

Elastic and dielectric measurements of the structural transformations in the ferroelectric perovskite $(\text{Na}_{1/2}\text{Bi}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$

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Abstract. NBT is a perovskite undergoing a series of structural and polar transitions starting from the high temperature paraelectric phase: tetragonal antiferroelectric, rhombohedral and finally ferroelectric. In solid solution with BaTiO_3 the ferroelectric phase changes from rhombohedral to tetragonal, at the so-called morphotropic phase boundary, and the phases at higher temperature become ill-defined, also because of the large lattice disorder induced by the coexistence of differently charged cations in the same sublattice. Combined dielectric and anelastic spectroscopy measurements are presented, which clarify some issues related to the phase transitions in NBT-BT. The influence of Ba substitution on the tetragonal antiferroelectric phase is determined for the first time, and the possibility that a monoclinic phase, although with very short coherence length, exists near the morphotropic phase boundary is discussed in view of a large maximum of the elastic compliance.

Introduction

The solid solutions of tetragonal (T) and rhombohedral (R) ferroelectric (FE) perovskites may have enhanced piezoelectric properties near the separation between the two phases, the so-called morphotropic phase boundary (MPB), where the free energies of R and T domains are similar and the reorientation of the polarization and distortion under electric field and stress is easier [1]. Indeed, the great majority of devices based on materials with high electromechanical coupling use $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) at compositions near its MPB. After decades of studies on its phase transitions and phase diagram, it has been found that PZT has an intermediate monoclinic (M) phase at the MPB [2], which is intermediate between the R and T structures and allows the polarization to rotate continuously between the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. Although the existence of the M phase in PZT is still debated [3], it is generally considered to be at the origin of the giant electromechanical coupling of PZT near the MPB [1,4].

Another perovskite which is much studied in the contest of high electromechanical coupling is $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ (NBT). At room temperature NBT is R-FE and in solid solution with BaTiO_3 (BT) or PbTiO_3 it becomes T-FE and hence NBT-BT is a possible Pb-free substitute for PZT [5,6]. Contrary to PZT, which has only mild disorder due to the coexistence of the similar ions Ti^{4+} and Zr^{4+} in the B sublattice of ABO_3 , NBT-BT has more severe disorder from the Na^+ , Bi^{3+} , Ba^{2+} in the A sublattice. This broadens the various structural transitions, including the ferroelectric one, making NBT-BT close to relaxors, and rendering the identification of the various phases very difficult. Two yet unanswered questions which will be addressed here are: when Ba is substituted, what happens to

the cubic-to-tetragonal transition, which is well documented in NBT [7]? Is there a M phase at the MPB?

Experimental

Ceramic samples of $(\text{Na}_{1/2}\text{Bi}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$ with $0 \leq x \leq 0.08$ have been prepared as described in [8] and cut as thin bars 4 cm long for both dielectric and anelastic experiments or sintered as discs for the dielectric ones. The dielectric permittivity $\epsilon = \epsilon' - i\epsilon''$ was measured between 200 Hz and 200 kHz with a HP 4284A LCR meter with a four wire probe during heating/cooling at 1–1.5 K/min between 300 and 570 K. The complex Young's modulus was measured between 100 and 1000 K by electrostatically exciting the flexural vibrations of the bars, whose first three resonant frequencies are in the ratios 1:5.4:13.3, the fundamental being ~ 1.5 kHz. We will show the reciprocal of the modulus, the elastic compliance $s = s' - is''$, in terms of real part and loss $Q^{-1} = s''/s'$.

Results and Discussion

Figure 1 presents the anelastic spectra of samples with $0 \leq x \leq 0.06$, which exhibit three main features. A sharp peak at the temperature $T_{\text{T-C}} = 820$ K of the T-C transformation of NBT, as determined by neutron diffraction [7], shifts to lower temperature and broadens with increasing x ; at $x = 0.05$ it is almost disappeared.

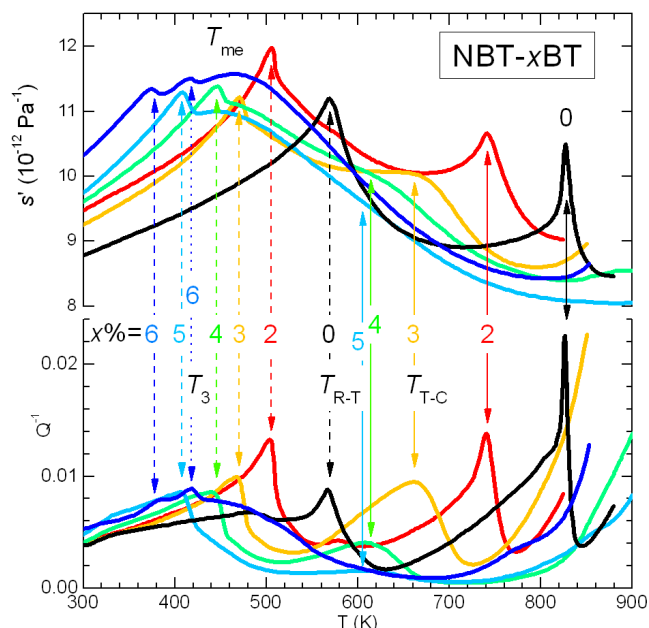


Fig 1 Elastic compliance s' and energy loss coefficient Q^{-1} of NBT-BT measured at ~ 1 kHz.

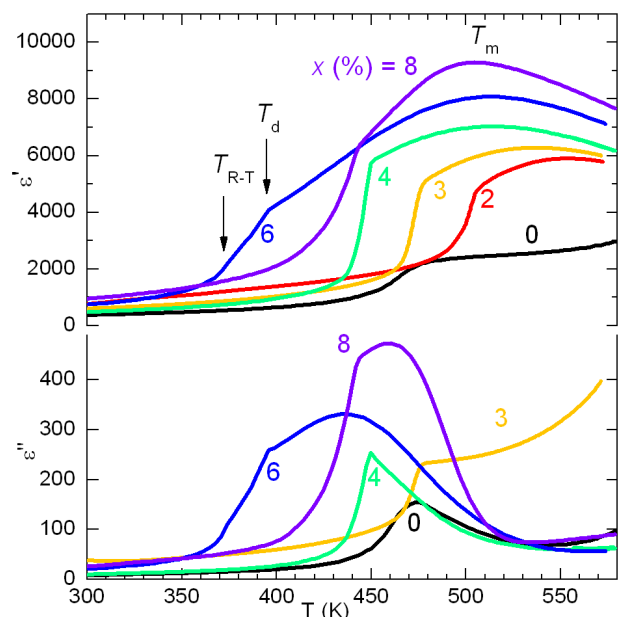


Fig. 2 Dielectric permittivity of NBT-BT measured at 10 kHz.

Another sharp peak at $T_{\text{R-T}} = 565$ K signals the onset of the R-T transformation of NBT; it also shifts to lower temperature and broadens with increasing x , transforming into a step. A broad component at T_{me} becomes preponderant for $x > 0.04$ and is associated with a transformation characterized by extremely short coherence length, but no glassy dynamics (there is no frequency dispersion as in glasses or relaxors). An additional step in the compliance, of unknown origin, appears at T_3 for $x > 0.05$.

The dielectric spectra are shown in Fig. 2, the main features are the kink measured during heating at the depolarization temperature T_d , where the FE phase becomes almost antiferroelectric (\sim AFE), and a broad peak at T_m , usually identified with the transition between AFE and paraelectric (PE). The T-C transition does not cause any anomaly in $\epsilon(T)$, while at the R-T transition there is a small step, usually not observed in the literature.

From the anelastic and dielectric spectra it is possible to complete the phase diagram proposed by Takenaka and co-workers [5,6], as shown in Fig. 3.

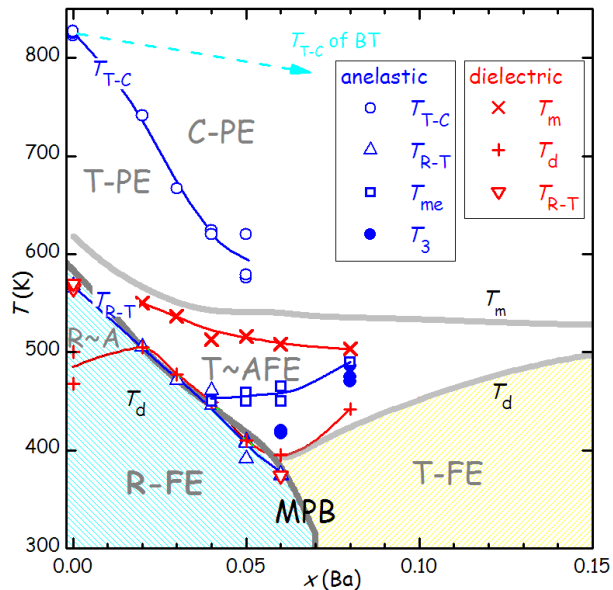


Fig. 3 Phase diagram of NBT-BT near the MPB. The grey lines are from Ref. [6], the blue and red symbols from the present data and Ref. [8].

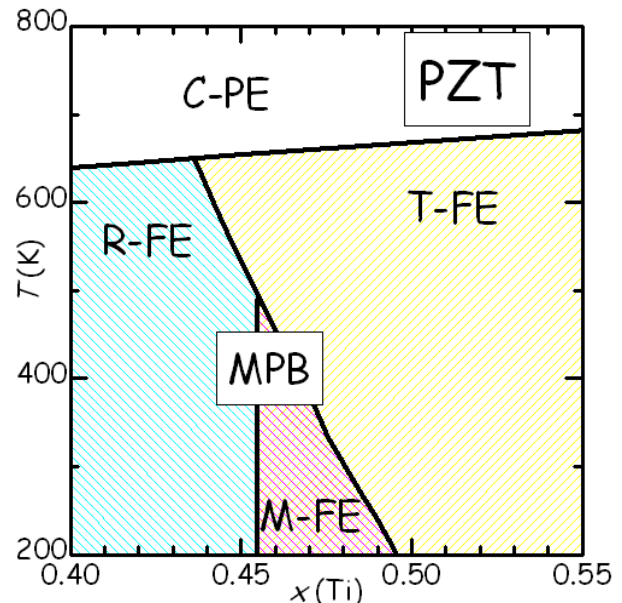


Fig. 4 Phase diagram of PZT, with the intermediate monoclinic region at the MPB separating R and T phases.

The main features revealed by the present measurements are as follows.

- 1) The T phase does not simply transform into a disordered pseudocubic phase, due to the severe additional disorder introduced by the Ba substitution. In fact, the rapid drop of T_{T-C} demonstrates that its stability range is only limited to compositions close to NBT. The dashed arrow in Fig. 3 points to the $T_{T-C} = 400$ K of the other end member of the phase diagram, BaTiO_3 , but the experimental line drops much faster to low temperature.
- 2) The structural R-T and the ferroelectric FE-AFE transition lines coincide for $0.02 \leq x \leq 0.06$.
- 3) The separation between R-FE and T-FE regions (MPB) starts at $x = 0.06$, $T = 390$ K, and is presumably rather steep, although only one additional point $x = 0.07$, $T = 315$ K is reported in the literature [6]. The two lines T_m and T_{me} of the broad dielectric and anelastic maxima should be considered as centroids of an extended region where a transition occurs between cubic paraelectric and ferroelectric phases.

The comparison of this phase diagram with the one of PZT, reported in Fig. 4, poses the question whether there is an intermediate M phase also at the MPB of NBT-BT; such a phase has never been reported and it would be probably impossible to ascertain its presence by diffraction, due to the large lattice disorder of NBT-BT. There is however another similarity between NBT-BT and PZT near the MPB: an enhanced and peaked elastic response, which has been interpreted as a signature of the M phase in PZT [9], as explained below.

According to Landau's theory of phase transitions, the elastic compliance s , which is the strain susceptibility, presents a peak only in the case that the order parameter is a strain ε [10,11]; in fact, in that case the compliance behaves like the dielectric susceptibility at a FE transition, with a Curie-Weiss peak. In the case of the FE transitions, however, the order parameter is the polarisation P , the lowest order coupling term between ε and P can be of the εP^2 type, and the compliance should have a step at the transition [10,11]. A peak in $s'(T)$ could in case of:

- 1) linear coupling between ε and P , forbidden by symmetry in the cubic phase for which the Landau expansion is written;

- 2) dynamic fluctuations due to coupling of the soft mode responsible for the transition with the acoustic mode related to the peaked compliance [11];
- 3) a transformation where ε is almost linearly related to the order parameter, like the shear strain and the rotation of P when passing from the T to the M structure [4].

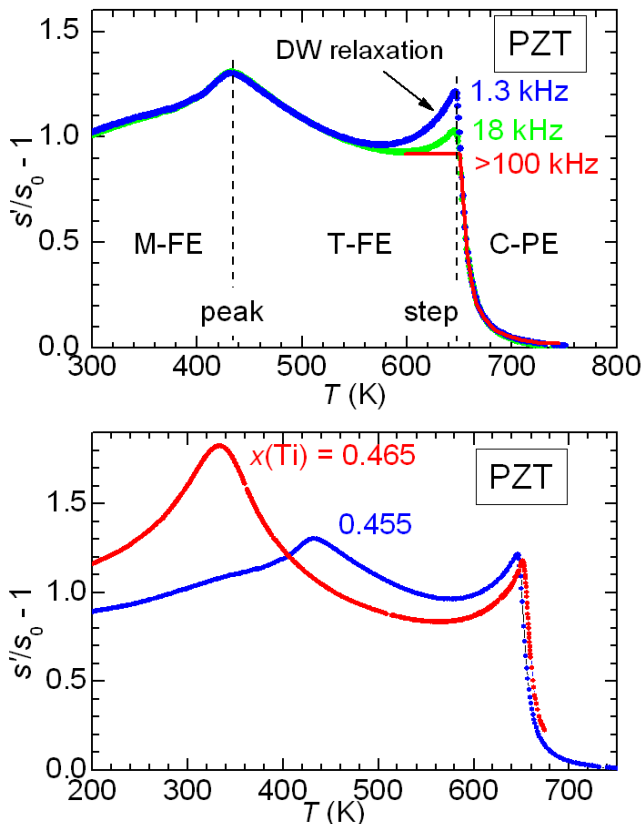


Fig. 5 Elastic compliance of PZT at compositions near the MPB. The continuous red line in the upper panel shows how the anomaly would become a step at much higher frequencies.

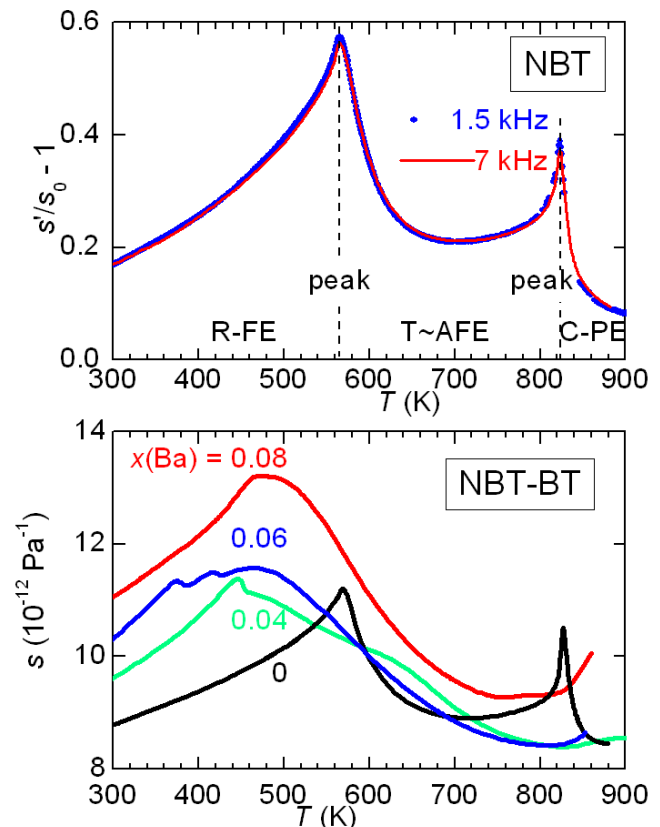


Fig. 6 Elastic compliance of NBT measured at two frequencies (upper panel) and of BNBT-BT at compositions near the MPB.

The case of PZT (Fig. 5) can be interpreted as follows [9]. At the transition between T-FE and C-PE the compliance has the expected step at the transition; in fact, the peaked component shifts to higher temperature with increasing frequency and is due to domain wall relaxation. At the M-T transition, instead, there is a genuine peak, without any frequency dispersion; it is small at a compositions at the border between M and R regions ($x = 0.455$, see Fig. 4) but it develops well within the M region ($x = 0.465$). This can be explained by observing that at the FE T-M transition there is mainly a rotation of the polarization from $\langle 100 \rangle$ toward $\langle 111 \rangle$, which is almost linearly coupled with a shear distortion, and therefore mimics the bilinear coupling term εP , which in turn induces a peak response of the compliance. In this sense, the peaked compliance would be an indicator of continuous rotation of the polarization, which is beneficial to the electromechanical coupling and is associated with a M phase.

The case of NBT-BT is more complicated (Fig. 6). On one hand there is a peak in the compliance, that becomes very large near the MPB, and hence would indicate the presence of M phase. On the other hand, the peak is also very broad, and also the T-C transition presents a peak (without frequency dispersion) instead of the expected step (the main order parameter in this case is the rotation of the TiO_6 octahedra about their c axes, which again cannot be linearly coupled to any strain in the symmetric cubic phase). In this case another explanation must be invoked for the peaked compliance, like dynamic fluctuations [11], observed *e.g.* in KMnF_3 [12], and arising from coupling of the soft mode with an acoustic mode. Then, the same mechanism might be responsible

also for the peak at the R-T transition in NBT, but two arguments should be considered. First, we observe that, among the two titanates PZT and NBT, only NBT, with much higher lattice disorder, has a peak in $s'(T)$ at the T-C transition. This suggests that static disorder is directly involved, *e.g.* producing bilinear coupling εP on a local scale, that does not completely average to zero and induces the peak. Secondly, the enhancement of the peak at lower temperature is so outstanding near the MPB, that it really suggests the possibility of continuous rotation of the polarization, as in PZT. Certainly, the lattice disorder does not allow a well defined monoclinic phase, and the broadening of the $s'(T)$ peak at 450-500 K indicates that the monoclinic distortions would have very short coherence length. This peak is also nearly independent of frequency, so excluding glassy dynamics, at least in the strain fluctuations responsible for the elastic maximum. This interpretation agrees with the proposal, made after experiments of X-ray diffuse scattering [13] and NMR [14], that at the local scale the displacements of Bi/Na, mainly along $\langle 100 \rangle$, have also a component along $\langle 111 \rangle$ producing monoclinic symmetry, .

Summary

The ferroelectric perovskite NBT-BT has similarities with the classical ferroelectric PZT, but its larger lattice disorder renders the study of its phase diagram and phase transitions more difficult. The combination of the dielectric spectroscopy with the anelastic spectroscopy allowed a more complete definition of the phase diagram of NBT-BT.

The region of stability of the antiferroelectric tetragonal phase of NBT rapidly shrinks in solid solution with BaTiO₃, besides merging into a disordered cubic phase near the composition of the morphotropic phase boundary. The latter separates the ferroelectric rhombohedral and tetragonal phases at compositions $>5\%$ Ba. The anomalous peaks in the elastic compliance at the cubic/tetragonal transformation and near the MPB are interpreted as due to the severe lattice disorder induced by the coexistence of differently charged cations in the same sublattice, but also as indication of continuous rotation of the polarisation, although with very short coherence length, near the MPB.

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