Characterization of a new photorefractive material: $K_{1-y}L_yT_{1-x}N_x$

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We report the growth and characterization of a new photorefractive material, potassium lithium tantalate niobate (KLTN). A KLTN crystal doped with copper is demonstrated to yield high diffraction efficiency of photorefractive gratings in the paraelectric phase. Voltage-controllable index gratings with $n_1 = 8.5 \times 10^{-5}$ were achieved, which yielded diffraction efficiencies of 75% in a 2.9-mm-thick sample. In addition, diffraction was observed in the paraelectric phase without an applied field. This effect is attributed to a growth-induced strain field.

The use of photorefractive materials to store volume holograms for optical computing and optical memories has long been an active area of research.[1-3] In addition, these materials show promise in the implementation of optical neural networks.

Potassium lithium tantalate niobate ($K_{1-y}L_yT_{1-x}N_x$) forms a solid solution for $y \leq 0.15$. Nevertheless, most research has been concentrated on the end members KLT[4,5] and KTN.[6,7] In general, most compositions of the solid-solution series have received little attention, possibly because they are considered difficult to grow.

We were able to grow large optical-quality crystals of KLTN using the top-seeded solution growth method by carefully choosing the constituent concentrations of the flux. Our primary motivation for adding lithium to KTN was to achieve a room-temperature phase transition[8] with a lower niobium concentration than that in conventional KTN's. Secondarily, the lithium ion is expected to be more mobile than the potassium ion that it replaces and is expected to weaken the transition from first order to order disorder.[9]

KLTN has the perovskite structure. In its highest symmetry phase it is cubic and, for small lithium concentrations, undergoes transitions to tetragonal, orthorhombic, and rhombohedral structures with decreasing temperature.[10] In our experiments the crystal was maintained just above the paraelectric/ferroelectric transition.

In the cubic phase the material's photorefractive properties are described by the quadratic electro-optic effect.[11] The birefringence is given by

$$\Delta n = \frac{n_0^3}{2} g P^2,$$

$$P = \epsilon_0(\epsilon - 1)E, \tag{1}$$

where g is the relevant quadratic electro-optic coefficient, n_0 is the index of refraction, and ϵ is the dielectric constant. P is the induced dc low-frequency polarization that we assume is linear with E. In this case, when an external field is applied to the crystal, an index grating is written with

$$n_1 \equiv \Delta n[E_0 + E_{sc}(x)] - \Delta n(E_0)$$

$$\cong \frac{n_0^3}{2} g \epsilon_0^2 \epsilon^2 [2E_0 E_{sc}(x) + E_{sc}^2(x)]$$

$$\Rightarrow n_{1_{eff}} = n_0^3 g \epsilon_0^2 \epsilon^2 E_0 E_{sc}(x), \tag{2}$$

where $E_{sc}(x)$ is the space-charge field due to the interfering light beams and E_0 is the applied field. $n_{1_{eff}}$ is the term of relation (2) that leads to Bragg matching. The space-charge field is thus transparent to the interfering beams unless a spatially uniform field is applied. By using this property, we have performed modulation of the nonlinear response at 20-kHz rates.

In this Letter we discuss the material properties of a KLTN crystal. We report a capacitive measurement of the dielectric constant that indicates that the KLTN undergoes a second-order phase transition. Diffraction experiments performed both with and without an applied field are described. Finally, KLTN is indicated to be a promising new photorefractive material.

The sample used in the following discussion was a 6.8 mm × 4.9 mm × 2.9 mm piece cut from a crystal grown by us using the top-seeded solution growth method. The crystal was pale olive green and free of striations. Its as-grown weight was 11.6 g. By using electron microprobe and atomic absorption analysis, the composition was determined to be $K_{0.950}Li_{0.04}Ta_{0.857}Nb_{0.129}:Cu_{0.004}$.

Figure 1 shows the absorption spectrum of the as-grown sample with peaks at 370 and 585 nm caused by Cu^{1+} donors and Cu^{2+} traps, respectively. The concentration of the impurities Cu^{1+} and Cu^{2+} can be determined from the absorption peaks by using

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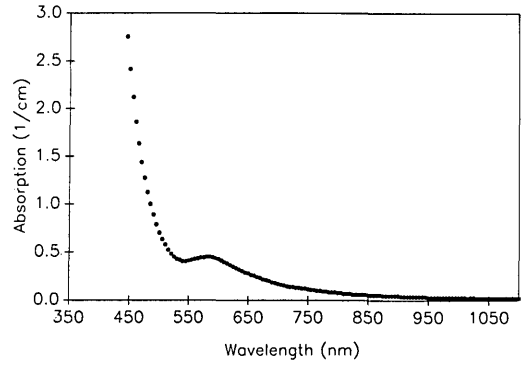

Fig. 1. Absorption spectrum of the as-grown KLTN:Cu.

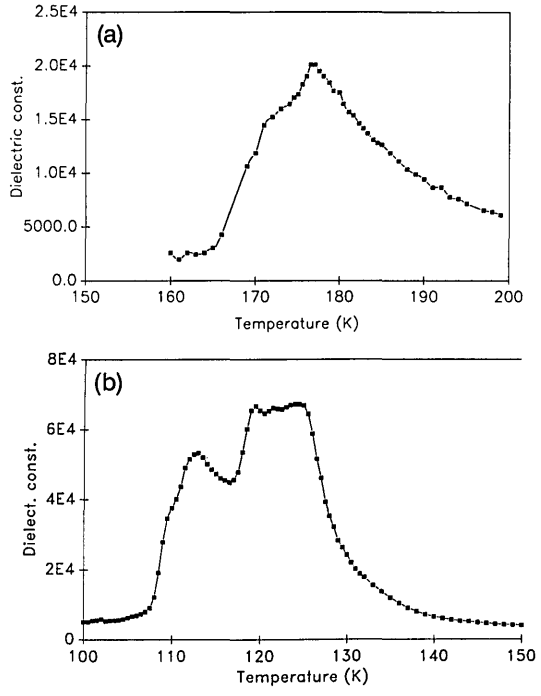

Fig. 2. (a) Dielectric constant of the $KLT_{0.857}N_{0.129}$. The phase transition is ~50 K higher than in a comparable KTN. (b) Dielectric constant of $KT_{0.86}N_{0.13}$.

Beer's law.[12] We calculate $[Cu^{1+}] = 6.0 \times 10^{19}/cm^3$ and $[Cu^{2+}] = 2.1 \times 10^{18}/cm^3$.

White-light birefringence measurements between crossed polarizers were used to measure the effective quadratic electro-optic coefficients. We determined $g_{11} - g_{12} = 0.186\ m^4\,C^{-2}$ to an accuracy of 5%.

The dielectric constant was monitored as a function of temperature by measuring the capacitance of the crystal, where $C = \epsilon_0 \epsilon A/d$. The results, shown in Fig. 2(a), are compared with those obtained from a KTN crystal with a similar tantalum:niobium ratio [Fig. 2(b)]. The cubic/tetragonal transition temperature has been raised approximately 60 K, to 178 K. The FWHM, i.e., the temperature range over which the dielectric constant drops to half its maximum value, is increased to ~10 K. Diffraction due to the linear electro-optic effect was weak directly below the transition and grew steadily as the temperature was lowered, indicating a second-order transition.

The diffraction experiments with applied field were performed as in Fig. 3 with the sample maintained at a temperature of 15 K above the transition. The writing argon laser beams were at either 488 or 514 nm. They were ordinary polarized to minimize beam interaction. The diffraction efficiency of the grating thus written was monitored with a weak extraordinary-polarized He–Ne beam at 633 nm. The 633-nm beam was verified not to erase the grating. The writing continued until the maximum diffraction was achieved.

After the gratings were written, the crystal was cooled to just above the transition, and the diffraction efficiency was determined as a function of applied field. The results are illustrated in Fig. 4. The three curves shown are for gratings that were written at +1450, 0, and −1450 V/cm. When the grating was optically erased with the argon beams, some residual diffraction (~1%) remained that was not optically erasable and could only be removed by heating the crystal to room temperature.

The highest diffraction efficiency observed for 488-nm writing beams was 75% for a sample of thickness 2.9 mm, where corrections were made for Fresnel losses. For 514-nm writing beams, the maximum value was reduced to 30%, and at 633 nm the diffraction was almost undetectable. The writ-

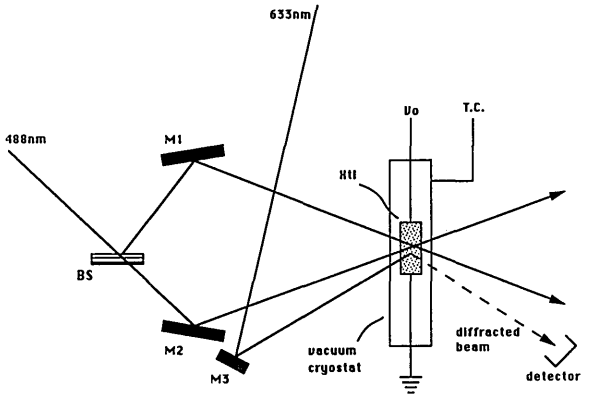

Fig. 3. Experimental setup for measurement of diffraction efficiency. Photorefractive crystal Xtl is mounted in a vacuum cryostat. Beam splitter BS and mirrors M1 and M2 create a 488-nm grating that is read with the Bragg-matched 633-nm beam and mirror M3. Diffraction is measured versus applied voltage Vo. The temperature was monitored by thermocouple T.C.

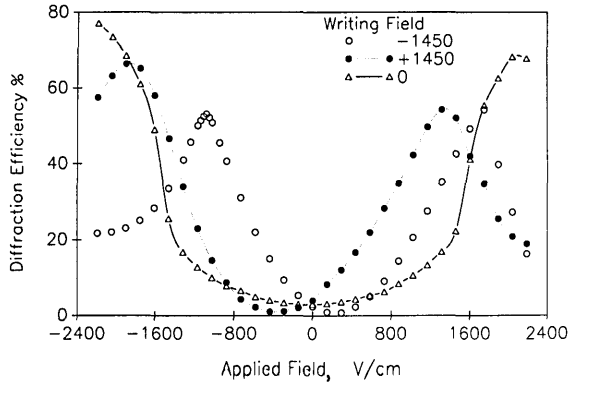

Fig. 4. Two-beam diffraction efficiency for gratings written at +1450, 0, and −1450 V/cm.

ing times for maximum diffraction roughly followed $\tau_{write} \approx 6\ s^2\,cm^2\,W^{-1}$ light intensity incident upon the crystal.

From the calculated index modulation of $n_1 = 8.5 \times 10^{-5}$, we determine the space-charge field to be $E_{sc} = 150$ V/cm. Using the writing time of 180 s at beam intensities adding up to 27.2 mW, we estimate the sensitivity for this KLTN crystal to be 7.30×10^{-6} cm^3/J for an applied field of 1.6 kV/cm. Following the procedure outlined above, the erase time near T_c was up to 2 orders of magnitude greater than the write time at $T_c + 15$ K.

KLTN was also observed to display weak diffraction without an applied field at as much as 120 K above the phase transition. At room temperature the diffraction efficiency in a 3-mm-thick sample was 0.65%. The effect was strongest with focused beams and weakened as progressively larger areas of the sample were illuminated. However, the diffraction efficiency measured with a given beam geometry was independent of beam intensity over several orders of magnitude.

In the diffraction experiments performed, an index grating was generated as in relation (2). Thus the diffraction efficiency in the crystal is a strong function of the dielectric constant ϵ. The largest effects occur near the phase transition. In KLTN the lithium raised the transition temperature 60 K over that of a KTN cyrstal with similar niobium concentration so that the temperature of maximum response was correspondingly raised. By choosing the proper niobium and lithium concentration, it may be possible to raise T_c to near room temperature while retaining a second-order transition.

As reported, the diffraction due to the linear electro-optic effect was weak directly below the transition and grew steadily as the temperature was lowered. The fact that the linear electro-optic coefficients are known to be large in this class of materials indicates that there is little spontaneous polarization at the transition. In other words, the transition displays second-order behavior and is at best weakly displasive. This agrees with KTN studies in which the phase transition is reported to become first order only for niobium concentrations exceeding 30%.[10]

In the experiments of diffraction with an applied field, the data are seen to follow a $\sin^2$ behavior with saturation (Fig. 4). This saturation is at least partly due to nonlinear polarizability of the medium at high field strengths.[6] From the data it is clear that a compensating dc field of approximately 300 V/cm is induced in the crystal under the influence of the writing field. As described previously, residual diffraction persisted when the gratings were optically erased. Also the erase/write time asymmetry was increased by up to 2 orders of magnitude. The asymmetry in the erasure time close to the transition may be due to the following mechanism: It is well known that in these crystals dipolar clusters are formed around impurities that move outside the center of inversion. In the vicinity of the phase transition the correlation length of these clusters becomes large and their relaxation time increases. Thus it is possible that a secondary grating is formed by these dipolar clusters in addition to the normal space-charge grating. The erasure time of the secondary grating is long in the vicinity of the phase transition, and this causes the asymmetry. This tentative explanation is currently under further investigation. We hope to harness this effect in the future to perform fixing in these materials.

In the experiments without an applied field, it was observed that substantial diffraction only occurs when the writing beams interfere over a small (uniformly strained) region of the crystal. We have determined that the effect arises from a weak semiuniform strain that is due to the growth process.

In conclusion, we have demonstrated the growth of a new photorefractive material, KLTN, and have characterized its photorefractive properties. Strong quadratic electro-optic coefficients, high diffraction efficiences, and sensitivities of 7.30×10^{-6} cm^3/J at 1.6 kV/cm were observed. Based on this research, KLTN crystals seem to be highly promising materials for volume hologram storage applications. In addition, the aspect of voltage control leads naturally to various interconnect schemes for neural networks.

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