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Cooperative phenomena induced by Nb admixture in $K_{1-x}Li_xTaO_3$

E Giulotto†, P Galinetto†, P Camagni†, G Samoggia†, V A Trepakov‡‖, L Jastrabik‡ and P P Syrnikov§

† INFM and Dipartimento di Fisica 'A Volta', Università degli studi di Pavia, Via Bassi 6, 27100 Pavia, Italy

‡ Institute of Physics AS CR, Na Slovance 2, 182 21 Praha 8, Czech Republic

§ A F Ioffe Physical and Technical Institute, 194 021 St Petersburg, Russia

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Abstract. Raman scattering observations were performed on samples of $K_{1-x}Li_xTa_{1-y}Nb_yO_3$, with x in the range 0.6–1.0 mol% and y in the range 0.2–0.3 mol%. Concentrations of Li and Nb, determined by analytical methods, were below the known thresholds at which these substituents can separately induce a ferroelectric transition in the quantum paraelectric $KTaO_3$. The temperature evolution of TO_1 and TO_4 spectra was monitored. The results show a critical behaviour below 50 K, characterized by an abrupt increase of first-order scattering strengths and by spontaneous splitting of the non-softening TO_1 mode. From our data, we infer the occurrence of a ferroelectric phase transition of order–disorder character. This proves that small additions of Nb enhance the tendency of the Li subsystem towards cooperative ordering in the $KTaO_3$ matrix.

1. Introduction

It is known that $KTaO_3$ (KTO) is an 'incipient ferroelectric', in which the lowest TO mode softens with decreasing temperature, and the dielectric constant ε' correspondingly increases with an extrapolated Curie–Weiss temperature of 1–4 K. However, ε' saturates below 20 K and the ferroelectric phase transition (PT) is prevented by quantum fluctuations. Upon addition of dipolar impurities, e.g. reorienting off-centre Li or Nb ions, various polar phases can occur, owing to instability of the matrix against polar distortions. These effects have been extensively investigated in the case of $K_{1-x}Li_xTaO_3$ (KLT) and $KTa_{1-y}Nb_yO_3$ (KTN) [1–3]. In KLT, the picture is dominated by large $\langle 100 \rangle$ displacement and slow relaxation of Li^+; softening of the TO_1 mode is generally frustrated [4]. The behaviour of KTN is characterized by small $\langle 111 \rangle$ displacement and fast relaxation of Nb^{5+}, with tendency to soft-mode-dominated PT [5, 6]. Depending on the concentration of the substituents, these compounds show a variety of phases [3]. For Li concentrations $x < 0.01$ or Nb concentrations $y < 0.007$, the behaviour of KLT and KTN is close to that of KTO. For $0.01 < x < 0.022$ or $0.007 < y < 0.008$, a low-temperature dipole-glass PT takes place. For $0.022 \leqslant x \leqslant 0.05$ and $0.008 \leqslant y \leqslant 0.06$ the low-temperature phase is a mixed ferro-dipole glass one for KLT and a soft-mode-dominated trigonal ferroelectric phase for KTN. For higher Li or Nb concentrations a cubic–tetragonal PT is observed in KLT, whereas three successive transitions to tetragonal, orthorhombic and rhombohedral phases take place in KTN.

‖ Permanent address: A F Ioffe Physical and Technical Institute, 194 021 St Petersburg, Russia.

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Fewer observations are known for KTO doped by both Li and Nb, i.e. $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ compounds (KLTN). In early studies [7, 8], the effects of Li^+ defects on the soft-mode PT were investigated using light depolarization, Raman spectroscopy and elastic compliance methods, and a phase diagram was suggested. New studies of permittivity and Raman scattering were reported recently [9, 10]. In this paper we discuss Raman scattering observations in KLTN samples with $0.6 \leqslant x \leqslant 1.0$ and $0.2 \leqslant y \leqslant 0.3$, thus covering a region that was not explored in past Raman studies [7]. The results show that even a small Nb admixture radically modifies the well known Raman signatures of KLT, in a way indicating the onset of a cooperative behaviour.

2. Experiment

The single crystals used here were grown in a platinum crucible, by spontaneous crystallization from a slowly cooled flux, in oxygen atmosphere. The batch consisted of high-purity (OSCh grade, 99.99%) Ta_2O_5, with ∼20% stoichiometric excess of K_2CO_3. The melt was cooled at a rate of $\sim 1\,^\circ C\ h^{-1}$ from 1360 to 1000 °C, then to room temperature, using a programmable temperature control system. To admix Li and/or Nb, the appropriate quantities of Li_2CO_3 and Nb_2O_5 oxides were added to the batch. The samples contained small additions of Cu, which facilitates crystal growth [11].

Absolute concentrations of Li, Nb and Cu were determined by flame emission spectroscopy, 'rodonide' photometry and absorption spectrophotometry, respectively. The compositions of the specimens under study are listed in table 1.

Table 1. Composition of $K_{1-x}Li_xTa_{1-y}Nb_yO_3$:Cu samples.

Batch	x	y	Cu (ppm)
PC-254	0.006	0.002	150
PC-297	0.009	$<9 \times 10^{-5}$	55
PC-301	0.010	0.003	50
PC-300	0.010	0.003	—

All specimens were grown from batches with a nominal Li concentration of 3%. The actual concentrations resulting from analyses are consistent with the conventional rule proposed for KLT on the basis of NMR studies [12]:

$$x = 0.35x_m$$

where x and x_m are the concentrations in the crystal and in the melt, respectively.

Specimens for Raman investigations were prepared from the quoted materials as polished parallelepipeds oriented along ⟨100⟩ cubic axes. Raman measurements were taken with a Ramanor spectrometer (Jobin & Yvon model HG-2S). Excitation was provided by the 514.5 nm line of an Ar-ion laser (Coherent Innova 300), with a beam intensity of 40 mW. The samples were mounted in a helium closed cycle optical cryostat (CTI-Cryogenics model 22) under the control of a Lakeshore Model 330 temperature module. The spectra were recorded after cooling the sample at a constant rate of $1\ K\ min^{-1}$ from 100 K to the lowest attainable point (11 K) and subsequently heating to the temperature of measurement. The latter was monitored by a Si-diode sensor placed in the vicinity of the sample. The spectral regions inspected were 8–120 and 520–600 cm^{-1}, where the low-energy TO_1 mode and the hard TO_4 mode can be observed. Spectral resolution was set at $2\ cm^{-1}$.

The spectra presented here were obtained in a 90° geometry, without polarization analysis of the scattered light. Samples PC-297, 300 and 301 were mounted with edges parallel to the

x, y and z laboratory axes. The thin-plate sample PC-254 was tilted so as to allow excitation of the large face in near-reflection geometry.

3. Results

Figure 1 shows the low-energy Raman spectra of sample PC-297 in which, according to table 1, Nb is absent and Li approaches 1%. One can observe below 70 K and all the way down to 13 K the regular growth of a broad spectrum, which remains unresolved even at the lowest temperature. Such behaviour is consistent with that of KLT systems of low Li concentration [4, 6], in which a separation between the symmetry species E and A_1 of the TO_1 spectrum is hindered by disorder-induced inhomogeneous broadening. In addition to the dominant spectrum one can notice the well known second-order 2TA band and a low-frequency peak, of uncertain attribution [4], vanishing progressively at the lowest temperatures.

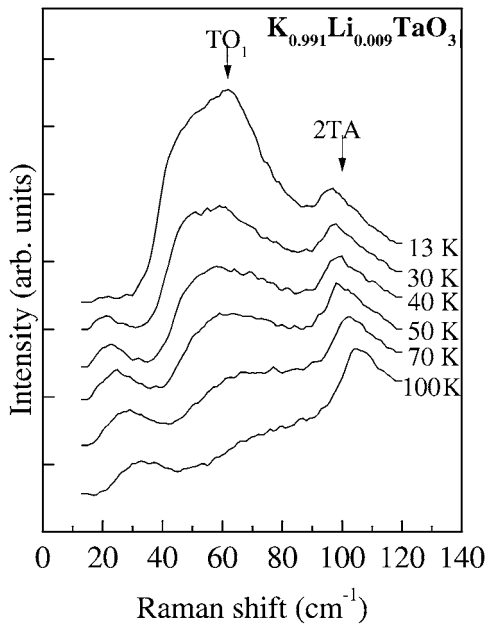

Figure 1. Low-energy Raman spectra of sample PC-297 at different temperatures.

We next consider the data for samples PC-254 and PC-301. According to table 1, these are KLTN systems having Li concentrations of 0.6% and 1.0% (comparable to PC-297) and Nb concentrations of 0.2 and 0.3%. Figures 2 and 3 show the temperature dependence of the low-energy spectra. Even in this case, there is initially the growth of a broad TO_1 spectrum. However, new features emerge below ∼45 K, where the spectrum begins to be resolved into three components A, B and C. The situation is also different concerning spectral intensities, which undergo a large and rapid increase not observed in pure KLT. Differences in the relative strengths of the components may derive from the different orientations of the two samples in the scattering experiments (see section 2).

The spectra of KLTN samples were analysed by fitting them to a superposition of three damped oscillators. Adequate fitting was obtained in each case below ∼40 K, and its quality was particularly good at the lowest temperatures, as shown in figure 4. Figure 5 plots the best fit values of the characteristic oscillator frequencies for the three component lines as a

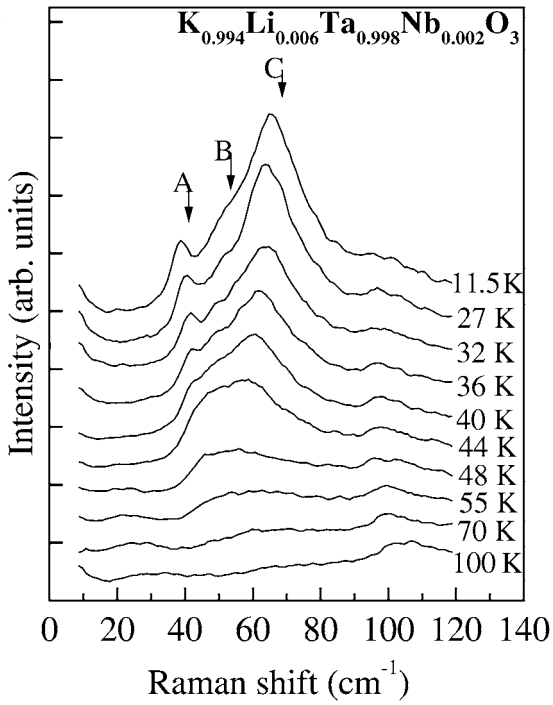

Figure 2. Same as figure 1, for sample PC-254.

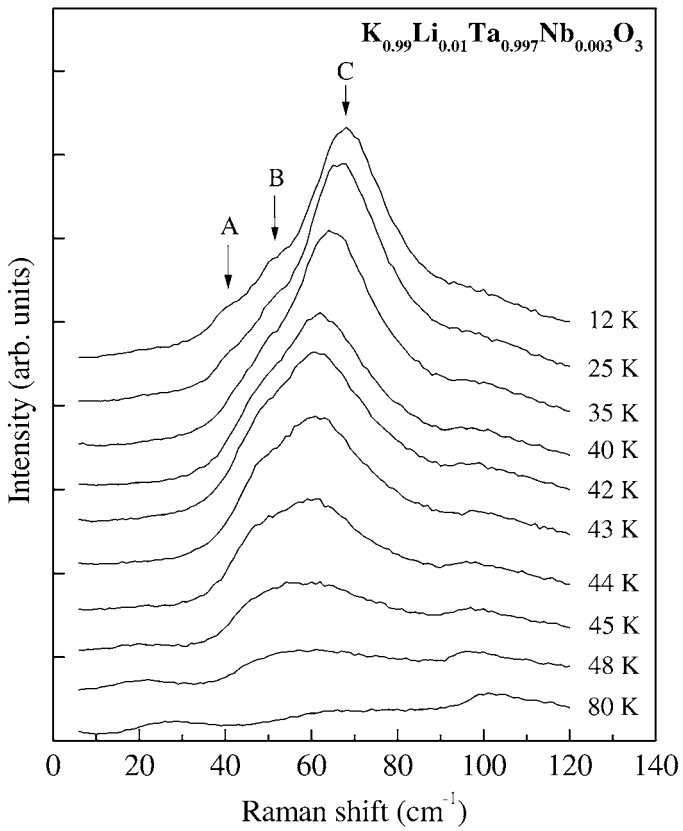

Figure 3. Same as figure 1, for sample PC-301.

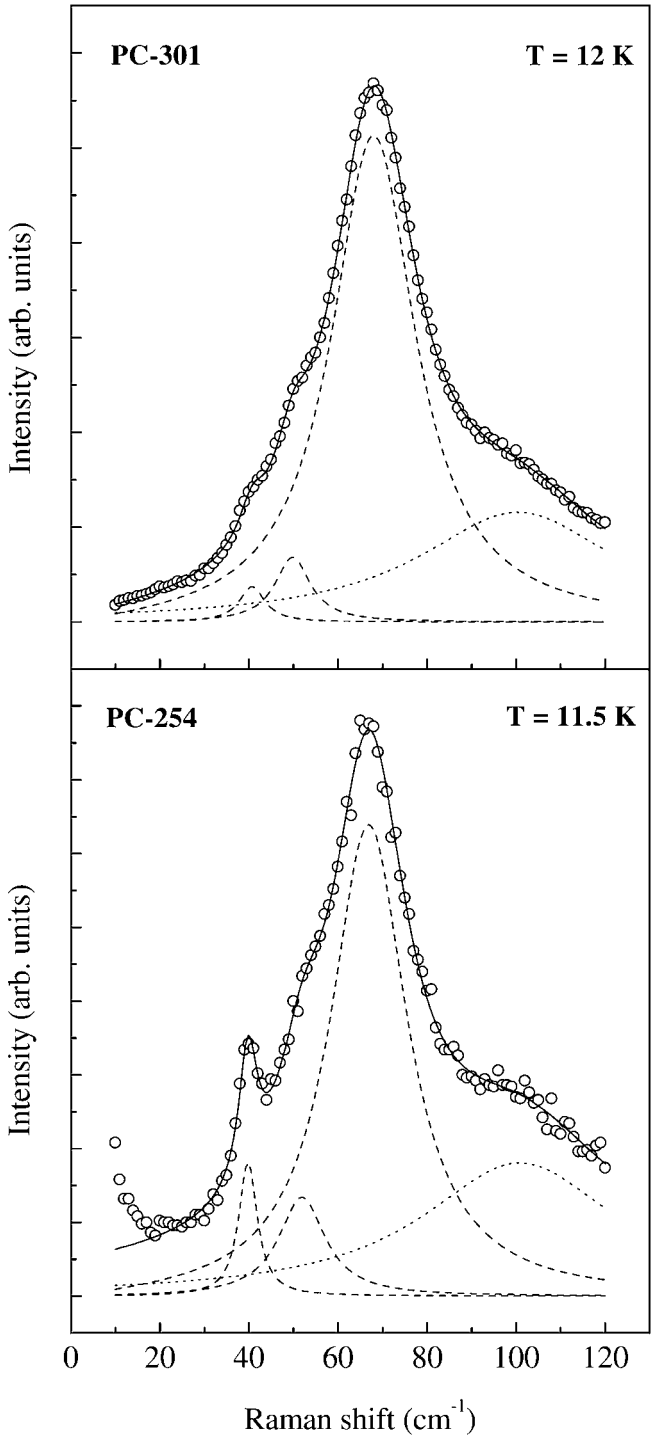

Figure 4. Examples of fit to low-temperature spectra of $K_{0.99}Li_{0.01}Ta_{0.997}Nb_{0.003}O_3$ (sample PC-301) and $K_{0.994}Li_{0.006}Ta_{0.998}Nb_{0.002}O_3$ (sample PC-254). The solid line is the best fit to as-measured experimental points in terms of three damped oscillators (dashed lines) plus a Lorentzian representing the 2TA band (dotted line).

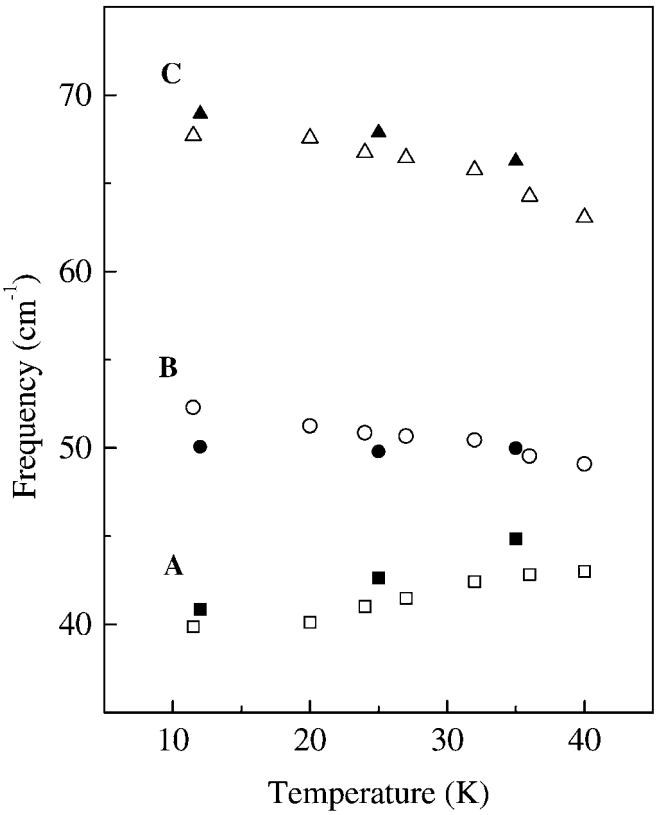

Figure 5. Temperature dependence of the oscillator frequencies for the A, B and C components of the low-frequency Raman spectrum of KLTN. Open symbols: sample PC-254; full symbols: sample PC-301.

function of temperature. The frequency behaviour is remarkably similar in the two samples. In both cases the three lines are still well separated at temperatures of 40 K or more; below that point, the extreme components A and C are seen to soften and to harden respectively, so that their splitting increases. As concerns the intermediate component B, we tend to exclude that it belongs to the TO_1 spectrum for the following reasons: (i) its position corresponds to a weak line often observed between 45 and 50 cm^{-1} in KTO-based systems, which was ascribed to disorder-induced scattering from the TA branch [4, 6]; (ii) its intensity does not grow in keeping with the other components, as it appears especially from the spectra of figure 2. Disregarding this component, the behaviour of the A and C lines demonstrates a large spontaneous splitting of the TO_1 mode.

Similar experiments were performed on sample PC-300, having the same composition as PC-301, without Cu doping. The evolution of the TO_1 spectra was closely comparable to that of figure 3, with minor differences in weight and resolution of the components, as well as in the temperature at which the critical increase begins to develop.

In parallel with the low energy spectra, the TO_4 Raman line was also investigated in the same crystals. This hard-phonon line has a simple Lorentzian shape and is easily deconvoluted from the nearby second-order TO_4+TA spectrum. Therefore it is a good tool for the monitoring of first-order Raman strength [6]. From a systematic survey, the integrated TO_4 intensities were

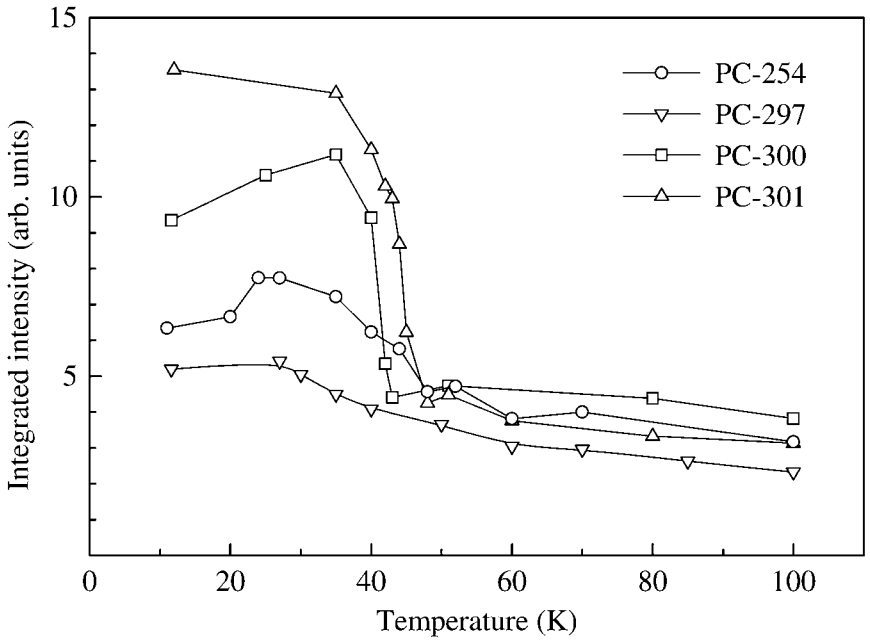

Figure 6. Temperature dependence of the TO_4 line strength in KLT and KLTN samples.

obtained as a function of temperature. They are reported in figure 6, after normalization to the RT intensity of the adjacent second-order spectrum. All these plots reveal the presence of a relatively strong TO_4 line even at 100 K or more. However, marked differences are found as temperature decreases. A weak increment takes place in PC-297, in accordance with past results on hard-phonon spectra in KLT [6], whereas a steep jump is found in PC-300 and PC-301 at 43 and 48 K respectively, i.e. in the range where the TO_1 enhancement occurs. The behaviour of PC-254 seems to be somewhat intermediate, revealing a moderate increase around 48 K.

4. Discussion

The present experiments have demonstrated that the simultaneous admixture of small amounts of Nb and Li in the KTO matrix gives rise to critical phenomena. In fact, it was shown that the presence of 0.2–0.3% of Nb and of 0.6–1.0% of Li is sufficient to induce a ferroelectric phase transition. Incidentally, this emphasizes the merit of the compositional analysis which was afforded in our work. Notice that Nb, in the quoted proportions, does not give rise to critical phenomena in KTN. On the other hand, no criticality should be expected from the action of Li alone at these levels. In view of this, our results are suggestive of a specific interplay between Nb and Li, capable of enhancing cooperative phenomena. This possibility has been explored in the past, applying a random field model to the specific case of KTO with two types of interacting random-site dipole [13].

The transition is marked by the critical increase of first order Raman scattering at $T_c \simeq 45$ K and by the appearance of a large splitting in the TO_1 mode, a few degrees below that point. The absence of softening of the TO_1 components suggests a classification of this PT as an order–disorder process. Past observations of optical anisotropy in KLTN systems [7]

have shown that the symmetry of the low-temperature phase is tetragonal, being dictated by ⟨100⟩ off-centre Li displacements even at low concentrations. In agreement with this are the persistence of first-order scattering and the inhomogeneous broadening of the TO_1 line, observed by us above T_c, which reveal the presence of quasi-static polar distortions, correlated over short distances.

In view of the low Nb content of our samples, it is not surprising that the general features are similar to those observed in KLT [4], except that critical cooperation now occurs at very low Li concentrations. According to theories on dipolar interactions in the presence of a ferroelectric soft mode [1], this would be consistent with an increased polarizability of the matrix, which is made softer by the presence of Nb.

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