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Shallow levels and photoconductivity in $K_{1-x}Li_xTaO_3$

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Abstract. We present the results of experiments performed on $K_{1-x}Li_xTaO_3$ as well as on Nb-doped and nominally pure $KTaO_3$ single crystals, in which we compared observations of thermally stimulated currents and photoconductivity. In the Li-doped compounds, the large enhancement of conductivity caused by ultraviolet excitation at low temperature was found to correlate with the filling of shallow trapping centres, giving intense charge release below 30–40 K. No sign of a corresponding release was shown by pure or Nb-doped $KTaO_3$, consistently with a very low yield of photocurrent which one observes in these cases. The depth of the trapping levels in $K_{1-x}Li_xTaO_3$ crystals was found to be between 50 and 70 meV. On the basis of past models and recent calculations, these levels can be identified with hole traps, originating from the perturbation of O^{2-} states at the top of the valence band. They are a plausible source of enhanced photoconductivity, via the quenching of electron–hole recombination.

1. Introduction

The mixed perovskites $K_{1-x}Li_xTaO_3$ (KLT) develop at low Li concentrations a dipole-glass state, characterized by an x-dependent freezing temperature T_f [1–3]. The polar structure is controlled by the interactions of dipolar and quadrupolar moments that are associated with substitutional Li^+ ions in off-centre position. The polar correlation length, which is of the order of a few nanometres in spontaneous conditions, can grow to much larger dimensions on cooling the sample in an applied electric field [4]. Birefringence and second-harmonic-generation measurements have shown that sample illumination with non-ionizing light of 2.41 eV (energy gap ∼3.6 eV) causes a quenching of ordering processes, which is consistent with the build-up of depoling fields due to space-charge formation [5]. Such phenomena are not surprising, in view of the sizable photoconductivity found in KLT under the same visible light [6, 7]. This extrinsic photoconductivity, not observed either in nominally pure or in Nb-doped $KTaO_3$, undergoes very large and abrupt increments at low temperatures.

Irrespective of visible or ultraviolet excitation, photo-Hall experiments have shown that the transport is of n type and that the electron mobility is weakly dependent on temperature [7]. The huge enhancement of photoconductivity found on going from 100 K to 13 K must then be ascribed to corresponding increases in the concentration of carriers, due to a radical increase of their lifetime. From this, one infers the presence of special centres that are able to quench electron–hole recombination processes. According to Klein *et al*, this role is played by O^{2-} shallow levels originating from O 2p non-bonding states, perturbed by off-centre Li^+ ions and

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acting as hole traps [6]. A light-induced EPR signal, characterized by an annealing temperature of 50 K, has indeed been ascribed to an O^- hole centre [8].

In recent experiments, thermally stimulated currents (TSC) were recorded in $K_{0.984}Li_{0.016}TaO_3$ and $K_{0.966}Li_{0.034}TaO_3$, after illumination with 2.41 eV light. Significant release structures were observed below 40 K [9], but the effects showed a complex dependence on the poling history. The associated trap depths were roughly estimated to be in the range 0.02 eV–0.10 eV. The authors tentatively identified these shallow levels with the centres responsible for the enhancement of photoconductivity.

More insight is needed to confirm the hypothesis of special traps as the controlling agent of these phenomena. In the first place, comparative TSC measurements on crystals of pure and doped $KTaO_3$ are required, in order to clarify whether the observed traps are specific to KLT. Furthermore, these measurements should be performed under better-controlled conditions. In this regard, it can be noticed that with visible light excitation, the low-temperature photoconductivity hardly attains a steady state in practical times. This prevents a full control of the starting conditions in the subsequent measurements of thermally stimulated currents. To overcome this difficulty, new experiments have been performed with ultraviolet light, having photon energy of the order of the band gap. In this way the photoconductivity attains a steady state fairly rapidly. Moreover, the photocurrent kinetics and saturation levels do not depend on the poling conditions [10].

In this paper we report on photoconductivity and TSC measurements made on single-crystal samples of $K_{1-x}Li_xTaO_3$ ($x = 0.016$: KLT-1; $x = 0.034$: KLT-2), of $KTa_{1-x}Nb_xO_3$ ($x = 0.024$: KTN) and of nominally pure $KTaO_3$.

2. Experimental procedure

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. Electrodes were obtained by painting silver paste on a pair of opposite faces. The sample dimensions were $2 \times 4 \times 6\ mm^3$ ($KTaO_3$), $2 \times 2 \times 5\ mm^3$ (KLT-1), $1.5 \times 2 \times 1\ mm^3$ (KLT-2), and $3 \times 3 \times 5\ mm^3$ (KTN), the first dimension indicating the inter-electrode spacing.

Thermally stimulated spectroscopies use the thermal excitation of charge carriers, from localized trapping centres to the conduction (or valence) band, to determine the energy levels and capture cross sections of the traps. In TSC experiments the sample is continuously heated, and the charge released by the traps, previously filled by illuminating the sample at low temperature, is driven to the electrodes by an external bias. A typical plot of current versus temperature consists of a series of peaks, corresponding to thermal emptying of different traps: the area of each peak is proportional to the density of specific traps, and the temperature of the maximum is related to their thermal ionization energy [11].

Typical experiments were performed with the following procedure: the sample was cooled in the dark to 13 K, at the controlled rate of 1 K min^{-1}, then it was uniformly illuminated with monochromatized light from an HBO–Hg lamp (irradiance $\sim 100\ \mu W\ cm^{-2}$ over a bandwidth of about 10 nm centred around 341 nm) until the steady state of the observed photocurrent was achieved. After a sufficient time from light shut-off for the current to relax to a nearly stationary background (typically of the order of one hour for KLT samples), heating at a controlled rate of 4 K min^{-1} began and the thermally stimulated current was measured. The current-driving and poling fields were 36 kV m^{-1}. All current measurements reported here were performed with a Keithley electrometer, model 6517. The overall sensitivity of the apparatus was 0.2 pA.

3. Results and discussion

As an example of photocurrent behaviour at 13 K, figure 1 shows the results obtained for the KLT-1 sample, with a comparison of ZFC and FC cases. After the light is turned on, the photocurrent readily reaches a stationary level that is practically independent of previous poling. Current relaxation is also clearly evidenced, showing an initial drop by two orders of magnitude in a few seconds, followed by a slower and slower decay in which the current remains well above the original dark level (50 pA) for several hours. Similar features, i.e. negligible influence of poling conditions and the presence of very long relaxation, were observed also for KLT-2.

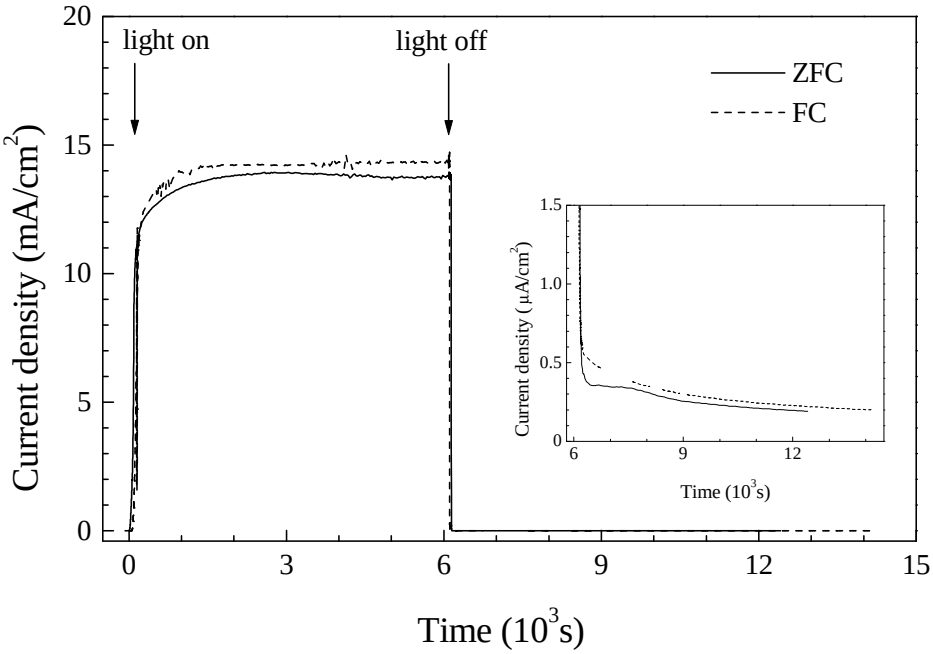

Figure 1. Growth and decay of the photocurrent in KLT-1 ($x = 0.016$), recorded at 13 K after preparation in ZFC and FC conditions. Exciting light: $\lambda = 341$ nm; $\Phi = 100$ μW cm^{-2}. (The inset shows later stages of the decay on an enlarged scale.)

Figure 2 shows the build-up of photocurrent density, observed in the various crystals for equal intensities of the exciting light and for equal driving field. One remarks immediately the huge increase in the yield of photocurrent (by 10^7 or more) on passing from pure or Nb-doped $KTaO_3$ to the KLT samples.

Figure 3 shows the structure of the TSC for the KLT-1 sample, observed by heating in the dark from 13 K to RT, after irradiation at the lowest temperature. The prominent feature is an intense and well defined peak at around 33 K. Its intensity and shape are nearly independent of the poling conditions: this is consistent with the behaviour of the photoconductivity, illustrated in figure 1, though it is at variance with the results of similar TSC experiments with visible light [7]. It is noteworthy that the intensity of this structure was independent of whether photocarriers were injected in the presence or in the absence of the field. This excludes artifacts due to space-charge separation. Considering the known freezing temperature of the KLT-1 sample (36.5 K) [4], it was also essential to ensure that the observed peak represents a true release of trapped charge rather than the displacement of polarization charge. This was

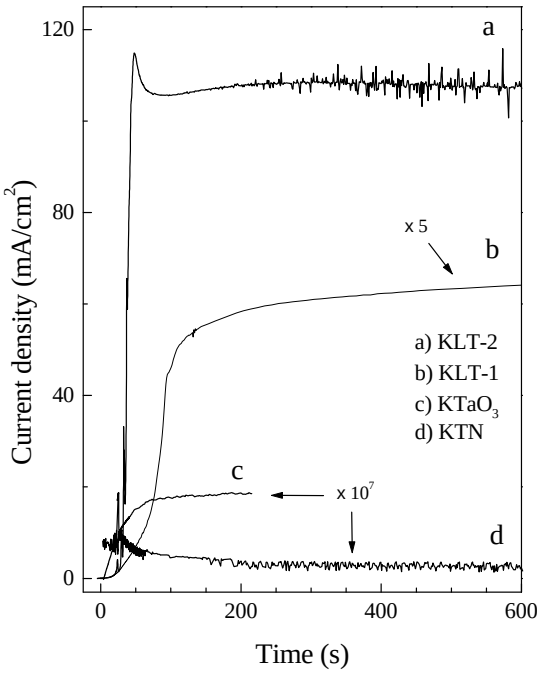

Figure 2. Build-up of the steady-state photocurrent at 13 K in pure and doped $KTaO_3$ (unpoled samples). The exciting conditions are as in figure 1.

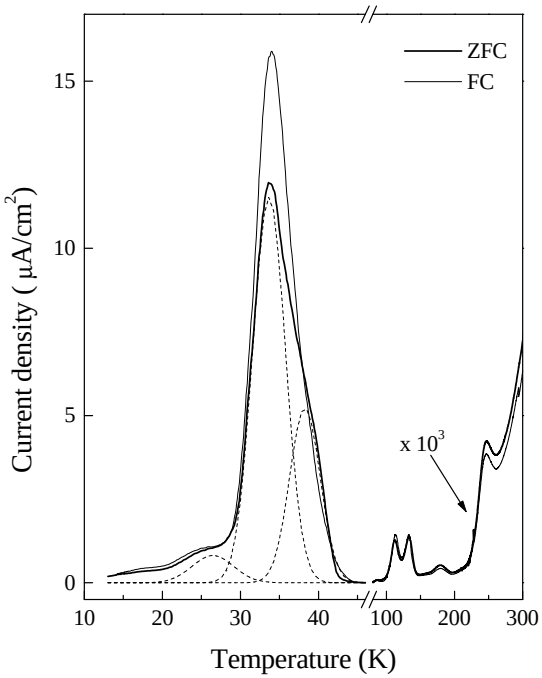

Figure 3. TSC spectra obtained from the KLT-1 sample after cooling to 13 K under different poling conditions, followed by prolonged illumination at $\lambda = 341$ nm and $\Phi = 100\ \mu$W cm^{-2}. Heating rate: $\beta = 4$ K min^{-1}. Broken lines represent fitting of the ZFC curve by Gaussian components.

checked by measuring polarization/depolarization currents during appropriate cooling and heating cycles in the non-illuminated sample with the same driving field. Such currents were found to be completely negligible with respect to the main TSC peak appearing in figure 3.

When the low-temperature peak is exhausted, the residual background current disappears and the dark level is recovered. Other peaks then follow in the range 100 K–300 K, with intensities that are three orders of magnitude smaller than the low-temperature one. One can conclude that the dominant population consists of relatively shallow traps, associated with the low-temperature peak.

In fact the shape of the peak at 33 K indicates a multicomponent character. In addition, the lack of significant broadening on the low-temperature side suggests second-order kinetics (i.e. a retrapping rate much higher than the recombination rate). The evaluation of peak parameters, such as the temperature at maximum (T_m) and the halfwidth, requires that each component be isolated, e.g. by standard procedures of thermal cleaning [11]. This could not be done here, because the thermal inertia of the cold finger plus sample holder prevented a sufficiently fast cooling. A simple line-shape analysis was then attempted by fitting the peak with three Gaussian functions (considering also the weaker shoulder on the low-temperature side). From best-fit values for T_m, it was possible to determine the trap depth, E, and capture cross section, S, by means of Fermi level analysis (see chapter 9 in reference [12]):

$$E = k_B T_m \ln\left(\frac{N}{n_m}\right) \tag{1}$$

$$\frac{\beta}{T_m^2} = k_B \frac{\nu_{th} S N}{E} \exp\left(-\frac{E}{k_B T_m}\right) \tag{2}$$

where k_B is the Boltzmann constant, n_m is the density of the carriers concerned at T_m, N is the effective density of states in the corresponding band, β is the heating rate, ν_{th} is the thermal velocity of the free carriers. In the evaluation of n_m, a carrier mobility of 100 $cm^2\ V^{-1}\ s^{-1}$ was considered, for this is the order of magnitude determined for this sample in previous experiments [7]. The electron rest mass was used for the estimate of N. The results for the ZFC case are reported in table 1. The case of FC, which is characterized by comparable amounts and structure of charge release, gave similar results. The estimated trap depths are between 50 and 70 meV; such values characterize the traps responsible for low-temperature release more precisely than previous work [9]. The values obtained for capture cross sections ($\sim 10^{-16}$ cm^2 or less) seem consistent with uncharged traps in a dielectric (see chapter 3 in reference [12]).

Table 1. The energy depths E and capture cross sections S of traps in KLT-1 as derived from low-temperature TSC peaks. T_m indicates best-fit values of the peak temperature.

T_m (K)	E (meV)	S (cm^2)
26.4	49.6	1.30×10^{-16}
33.7	58.5	6.05×10^{-18}
38.3	68.7	1.24×10^{-17}

Comparable release currents were observed in the KLT-2 sample, as shown in figure 4. Here the TSC spectrum is characterized by a broad structure around 30 K, followed by several narrow peaks overlapping on the high-temperature side, between 38 and 43 K. Release vanishes above 45 K; hence a role for the depolarization current can be excluded, as we know that the freezing temperature of the compound is 52 K [3]. Peaks of very weak intensity (not shown here) were found above 100 K.

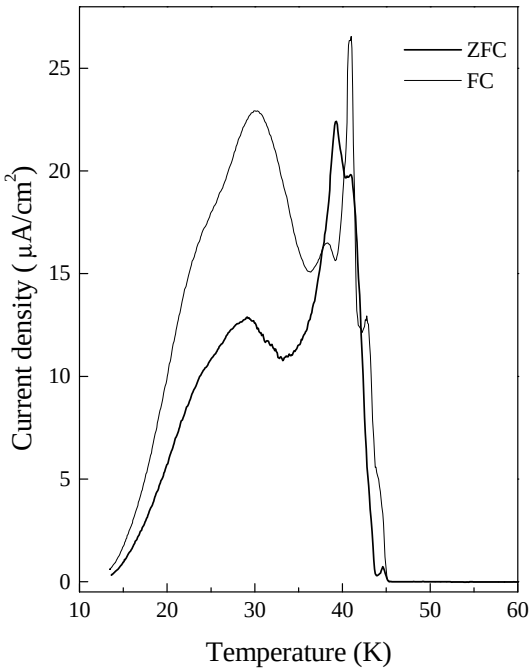

Figure 4. TSC spectra from KLT-2, limited to the low-temperature region. The other conditions are as for figure 3.

A full Gaussian analysis proved unable to describe the complex structures of figure 4. However, an estimate of individual intensities and positions can be readily made for the sharp peaks. Using equation (1), trap depths of 67 and 69 meV were derived for the two main peaks, with a deviation of at most ± 0.5 meV between the poled and unpoled cases. We note the close similarity of these figures to that derived from the peak at 38.3 K for KLT-1.

The results of TSC observations on KTN and nominally pure $KTaO_3$ performed under similar conditions are reported in figure 5. The remarkable feature in both cases is the complete absence of charge release in the region below 40 K, in radical contrast with the case for the KLT samples. In the Nb-doped compound, the negligible release allows us to appreciate the depolarization peak, in good correspondence with the known critical temperature of 32 K [13]. Minor release peaks appear at 85 K (pure) and 55 K (KTN). These structures do not coincide with any of the release peaks found for KLT samples and are much less pronounced. The structure observed for $KTaO_3$ was analysed by the initial-rise method, from consideration of its shape, which is suggestive of simple first-order kinetics (i.e. a recombination rate much higher than the retrapping rate) [11]. In this way, a trap depth of about 90 meV was estimated.

4. Conclusions

Two main results are evidenced by the present experiments. In the first place, large photocurrents can develop in $K_{1-x}Li_xTaO_3$, but not in nominally pure and Nb-doped $KTaO_3$ even under illumination with ionizing light. Moreover, TSC data demonstrate that in $K_{1-x}Li_xTaO_3$ the high level of photoconductivity correlates with a substantial production of trapped carriers, which are easily de-trapped at low temperature. On the other hand, in samples not containing Li the very small values of photoconductivity correspond to negligible release. This appears

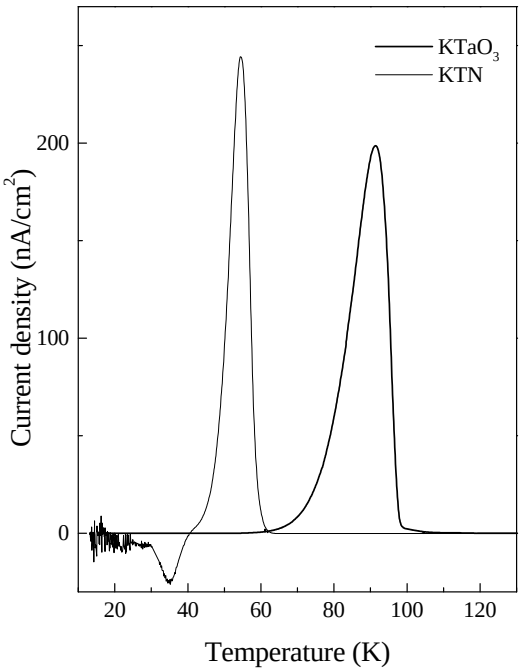

Figure 5. TSC spectra from unpoled $KTaO_3$ and KTN. The other conditions are as for figures 3 and 4.

to confirm that in KLT there is a specific role of shallow centres, which are able to enhance photoconductivity by trapping one of the carriers and hindering recombination. Considering the proven n-type character of photo-transport [7], one can argue that holes are the trapped entities. As to the nature of the traps, theoretical arguments [6] and EPR data [8] have been presented in support of their identification with oxygen sites, perturbed by off-centre Li^+ ions. *Ab initio* calculations on the electronic structure of $K_{0.985}Li_{0.15}TaO_3$ have recently provided a test of this hypothesis, and shown that substitutional Li introduces new levels at 60 and 90 meV above the top of the valence band of $KTaO_3$, originating from O^{2-} states [14].

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