Photoinduced electronic transport in $K_{1-x}Li_xTaO_3$

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Photocurrent and Hall effect measurements were performed on $K_{0.984}Li_{0.016}TaO_3$ and $K_{0.966}Li_{0.034}TaO_3$ single crystals under illumination with 514.5-nm and UV light. The currents observed are carried by electrons, whose mobility does not undergo large variations on cooling across the dipole-glass freezing temperature T_f. The sharp increase of photocurrent occurring in the polar phase is primarily due to enhancement of carrier density. The effect is much larger after field cooling, being accompanied in this case by persistent currents. The present results lead us to conclude that hole traps with vanishing cross section for electron recombination are active below T_f. [S0163-1829(98)04708-0]

INTRODUCTION

In the past twenty years the mixed perovskite $K_{1-x}Li_xTaO_3$ (KLT) has been extensively investigated in order to clarify the role of substitutional Li^+ ions in off-center positions.[1,2] At low Li concentrations ($x<0.02$) this compound develops an orientational glass state characterized by an x-dependent freezing temperature T_f. Upon cooling in the presence of a forcing electric field, the nanometric polar regions tend to align and the correlation of polarization scales up to large dimensions (1 μm or larger).[3–5]

Recently, it was shown that large photocurrents can be induced in this material below 80 K, by irradiation with 2.41 eV photons, which is less than the band gap (3.65 eV).[6] Photocarriers are thought to arise from two-step excitations that are allowed by intragap impurity levels. However, no effects of comparable magnitude have been reported in nominally pure or in Na- and Nb-doped $KTaO_3$. Therefore, this extrinsic photoconductivity seems to be correlated to some structural peculiarity of KLT. It has been proposed that shallow O^{2-} levels induced by the off-centering of Li^+ ions act as hole trapping centers so as to hinder electron-hole recombination and to enhance the photocurrent.[6,7]

The onset of large photocurrents has also been observed in $Sr_{1-x}Ca_xTiO_3$ near the ferroelectric critical temperature T_c.[8] In this case the authors claim that the effect is due to enhanced carrier mobility associated with the growth of ferroelectric order. In both materials photoconductivity was assumed to be n-type. However, no data are available about the sign, the number, and the mobility of photocarriers.

In order to clarify the photoassisted transport in KLT, we have undertaken a combined study of photoconduction and the photo-Hall effect. In this paper we report on extensive experiments performed in $K_{0.984}Li_{0.016}TaO_3$ single crystals. Results obtained from $K_{0.966}Li_{0.034}TaO_3$ are also included. The samples were parallelepipeds of high optical quality, oriented along the (100) directions. They were cut from single crystals grown by the spontaneous nucleation technique. These materials were characterized as having freezing temperatures T_f = 36.5 K ($x=0.016$) and T_f = 52 K ($x=0.034$).[3,4] We indicate the transition temperatures of our samples of both concentrations by T_f, even though the nature of the low-temperature phase is debated for $x>0.02$. Electrodes for current measurements were obtained by Pt sputtering on a pair of opposite faces. The current driving field was 36 kV/m. The same contacts were used to apply the poling field. Pointlike electrodes were applied on a lateral pair of faces for Hall experiments. Currents and Hall voltages were measured by Keithley electrometers model No. 6517. The crystals were placed for photocurrent measurements in a closed-cycle optical cryostat, Leybold model No. R210, which allowed working temperatures as low as 15 K. To perform photo-Hall experiments the samples were mounted in an optical cryostat, CTI-Cryogenics Cryodyne model No. 22, with amagnetic extension. Magnetic fields up to 1.2 T were provided by a Bruker electromagnet, model No. B-M10.

The experimental procedure was as follows: The sample was cooled in the dark from room temperature down to the point of measurement. Then it was uniformly irradiated with 514.5-nm light from an Ar-ion laser or from a monochromatized HBO-Hg lamp and measurements were started. All cooling runs were performed at a controlled rate of 1 K/min. A fixed value of 36 kV/m was used for the poling field during field-cooling preparation. In the attempt to reduce possible effects of space charge,[9] this field was applied below 70 K. After each run the crystal was heated to 300 K and regenerated in short circuit overnight to avoid memory effects.[10]

EXPERIMENTAL RESULTS

Unless otherwise specified, results refer to $x=0.016$ samples. As a general feature, we observe that the freezing temperature T_f is a point of discrimination between two distinct regimes of photoconduction. At $T>T_f$ the photocurrent has the same intensity and the same saturating behavior irrespective of zero-field cooling (ZFC) and field cooling (FC) conditions. Its saturation value was found to depend linearly on the illumination flux over the range 0.01–5 kW/m^2. This result is at variance with that reported in Ref. 6. On cooling across T_f, the photocurrent undergoes rapid enhancement, accompanied by a remarkable change of kinetics. Both as-

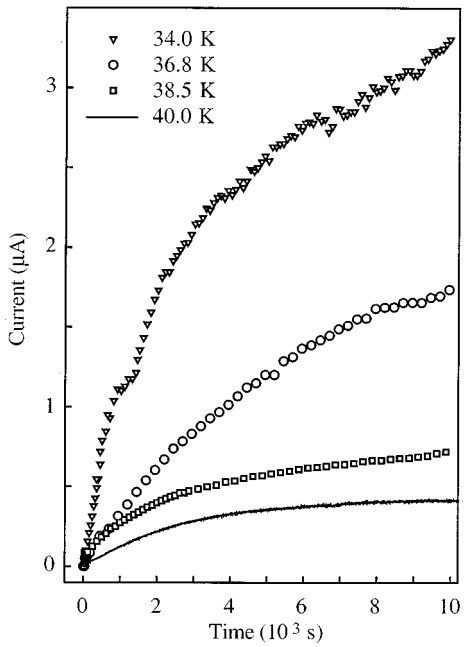

FIG. 1. Photocurrent vs time recorded in the field-cooled sample ($x=0.016$) at different temperatures around T_f (36.5 K), under a fixed illumination flux of 1 kW/m^2.

pects are drastically dependent on the cooling conditions, namely, FC vs ZFC. We took care to verify whether these effects had any significant component of photovoltaic origin. This possibility was ruled out by observing that short-circuit photocurrents (less than 10^{-10} A) were regularly orders of magnitude smaller than those observed with the driving field.

In Fig. 1 several plots of photocurrent vs time at fixed illumination flux are reported in the FC case. In a narrow range around T_f, one observes a rapid increase of intensity and a remarkable change of time dependence, from a saturating to a nonsaturating regime. In the polar phase the phenomena are further enhanced: At 15 K the increase is at least two orders of magnitude and photocurrent assumes a linear growth over the entire range of our observations (3×10^4 s), after a transient stage at the beginning of illumination, usually terminating with a kink at 10^3 s (Fig. 2). Following accepted models, the initial stage, characterized in many cases by an S-like shape, may be connected with some type

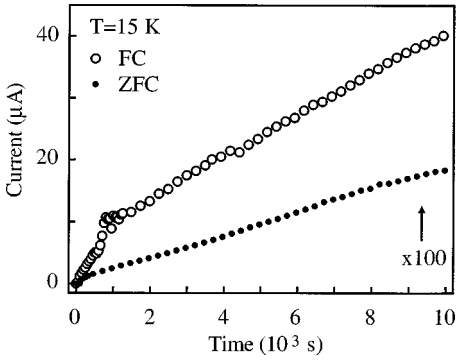

FIG. 2. Photocurrent vs time recorded at 15 K in field-cooled (FC) and zero-field-cooled (ZFC) samples ($x=0.016$), under a fixed illumination flux of 1 kW/m^2.

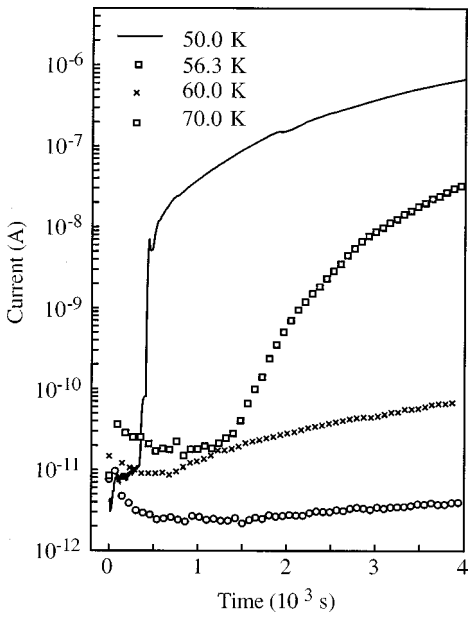

FIG. 3. Photocurrent vs time recorded in the field-cooled sample ($x=0.034$) at different temperatures around T_f (52 K), under a fixed illumination flux of 0.5 W/m^2.

of trap being filled by photocarriers.[11] Figure 2 compares the kinetics observed at 15 K after FC and ZFC. Notice that for equal conditions the rates of linear growth for the two cases are in a ratio of 100 or more. The role of T_f in determining photocurrent levels is confirmed by the results for $x=0.034$, illustrated in Fig. 3. In this case the increase of intensity near T_f appears to be even stronger.

Depending on poling conditions, a qualitative difference is also found in the decay of current after shutoff of the exciting light, as illustrated in Fig. 4. Starting from equal levels, obtained after different waiting times, two widely different regimes are obtained at low temperature. In the field-cooled sample, the current decays rapidly to a stationary value, which is orders of magnitude larger than the dark value (2×10^{-11} A) and persists for several days in the

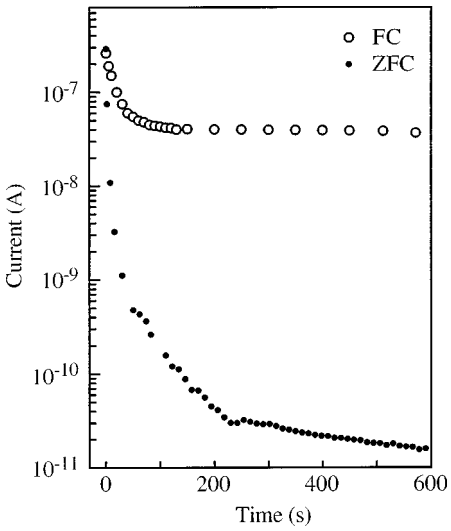

FIG. 4. Current decay after shutoff of the exciting light at 15 K, starting from equal levels of current in both FC and ZFC samples ($x=0.016$).

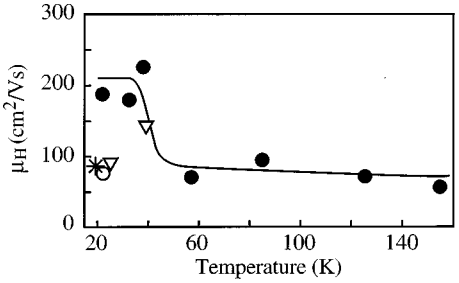

FIG. 5. Hall mobility μ_H vs temperature under illumination with UV light, after FC (○) and ZFC (●) for $x=0.016$. Data obtained with 514.5-nm light after FC (▽) and ZFC (*) are also reported. The continuous line is a guide to the eye.

absence of illumination. This persistent current can be observed with weaker intensity at temperatures up to 40 K. On the contrary, a nearly complete relaxation always occurs in the ZFC sample within a few minutes from the end of excitation. In all cases the decay is markedly nonexponential, with an instantaneous rate that decreases with time. The results hold qualitatively even if waiting times are kept the same: The shutoff of light after 1.8×10^4 s implies a rapid drop from 3×10^{-7} A to less than 10^{-10} A in the ZFC case, while in the FC sample a current of 2 μA is sustained, to be compared to the initial 70 μA. To the authors' knowledge this is the first report of persistent currents in an oxidic perovskite.

The sign, mobility, and concentration of the photocarriers were investigated by means of photo-Hall experiments. The Hall coefficient R_H, associated with the presence of photocurrent, was regularly negative and its value was independent of the magnetic field in the range 0.3–1.2 T. This implies that the photocarriers are electrons.

From the knowledge of R_H and of the measured conductivity σ, the Hall mobility $\mu_H = R_H \sigma$ was derived. Mobility data are reported in Fig. 5 as a function of temperature in the range 20–160 K. We notice that most of the data presented here were obtained under illumination with the multiline UV light from the Ar-ion laser (363.8, 351.4 and 351.1 nm). This was required to obtain carrier concentrations, sufficient to measure Hall voltages with adequate sensitivity. The ensemble of the UV data obtained after ZFC shows that μ_H is nearly constant in the range 50–160 K and is approximately doubled on further cooling. Anyway, it appears from Fig. 5 that the Hall mobility as determined under illumination with UV or green light and in any cooling conditions is always between 50 and 250 cm^2 V^{-1} s^{-1}. Therefore, one infers that the large photocurrent variations are mainly due to variations in the density of free electrons. Referring to the data of Fig. 2 and assuming a representative value $\mu_H = 200$ cm^2 V^{-1} s^{-1}, the carrier concentrations estimated at the end of the illumination process (3×10^4 s) are about 1.5×10^{10} and 7×10^7 cm^{-3}, respectively, for the FC and ZFC experiments.

DISCUSSION

Our results demonstrate that the behavior of photoconduction in KLT is closely correlated with the freezing temperature. This correlation, which could only be guessed from previous data,[6] is now firmly established by the abrupt changes of intensity and kinetics that accompany the onset of the polar phase at different Li concentrations.

Previous interpretations[6,7] ascribed the temperature dependence of photoconductivity in KLT to the combination of (i) an electron mobility following the law $\mu \propto T^{-3}$ (Refs. 12 and 13) and (ii) a free-carrier lifetime $\tau \propto T^{3/2} \epsilon^2$, controlled by capture in a charged recombination center. However, the present photo-Hall experiments show that the mobility is scarcely sensitive to temperature variations and much lower than in n-doped $KTaO_3$ (Ref. 13) (probably this is due to the dominance of impurity scattering associated with the presence of lithium disorder). Even more remarkably, μ_H is quite independent of cooling conditions and light excitation, which, on the contrary, greatly affect current levels. On the other hand, no simple conjecture concerning lifetime seems to be able to explain the huge increments of photoconductivity in the polar phase or the presence of persistent currents.

Two main effects can account for the increased photocurrent levels at low temperatures. If carriers of both signs are created by illumination, one might argue that holes are efficiently swept away by special hole traps, so that recombination with the other carrier is prevented. Traps acting in this way could be identified with the shallow acceptor centers that, according to Ref. 6, arise from O $2p$ nonbonding levels as a result of perturbation by off-center Li^+ ions. We expect these centers to be sensitive to the onset of the polar phase, in the sense that their stability should be radically increased below T_f, due to the off-center freezing of the Li^+ ions. Actually, this interpretation is plausible, but not sufficient to justify the behavior in the low-temperature phase. The mere stability of hole traps is unable to explain the temperature dependence of the growth rate or its dramatic increase from the unpoled to the poled sample. Therefore, one should admit the presence of an additional mechanism, linking the effectiveness of carrier generation with temperature and the poling field. Concerning persistent currents, an explanation might be based again on the presence of hole traps, which prevent electron recombination. However, this is not easily reconciled with the fact that persistent currents are only observed in the poled state. The possible role of an electret state in the phenomena deserves consideration.

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