The sample was then reduced, converting Cu^{2+} ions to Cu^+ ions, with the use of a thermal heat treatment. This involved sealing the sample in an ampule filled with 0.3 atm of nominally pure Ar gas, which was then heated to 800°C and kept there for 12 h before being cooled to room temperature. Cr and Au electrodes were evaporated perpendicular to the 0.69-cm edges. The chemical composition was determined from electron microprobe analysis to be $KTa_{0.87}Nb_{0.13}O_3$. Cu was found to be present at a concentration of $(3.0 × 10^{19})/cm^3$. The V concentration was below the detection limit of $10^{18}/cm^3$. The sample was then mounted in a low-temperature cryogenic system that permitted the temperature to be stabilized to within 0.1 K.

The ferroelectric phase transition temperature of KTN is roughly linearly dependent on the Nb concentration.[7] It varies from that of $KNbO_3$ at 435°C to that of $KTaO_3$, which approaches a ferroelectric transition at 0 K. The transition is second order for $x < 0.3$ and first order for $x > 0.3$. The temperature dependence of the low-frequency dielectric constant of the KTN:Cu,V sample, determined from capacitance measurements, is given in Fig. 1. The peaks roughly correspond to the phase transition temperatures of KTN. The high-temperature paraelectric phase is cubic. As it is cooled it undergoes ferroelectric transitions from the tetragonal phase to the orthorhombic phase to the rhombohedral phase. In these ferroelectric phases the spontaneous polarization lies, respectively, along the [001], [011], and [111] directions. Also shown in Fig. 1 is the temperature dependence of the spontaneous polarization along the [001] direction.
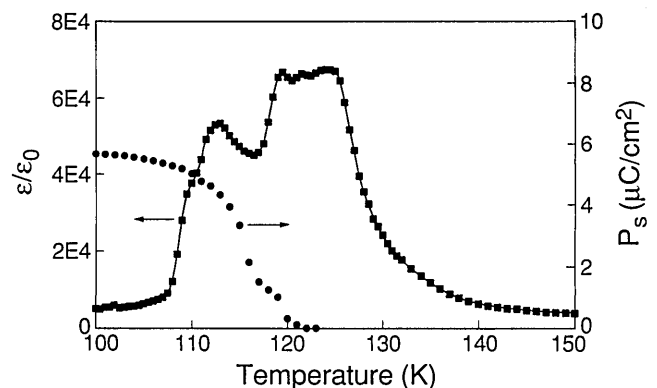

Fig. 1. Temperature dependence of the static dielectric constant and the spontaneous polarization of a KTN sample.
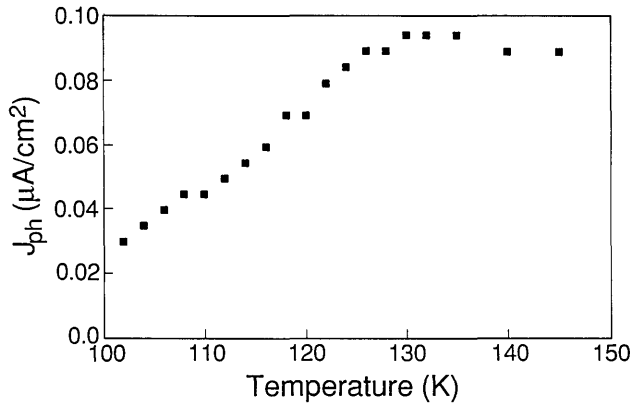
Fig. 2. Temperature dependence of the photocurrent measured with 514-nm illumination under a 1000-V bias.

It was determined by measuring the pyroelectric current on heating the sample after it was cooled to the low-temperature phase under a 1000-V bias. The spontaneous polarization decreases rapidly on approaching the tetragonal phase. A similar temperature dependence of the spontaneous polarization was measured in a $K_{1-x}Li_xTaO_3$ sample.[8] The cubic to tetragonal transition is found to be of second order, which reduces the danger of damaging the sample on cooling through the phase transitions.

The temperature dependence of the photocurrent under a 1000-V bias was also measured. The sample was illuminated uniformly with an expanded 20-mW/cm^2 514-nm beam. The light was polarized along the direction of the applied field. The measurements were made on cooling the sample from the cubic phase. The photocurrent is seen to be roughly constant in the cubic phase and to drop steadily on cooling through the ferroelectric region (Fig. 2).

Photorefractive diffraction gratings were written using two equal-intensity 150-mW/cm^2 beams from a 514-nm Ar laser. The beams were expanded to illuminate uniformly the sample, to which an electric field was applied in the plane of incidence. The beams crossed at a 16-deg angle and were ordinary polarized to prevent strong beam fanning and coupling. An expanded beam normally incident from the reverse side was used as an erase beam. In order to monitor the diffraction efficiency of the grating, an extraordinary-polarized 15-μW 632.8-nm He–Ne beam was aligned at the Bragg angle. The He–Ne beam was chopped, and a lock-in amplifier was used to detect the diffracted signal.

Photorefractive measurements were made at $T =$ 135 K in the paraelectric cubic phase under a 1000-V bias voltage. At this temperature photorefractive diffraction gratings could be written and erased in the usual manner. The gratings had an erase time of 3 s under 250-mW/cm^2 illumination. A grating with a diffraction efficiency η of 10% was written, after which the writing beams were turned off. The dark storage time of these gratings has been determined to be of the order of several days. The sample was then cooled from the cubic phase through the tetragonal and orthorhombic phases to $T = 108$ K in the rhombohedral phase. During the cooling the He–Ne probe beam was

used to monitor the strength of the grating (Fig. 3). The diffraction efficiency increased on approaching the ferroelectric transition and peaked at a value of 38% before falling to $\eta = 10\%$ at $T = 108$ K. The bias voltage was then removed, and the sample was illuminated with the normally incident 250-mW/cm^2 erase beam. The diffracted intensity initially rose and within a few seconds decreased to its original value of η = 10% (Fig. 3). The diffraction efficiency of the fixed grating was observed to remain at this value for half an hour. The bias voltage was then reapplied, and the sample was slowly reheated under illumination with the erase beam. The grating remained fixed until $T =$ 123 K, at which point the grating was abruptly erased.

The fixing procedure was repeated under varying conditions. The fixed gratings have been observed to undergo no change in diffraction efficiency after several hours of illumination. To create a fixed grating, it was necessary to cool the sample from the cubic phase to the low-temperature rhombohedral phase. If the sample is cooled to temperatures slightly above that of the tetragonal to rhombohedral transition, the photorefractive grating is erased under illumination. However, once a grating is fixed it remains so on heating
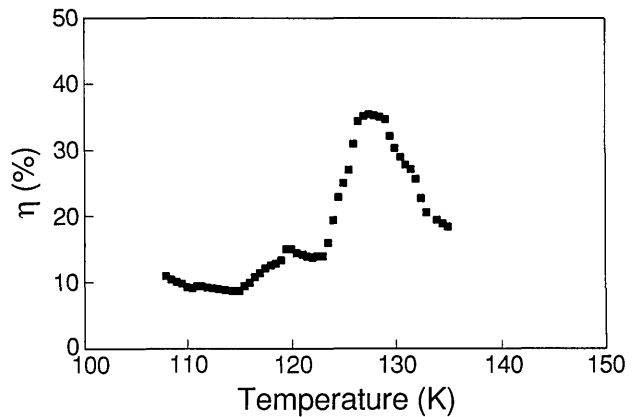

Fig. 3. Diffraction efficiency of the grating on cooling the sample with the writing beams blocked from the cubic phase to the rhombohedral phase under a 1000-V bias.
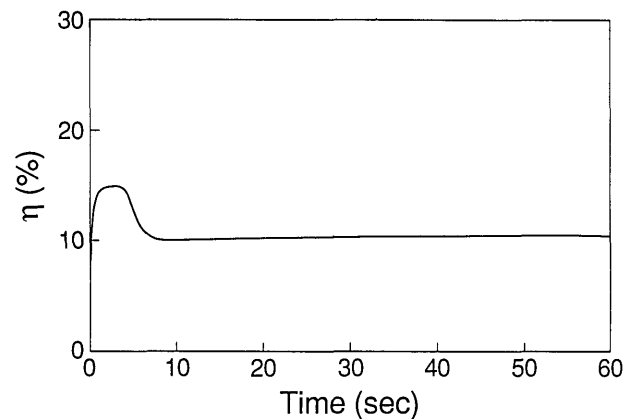

Fig. 4. Temporal dependence of the diffraction efficiency from the fixed grating in the rhombohedral phase after it was illuminated with a 514-nm erase beam.

into the orthorhombic and tetragonal phases. Also, the quality of the grating as determined by the amount of scattered light improved with increasing temperature. It has been observed that even after a single grating is fixed it is still possible to write and erase other unfixed gratings. Other evidence for this is the existence of dynamic beam fanning in the sample in the presence of a fixed grating. After a grating has been fixed it can be restored to its unfixed state, one in which it is erasable under illumination, simply by reheating the sample back to the cubic phase.

The above fixing process is not similar to those that rely on an ionic compensation of the photorefractive space-charge field.[1-3] From Figs. 3 and 4 it is observed that the space-charge grating is not canceled by an oppositely charged space-charge grating. The fixing procedure is not similar to those that locally switch ferroelectric domains either. In these procedures the electronic space-charge field is erased after domain formation. In addition, the applied field parallel to the grating vector during cooling ensures that the sample has a large spontaneous polarization along the [001] direction.

The above results are consistent with the existence of two types of photorefractive species. In the cubic phase both species are absorbing and contribute to the photorefractive effect. As the temperature is lowered into the rhombohedral phase, the species responsible for the fixed grating becomes photorefractively inactive. That is, it neither photoexcites nor traps free carriers. Evidence for this is the steady drop of the photocurrent on cooling into the ferroelectric region. On reheating the fixed grating to the cubic phase this species once again becomes photoexcitable, and the grating becomes erasable. The second species, possibly present at lower concentrations, remains photoexcitable at all temperatures. It is responsible for the observed dynamic photorefractive effect in the rhombohedral phase in the presence of a fixed grating.

Such a process would involve the interaction of the photorefractive species with the ferroelectric phase transition. The ferroelectric properties of perovskites are strongly affected by the symmetry and dynamics of impurities.[9-11] In KTN it is believed that in the cubic phase the Nb ions hop between eight equivalent sites along the [111] directions of a cube.[11] The tetragonal and rhombohedral phases, respectively, are the result of the Nb ions' being constrained to hop between sites in the direction of the corners of a half-cube and in the directions of two adjacent corners of a cube. The rhombohedral phase is due to the Nb ions' being constrained to a single off-center site in the direction of the corners of a cube. For the case of a photoexcitable impurity center, Levanyuk and Osipov

have shown that interaction with the ferroelectric soft mode or phase transition can cause the ion to be displaced from its symmetric position.[12] This off-center displacement can then raise the energy required for photoexcitation high enough so that the state no longer is absorbing. In KTN:Cu,V, Cu has been determined to be the predominant photorefractive species in the cubic phase.[6] On cooling into the rhombohedral phase the Cu ions, as do the Nb ions, may freeze out at an off-center site. Such a distortion may result in the Cu ions' becoming photorefractively inactive or fixed. On reheating into the cubic phase the distortion vanishes, and the center may once again become photorefractively active.

In summary, we have demonstrated a procedure to fix photorefractive gratings in KTN. It involves the writing of a photorefractive grating in the cubic phase and cooling a sample through the tetragonal and orthorhombic phases to the rhombohedral phase under an applied bias. Diffraction efficiencies of 10% in a 0.43-cm-thick sample were reported for a fixed grating. The fixed grating can be restored to the erasable state by reheating the sample to the cubic phase. The mechanism responsible for this effect is believed to be due to the displacement of an impurity center on cooling to the rhombohedral phase, which causes it to become photorefractively inactive.

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