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## Glassy and ferroelectric aspects of potassium tantalate niobate

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**Abstract.** The dielectric susceptibility obtained for a crystal of  $\text{KTaO}_{0.96}\text{Nb}_{0.04}\text{O}_3$  is presented as a function of temperature and frequency. The data are analysed in terms of parameters describing the relaxation strength and the width of the relaxation time distribution around an average value. The results are compared with those reported for  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  crystals with lower niobium concentration ( $x = 0, 0.0075$  and  $0.02$ ). The degree of disorder introduced by niobium is thus described as function of niobium concentration. It is shown that the phase transition in  $\text{KTaO}_{0.96}\text{Nb}_{0.04}\text{O}_3$  cannot be interpreted by the *usual* ferroelectric picture, nor by the glass-like behaviour.

### 1. Introduction

$\text{KTaO}_3:\text{Nb}$  (KTN) had been considered as a prototype ferroelectric for a long time [1, 2] until Samara [3] suggested that it was actually glass like. His proposal rested on the observation of dielectric dispersion in the kilohertz range under hydrostatic pressure. He concluded that at ambient pressure, where no dielectric dispersion was observed, Nb ions stay off-centre for arbitrarily long times and that they were not correlated over macroscopic ranges. According to this picture KTN would be glass like.

Samara's findings prompted a search for other evidence of glass formation in KTN. In particular, it was found that microscopic ferroelectric regions already existed in pure  $\text{KTaO}_3$  [4] and critical non-linear polarizability results were interpreted in terms of glass formation [5]. On the other hand the relaxation rates of both the Ta and the Nb nuclear moments in a magnetic field were critical, i.e. they behaved as  $\tau^{-1} \propto T - T_c$  as in ordered material undergoing a phase transition rather than Arrhenius like, i.e.  $\tau^{-1} \propto \exp(-E_b/kT)$ , as in  $\text{KTaO}_3:\text{Li}$  glass [6]. Furthermore the lattice mode of relaxation in  $\text{KTaO}_3$  observed at some  $10^8$  Hz was little influenced by Nb doping and showed critical slowing down as well [7].

In this paper we attempt to reconcile these findings. With this aim we present dielectric dispersion measurements on samples in a wider concentration range. The

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data are evaluated quantitatively in terms of parameters describing the relaxation strength, time scale and, for the first time in KTN, width of relaxation time distribution. By relating the three parameters for ordered and disordered systems we hope to gain insight into the degree of disorder produced by Nb and its evolution with Nb concentration.

## 2. Experiment

The samples have been grown by the spontaneous-nucleation technique [8], cut along (100) crystallographic axes, polished and electroded by Au vapour deposition. The concentrations  $x$  were determined by laser-induced mass spectroscopy. The samples were placed into cryogenic environment with a long-term temperature stability of 10 mK. In this section, we present dielectric susceptibility data obtained for a crystal of  $\text{KTa}_{0.96}\text{Nb}_{0.04}\text{O}_3$ , compared with the results previously reported for KTN samples with  $x = 0$ ,  $x = 0.0075$  and  $x = 0.02$  [7].

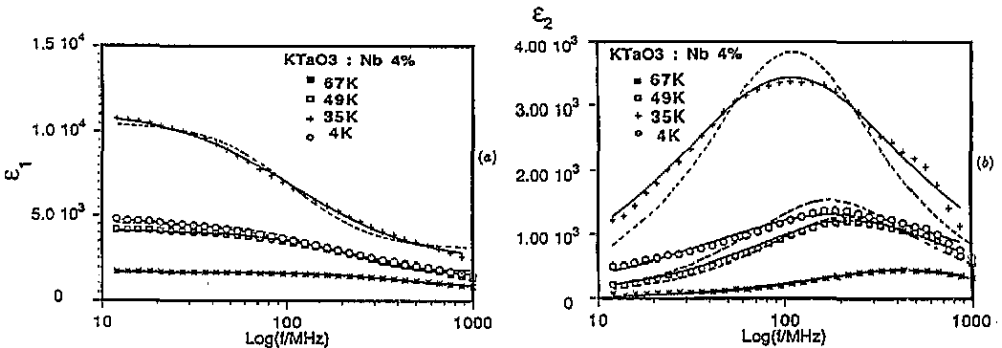


Figure 1. (a) Real and (b) imaginary parts of the dielectric susceptibility versus  $\log f$ : ---, fit to the Debye function (equation (1)) (unsatisfactory); —, fit to the Debye-Wagner function (equation (2)).

The real and imaginary parts of the susceptibility obtained for  $\text{KTaO}_{0.96}\text{Nb}_{0.04}\text{O}_3$  are shown in figure 1 as functions of frequency:

$$\epsilon - \epsilon_\infty = \Delta\epsilon / (1 - i\omega\tau) \quad (1)$$

which obviously do not fit the data. We have thus adopted a generalization of the Debye dispersion curves of the form [9]

$$\epsilon - \epsilon_\infty = \Delta\epsilon \int \frac{g(\tau) d\tau}{1 - i\omega\tau} \quad (2a)$$

where  $g(\tau)$  is a log-normal distribution given by

$$g(\tau) = (\pi\Delta)^{-1/2} \exp\left\{[\ln(\tau - \tau_m)]^2 / \Delta^2\right\}. \quad (2b)$$

This Debye–Wagner function contains a parameter  $\Delta$ , describing the width of the relaxation time distribution on a  $\ln$  scale around the average value  $\tau_m$ , in addition to the parameter  $\Delta\epsilon$  common to both expressions. The Debye–Wagner expression reduces to the Debye-like expression for  $\Delta = 0$  ( $\tau = \tau_m$ ).

A fit of equation (2) to the data is also shown in figure 1 and is much more convincing than the fit of equation (1) to the data. The parameters obtained are for 35 K:

$$\Delta\epsilon = 9054 \quad \epsilon_\infty = 2368 \quad \tau_m = 1.5 \times 10^{-9} \text{ s} \quad \Delta = 1.2.$$

Now we compare the behaviour for KTN with  $x = 0.04$  with the behaviour of other samples with smaller amounts of niobium or with no niobium at all. We present in figure 2 the average relaxation rate as a function of temperature for four niobium concentrations. For  $KTa_{0.96}Nb_{0.04}O_3$ ,  $\tau^{-1}$  does not fit a law  $A(T - T_c)^\gamma$  in contrast with the situations for the crystals with  $x = 0.0075$  and  $x = 0.02$  where  $T_c < 3$  K and  $\gamma = 1.7T_c = 34.5$  K and  $\gamma = 1$ , respectively, are found [7]. The dispersion step  $\Delta\epsilon$  is plotted as a function of temperature in figure 3 for the various concentrations. Again  $\Delta\epsilon^{-1}$  was found to fit  $(T - T_c)^\gamma$  for crystals with  $x \leq 0.02$  [7], whereas a more complex behaviour is reported for  $x = 0.04$ .

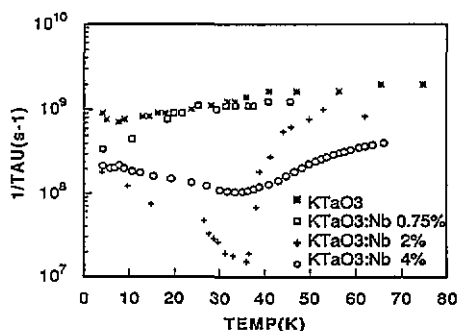


Figure 2. Temperature dependence of the relaxation rate  $\tau^{-1}$  for various Nb concentrations.

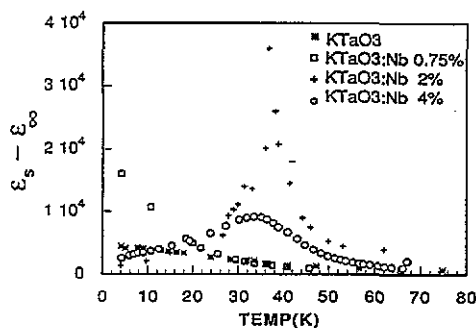


Figure 3. Temperature dependence of the relaxation strength  $\Delta\epsilon$  for various Nb concentrations.

All this indicates that both the susceptibility and the relaxation rate are critical functions of temperature as predicted for the ferroelectric limit as long as  $x \leq 0.02$ . In figure 4 we report the distribution width  $\Delta$  as a function of temperature. For the concentration  $x = 0.04$ , large values of the width  $\Delta$  are found,  $0.7 \leq \Delta \leq 1.6$ , clearly indicative of a polydisperse behaviour.  $\Delta$  appears to be a monotonic function of temperature without any sign of criticality at any temperature. For  $x = 0$  and  $x = 0.0075$ ,  $\Delta$  is very small for all temperatures whereas  $0.4 \leq \Delta \leq 0.8$  is found for  $x = 0.02$ . For this concentration, these values are nevertheless too low to conclude the relevance of Debye–Wagner law as a fit for the dielectric susceptibility. This can be clearly seen in figure 1 where at 67 K no significant difference between the data for the fits with equations (1) and (2) for  $\Delta = 0.8$  is found.

Up to the concentration  $x = 0.02$ , KTN can thus be considered as ferroelectric with regards to the susceptibility since its frequency dependence is monodispersive and its temperature behaviour is essentially given by the Curie–Weiss law even if

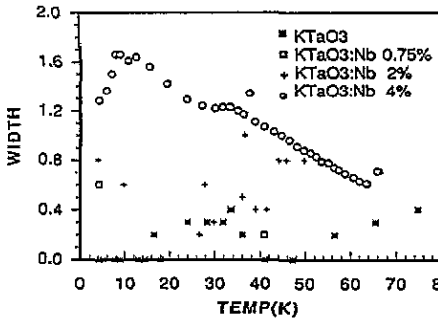


Figure 4. Width of log-normal distribution of relaxation times  $\Delta$  versus temperature, as obtained for various Nb concentrations.

some deviations from  $\gamma = 1$  are noticed for  $x = 0.0075$ . These features are quite comparable with those found in prototype ferroelectrics such as  $\text{BaTiO}_3$  [10]. An order-disorder mechanism can be associated with both compounds but subsequent differences exist. For KTN with  $x \leq 0.02$  no bulk distortion is observed [11] at the transition and the long-range displacement correlation is never infinite. The sample doped with 4 at.% Nb requires, however, a particular interpretation to which we now turn.

### 3. Interpretation

The character of the dielectric dispersion changes quantitatively and qualitatively with the Nb concentration; there are essentially two regimes. For  $0 \leq x \leq 0.02$  both the relaxation rate and  $\epsilon^{-1}$  vary with temperature as  $(T - T_C)^\gamma$ . The relaxation step is monodispersive. These findings are compatible with the notion of an order-disorder transition. We imagine pentavalent ions Ta and Nb which move in phase. Their coherence length increases and their motion slows as  $T$  goes to  $T_C$  [7]. Below  $T_C$  they form a polar phase with a domain structure of macroscopic size [12, 13]. Deviation from this behaviour occurs at 4 at.% Nb; the relaxation rate and  $\epsilon^{-1}$  go through a flat minimum at a temperature which can hardly be called critical and the relaxation step is polydispersive at all temperatures.

Often in the past [2, 14] such behaviour has been related to compositional inhomogeneity of the sample on a macroscopic scale. This implies that  $T_C$  is distributed in the sample which leads to a convolution of the responses with this distribution. However, within this model the distribution width  $\Delta$  should not be temperature dependent as shown in figure 4. Compositional inhomogeneity does therefore not account for the observed feature.

Having discarded this rather trivial explanation, we focus our attention on the role of Nb in KTN. It has been pointed out [15] a long time ago that Nb has a stronger affinity to oxygen than Ta has. Accordingly, the average interaction between B site ions and oxygen in perovskite is enhanced by Nb addition and  $T_C$  is raised. In this model, periodic symmetry is not broken and the predictions for the dielectric response are thus exactly like those for ferroelectrics:

$$\epsilon \propto (T - T_C)^{-\gamma} \quad \tau \propto (T - T_C)^{-\delta} \quad \Delta = 0.$$

If the Nb ions do, however, go off centre, they carry a dipole moment and accordingly they interact with one another. This interaction should be random in view of the

random occupation of sites [16]. The predictions of the model involving random interaction only are as follows:  $\epsilon \propto (T - T_C)^{-1}$  above  $T_C$  and constant below  $T_C$ ;  $\tau$  monotonic with temperature and  $\Delta > 0$ . We note that the predictions of the ferroelectric model describe the findings for the low Nb concentration  $x = 0.0075$  and  $0.02$  but not for  $x = 0.04$  whereas the predictions of the glass models are at variance with all findings except for the observation of a non-zero  $\Delta$  at  $x = 0.04$ . This complexity requires a model which is more complex than the simple models of ferroelectricity and of spin glasses [3].

We discuss our results in the framework of the independent-cluster approximation. In this model, each Nb ion polarizes in  $KTaO_3$  unit cells. The relaxation motion of these polarized clusters gives rise to the observed radio-frequency dielectric dispersion. When the clusters are not interacting, the dispersion step  $\Delta\epsilon$  may be described by the Debye-Langevin equation

$$\Delta\epsilon = Np^2/3k_B T\epsilon_0 \quad (3)$$

where  $N$  is the number of clusters and  $p$  is the effective dipole moment of each cluster. Since the soft-mode frequency decreases on approaching  $T_C$  from above and below, the vibrational amplitude as well as the ionic polarizabilities along  $\langle 100 \rangle$  axis increase [15]. This leads to an increase in  $p$  and to the divergence of  $\Delta\epsilon$ .

In the dilute case, (Nb concentrations  $x = 0, 0.0075$  and  $0.02$ ) the cluster size can be extended to a long range owing to the large distance between the two first niobium neighbours. This explains the large dispersion step at  $T_C$  and the slow relaxation rate  $\tau^{-1}$  at  $T_C$ . The increase in  $\Delta\epsilon(T_C)$  and decrease in  $\tau^{-1}(T_C)$  when  $x$  goes from 0 to 0.02 can be related to the increasing number of non-interacting clusters (see equation (3)). For  $x > 0.02$ ,  $N$  is so high that the size of each cluster has to decrease. Consequently,  $p$  and thus  $\Delta\epsilon$  decrease whereas the relaxation rate becomes higher. The Nb concentration  $x = 0.02$  can therefore be considered as the percolation threshold. This picture is consistent with the analysis of the NMR results given by Van der Klink *et al* [17]. These workers show that, in the dilute case, each off-centre Nb ion is able to polarize 100  $KTaO_3$  unit cells. When  $x$  is higher than 0.02, our results show that this number cannot increase and can be considered as a maximum, yielding a distance between two Nb ions corresponding to the percolation threshold. Above this percolation threshold, for  $x = 0.04$ , the interaction between the clusters should be random in view of the random occupation of sites [16].

A decrease in  $\tau^{-1}$  and an increase in the correlation length  $\xi$  are expected as the temperature approached  $T_C$  from above or as the niobium concentration  $x$  (or cluster size) increases. Inspection of figure 2 shows that these predictions are valid. Thus the relaxation rate decreases with increasing  $x$  in the paraelectric phase whereas it slows down on approaching  $T_C$  for  $x = 0.02$ . A deviation is detected for  $x = 0.04$  in the close vicinity of  $T_C$ . The relaxation rate indeed stays large and therefore  $\xi$  is finite. This is probably related to the number of clusters which is so large that the size of each cluster can no longer increase. The niobium concentration of 0.04 consequently reduces the polar correlation into the cluster. Such a finding is contrary to the notion of ferroelectricity where the correlation length should diverge at  $T_C$ . The explanation in terms of finite correlation lengths is supported by observation by light scattering [5, 11], second-harmonic generation [12], x-ray [13], hyper-Raman [18] and NMR [17] investigations.

In view of the virtual-crystal approximation,  $T_C$  increases with increasing  $x$ . Furthermore, Nb is a source of a local field as well. These fields have random sites

and lead to random interactions between Nb, increasing with increasing  $x$  as well. Random interaction gives rise to flattening of otherwise sharp Curie–Weiss branches of  $\epsilon^{-1}$  versus temperature. If dominant, they lead to a dipole–glass transition. At 4 at.% Nb, random interactions are still not dominant, in contrast with interactions between strongly off-centre Li ions in KTL [16]. In fact the relaxation time is neither of the critical type ( $\tau^{-1} \propto T - T_C$ ) nor Arrhenius like and the distribution of relaxation times is only moderately wide ( $\Delta < 2$ ) rather than wide as for KTL. Despite signs of disorder we believe that KTN is essentially ferroelectric and suggest that the transition may be termed diffuse but not glass like.

#### 4. Conclusions

KTN shows essentially ferroelectric features for  $x \leq 0.02$ : a Curie–Weiss branch for the monodispersive dielectric susceptibility and critical slowing down. If  $x = 0.04$ , the Curie–Weiss branches are rounded, and relaxation is uncritical and polydispersive. These features are traced back to the onset of interaction between Nb dipolar impurities at random site. The polar phase of KTN is ferroelectric with much reduced polar correlation but not glass like in the terminology of spin glasses.

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