

Polaronic relaxation in perovskites

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We report a low-temperature loss anomaly in several oxidic perovskites such as KTaO_3 , $\text{KTaO}_3\text{:Nb}$, SrTiO_3 , $\text{SrTiO}_3\text{:Ca}$, $\text{PbTiO}_3\text{:La}$, Cu , and $\text{BaTiO}_3\text{:La}$. We show that this anomaly arises from a low-frequency dielectric relaxation. The activation energy and the relaxation time of this process are nearly the same for all the investigated perovskites disregarding their composition, texture, and ferroelectric properties. We thus ascribe the loss anomaly to the localization of polarons on residual defects. Although the dielectric losses in SrTiO_3 and $\text{SrTiO}_3\text{:Ca}$ are qualitatively similar to other perovskites, the loss anomaly occurs at much lower temperatures: 10 instead of 40 K.

I. INTRODUCTION

Residual defects may contribute to the macroscopic susceptibility of dielectric materials, mainly at low temperature. In this respect, oxidic perovskites (ABO_3) are very interesting for at least two reasons: they display a large variety of lattice properties, and very good crystal quality has been achieved.

Potassium tantalate (KTaO_3) and strontium titanate (SrTiO_3) are perovskites which have nearly the same lattice properties. They remain paraelectric down to very low temperatures.¹ An incipient ferroelectric state is canceled by the quantum fluctuations for $T < 10$ K.² As a result, their dielectric susceptibility increases when T decreases following a modified Curie law $\epsilon_1 \approx C/T^\gamma$. At 4 K, ϵ_1 is usually of the order of 5000 and no dielectric dispersion was observed at low frequency ($f \leq 10^6$ Hz) in the early experiments.

Recently, a very small anomaly in KTaO_3 at $T \approx 40$ K ($f = 1$ kHz) both in pure and slightly doped KTaO_3 was reported.³ This dielectric relaxation was fitted using a Cole-Cole equation. The temperature variation of the mean relaxation time was Arrhenius like, leading to an activation energy of about 75 meV. The relaxation strength was about 200 times smaller than the low-frequency dielectric susceptibility. This explains why this relaxation escaped early dielectric investigations.⁴ Moreover, the relaxation strength could be decreased when the $\text{KTaO}_3\text{:Fe}$ sample was reoxidized, showing that oxygen vacancies play some role in this relaxation. Recently a maximum of the dielectric losses has been found below 20 K in SrTiO_3 (Ref. 5) and a connection was made with the possible novel phase of SrTiO_3 below 40 K.

Moreover, a slight loss anomaly was observed in the vicinity of 40 K in intentionally doped compounds. This was the case of La-doped perovskites $\text{SrTiO}_3\text{:La}$ (Ref. 6) and $\text{BaTiO}_3\text{:La}$.⁷ Thus a number of such anomalies has already been reported in several perovskites of different composition, texture, and ferroelectric properties. How-

ever, the interpretations were up to now different from one compound to another.

In the present study, we wish to collect a number of data in several doped perovskites. To this aim, dielectric measurements in $\text{SrTiO}_3\text{:Ca}$, $\text{PbTiO}_3\text{:La,Cu}$, and in $\text{BaTiO}_3\text{:La}$ were performed.

It is also important to check whether the 40 K anomaly is still observed in crystals with very different lattice properties. That is why we have investigated up to ten samples of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ ($0 \leq x \leq 5\%$) in order to clarify the lattice dynamical contribution to the above-mentioned relaxation. In fact, the lattice properties of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ are strongly dependent on the Nb content: for $x_{\text{Nb}} \leq 0.75$, $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ remains paraelectric while it is ferroelectric for $x_{\text{Nb}} \geq 2\%$ with some glasslike properties in the intermediate range $0.75\% \leq x_{\text{Nb}} \leq 2\%$.⁸

We have found a dielectric anomaly below 40 K in all the investigated samples disregarding their composition, growth, texture, and ferroelectric properties. The strength and activation energy of this relaxation are similar for all the compounds apart from SrTiO_3 and $\text{SrTiO}_3\text{:Ca}$, where a thermally activated Arrhenius law is not observed. We thus propose a common model for all these observations, namely, the relaxation of polarons resulting from the occurrence of residual point defects in all compounds.

SAMPLES AND EXPERIMENTS

We have used up to forty samples: crystals and ceramics. The ceramics were all produced in our laboratory. The BaTiO_3 ceramic specimens doped with La_2O_3 and PbTiO_3 doped with La_2O_3 and CuO were prepared by the conventional solid-state technique from the oxides as raw materials. Their structure and homogeneity were checked by powder x-ray measurements and electron microscopy.

From x-ray and chemical analysis on La-doped

perovskites (ABO_3 :La), most of the La^{3+} ions are expected to substitute only for A^{2+} ions. Lanthanum ions carry excess positive charges which, for electric neutrality, can be compensated in two ways: on one hand, by the formation of conducting electrons, and on the other hand by A vacancies. In slightly La-doped $BaTiO_3$ ceramics, the substitution of Ba^{2+} by La^{3+} releases a negative charge carrier and reduces partially Ti^{4+} to Ti^{3+} . Thus these compounds correspond to the chemical formula $Ba^{2+}_{1-y}La^{3+y}(Ti^{4+}_{1-y}Ti^{3+}_y)O_3$, whereas cationic vacancies form at higher concentrations.⁹ In the case of La-doped $PbTiO_3$, vacancies are introduced in the lattice and the sample compositions can be expressed as $(Pb_{1-3/2y}La_y\Box_{1/2y})TiO_3$ ($0 \leq y \leq 35\%$).¹⁰ All the $PbTiO_3$:La samples have a lemon-yellow color and a specific resistance of more than $10^{11} \Omega m$ at room temperature.

As earlier described,¹¹ the Copper ions are incorporated on B sites in $(Pb,La)TiO_3$, as in the case of Mn doping. Thus the incorporation of La^{3+} on A sites is partly compensated by Cu^{2+} on B sites. The density of vacancies will decrease when increasing the Cu content in $(Pb,La)TiO_3$, leading to the chemical formula $(Pb_{1+x-3/2y}La_y\Box_{1/2y-x})(Ti_{1-x}Cu_x)O_3$. According to x-ray diffraction results, solid solution can be obtained for x ranging from 0 to $y/2$. Meanwhile, the conductivity of $BaTiO_3$:0.2% Cu is several orders of magnitude higher than in pure $BaTiO_3$;¹² the incorporation of Cu in $(Pb,La)TiO_3$ does not sensibly modify the conductivity properties of the raw samples.¹¹ On the other hand, the temperature-dependent resistivity measurements carried out on reduced samples exhibit a net evolution with copper doping. These specimens will be numbered using a terminology such as PLTC (20,1), where the first number denotes the amount (at. %) of lanthanum and the second the amount (at. %) of copper.

The crystals of $KTa_{1-x}Nb_xO_3$ ($0 \leq x_{Nb} \leq 5\%$) used in this study were produced by three different crystal growers (Boatner, Rytz, and Rod) in three different laboratories. In this way, the defect content of the raw materials will not be the same. This is to be noted since the unwanted impurities (mainly Fe, Sr, and Ca ions) usually have a strong contribution to the observed dielectric properties of $KTa_{1-x}Nb_xO_3$. We also probed two different single crystals of $SrTiO_3$ and a $SrTiO_3$:Ca (0.2%) one.

The ceramics and crystals used in the dielectric experiments were cut on a rectangular shape and the sample size ranged from $1 \times 1 \times 1 \text{ mm}^3$ up to $6 \times 2 \times 1 \text{ mm}^3$. The major faces were electroded using either chromium-gold or gold vapor deposition. For the dielectric susceptibility measurements we have used a Hewlett Packard 4192 or 4284 impedance analyzer in a frequency range from 20 up to 10^6 Hz with a peak-to-peak amplitude of 1 V. The permittivity was determined by measuring the capacitance and loss tangent as functions of temperature and frequency. The sample temperature could be monitored between 5 and 300 K with an accuracy better than 0.1 K. Since the dielectric anomaly is very small, we took some care to achieve a good grounding and shielding of the sample.

RESULTS

The dielectric data were recorded in two ways: either at several spot frequencies while cooling the sample down to 5 K at a rate of -1 K/min or at fixed temperature and sweeping the frequency. The former process gives a qualitative insight into the low-frequency dielectric anomaly as reported in Fig. 1 for several $KTa_{1-x}Nb_xO_3$ samples. The maximum of ϵ_2 which evidences this anomaly is always detected at nearly the same temperature, T_{max} , for all the samples. T_{max} increases when the frequency increases [compare Figs. 1(a) and 1(b)] and the absolute value ϵ_{2max} of ϵ_2 at $T_{max}(f)$ increases when the Nb content of the sample increases. We recall that the samples $KTa_{1-x}Nb_xO_3$ ($x > 0.75\%$) undergo a ferroelectric phase transition. This is evidenced by the step in ϵ_2 at about $T = 40 \text{ K}$ for $x_{Nb} = 3\%$.

The frequency shift of T_{max} is more clearly demonstrated in Fig. 2 for $x_{Nb} = 1.5\%$. This gives a first insight into the microscopic process which leads to the dielectric anomaly. Namely, it is a thermally activated polar

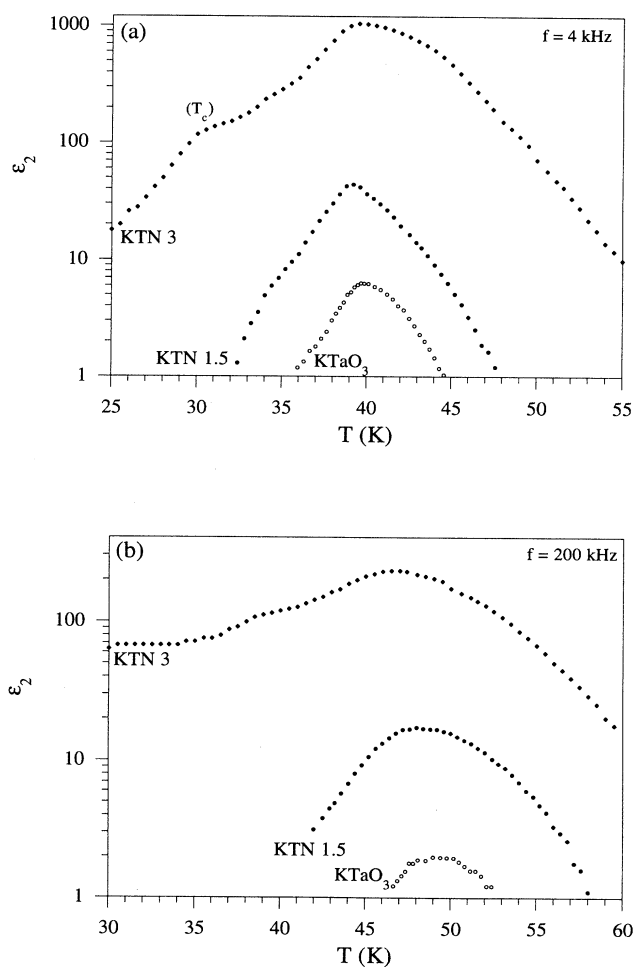


FIG. 1. Imaginary part of ϵ^* versus temperature for different $KTa_{1-x}Nb_xO_3$ crystals at 4 kHz (a) and 200 kHz (b). Note both anomalies occur at the same temperature for all the Nb contents and the increasing of the anomaly with Nb content.

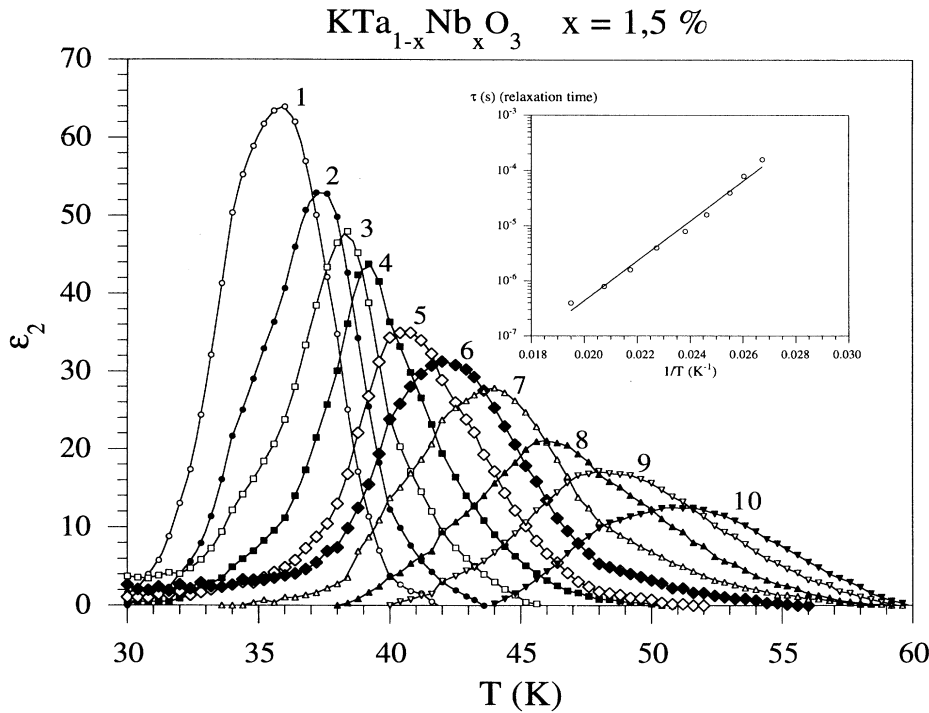


FIG. 2. Temperature dependence of the imaginary part of ϵ^* for various frequencies in a $\text{KTa}_{0.985}\text{Nb}_{0.015}\text{O}_3$ crystal. The solid lines are guides for the eyes. Inset: Debye relaxation time τ as a function of $1/T$ deduced from the ϵ_2 maximum.

motion whose activation energy may be deduced from an Arrhenius plot of f versus T_{\max} (inset Fig. 2). This will be discussed.

Figure 3 shows a typical result for the specimen PLTC (20,0). The main feature is the two maxima of $\tan\delta$ which shift to higher temperatures as the frequency is increased: a first peak appears at 35–50 K as in the $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ crystals and a second at 85–100 K. At

lower temperature a saturation effect is detected and $\tan\delta$ becomes nearly independent on temperature. The high-temperature anomaly has been previously described as a lattice perturbation due to the La^{3+} heterovalent substitution. The activation energy of this 90 K dielectric anomaly is about 220 meV. A similar model to the one proposed originally by Skanavi and Matveeva¹³ could be an explanation. The distortions introduced by the La^{3+}

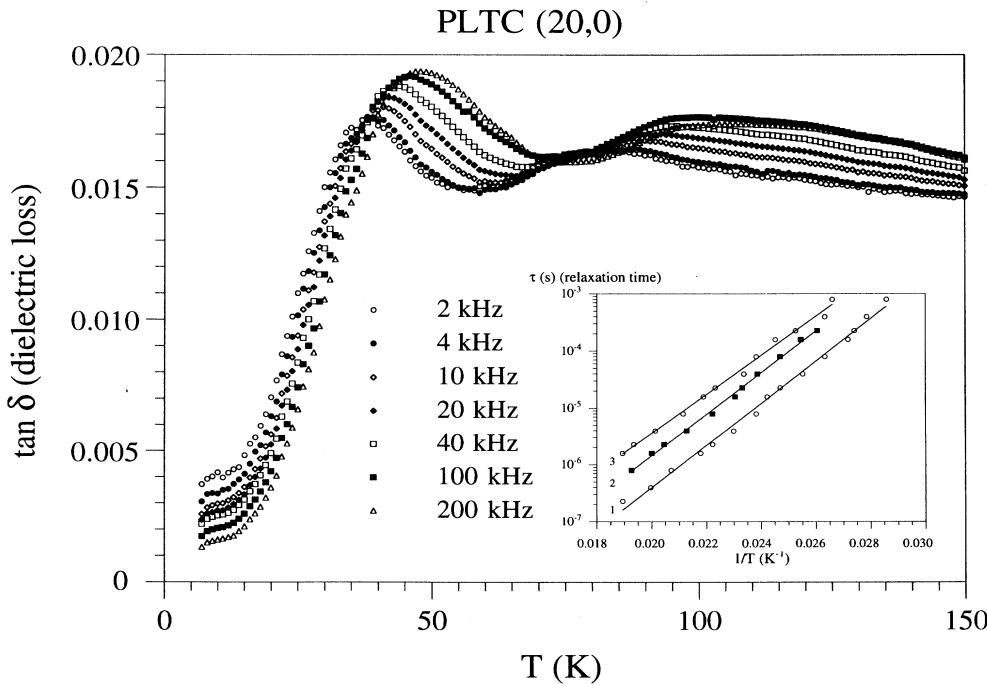


FIG. 3. Temperature dependence of the dielectric loss $\tan\delta = \epsilon_2/\epsilon_1$ at various frequencies in PLTC (20,0). Inset: Relaxation time versus $1/T$ from $\tan\delta$ maximum for three ceramics: (1): PLTC (20,0), (2): PLTC (20,1), and (3) PLTC (20,3).

ions and associated vacancies are sufficient to produce more than one off-center equilibrium position for the Ti^{4+} ion. The observed relaxation is then associated with thermally activated motion between these equivalent potential minima. Dielectric relaxations were already observed in SrTiO_3 samples doped with trivalent rare-earth ions and especially in $\text{SrTiO}_3:\text{La}$ (Ref. 6) at about 70 K. These relaxations were thermally activated with an activation energy of 260 meV.^{6,13}

In the following, we will focus on the low-temperature anomaly.

We now turn to the PLTC (20, x) sample containing copper. The temperature dependence of the loss at constant frequency shows the two loss peaks observed in PLTC (20,0). All these materials undergo just one phase transition from the cubic to the tetragonal phase at about 400 K. Thus these Debye-like anomalies are not related to a phase transition. Moreover, their amplitude may be systematically decreased when the heterovalent substitution $\text{Cu}^{2+}/\text{Ti}^{4+}$ is increased. The first maximum (30–50 K) disappears for $x=10\%$ and the second for $x=8\%$. At the same time, it is interesting to note that the 40 K anomaly shifts to higher temperatures, from 45.9 ($x=0$) to 53 K ($x=8\%$). It is also interesting to note that, reducing PLTC (20,8), the temperature anomaly decreases from 53 to 30 K.

The most quantitative description of this thermally activated process is gotten from the fixed-temperature experiments, an example of which is plotted in Fig. 4. In all the $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ and $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ samples investigated, a maximum of ϵ_2 is observed. This maximum is monotonously shifted to low frequencies when the temperature decreases. The dispersion curves were fitted using a Debye-type formula,

$$\begin{aligned} \epsilon^*(\omega) &= \epsilon_1(\omega) - j\epsilon_2(\omega) \\ &= \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega\tau)^{(1-\alpha)}}, \end{aligned} \quad (1)$$

where ϵ_∞ is the high-frequency ($f > 1$ MHz) limit of the dielectric susceptibility, ϵ_s is the low-frequency limit ($f < 100$ Hz), and τ the relaxation time. The Davidson and Cole parameter α is used to fit the relaxation broadening. For all the samples and at all temperatures, α is small ($\alpha < 0.2$), which means that the relaxation remains monodispersive: the concentration of electric dipoles is small enough to preclude any interaction between them. The fittings were mainly attempted on the imaginary part of the dielectric susceptibility $\epsilon_2(\omega)$. Since for the lowest Nb contents the relaxation amplitude is very small [Figs. 1(a) and 1(b)], the fitting of $\epsilon_1(\omega)$ was sometimes not efficient enough. Among the fitting parameters, the most interesting is τ , the relaxation time.

In the La^{3+} -doped ceramics, due to the relatively flat loss in the vicinity of the temperature maximum, it is unfortunately difficult to fit $\epsilon_2(\omega)$. However, it is equally valid to take the data as a function of frequency with temperature as a constant parameter, or with variable temperature at a constant frequency, provided that the sample follows the Debye characteristics.¹⁴ Thus from the curves $\epsilon_2(T)$ at spot frequencies, we got T_{max} , the loss peak temperature. The curves of the Debye relaxation time $\tau = 1/2\pi f$ as a function of $1/T_{\text{max}}$ for the different PLTC ceramics exhibit straight lines, which shift to higher temperature as the Cu content is increased (inset Fig. 3).

In the following, we will be mainly concerned with the temperature variation of τ , which may be described by a thermally activated Arrhenius law as evidenced by the insets in Figs. 2–4:

$$\tau = \tau_0 \exp \left[\frac{E}{kT} \right]. \quad (2)$$

SrTiO_3 and $\text{SrTiO}_3:\text{Ca}$ samples for which the dielectric anomaly appears at lower temperature ($T=13$ K) cannot be described by such an equation (Fig. 5). The Arrhenius

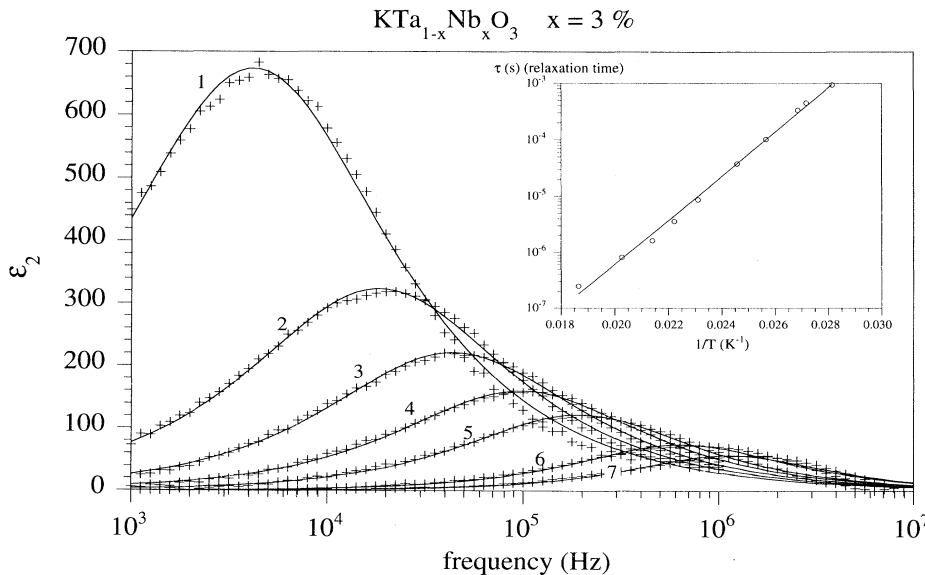


FIG. 4. Imaginary part of the dielectric susceptibility versus f obtained for $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ with $x=3\%$. Solid lines: fit to a Debye-type dispersion (see text). Inset: Debye relaxation time τ as a function of $1/T$ calculated from the Debye fits.

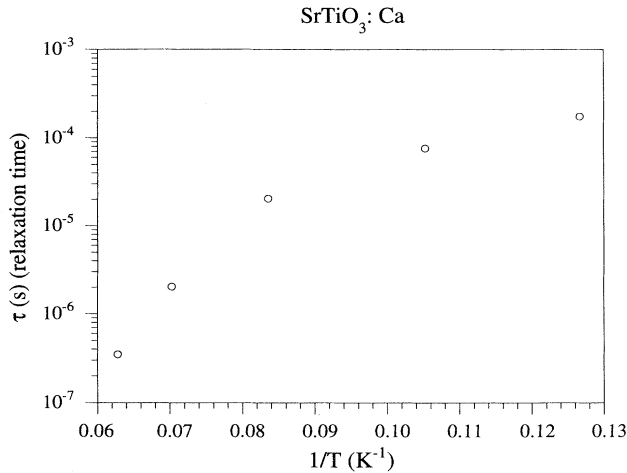


FIG. 5. Debye relaxation time τ as a function of $1/T$ for a $\text{SrTiO}_x\text{:Ca}$ crystal. Note the non-Arrhenius variation of τ in agreement with similar data in pure SrTiO_3 (Ref. 5).

fit leads to the high-temperature relaxation time τ_0 and to the activation energy E_a . Tables I(a), I(b), I(c), and I(d) summarize the Arrhenius parameters. The most important result is that the activation energy (about 75 meV or 870 K) is very close in all the investigated samples and independent of impurity substitution. Moreover, the pre-factor τ_0 is always very small. For usual lattice dipole re-

laxation τ_0 is of the order of 10^{-12} s, while it is of the order of 10^{-14} s in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ and PLTC. Since the lattice dynamics of the investigated $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ crystals is very different (from quantum paraelectric to ferroelectric), any purely ionic motion should be connected to the bulk lattice properties. It is worth pointing out that neither the relaxation time nor the relaxation amplitude is critical, i.e., they do not behave as $\tau^{-1} \propto T - T_C$, but follow an Arrhenius law. This lack of criticality for all the Nb contents in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ is the signature of an anomalous dipolar relaxation.

To summarize these experimental findings, we stress that the observed relaxation arises from unusual dipoles in all the PLTC, $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, and $\text{SrTiO}_3\text{:Ca}$ samples: The activation energy of the thermally activated dipolar relaxation is small and independent of the impurity content and of the lattice dynamic. The high-temperature extrapolation of the relaxation time τ_0 (10^{-14} s) stays several orders of magnitude below the usual phononic frequencies (10^{-12} s).

DISCUSSION

Several previously reported dielectric dispersion experiments were performed in pure and doped KTaO_3 . In $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ and $\text{K}_{1-x}\text{Na}_x\text{TaO}_3$, the observed relaxations were ascribed to lattice or impurity induced dipoles.^{15,16} These purely ionic dipoles lead either to monodispersive or to polydispersive relaxations. In the former

TABLE I. Activation energy (E_a) and Debye relaxation time at high temperature (τ_0) deduced from the Arrhenius plots. (a) $\text{PbTiO}_3\text{:La,Cu}$ results. (b): $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN). Underlined values are recorded at spot frequencies while cooling the sample, whereas the others are at fixed temperature while sweeping the frequencies. (UHP means ultrahigh purity.) (c): Pure and Ca-doped SrTiO_3 data. (d): $\text{BaTiO}_3\text{:La}$ -doped and reduced TiO_2 results. Note the agreement between our results in $\text{BaTiO}_3\text{:La}$ and the literature (Ref. 7).

	PLTC (20;0)		PLTC (20;1)		(a) PLTC (20;3)		PLTC (20;8)	PLTC (20;8) (reduced)		PLTC (30;0)
E_τ (meV)	73,7	72,2	64,0	73,9	54,0	64,5				
τ_0 (10^{-14} s)	1,6	5,8	139	15,5	0,75	2,6				
(b)										
	KTaO_3 UHP Boatner	KTN $x=1,5\%$ Boatner	KTN $x=2\%$ Rytz	KTN $x=2,5\%$ Rod	KTN $x=2,9\%$ Rytz	KTN $x=3\%$ Rytz	KTN $x=3\%$ Boatner	KTN $x=5\%$ Boatner		
E_τ (meV)	<u>75,3</u> 73,6	<u>70,6</u>	<u>68,0</u>	77,3	79,4	74,9	<u>78,6</u> 74,4	68,0		
τ_0 (10^{-14} s)	<u>1,5</u> 2,2	<u>3,8</u>	<u>2,2</u>	0,78	1,4	5,2	<u>0,43</u> 2,9	74		
(c)										
	SrTiO_3			$\text{SrTiO}_3\text{:0,2\% Ca}$						
E_τ (meV)	5,7			8,6						
τ_0 (s)	$2 \cdot 10^{-8}$			$2 \cdot 10^{-9}$						
(d)										
	$\text{BaTiO}_3\text{:0,03\% La}$ (Ref. 7)	$\text{BaTiO}_3\text{:0,5\% La}$	$\text{BaTiO}_3\text{:1\% La}$	TiO_{2-x} (Ref. 19)						
E_τ (meV)	68,0	43,0	83,2	at 4 K	at 11 K	at 15 K				
τ_0 (s)		$\approx 10^{-14}$	$\approx 10^{-16}$	10^{-6}	10^{-7}	10^{-8}				

case,¹⁵ it is the individual motion of correlated chains (or clusters) of off-centered Ta⁵⁺ ions which was held responsible for the relaxation. In the latter, the correlation between randomly distributed impurities strongly increases the distribution of relaxation time.¹⁷ This effect may induce a low-temperature polar phase with some glassy features.¹⁸ The relaxation that we have reported here cannot be classified in either of these two families.

In PLTC (20,0) we have found two dielectric anomalies in the investigated samples. They arise from the slowing down of Debye relaxations. The low temperatures ($T < 150$ K) allow us to observe in our frequency window (10 Hz to 1 MHz) polar motion with energies less than 0.3 eV. The two separate regions of frequency dependence characterize two different physical mechanisms: the 90 K anomaly ($E_r \approx 250$ meV) is closely linked with the properties of the lattice, while the low-temperature one ($E_r \approx 75$ meV, $\tau_0 \ll 10^{-12}$ s) may be regarded as being associated with unusual dipoles present in these materials. Indeed, the possibility that such a dielectric relaxation is due to ion jumping is immediately ruled out by comparing the activation energies involved (0.07 eV compared to 0.2–1 eV for ion jumping).

The sensitivity of the low-temperature dielectric anomalies to Cu doping (inset Fig. 3) led us to the conclusion that heterovalent substitution may play a role in the observed losses. In KTaO₃, it is only very recently that additional unwanted impurities such as Fe³⁺ substituted to Ta⁵⁺ or oxygen vacancies were considered. These point defects can both induce a dielectric relaxation in pure KTaO₃ in the temperature range of interest.³ Our observations are basically in agreement with this description. However, due to the unusual temperature behavior that we have observed, we propose an alternative model. In fact, several dielectric relaxations in the 30–50 K temperature range were already reported in different oxides. In rutile TiO₂, Dominik and MacCrone¹⁹ found a relaxation in this temperature range only in oxygen-deficient samples. In La³⁺ and Gd³⁺ BaTiO₃-doped ceramics a slight loss anomaly, again in the same temperature and frequency range and with an activation energy of 70 meV, was reported.¹⁷ However, in this later case, only $\tan\delta$ displays a steplike temperature variation and a Debye-like dispersion was not evidenced. We can try to find a connection between these early investigations in TiO₂ and BaTiO₃:La,Gd and ours. Following Dominik and MacCrone and Iguchi *et al.*,⁷ we may attribute the loss anomaly to a polaronic-like relaxation. In such a case, it is the interaction between free charges and the lattice which induces the local dipoles.

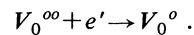
The polaron mobility in ionic crystals is usually evidenced by optical absorption and conductivity. The local relaxation of polarons can also induce a dispersion in the dielectric susceptibility of those systems. It is well known that charge carriers do not exclusively produce direct current conduction but also make a contribution to the dielectric behavior. The dielectric effects of free charge carriers become significant at frequencies of the order of the reciprocal collision time ($f \approx 10^{16}$ Hz) and thus cannot be observed in our frequency range. Nevertheless, dielectric responses are to be expected from any localized

charge carriers, especially at low temperature, where the effects of free charge carriers are not dominant. Under the action of an ac field, the charge may hop between the equivalent lattice sites available, related to the crystal symmetry. This hopping is equivalent to the reorientation of an electric dipole, which gives a frequency-dependent complex dielectric constant exhibiting Debye-type behavior.

Localization in a solid is connected with disorder, such as structural or compositional defects or with the polarizability of the lattice. If the medium is sufficiently strongly polarizable resulting from a local lattice distortion, the carrier may occupy a bound state. Then the polaron may move by hopping when sufficient energy becomes available for their excitation out of the local potential well. The transition probability for a carrier hopping from an occupied to an unoccupied site depends upon the overlap of the wave functions centered on the respective sites. Hopping over large distances is thus not favored. Moreover, polaron hopping may occur at higher temperatures as the hopping distance involved is larger.

Thus, the polaron effective mass is expected to be both higher than the free charge one and smaller than the ionic one [$m_{\text{polaron}} \approx 100 \times m_{\text{electron}}$ (Refs. 20 and 21)]. This leads to an Arrhenius prefactor τ_0 between the free electron time scale (10^{-16} s) and the phononic one (10^{-12} s). In all the investigated perovskites, we have found $\tau_0 \approx 10^{-14}$ s. Moreover, we note that a polaronic model gives an activation energy value in agreement with our experiments findings.⁷

It is also useful to understand why the 35 K anomaly is disconnected from the lattice properties. Oxygen vacancies (or unwanted heterovalent impurities, such as Fe³⁺ ...) are the source of free charges and the soft lattice provides the elastic energy which is necessary for a polaronic state to occur.¹⁹ The polaronic-type defects could be oxygen vacancies whose ionization state gradually changes for temperatures lower than 60 K:



The direct experimental evidence for the dependence of peak height on oxygen vacancies density has been observed in KTaO₃.³ This can also be an explanation for the decrease of the amplitude anomaly when Cu doping increases. As recalled in the introduction, the cation vacancies concentration decreases with Cu substitution. They may weaken the bond strength of the oxygen sublattice with respect to cations.²² As a result, oxygen vacancies density, formed at elevated temperatures from thermal dissociation, is all the higher as Cu doping increases.

A very localized nature of the dipoles and a relatively small activation energy are the main features of these polarons. The low activation energy (75 meV) and the high mobility of the relaxation ($\tau_0 \approx 10^{-14}$ s) show that our observations fit in this model. Moreover, a polaronic picture is useful to understand why the 30–40 K dielectric relaxation is disconnected from the polar properties of KTa_{1-x}Nb_xO₃. At last, we recall that the very specific dispersion of acoustic phonons in KTaO₃ together with a

strong TO mode softening may be the driving source of the polaronic state.²³ Unfortunately, due to the very high resistivity of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, it was up to now impossible to find conductivity evidence for such polarons.

Resistivity and electron paramagnetic resonance experiments are actually in progress in $\text{PbTiO}_3\text{:La,Cu}$ showing that the localization of free charges at low temperature

does happen in these compounds.²⁴

At last, we point out that SrTiO_3 and $\text{SrTiO}_3\text{:Ca}$ crystals display qualitatively the same loss anomaly. It is only the temperature range ($T < 15$ K) and the non-Arrhenius behavior of the relaxation frequency which are specific to strontium titanate.²⁵

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