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LETTER TO THE EDITOR

Infrared spectroscopy of $KTa_{1-x}Nb_xO_3$ crystals

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Abstract

Fourier-transform infrared and time-domain THz dielectric spectroscopy measurements on $KTa_{1-x}Nb_xO_3$ crystals for $x = 0.018$ and 0.022 were performed. The temperature behaviour of the soft mode frequency and damping have been determined above the ferroelectric phase transition. No dielectric dispersion in the frequency range below the polar phonon absorption is observed down to kHz frequencies at temperatures from room temperature down to 60 K. At lower temperatures the $KTa_{1-x}Nb_xO_3$ samples become opaque due to additional losses, which persist down to liquid helium temperatures. This supports the nanoscopic dipolar glassy state rather than macroscopic ferroelectricity at low temperatures.

1. Introduction

Pure $KTaO_3$ belongs to the group of incipient ferroelectrics. The permittivity of these materials obeys the Curie–Weiss law at high temperatures but saturates at low temperatures due to the quantum fluctuation effects. The structure of $KTaO_3$ remains cubic perovskite down to 0 K. The permittivity of a pure crystal is fully determined by the contribution of three IR-active polar phonon modes. The most significant contribution is due to the lowest TO_1 mode which softens on cooling.

Substitutional doping of $KTaO_3$ with certain ions (e.g. Nb or Li) is known to induce the ferroelectric phase transition or lead to relaxor-type behaviour [1]. The formation of a dipolar glass-like state is also possible in such systems [2, 3]. A large variety of phenomena such as competition between short- and long-range order, relaxation of nanoscale polarization clusters, glass-like freezing of polar cluster dynamics etc have been revealed and studied during the last two decades. The relative simplicity of the system and the possibility to vary the concentration of the doping ions made $KTa_{1-x}Nb_xO_3$ (KTN) and $K_{1-x}Li_xTaO_3$ (KLT) model systems for experimental and theoretical study of the mentioned phenomena.

It is reliably established that the small Li^+ ions occupy off-centre positions on the potassium sites, creating a local dipole moment. The approximate value of the off-centre shift is 1.3 Å according to different experimental results [4–6]. Thus the local dipole moment of the Li^+ ion is relatively large.

The situation in KTN is different because Nb^{5+} and Ta^{5+} ions have approximately the same radius so that the off-centre displacement should be rather small. According to the theoretical model of Girshberg and Yacoby [7] a strong non-uniform electron–phonon interaction leads to some off-centre displacements of Nb ions in KTN. The value of this displacement in $KTa_{0.91}Nb_{0.09}O_3$ found by means of x-ray absorption fine-structure measurements [8] is 0.14 Å along the ⟨111⟩ direction, i.e. smaller by an order of magnitude than Li displacements in KLT. On the other hand, *ab initio* calculations [9] predict narrow a potential well for Nb atoms in KTN without off-centre minima. The conclusion about the centrosymmetric position of Nb in KTN (above the phase transition) has been drawn from the experimental NMR study [10]. Thus the question about the value of Nb displacement in $KTa_{1-x}Nb_xO_3$ and about its role in the observed phase transition is still under discussion.

A great deal of experimental work has been devoted to the investigation of KTN and KLT systems. However, concerning far-infrared and THz spectroscopy, there is a lack of published experimental data. To the best of our knowledge, no systematic study by means of infrared (IR) and THz spectroscopy has been published yet, except for our preliminary data [11–13]. Nevertheless, such measurements bring valuable information about polar excitations including the soft mode and build a bridge between the IR and microwave (MW) ranges of the dielectric spectrum in these materials, which is usually quite complex in ferroelectrics and related materials.

The aim of the present study was to apply time-domain terahertz transmission spectroscopy (TDTTS) to the investigation of the dielectric response of $KTa_{1-x}Nb_xO_3$ systems and combine the results with those of Fourier transform IR (FTIR) spectroscopy, in order to determine the soft mode dynamics, possible structural changes in the materials and the existence of 'central mode'-like excitations.

2. Experimental details

KTN single crystals with orientation (100) were grown using a spontaneous crystallization process. Two KTN samples with Nb concentration $x = 0.018$ (provided by Dr L A Boatner, Oak Ridge National Laboratory, USA) and $x = 0.022$ (provided by Dr P P Syrnikov, A F Ioffe Physico-Technical Institute, St Petersburg, Russia) were studied. The niobium concentration was checked by various analytical methods with the precision around 100 ppm (see [14] for details).

The complex permittivity of KTN samples in the THz frequency range (3–80 cm^{-1}) was measured by a home-made TDTTS set-up [15]. The samples for transmission measurements were prepared in the form of plane-parallel plates. In view of the very high losses at low temperatures the samples were made as thin as possible, having thickness 55 μm. The far-IR reflectivity (20–650 cm^{-1}) was measured using a Bruker 113v FTIR spectrometer. The combined fitting of the reflectivity spectra was performed using a factorized oscillator model [16]

$$\epsilon^*(\omega) = \epsilon_\infty \prod_{j=1}^{n} \frac{\omega_{\mathrm{LO}_j}^2 - \omega^2 + \mathrm{i}\omega\gamma_{\mathrm{LO}_j}}{\omega_{\mathrm{TO}_j}^2 - \omega^2 + \mathrm{i}\omega\gamma_{\mathrm{TO}_j}}, \tag{1}$$

where ω_{TO_j} and ω_{LO_j} are transverse and longitudinal frequencies of the jth polar phonon mode, respectively, γ_{TO_j} and γ_{LO_j} their respective damping constants and ϵ_∞ the optical

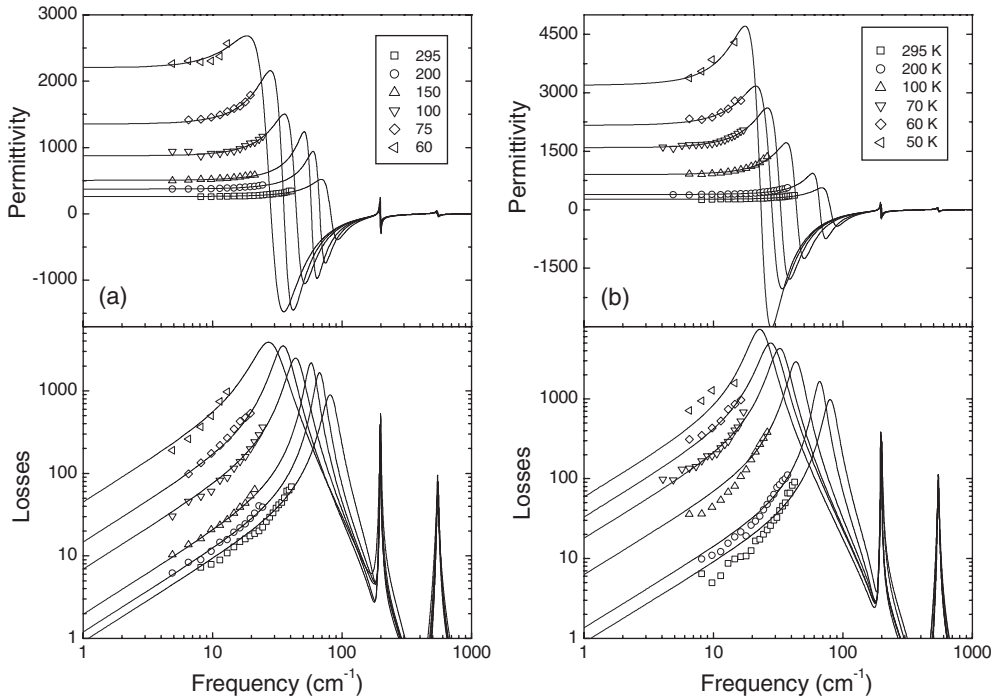

Figure 1. THz permittivity and losses in $KTa_{1-x}Nb_xO_3$ for $x = 0.018$ (a) and 0.022 (b). Solid lines are fits to the oscillator model.

permittivity due to the electronic polarization processes. The parameters of equation (1) were fitted to describe simultaneously the complex permittivity obtained by TDTTS and normal incidence reflectivity from FTIR measurements. The combined fitting of the reflectance and transmittance spectra also suppressed the influence of the sample surface.

3. Results and discussion

Some results of the THz complex permittivity measurements together with fitting curves of IR reflectivity are presented in figure 1. The factorized oscillator model provides satisfactory agreement with permittivity and losses for all the measured spectra. Below 50 K down to liquid helium temperature the samples were completely opaque in the THz range. The permittivity increases on cooling as a result of the TO_1 mode softening. The other two IR-active phonon modes TO_2 and TO_4 have only slightly different parameters compared to those of pure $KTaO_3$.

It should be stressed that no polar excitation recalling the central peak is observed in KTN samples in the investigated temperature range within the experimental accuracy of the TDTTS and FTIR technique. This is in contrast to KLT samples, where the mode assigned to relaxational hopping of Li ions among off-centre positions has been observed near room temperature [13, 17]; however, it agrees with the negligible off-centring of the Nb ions.

Further evidence for the weak character of Nb-ion relaxation in KTN apart from T_c comes from the comparison of phonon contribution to permittivity with low frequency permittivity of the same sample taken from [14]. The results for $KTa_{1-x}Nb_xO_3$ with $x = 0.018$ are shown in figure 2. One can see that within the experimental error there is no dielectric dispersion from kHz up to the THz range at temperatures above 60 K.

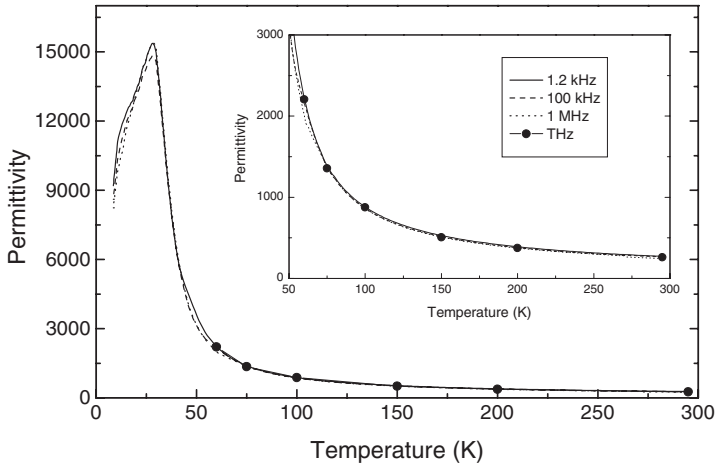

Figure 2. Low frequency permittivity as a function of temperature and the phonon contribution to permittivity determined from the fits for $KTa_{1-x}Nb_xO_3$ with $x = 0.018$.

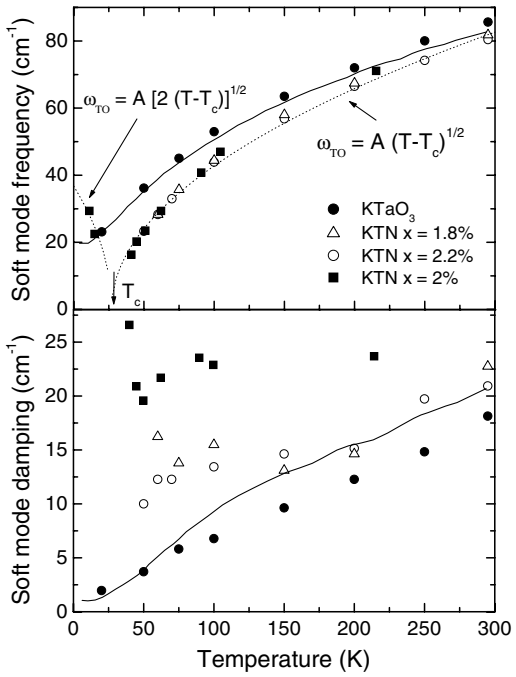

Figure 3. Frequency and damping constant of the soft mode in KTN and $KTaO_3$ as a function of temperature. Solid lines and full squares correspond to hyper-Raman results for pure $KTaO_3$ taken from [18] and $KTa_{1-x}Nb_xO_3$ with $x = 0.02$ from [19], respectively. The dotted line for KTN is the approximate fit to the Cochran law ($T_c = 27$ K).

The soft mode frequency and damping constant as a function of temperature obtained from the fits are shown in figure 3 for $x = 0$; 0.018 and 0.022 compared with hyper-Raman results of Vogt [18] for pure $KTaO_3$ and Kugel *et al* [19] for $x = 0.02$. The agreement between our IR results and the hyper-Raman data of Vogt is rather good, especially concerning the soft

mode frequency, in contrast to the recently published data of Ichikawa *et al* [20], where IR results deviate from hyper-Raman data near room temperature. Perhaps the better agreement of our results is due to the combination of THz data with FTIR reflectivity, which takes into account all IR-active modes.

The Nb doping of $KTaO_3$ decreases the soft mode frequency and induces its critical slowing down in the vicinity of the phase transition temperature $T_c \simeq 27$ K. This behaviour is in contrast with the Li doping, which stiffens the soft mode and does not show any temperature anomaly near the phase transition in the far IR response. Our results on the soft mode frequency are in good agreement with the hyper-Raman measurements for KTN with $x = 0.02$. The damping constants extracted from the fits are higher than for pure $KTaO_3$ and are almost temperature independent but somewhat lower than those found from hyper-Raman measurements. The temperature dependence of the soft mode frequency for both investigated KTN crystals can be approximately fitted to the Cochran law (see figure 3). Deviations from this law are expected in the vicinity of T_c as predicted for quantum ferroelectrics; however, measurements of the soft mode response were not possible because the samples become opaque near the transition. In hyper-Raman scattering the soft mode becomes overdamped near T_c and the measurements are also not accurate enough. Below the phase transition, where the samples are opaque in the THz range, the hyper-Raman [19], neutron and Raman scattering [21] experiments reveal a soft mode which stiffens approximately following the Cochran law with proportionality constant renormalized according to thermodynamic mean-field theory [22] (see figure 3). In the immediate region of T_c its softening is, however, incomplete to about 10 cm^{-1} at T_c as found in [21].

On further cooling below T_c, the soft mode should move again to higher frequencies (hardening) and the material should become transparent. This is, however, not the case for KTN, which remains opaque below the phase transition. It is seen in figure 3 that at 10 K the soft mode should appear near 30 cm^{-1} from the hyper-Raman scattering, which could also be seen by TDTTS. In KTN with $x = 0.022$ at 50 K the detected soft mode frequency is 23.3 ± 0.5 cm^{-1}. The soft mode splitting measured by Raman spectroscopy below T_c (at 15 K) is rather small: 3 cm^{-1} for KTN with $x = 0.018$ [23] and 6.5 cm^{-1} for KTN with $x = 0.024$ [24], and the effective IR soft mode response itself seems not to be sufficient to make the KTN samples opaque. Therefore, some additional mechanisms of dielectric losses in the THz range start to be effective below T_c. One of them may be piezoelectric resonances in polar regions [25], which should be smaller than a few tens of nanometres in order to bring the resonance frequencies up to the THz range. This is in reasonable agreement with recent dielectric and Raman study of the same KTN sample with $x = 0.018$ [23], which suggests a short-range dipole order in KTN below the phase transition. The physical picture proposed in that paper is the following. On cooling from room temperature, the system behaves as a conventional displacive-type ferroelectric. However, the soft mode softens only locally in the regions enriched by Nb ions. Below T_c these regions of nanoscale size acquire dipole moments which interact with each other, leading to their freezing into a glass-like state. This so-called re-entrant glass scenario has also been recently supported by dielectric measurements [26]. Further evidence for short-range order in KTN at liquid helium temperatures was found by Kleemann *et al* [27] from the measurements of the refractive index and linear birefringence as a function of temperature. For $KTa_{1-x}Nb_xO_3$ with $x = 0.02$ they found that about 80% of the polarization contribution to the change of refractive index consists of short-range polarization fluctuations and only 20% is due to long-range order also contributing to linear birefringence.

Another mechanism responsible for the non-transparency below T_c can be a quasi-Debye relaxation based on microscopic phonon transport theory [28]. It predicts that far below the eigen-frequency, two-phonon difference decay processes dominate the dielectric spectrum. These processes can only be activated in a polar medium and induce additional absorption.

4. Conclusion

Far-IR spectroscopic measurements on $KTa_{1-x}Nb_xO_3$ crystals with $x = 0.018$ and 0.022 above the ferroelectric transition temperature have demonstrated a critical softening of the soft mode following the Cochran law. The soft mode frequencies and damping constants extracted from combined fits of FTIR reflectivity and TDTTS complex permittivity spectra are in good agreement with previously published Raman and hyper-Raman data. The phonon contribution to permittivity coincides with the permittivity measured in the kHz range, proving absence of noticeable dielectric dispersion below the IR range down to 60 K. No indication of central-mode type dispersion related to Nb hopping among potential minima is observed in the THz spectra. Below 60 K the KTN samples become opaque due to the enhanced losses, which persist down to liquid helium temperatures. Taking into account the soft mode hardening [21, 19] at these temperatures, we assume the appearance of polar excitations related to the piezoelectric resonances inside the polar nanoclusters similarly to the $K_{1-x}Li_xTaO_3$ system or quasi-Debye losses.

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