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(abstract) We investigated dielectric and hypersonic properties of NBT over a wide temperature range. The dielectric permittivity and loss measured from 20 Hz to 300 kHz agree at lower temperature with previous results. At higher temperature in and near the tetragonal phase the lower frequencies show a very large permittivity peak with considerable dispersion and large loss. This behavior is very similar to that found in other perovskite crystals and ceramics, in some cases far above T_c . We attribute it to extrinsic bulk conductivity. The phase shift giving nonzero σ'' in $\sigma = \sigma' + j\sigma''$ may be caused by a spread in mobility activation energy. The Brillouin scattering data at 514.5 nm show a very broad dip in sound velocity and a very large and broad attenuation peak, both centered in the tetragonal phase temperature range. This behavior is attributed to hybridization of order parameter and cluster fluctuation contributions.

INTRODUCTION

Sodium bismuth titanate (NBT, formula $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$) is a relaxor ferroelectric with unusual dielectric, optical and other properties.[1] The Na^+ and Bi^{3+} ions randomly occupy the "A" cation sites. This random ion placement broadens the phase transitions and changes the nature near the transitions of the anomalies in permittivity and in sound velocity and attenuation determined by Brillouin scattering.

In this paper we first describe our Brillouin scattering and lower-temperature dielectric results. Most of the paper is devoted to the large low-frequency permittivity peak seen by us[1] at high temperature in NBT. This peak and associated loss resemble behavior of other perovskite crystals and ceramics.[2-5] We explain these phenomena in terms of extrinsic bulk conductivity with a spatial distribution of mobility activation energies.

BRILLOUIN SCATTERING RESULTS

Our Brillouin scattering results are summarized in Fig. 1. Only the background intensity shows an obvious anomaly right at a transition, namely the jump at the trigonal-tetragonal transition. The dip in Brillouin shift, and the peaks in linewidth and background intensity, all appear in the tetragonal phase between its transitions to the trigonal and cubic phases. We believe the usual anomalies caused by Landau-Khalatnikov-type (order parameter) variations are absent because of the presence of large fluctuations which must cause "hybridization" mixing of the fluctuation and Landau-Khalatnikov contributions.[6] We attribute the location of the anomalies **between** two transitions to an interaction between the two types of fluctuations associated with these two transitions. Further details of the Brillouin experiment and results, and comparison with results for other relaxor ferroelectrics, have been submitted for publication elsewhere.

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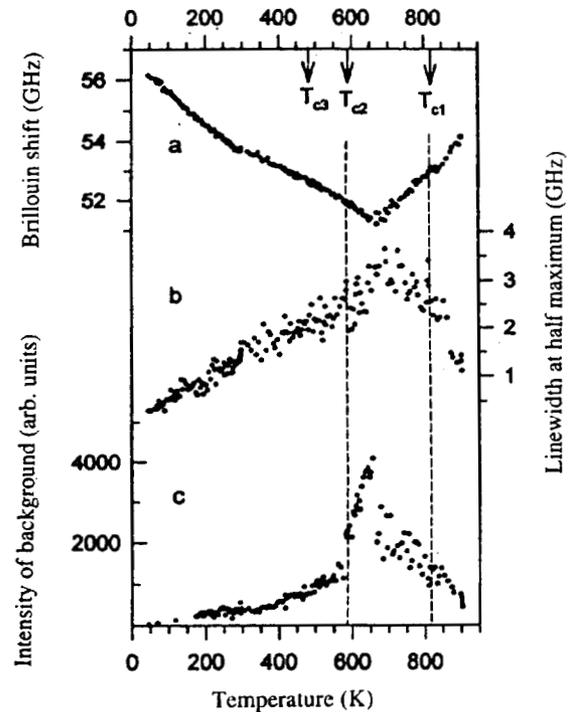


Figure 1. Brillouin scattering results for NBT. T_{c1} and T_{c2} represent the transitions from the orthorhombic to the cubic and trigonal phases respectively. T_{c3} denotes the transition from the antiferroelectric to the ferroelectric phase as temperature decreases.

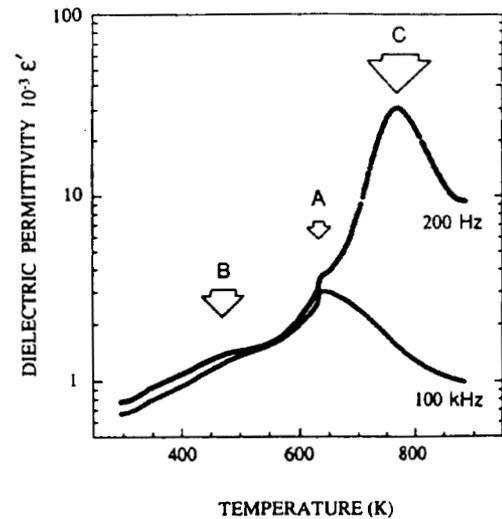


Figure 2. (from Ref. 1) The dielectric permittivity of NBT upon heating. A and B correspond to T_{c2} and T_{c3} of Fig. 1 respectively. C represents a peak whose temperature is frequency-dependent.

DIELECTRIC RESULTS AT LOWER TEMPERATURES

These results, going upward from room temperature as shown in Fig. 2, begin with a steady increase in permittivity. The only indication of the transition at T_{c3} near 550 K is disappearance of the weak dispersion. The slope then increases to a cusp at T_{c2} . The phase between T_{c3} and T_{c2} is antiferroelectric or antiferroelectric incommensurate. Our results agree with those of others to an extent determined by crystal quality variations. Comparison and further interpretation of these results appears elsewhere.[1]

The 100 kHz permittivity is quite large just above T_{c2} in the tetragonal phase. It decreases gradually as temperature increases, but shows no anomaly at T_{c1} .

A striking feature of Fig. 2 is the huge permittivity peak (ϵ') at 200 Hz in the tetragonal phase. At this low frequency also, there is no anomaly at T_{c1} . We previously[1] attributed this peak to superparaelectric clusters whose switching is related to the conductivity mechanism. Very recently we learned of such peaks far inside the cubic phase for other perovskites. The remainder of this paper is devoted to our new explanation for such peaks.

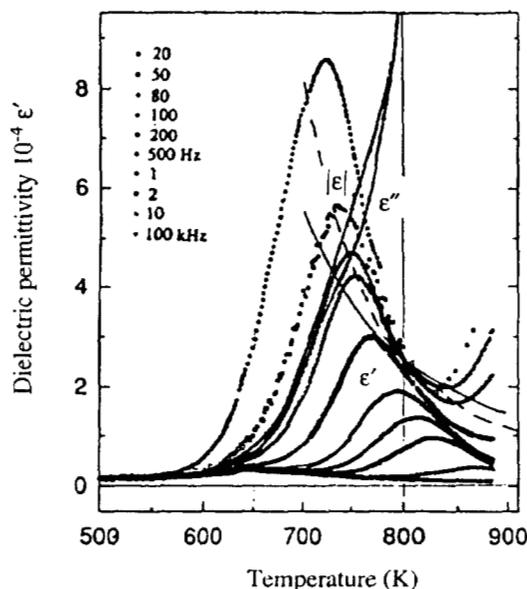


Figure 3. (from Ref. 1) Permittivity ϵ' vs. temperature for NBT, with scale chosen to emphasize the large low-frequency peaks. The upturns at the right may be artifacts resulting from the very much larger ϵ'' values at high temperature. The solid and dashed lines indicate fits to a model we no longer consider applicable.

THE HIGH-TEMPERATURE DIELECTRIC BEHAVIOR IN VARIOUS PEROVSKITES

The strong dispersion associated with the largest (ϵ') permittivity peak in NBT is illustrated in Fig. 3. An important feature, discussed later, is the overlap envelope on the high-temperature side. Two other important features are that both the peak height and peak frequency approximately obey the Arrhenius law. Although these permittivity peaks are high, the lossy component ϵ'' of the permittivity at each peak is even higher.

The physical nature of the dielectric loss ϵ'' is better understood by plotting it logarithmically as σ' , using the relation $\sigma' = 2\pi f \epsilon_0 \epsilon''$, where f is frequency and ϵ_0 is the MKS constant $8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$. This plot appears in Fig. 4. There are two distinct envelopes where curves for different frequencies overlap. The upper one is the ac conductivity limit, and the lower one the dc conductivity limit. Both envelopes obey the Arrhenius law, with the

dc envelope having the higher activation energy. A kink appears in the ac envelope at T_{c2} near 640 K, and a rounded bend occurs in the ac and dc envelopes at T_{c1} near 820 K.

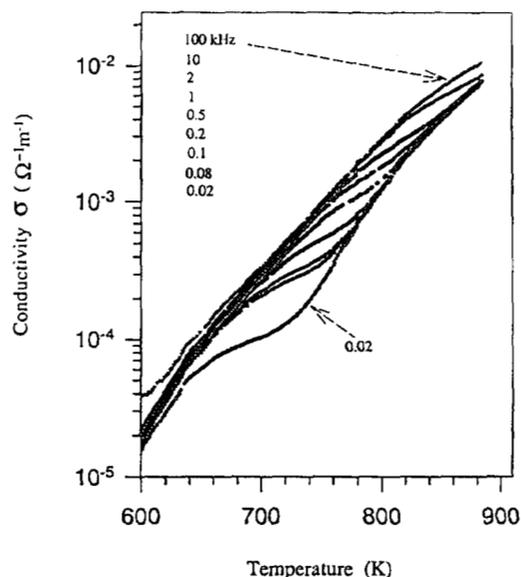


Figure 4. Electrical conductivity σ vs. temperature for NBT for several frequencies.

Figure 5 shows similar behavior found by Stumpe *et al.*[2] for a 0.24 mm thick SrTiO_3 crystal (but plotted as ρ vs. $1/T$). Both our results and theirs show ac and dc conductivity envelopes which tend toward convergence at finite temperature. The permittivity plot[2] for their 1.02 mm thick SrTiO_3 crystal is similar to our Fig. 3. For their 0.24 mm crystal this dispersive behavior is superimposed on broad permittivity humps peaking near 950 K and showing little dispersion. This may be a surface effect appearing only in the thinner crystal, which may cause the S-type upward distortion of resistivity with decreasing temperature in Fig. 5. Unfortunately they provided no resistivity data for their 1.02 mm crystal.

Similar permittivity behavior to ours was seen by Kuwabara *et al.*[3] in a ceramic sample of $\text{Pb}_{1-x}\text{La}_{2x/3}\text{TiO}_3$ (PLT10) with $x=0.10$, as shown in Fig. 6. The lowest-frequency peaks are distorted by the proximity of the ferroelectric transition at 378 °C (651 K; pure PbTiO_3 has $T_c=490$ °C). For $x=0.05$ they observed broad nondispersive peaks centered near 462 °C which may be locked onto the ferroelectric transition.

The NBT, SrTiO_3 , and PLT10 samples are compared in Fig. 7 where the σ' and σ'' components of the conductivity $\sigma = \sigma' + j\sigma''$ are plotted at the temperatures for which the ϵ' (or σ'') peaks occur. Striking similarity is noted for these results from quite different samples. The σ' values always exceed the σ'' values, supporting the idea that a phase-shifted conductivity is being observed. The σ' values obey the Arrhenius law, while the σ'' values show curvature.

Large and dispersive permittivity peaks were also observed by Bidault *et al.*[5] in BaTiO_3 single crystals far above T_c . The peak height increased for reduced samples, and decreased for oxidized samples. Similar behavior was noted for a CaTiO_3 single crystal and various PLT ceramics. Ujma and Dmytrów[4] found dispersive peaks above the ferroelectric (233 °C and antiferroelectric (225 °C) transition sequence in PbZrO_3 single crystals and ceramics. Neither group[4,5] provided conductivity data for their samples.

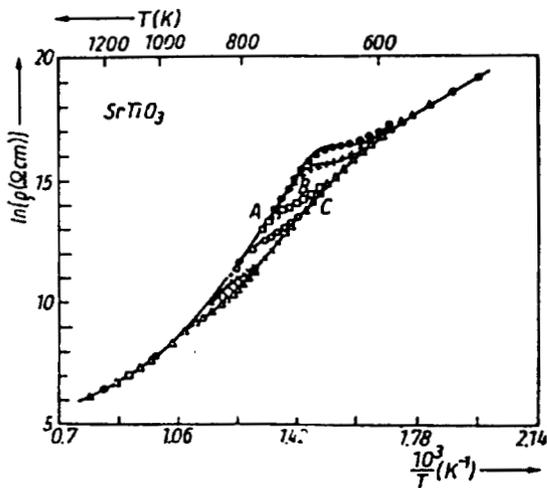


Figure 5. (from Ref. 2) Logarithm (to base e) of resistivity of 0.24 mm thick SrTiO₃ single crystal vs. inverse temperature for frequencies 0.1 kHz (filled circles), 0.2, 1, 4, 20 kHz, and 100 kHz (open triangles).

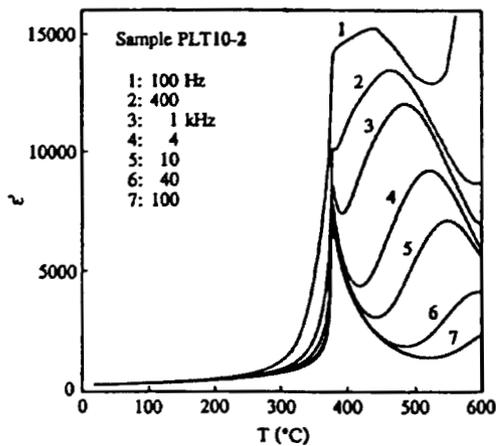


Figure 6. Temperature dependence of permittivity ϵ' vs. temperature for various frequencies for a lead lanthanum titanate ceramic sample with 90% lead.

CONDUCTIVITY MODEL FOR HIGH-TEMPERATURE DIELECTRIC PEAK

This model for the very large low-frequency permittivity and loss was reached by a process of elimination. First, any model based on microdomains[3] or superparaelectric clusters[1] seems ruled out, because such ordered regions should not exist in the 700 to 900 K range in the quantum paraelectric strontium titanate,[2] or hundreds of degrees above T_c in barium titanate,[5] in which similar large peaks were found. Given that the basic dielectric behavior is not anomalous for these two materials in this temperature range, and noting that the lossy part of the permittivity shows thermal activation, we are led to consider the phenomena as electrical conductivity phase-shifted enough to provide the permittivity ϵ' peaks.

Given that conductivity is important, are we dealing with a bulk or a surface-modified effect? Stumpe *et al.*[2] and Bidault *et al.*[5] attributed the phenomenon to a high-impedance surface layer. We followed Stumpe in describing the bulk as a parallel RC circuit, in series with another parallel RC circuit representing the two surfaces. We provided both R's with thermal activation, but kept the C's independent of temperature as required, to approximate such

materials as SrTiO₃ and BaTiO₃. This model reproduces, for some parameter choices, the shoulder in ϵ'' representing upward deviation from an Arrhenius law, as seen in Fig. 8. However, Fig. 8 also shows only a plateau in ϵ' could be achieved, and not a peak. The plateau level is independent of frequency whereas experimentally the peak amplitude increases rapidly with falling temperature. The failure to reproduce this characteristic peak behavior seems to rule out the blocking surface interpretation.

We are thus led to consider the behavior as a bulk conductivity phenomenon, but not of the usual type for which $\sigma''=0$ and σ' lacks frequency dependence. The only evident way of causing such dependence is to assume a spatial distribution of mobility barrier heights. We decide on the basis of the following discussion whether this distribution starts at zero energy. The conductivity (Figs. 4 and 5) shows a dc limit envelope where data at some frequencies overlap, and a higher ac limit envelope with lower activation energy where data for other frequencies overlap. The difference between the ac and dc slopes corresponds to a rather small activation energy, several times kT but much smaller than the overall conductivity activation energy.

One might attribute this small difference to mobility activation energy resulting from a spatial distribution of relatively small barriers, and attribute the major part of the activation energy to the carrier concentration n . This assumption fails because it would require the permittivity peaks to occur at much higher frequencies than observed. The conductivity instead appears to be extrinsic, with a fixed number of carriers and a high mobility activation energy which has a relatively small spatial spread to account for the nonzero σ'' .

The conductivity is related to sample preparation and treatment, as seen in relation to oxidation or reduction of barium titanate.[5] Both the extrinsic carrier concentration and the barrier distribution can be affected.

We accordingly are led to a model with extrinsic conductivity. The large conductivity activation energy is associated with the high barrier for the carrier to hop from one site to the next. This energy is comparable to that for diffusion of metal ions in NaCl, for instance.[7] The required distribution in barrier heights is caused by crystal imperfections. The nature of the distribution and its effects will require considerable analysis. We present here only a first attempt at such analysis.

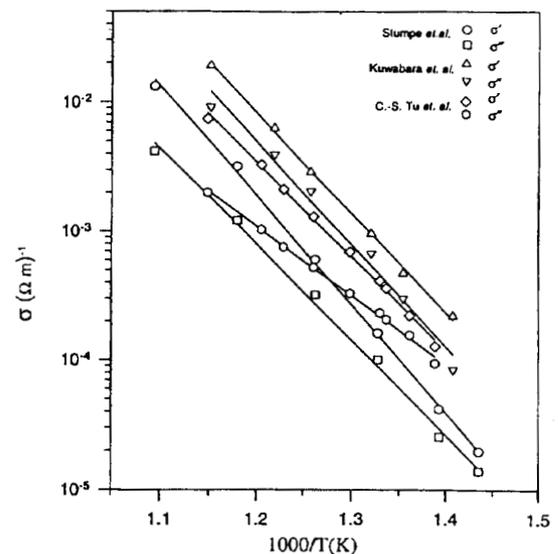


Figure 7. Semilogarithmic plot of real (σ') and imaginary (σ'') conductivities vs. inverse temperature at the temperatures for which the ϵ' (or σ'') peaks occur, for the NBT (Ref. 1), SrTiO₃ (Ref. 2), and PLT10 (Ref. 3) samples described in the text.

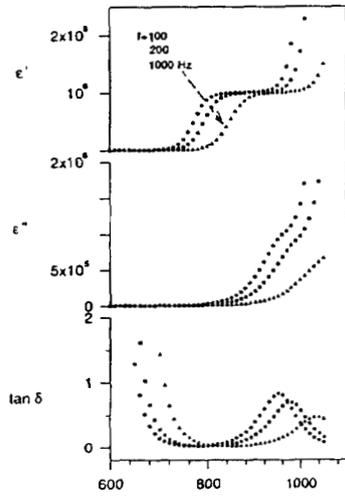


Figure 8. Plots of real and imaginary parts of permittivity for a crystal and its surface modelled by two parallel RC circuits in series, with thermally activated R's and temperature-independent C's. Parameters are $d_{\text{bulk}}=1$ mm, $d_{\text{surf}}=10^{-4}$ mm, $W_{\text{bulk}}=20000$ K, $W_{\text{surf}}=30000$ K, $\epsilon'_{\text{bulk}}=\epsilon'_{\text{surf}}=100$, $\sigma_0=10^7$ (ohm-m) $^{-1}$.

We assume a spatial power law for the distribution of barrier heights about the mean height B. We force the distribution to reach a maximum value B_0 by writing it as

$$U(r)=B+B_0[r/(R+r)]^\gamma \quad (1)$$

In this paper we apply this model and the above distribution only to the SrTiO₃ data,[2] because these are farthest from complicating effects of phase transitions. This is not a perfect test case, because these data may be shifted by surface impedance effects, as discussed both above and below. We will try to fit the SrTiO₃ ac and dc conductivity envelopes and the permittivity envelope discussed above.

The ac conductivity envelope should have the activation energy B in Eq. (1). We take the $f=4$ kHz curve which departs from the ac envelope at $T=700$ K in Fig. 5, use $B/k=15960$ K as the measured slope of that envelope, and assume an attempt frequency $\nu=3 \times 10^{12}$ Hz. At this departure point the relation

$$\nu^{-1} \exp(B/T)=1/2\pi f \quad (2)$$

should hold. If B is taken as the unknown in Eq. (2), we actually get $B=12730$ K.

If we assume hopping conductivity with steps of $a_0=0.4$ nm (one lattice constant) obeying the equation $\sigma=\nu \exp(-B/kT)e^2 a_0^2/kT$, we can solve for the (assumed temperature-independent) carrier concentration and obtain (for $\sigma=1.24 \times 10^{-4}$ ohm $^{-1}$ m $^{-1}$ and $B=12730$ K) the value $n=7.71 \times 10^{27}/\text{m}^3$. This value is somewhat large, because the unit cell concentration is only $(4 \text{ nm})^{-3}=1.56 \times 10^{28}/\text{m}^3$. Either the activation energy B must be lower, or the mobility must be higher, as it could be if electrons rather than ions are the carriers.

The $f=4$ kHz curve joins the dc envelope at $T=800$ K, and the measured slope of that envelope is $(B+B_0)/k=20080$ K. Employing the same attempt frequency in the analog to Eq. (2) yields $B+B_0=14880$ K. The agreement both for B and for $B+B_0$ is only fair, but as mentioned above, the measured envelopes in Fig. 5 may be too steep because of surface impedance. The important point is that this model qualitatively reproduces the curves of Fig. 5, with low frequencies as observed at the ac to dc envelope crossovers.

Obtaining the permittivity envelope for the barrier height distribution of Eq. (1) is a difficult problem. As an initial

approximation we assume that at the temperature T at which the permittivity peak at frequency f occurs, the effect of the barriers is the same as that of an infinite barrier at a radius r_b where from Eq. (1) $U(r_b)=B+B_0-kT$. The motivation for this assumption is that the carriers in one period can just diffuse to the radius where thermal motion is sufficient to let them drift without appreciable additional trapping. This radius is given by

$$r_b/R=[(1-kT/B_0)^{-1/\gamma}-1]^{-1} \quad (3)$$

The dipole moment p per carrier is $e^2 E r_b^2/5kT$ for this spherical radius. A reasonable fit using $\epsilon'=\nu p/\epsilon_0 E$ to the peak ϵ' amplitudes at various frequencies is obtained by choosing $\gamma=1/3$, B_0 smaller than found above, only 1200 K, $B=13000$ K near the value found above, and $R=30 \mu\text{m}$. This γ value gives r_b strong temperature dependence, as seen in Fig. 9. Such strong dependence gives the observed strong temperature dependence of the peak ϵ' values.

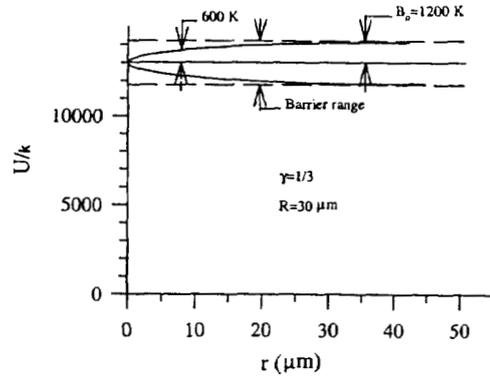


Figure 9. Shape of the mobility barrier height distribution of Eq. (1) for parameters given in the text.

CONCLUSIONS

The relaxor ferroelectric nature of NBT is evident in the unusual Brillouin scattering and lower-temperature dielectric behavior. The large ac dielectric peaks and their dispersive behavior in the 700 to 900 K range are a common feature of perovskite crystals and ceramics, and appear to result from a phase-shifted conductivity. A spatial distribution of mobility barriers for extrinsic bulk conductivity seems the likeliest origin of the phase shift.

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