Order and disorder processes in the Raman spectrum of KTa$_{1-x}$Nb$_x$O$_3$

Order and disorder processes in the Raman spectrum of $KTa_{1-x}Nb_xO_3$

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Abstract. We present light scattering measurements up to 800 cm^{-1} for $KTa_{1-x}Nb_xO_3$ crystals with high niobium (9 at.%) and low niobium (2 at.%) concentrations. The spectra in the ordered cubic phase (at high temperatures) and rhombohedral phase (at low temperatures) are characterised by normal second- and first-order lines, respectively, as required by symmetry. Nevertheless, in the cubic phase, within a temperature range depending on the niobium concentration, the spectrum exhibits a broad central peak and lines activated by local symmetry breaking. This intermediate state can be defined as a precursor ferroelectric ordering state above T_c. The continuous change in the Raman spectrum with decreasing temperature can therefore be attributed to a gradual dipolar clustering process induced by relaxing Nb ions in the $KTaO_3$ lattice.

1. Introduction

Considerable interest has recently been devoted to the competition between the long-range order and the freezing in of random-cluster or glassy behaviour, in magnetic and electric systems (for more details of electric dipole glasses see, e.g., [1]). Some changes in the competitive effects are expected to result from the introduction of impurities in a host lattice.

Dipolar systems of $KTaO_3$ containing a small concentration of impurities are very suitable for such studies and have been extensively investigated. While pure $KTaO_3$ does not undergo any phase transition down to 0 K, replacing K by Li or Na, or Ta by Nb, destabilises the host lattice and leads to a transition temperature which is dependent on the dopant concentration. At the present time these systems are not definitively understood and the mechanism of the phase transition remains controversial (see, e.g., [2]).

Here we are especially interested in the $KTa_{1-x}Nb_xO_3$ (KTN) system. The existence of disorder due to Nb off-centre positions in the high-temperature phase [3] has been particularly questioned together with the real nature (ferroelectric [4, 5] or dipolar glassy [6–8]) of the low-temperature phase. The displacive [9], order–disorder [10–12] and diffuse [7] mechanisms have also been suggested successively to explain the niobium-induced phase transitions. Further, the clear phonon softening detected by hyper-Raman [9] or electric-field-induced Raman [3] scattering is seemingly in conflict with the existence of disorder revealed by light quasi-elastic scattering [10, 11] and the most recent dielectric measurements [12].

In this work we describe light scattering measurements performed on KTN crystals as a function of temperature. We attempt

(i) to confirm in a sole investigation several experimental features which were separately displayed in the Raman spectra previously reported [3, 8, 10], i.e. the soft phonon peak, the disorder-induced lines and the central peak onset,

(ii) to establish the relation between all these features and the mechanism of the phase transition in KTN and

(iii) to study the influence of the niobium concentration upon these phenomena.

In contrast with earlier Raman experiments on the KTN system which usually concerned crystals with a low niobium concentration ($x \leqslant 0.03$) and low-frequency scattering only [3, 8, 10], our studies include crystals with a larger niobium concentration ($x \leqslant 0.11$) and are extended to high frequencies (up to 800 cm^{-1}). Indeed, whereas the behaviour of the low-frequency scattering is interesting for understanding the critical dynamics at the phase transition, the measurement of the entire Raman spectrum is of particular importance to knowledge of the various phases exhibited by the crystal as a function of temperature.

We present in this paper the Raman results which were made on KTN crystals with two different niobium concentrations: $x = 0.09$ and $x = 0.02$. The $KTa_{0.91}Nb_{0.09}O_3$ crystal should exhibit successive cubic-to-tetragonal-to-orthorhombic-to-rhombohedral phase transitions [13], as in pure $KNbO_3$ whereas the $KTa_{0.98}Nb_{0.02}O_3$ crystal is expected to undergo only the direct transition from the cubic phase to the rhombohedral phase [13].

2. Results

Raman measurements are performed in right-angle scattering geometries on KTN samples with (100) faces. Spectra are obtained with a Spex double monochromator using the 632.8 nm He–Ne laser line.

2.1. Analysis of the low-frequency spectrum

Figure 1 displays the Raman spectrum recorded at a low frequency in the $KTa_{0.91}Nb_{0.09}O_3$ crystal for several temperatures in the $Z(XX)Y$ configuration. Successive phase transitions are expected to occur at 91, 88 and 84 K. A 50 μm entrance slit of the spectrometer was chosen for these measurements. An intense phonon peak is detected in the spectra at 80, 70 and 20 K. This phonon exhibits a clear increase in frequency and intensity with decreasing temperature. Between 120 and 90 K, only a broad shoulder is observed at low frequencies in the spectrum. The double structure of the intense soft phonon peak (seen in the spectrum at 70 and 20 K) reveals degeneracy lifting of the lowest-frequency cubic F_{1u} (TO1) mode into the A_1 and E lines, according to the rhombohedral symmetry expected for the low-temperature phase. The small frequency difference between these lines is consistent with the weak cell distortion revealed by x-ray data [14].

Below 110 K, quasi-elastic scattering emerges between the Rayleigh line and the soft-phonon peak. As shown in figure 1, the intensity of this central peak is found to increase on cooling to 80 K, then to decrease and finally to vanish at around 40 K. Such a central peak is detected for 2, 5, 9 and 11 at.% Nb samples in our investigations and seems to be analogous to that previously reported for 0.8 and 3.2 at.% Nb samples
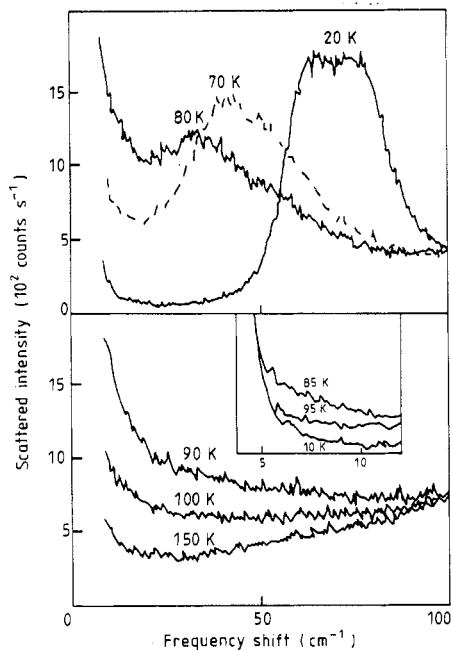
Figure 1. Low-frequency Raman spectrum in $KTa_{0.91}Nb_{0.09}O_3$ crystal recorded at various temperatures with a slit width of $50\,\mu m$ in the spectrometer entrance. The inset shows the onset of the quasi-elastic scattering as well as the Rayleigh line.
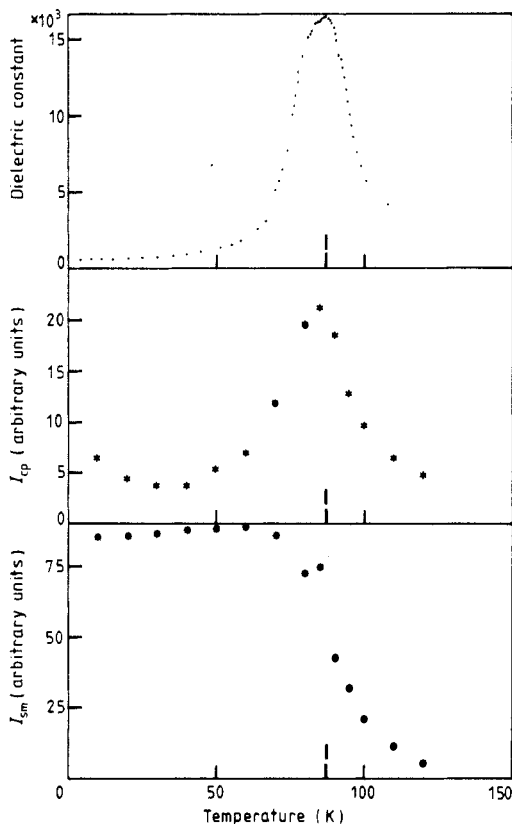

Figure 2. Temperature dependence of the integrated intensity I_{sm} for the soft mode and the integrated intensity I_{cp} for the central peak of $KTa_{0.91}Nb_{0.09}O_3$. These intensities are compared with the dielectric behaviour recorded at 10 MHz. T_c is taken to be equal to 88 K.

[8, 10] as well as for $KNbO_3$ [15]. Broad quasi-elastic scattering can be clearly discerned from the Rayleigh line (see the inset of figure 1) so that the I_2 filter absorption technique is not really needed in our investigation. The occurrence of the central peak at around T_c is confirmed by additional high-resolution measurements using a 10 μm spectrometer entrance slit, which allows us to determine the spectrum down to 1 cm^{-1}.

The above observations can be thoroughly understood in relation to the structural phase transitions when reporting the temperature dependence of the integrated intensity I_{cp} for the central peak and the intensity I_{sm} of the soft-mode peak. The integrated intensity is calculated from the following formula:

$$I = \int_a^b \frac{I(\omega)/\omega}{n(\omega) + 1}\, d\omega$$

where $n(\omega) + 1$ is the population factor for the Stokes scattering. For both quasi-elastic scattering and the soft mode the integrating limits a and b depend on the lineshape and thus on the temperature. In fact the scattered intensities arising from the central peak

and the soft mode can be superimposed in some frequency ranges. Therefore a value of $18 \, \text{cm}^{-1}$ is taken as the arbitrary limit between both peaks in the calculations for each temperature. The integrated intensities provide respective contributions from each peak to the dielectric permittivity, according to the Kramers–Kronig relation. The temperature dependence of the central-peak integrated intensity is therefore compared in figure 2 with that for the dielectric constant which is directly measured for the same KTN sample [16]. The reported dielectric data were taken at a frequency (10 MHz) below the large dispersion step which is detected versus frequency. A very pronounced peak at around 88 K is observed in the dielectric behaviour shown in figure 2. Two slight peaks at 84 and 91 K are estimated to lie one on each side of the large peak. Nevertheless, since the dielectric measurements together with the Raman data, shown below, do not yield a clear indication of successive phase changes, 88 K is taken as the sole transition temperature T_c.

The comparison between the intensity I_{cp} and the ε data shows that the maximum of the central peak occurs at a temperature (85 K) very close to T_c. Further, $\varepsilon(\text{expt})$ and I_{cp} exhibit very similar behaviours. The quasi-elastic scattering detected at around T_c can therefore be interpreted as the signature in the Raman spectrum of the relaxation mode found in the dielectric measurements [16].

We now turn to the behaviour of the integrated intensity I_{sm} of the soft-phonon mode. This intensity has a nearly constant value in the low-temperature phase from 10 to 75 K and then exhibits a steep fall at around T_c. Above T_c, it has a significant value which decreases with increasing temperature, so that it vanishes at around 120 K. This result is completely unexpected in that the one-phonon scattering forbidden by the cubic symmetry is present. The origin of this scattering strength which remains above T_c will be discussed below. By comparing the behaviour of the integrated intensities I_{cp} and I_{sm}, the decrease in the central-peak intensity seems to be connected with an increase in the soft-phonon peak below T_c. In addition, it is noticeable that both intensities vanish at around 120 K.

2.2. Analysis of the high-frequency spectrum

The Raman spectrum for the 9 at.% Nb sample extended to high frequencies is plotted as a function of temperature in figure 3. The spectrometer entrance slit was larger (200 μm) than for the low-frequency measurements, in order to detect the main first- and second-phonon scattering features, in addition to the broad central component and the soft-phonon peak. The presence of intense second-order scattering (denoted S in figure 3) makes it difficult to observe first-order Raman lines (denoted F) which could be induced by any disorder or structural change. Hopefully the second-order scattering bands were satisfactorily determined in a previous investigation [17].

The Raman spectra at 150, 80, 70 and 10 K plotted in figure 3 can be easily analysed. First, the spectrum at 150 K does not exhibit any feature induced by disorder and shows only well assigned second-order bands, which follow the normal light polarisation effect. At 80 and 70 K, in addition to the remaining second-order bands S_1 and S_5 the spectrum exhibits only first-order lines which can be seen more clearly in the spectrum at 10 K. The lines denoted F_1, F_2, F_3 and F_4 correspond to phonons issued from the soft F_{1u} (TO1), $F_{1u}(2)$, F_{2u} and F_{1u} (TO3) modes respectively of the cubic phase (according to the notation used for $KNbO_3$ [18]. The Raman spectrum below 80 K is shown to be independent of the light polarisation, consistent with the rhombohedral structure assumed for this phase [13].
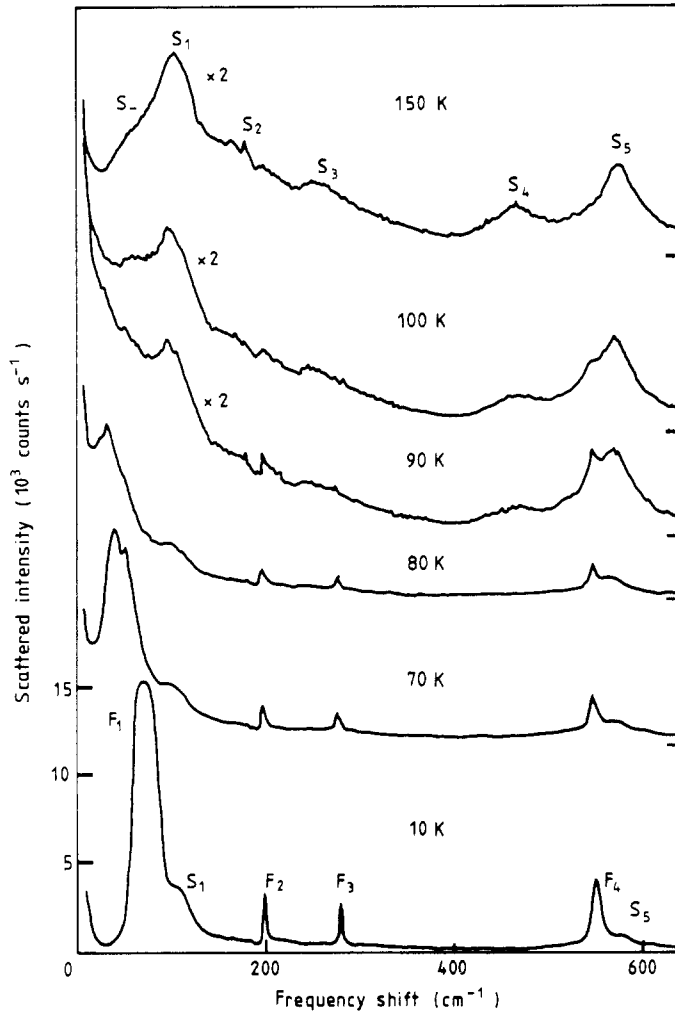
Figure 3. Temperature dependence of the whole Raman spectrum in a $KTa_{0.91}Nb_{0.09}O_3$ crystal. F denotes the first-order lines and S corresponds to second-order scattering peaks. These spectra are recorded with a slit width of 200 μm in the spectrometer entrance.

The spectra at 90 and 100 K are more complicated to analyse. First-order and second-order processes can be distinguished by their individual temperature dependences. Indeed, whereas the second-order bands decrease in intensity as expected when the temperature decreases, the first-order lines display a surprising increase in intensity. Compared with the spectrum at 80 K, some bands detected above T_c (88 K), but below 120 K, are indicative of some disorder process in the cubic phase or a precursor effect of the low-temperature phase. Thus, the scattered intensity between the central peak and the S$_-$ peak (arising from a second-order difference process TO1–TA [17]) exhibits an increase between 130 and 90 K, as already shown above (intensity I_{sm} above T_c in figure 2). This scattering may result from the activation above T_c, either of the TO$_1$ phonon or of the one-phonon density of states related to it. The continuous change in the low-frequency Raman spectrum through the transition temperature seems to show
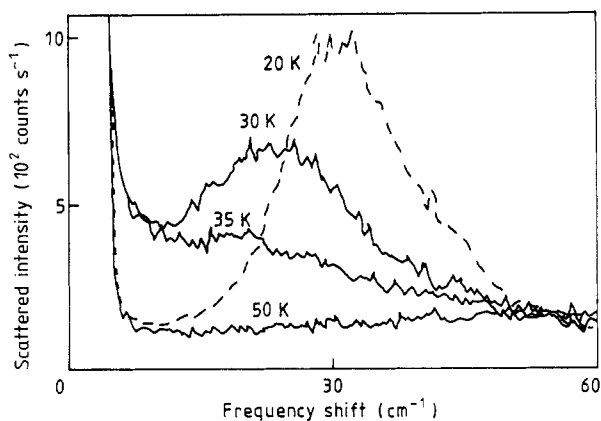
Figure 4. Low-frequency Raman spectrum of $KTa_{0.98}Nb_{0.02}O_3$ obtained at several temperatures, with a slit width of 50 μm in the spectrometer entrance.

that scattering above T_c has the same origin as the phonon peak in the low-temperature phase. The low-frequency intensity above T_c can therefore be attributed to the disorder-induced one-phonon process.

Likewise the shoulder which occurs on the low-frequency side of the S_5 peak for the spectra at 100 and 90 K is located at a frequency very close to the one-phonon peak F_4 detected below T_c. In addition the peak F_2 can also be estimated to appear in the spectrum at 90 K.

We can summarise the above observations as follows. The only phase transition in the $KTa_{0.91}Nb_{0.09}O_3$ crystal which is revealed by a significant change in the Raman spectrum should occur at around 88 K, between the high-temperature phase of average cubic symmetry and the low-temperature rhombohedral phase. This transition is reflected in the appearance of a well defined and intense first-order phonon peak which displays a large softening when T_c is approached from below. This phase transition seems to be connected to a broad central peak which is found to be a maximum at T_c. No evidence of intermediate orthorhombic and tetragonal structures is provided by our Raman investigations. The spectrum displays only phonon bands which are required by cubic symmetry for temperatures above 120 K and by rhombohedral symmetry below T_c (88 K). In the intermediate-temperature range between 120 and 85 K the Raman spectrum exhibits some features characterising the low-temperature phase and rendered active by local symmetry breaking which is also reflected in the existence of a central peak in the same temperature range.

2.3. Analysis of the Raman data in KTN with 2 at.% Nb

Similar observations to those above can be made for a crystal with a more dilute niobium concentration, namely the $KTa_{0.98}Nb_{0.02}O_3$ crystal which should undergo only a direct cubic-to-rhombohedral phase transition. Low-frequency Raman data are reported in figure 4. They reveal the existence of a broad central peak, besides a clear soft-phonon peak. The central-peak intensity is a maximum at 32 K close to T_c revealed by second-harmonic generation [9]. The spectrum at 50 K corresponds to the cubic phase whereas the spectra at 30 and 20 K characterise the rhombohedral structure. The spectrum at
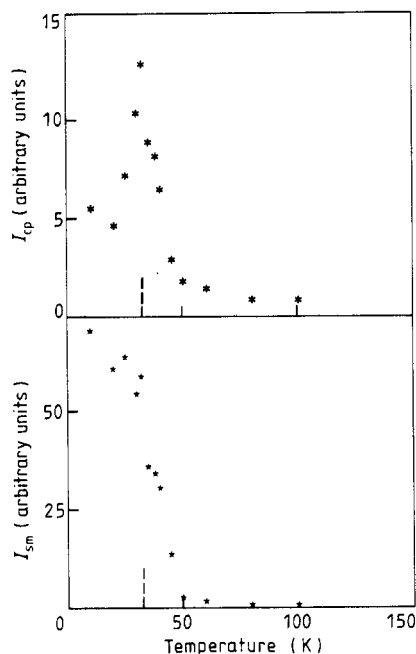
Figure 5. Temperature dependence of the integrated intensity I_{sm} for the soft mode and the integrated intensity I_{cp} for the central peak of $KTa_{0.98}Nb_{0.02}O_3$. T_c is taken to be equal to 32 K.

35 K reflects the intermediate state related to the local disappearance of the inversion centre.

Figure 5 displays the temperature dependences of the integrated intensities of the central peak and the soft phonon. In these calculations a frequency of 10 cm^{-1} is chosen as the limit between the two peaks for each temperature. The soft-phonon intensity displays an increase on cooling in the rhombohedral phase and a large jump at T_c. The scattering remaining at low frequencies above T_c completely disappears at around 50 K simultaneously with the central peak.

The KTN crystals with 2 and 9 at.% Nb therefore reveal similar features concerning critical dynamics. Only the width of the temperature range where these features are detected is different.

2.4. Interpretation

We can now tentatively propose a unified view of the mechanism of the phase transition in KTN. For this we consider the main experimental features revealed by our Raman spectra, namely the central-peak onset at around T_c, the existence of disorder-induced first-order lines above T_c and the vibrational soft mode below T_c.

At very high temperatures the structure is cubic and the niobium ions are on site. The Raman spectrum consistently exhibits only second-order phonon bands. When the temperature is decreased and approaches the phase transition, the niobium ions hop between several off-centre positions, as revealed by the appearance of quasi-elastic scattering. The dipolar clusters which form around relaxing niobium locally break the selection rules and thus lead to activation above T_c of the first-order phonon lines which are normally forbidden in the cubic phase. These lines concern the soft-phonon mode and the three hard modes associated with the KTN lattice. These phenomena characterise an intermediate state which on average retains cubic symmetry and is locally a precursor

of the rhombohedral structure of the low-temperature phase. At T_c the relaxation mode slows down [12] and the dipolar clusters are mainly growing. Below T_c, the off-centre Nb ions are frozen in, giving rise to polarisation along the $\langle 111 \rangle$ axis, consistent with the rhombohedral structure. As shown by the increase in the intensity of the soft and hard vibrational modes as the temperature decreases, the niobium ions move more cooperatively in the low-temperature phase, so that the ferroelectric long-range order can be reached.

This description can hold for a highly concentrated KTN crystal (9 at.%) as well as for dilute crystals (2 at.%). The Raman spectrum in the $KTa_{0.91}Nb_{0.09}O_3$ crystal displays no signature of the tetragonal and orthorhombic phases expected according to the low-frequency dielectric measurements. These phases are included in the temperature range covered by the intermediate state defined above. Consequently they can be interpreted as arising from a partial ordering of hopping off-centre niobium ions along the $\langle 001 \rangle$ and $\langle 101 \rangle$ axes, respectively.

3. Conclusion

The phase transitions in the KTN crystals can be described by a mechanism induced by relaxing dipoles around off-centre niobium ions which progressively break the cubic symmetry of the host lattice. In view of our low- and high-frequency Raman scattering measurements there is no qualitative difference in the dynamical behaviour between KTN crystals with 9 at.% Nb and those with 2 at.% Nb. An intermediate state seems to exist between the cubic and the rhombohedral phases in both crystals and is regarded as precursor ordering of the low-temperature phase. This intermediate state which does not obey cubic symmetry concerns a temperature range which increases with increasing niobium concentration (KTN crystals with 2, 5, 9 and 11 at.% Nb are considered for this). This temperature range is shown to be much larger than that covered by the expected tetragonal and orthorhombic phases.

Regarding the previous Raman studies in KTN we have emphasised in our own investigation the relation between the dynamics at high and low frequencies in the understanding of the phase transition mechanism.

We have particularly pointed out the presence of gradually growing clusters around off-centre niobium ions which are revealed by the simultaneous occurrence of the first-order phonon lines and the quasi-elastic scattering above T_c.

Acknowledgments

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