Evolution of the tetragonal to rhombohedral transition in 
\[(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - x\text{BaTiO}_3 (x \leq 7\%)\]

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Abstract

\[(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - x\text{BaTiO}_3\] has been the most studied Pb-free piezoelectric material in the last decade; however, puzzles still remain about its phase transitions, especially around the important morphotropic phase boundary (MPB). By introducing the strain glass transition concept from the ferroelastic field, it was found that the phase transition from tetragonal (T, \(P4_{2}bm\)) to rhombohedral (R, \(R_{3c}\)) was affected by a strain glass transition at higher temperature for \(x \geq 4\%\). In these compositions, the T–R transition was delayed or even totally suppressed and displayed huge thermal hysteresis upon cooling and heating. Also, isothermal phase transitions were predicted and realized successfully in the crossover region, where the interaction between the T–R transition and the strain glass transition was strong. Our results revealed the strain glass nature in compositions around the MPB in this important material, and also provide new clues for understanding the transition complexity in other \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\)-based Pb-free piezoelectric materials.

Keywords: Pb-free piezoelectrics, morphotropic phase boundary, phase transition, dynamic mechanical analysis

1. Introduction

Owing to increasing environmental and health concerns, there is a rising need for high-performance Pb-free piezoelectric materials to replace the toxic Pb-based ones \([1–4]\). Usually, high piezoelectricity can be obtained at the morphotropic phase boundary (MPB), a phase boundary separating two different ferroelectric phases and, in most cases, the MPB is a boundary between tetragonal (T) and rhombohedral (R) phases \([1, 5–7]\). The structural instability as well as the easy polarization variation at MPB would result in high permittivity and piezoelectricity \([5, 7–13]\).

Because of the existing MPB between T and R as well as the similarity in electron configuration of \(\text{Bi}^{3+}\) and \(\text{Pb}^{2+}\), \((1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - x\text{BaTiO}_3\) (BNT–xBT) has attracted much attention in the last decade as a promising candidate for Pb-free piezoelectrics \([4, 6, 14–22]\). However, its piezoelectric property is still not good even at its suggested MPB \(x = 6–7\%\) \((d_{33} = 120–180\ \text{pC N}^{-1})\) \([3, 6, 16]\), in contrast to \(d_{33} > 400\ \text{pC N}^{-1}\) for other BT-based MPB...
compositions [5, 23–25], and the depolarization temperature ($T_d$) in BNT–xBT drops significantly around MPB, restricting its practical applications [3, 4].

The major difference of BNT–xBT as compared to other MPB systems is the fact that the MPB and $T_d$ in BNT–xBT appear only after electric poling [6, 16, 26]. In the unpoled state, the MPB compositions only show a pseudo-cubic (p-C) structure with nano-sized domains and no macro phase transition between T and R, in other words, no actual MPB ($p$–$C$) structure with nano-sized domains and no macro phase transition, especially in their interaction/crossover region where peculiar transition phenomena occur. Hence, compositions near the MPB ($p$–$C$) are characterized by apparent heat flow peaks/dips in DSC (neither in other structure measurements such as XRD and permittivity measurement, to characterize the T–R transition and to further understand the nature of the previously suggested MPB in BNT–xBT, we used multi-frequency dynamic mechanical analysis (DMA), combined with differential scanning calorimetry (DSC) and permittivity measurement, to characterize the T–R transition in BNT–xBT. It should be emphasized that DMA is particularly effective in clarifying transitions in BNT–xBT because DMA is very sensitive to strain change caused by various transitions (strain resolution ~1 nm). Previously, we have used DMA to characterize the transition in BNT–xBT upon heating, and we found that the T–R transition finally evolved into a strain glass transition, a glass-frozen process instead of a typical phase transition [14]. In this paper, different methods were used to study the T–R and strain glass transition, especially in their interaction/crossover region where peculiar transition phenomena occur.

2. Experimental

Ceramic samples were fabricated via a conventional solid-reaction method with starting materials of carbonate (BaCO$_3$, Na$_2$CO$_3$) and oxide (Bi$_2$O$_3$, TiO$_2$) powders (purity 99.9%). The calcination was performed at 900 °C for 4 h and sintering at 1100–1200 °C for 2 h. To reduce the volatilization of Bi and Na, calcination and sintering were performed in a closed crucible, with pellets buried in excess of protective powders that had the same composition as the sample. Heat flow was analyzed with a DSC-Q200 from TA Instrument at a heating/cooling rate of 10 °C min$^{-1}$. Dielectric constants were measured using a HIOKI LCR meter at 100 Hz, 1 kHz and 10 kHz at a heating/cooling rate of 2 °C min$^{-1}$. Crystal structure was analyzed with an x-ray diffractometer (Shimadzu 7000 XRD). DMA was carried out with a DMA-Q800 system from TA Instruments at 0.2, 0.4, 2, 4, 10 and 20 Hz at a heating/cooling rate of 2 °C min$^{-1}$.

3. Results and discussion

3.1. The compositional evolution of the T–R transition in BNT–xBT

Figures 2(a)–(d) show typical DSC and permittivity curves of BNT–xBT, revealing its T–R phase transition (the cooling run was seldom reported previously). The T–R transition is characterized by apparent heat flow peaks/dips in DSC and kinks in permittivity curves, denoted $T_m$ and $T_m^+$ in figure 2, for critical temperatures during cooling and heating runs, respectively. One can note that at the permittivity peak temperature ($T_m$), there is no corresponding transition signal in DSC (neither in other structure measurements such as XRD).
or neutron [27, 29–32], nor in our later DMA), which means that this anomaly only appears in permittivity measurement and does not represent a typical ferroelectric transition, thus this temperature will not be discussed further in this work.

The structure phase transition temperatures $T_{s-}$ and $T_{s+}$ were plotted in figure 2(e) against the composition $x$. It can be seen that both temperatures decrease with increasing BT content. Interestingly, the transition becomes abnormal for $x \geq 4\%$. In BNT–4BT, there is an apparently increased thermal hysteresis (≈45 °C) compared with lower BT content compositions. Furthermore, BNT–5BT shows an asymmetric transition behavior with clear transition signal only upon heating (see figure 2(c)). In compositions $x = 6$ and 7% in the unpoled state, the T–R transition no longer appears to occur.

### 3.2. The presence and impact of a strain glass transition

We then used DMA to characterize the T–R transition in BNT–$x$BT (only the cooling run is shown). For pure BNT (figure 3(a)), the structure transitions from C to T to R ($T_{c-}$ and $T_{c+}$) are characterized by sharp peaks in tan delta and dips in modulus. For BNT–7BT (figure 3(b)), even though no transition was detected by DSC measurement, the DMA curve reveals a broad transition-like signal at $T_{g-}$. Importantly, the transition temperatures are frequency dependent (inset in figure 3(b)) and show a little divergence between that of modulus and that of tan delta. Also, it can be noted that the change of modulus and the tan delta caused by this transition is rather small compared with that of BNT if putting into the same scale. These features indicate that the transition in BNT–7BT is not a typical phase transition which reforms the material and occurs at nearly the same temperature for different frequencies and different measurements; rather, they fit well with the criteria of a strain glass transition [14, 33, 34].

Strain glass transition is the conjugated glass transition of structure/ferroelastic transition. It represents a process of kinetically frozen short-range strain ordering domains, which is different from a thermodynamic transition that involves long-range order phase transition [33, 34]. Here ‘frozen’ means that the short-range ordering domains (nano domains) become non-ergodic due to the lack of thermal activation energy [35, 36]. Strain glass is a ferroic glass state with strain ordering as the primary order parameter, and is physically parallel with cluster spin glass [37] in ferromagnetic materials and relaxor [38] in ferroelectric crystals. Similar to cluster spin glass and relaxor transition, strain glass transition is characterized by the absence of macro phase transition (no phase transition signal in DSC measurement), and by the freezing of nano domains (frequency dispersion in DMA measurement at the frozen region) [14, 33, 34].

For intermediate compositions, BNT–4BT and BNT–5BT, both the strain glass transition and the T–R
Figure 3. DMA characterization during cooling for (a) BNT, and (b) BNT–7BT at 0.2, 2 and 20 Hz. \( T_{c-} \) stands for structure transition of C–T and \( T_{s-} \) for T–R; \( T_{g-} \) stands for the strain glass transition. The inset in (b) is a close view of the modulus at \( T_{g-} \) for BNT–7BT.

Figure 4. DMA characterization during cooling of (a) BNT–4BT and (b) BNT–5BT. Panels (c1)–(c4) are the temperature-dependent XRD profiles for BNT–5BT during cooling at 300, 100, 50 and −20 °C. P stands for parent phase and S stands for subphase in the XRD peak index.

In addition, a broad transition signal at temperatures below \( T_{g-} \) appears for BNT–5BT, but is very weak and diffuse. Also, the temperature region of transition is similar for modulus and tan delta, indicating a possible diffuse phase transition. To identify the nature of this broad transition, we recorded XRD profiles for BNT–5BT at different temperatures during cooling (figures 4(c1)–(c4)). The XRD result provides direct evidence for the gradual development of the long-range order state during this broad transition. Thus, this transition is confirmed to be a diffuse phase transition which occurred in a large temperature range, and apparently it is too weak and too diffuse to be clearly detected by DSC and permittivity measurements.

This diffuse phase transition was further proved by DSC thermal cycle experiments, as shown in figure 5(a). The sample was cooled from higher temperature to different holding temperatures and then heated. From the transition latent heat released on heating, the ordering degree of the sample when cooled to that holding temperature can be estimated. During all the cooling run, no clear transition signal was detected because the cooling transition was weak and diffuse. However, upon heating, different holding temperatures gave different heating transition behaviors. One can find that the transition latent heat gradually appeared and increased with lowering holding temperatures. Also, the transition signal upon heating is relatively sharp and \( T_{s+} \) is almost independent of the holding temperatures, being different from the diffuse transition upon cooling. The quantitative transition heat versus holding temperature was plotted in figure 5(b). The diffuse T–R transition starts at a temperature of about 80 °C. By further lowering the holding temperature, the transition becomes more and more evident with a nearly linear amount of heat released. When the holding temperature reaches −20 °C and below, the transition heat gets saturated, indicating that the transition is nearly complete. From figure 5(b), the diffuse T–R transition in BNT–5BT occurs from 80 to 0 °C, similar to the DMA result shown in figure 4(b).

3.3. Phase diagram incorporating T–R and strain glass transition

Based on the dynamic mechanical measurement data, a transition diagram concerning the T-R and strain glass
transitions can be constructed, as shown in figure 6. For the heating run (figure 6(a)), compared with previously reported data (figure 1), the main structure transition signals are the same; however, new strain glass transition is defined according to the frequency dependence of transition temperatures revealed by DMA. Actually, this strain glass transition temperature matches well with \( T_{me} \) (maximum elastic compliance) in the anelastic measurement by Cordero et al \[18\]; however, only single frequency was used in determining \( T_{me} \) in the previous work, thus the nature of the transition at \( T_{me} \) was not clearly explained.

For the cooling run (figure 6(b)), which has been seldom reported, new strain glass transition was found for BNT–xBT with \( x \geqslant 4\% \) as compared with previous diagrams based on DSC and permittivity (figure 2(e)). It is worth noting that a structure phase transition occurred after a glass transition has been defined as spontaneous transition, which means that the frozen glass state (after glass transition, a non-ergodic state) can spontaneously transform into a long-range order state by further cooling rather than by an external field \[39, 40\]. Accordingly, we suggest that the structure transition occurred after the strain glass transition during cooling in BNT–4BT and BNT–5BT as a spontaneous transition (\( T_{sp} \)).

3.4. Puzzles unfolding

As indicated in the diagram, for \( x \leqslant 3\% \), the ceramic samples undergo thermodynamic structure phase transitions between T and R, while for \( x \geqslant 6\% \), they undergo kinetically frozen strain glass transitions, namely only a very few nanosized R domains are formed, while most parts of the sample remain unchanged, proved by the \textit{in situ} transmission electron microscopy observations of Ma et al \[21, 22\]. Thermodynamic phase transition and kinetic glass transition are different in nature and correspond to two different non-ergodic states, and thus only one transition, either to a long-range order phase or to a frozen short-range glass, is expected in a sample.

However, BNT–4BT and BNT–5BT have the unique combination of these two different transitions. Upon initial cooling (figure 6(b)), BNT–4BT and BNT–5BT presumably experience the T–R structure transition at certain temperatures similar as \( x \leqslant 3\% \) (thermodynamic favorable state); however, they first undergo a strain glass transition and become non-ergodic before this transition could happen (kinetically frozen). In order to escape from the frozen state and become the thermodynamically favorable state, they undergo
a spontaneous transition at much lower temperatures with increasing thermodynamic driving force [41]. In BNT–6BT and BNT–7BT, the spontaneous transition, if it exists, is shifted to temperatures below $-140^\circ$C (the lowest temperature our DMA can reach).

On the other hand, the structure transition upon subsequent heating (figure 6(a)) is relatively normal, as evidenced by the linear relation of $T_\text{i}$ with composition $x$, except that $T_\text{i}$ suddenly disappears for BNT–6BT and BNT–7BT. This can be explained by the different transition sequence upon cooling and heating. During cooling, the strain glass transition occurs prior to the T–R transition, hence it greatly affects the T–R transition and drives the transition to a much lower temperature; while upon heating, the structure transition occurs prior to the strain glass transition, thus the T–R transition is not influenced.

The T–R transition is significantly affected upon cooling, but not affected upon heating. Therefore, it becomes easy to understand why there is a huge thermal hysteresis for BNT–4BT as well as BNT–5BT (if we choose the peak temperature of diffuse phase transition as $T_\text{s}$, then the thermal hysteresis is about 100 °C for BNT–5BT). Also, the abrupt disappearance of the T–R transition in BNT–6BT and BNT–7BT comes from the fact that there is no spontaneous transition upon cooling, therefore no T–R transition can be expected on the subsequent heating run.

With this newly found strain glass transition at high temperature and the reversed transition sequence during heating/cooling in BNT–xBT, the puzzles mentioned in the introduction section can be explained. (i) The T–R transition abruptly disappears in BNT–6BT and BNT–7BT (upon heating) because it is suppressed/prevented by the high-temperature strain glass transition upon cooling and therefore no T–R transition can be expected upon heating; (ii) the mysterious transition at $T_\text{me}$ previously revealed by anelastic measurements is just this strain glass transition; and (iii) the huge thermal hysteresis and asymmetric transition are caused by the asymmetric influence of the strain glass on the structure transition upon cooling and heating.

It is worth noting that researchers also claim that the MPB region in BNT–xBT (unpoled state) is a relaxor state since strong permittivity relaxation and nano-sized ferroelectric domains were found in this region [21, 22, 32]. However, owing to the high-temperature permittivity peak at $T_\text{m}$, direct evidence of the relaxor frozen process can hardly be obtained. Here, by DMA, the glass transition nature in this region is validated (unpoled state).

For other BNT-based Pb-free piezoelectric materials, such as $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - \chi (\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ [19, 42–49], they show very similar transition complexity as BNT–xBT, like abrupt disappearance of T–R transition as well as the unexpected lowering of $T_\text{d}$ at MPB compositions in the unpoled state. Therefore, the abovementioned strain glass transition and related peculiar transition phenomena are also expected and explainable for those materials. In fact, lots of reported data suggest our assumption.

### 3.5. Isothermal transition at the crossover region

For the purpose of the following discussion, we define the linear extrapolation of $T_\text{s}$ (dashed red line in figure 6(b)) as the ‘ideal $T_\text{s}$’ for those whose transition was affected by the high-temperature strain glass transition. Accordingly, a region between the ‘ideal $T_\text{s}$’ and the ‘measured $T_\text{s}$’ marks the interaction region between the structure transition and the strain glass transition and is referred to as the crossover region in the transition diagram (filled with green lines in figure 6(b)).

In this crossover region, the kinetically frozen glass state is caused by the strain glass transition, but the thermodynamically favorable state is the long-range order state. This means the glass state here is a metastable state and has a tendency to evolve into a long-range order state. If this is true, then a time-induced transition from the metastable glass to a long-range order state would be expected, since an increase in holding time increases the accumulated transition possibility to a thermodynamically favorable long-range order state.

Figures 7(a) and (b) show the isothermal (time induced) phase transition in BNT–xBT at the crossover region. To reveal what happened during isothermal holding, we compared the subsequent heating DMA curves without holding (3 min in experiments) and after 5 h holding. For BNT–4BT heated from 135 °C without holding (red curves), the DMA heating curves only show a strain glass transition at $T_\text{gs}$. However, after isothermal holding for 5 h at 135 °C, the subsequent heating curves (blue) show a clear transition.
signal in both modulus and tan delta, labeled as \( T_\alpha \) (iso). A similar result for BNT–5BT at 70 °C is shown in figure 7(b). This means BNT–4BT at 135 °C and BNT–5BT at 70 °C (crossover region) are in a strain glass state initially, but can transform into a long-range order state after holding for 5 h at that temperature. This is clear evidence that during isothermal holding, both compositions undergo isothermal phase transitions from a strain glass to a long-range order state.

The \textit{in situ} time-dependent modulus curves for the two compositions are shown in figure 7(c). For BNT–4BT and BNT–5BT, the modulus increases through several ‘V’-shaped valleys at the beginning, similar to the modulus softening effect in the transition region. The \textit{in situ} time-dependent XRD profiles for BNT–5BT at 70 °C (figure 7(c) inset) shows that the gradual development of long-range ordering domains, especially in the initial 2 h, were consistent with the time period of the modulus valleys. After the ‘stepwise increase’, the modulus becomes saturated with time evolution, indicating that the isothermal transition is nearly complete and an ageing effect becomes dominant [50–53].

For BNT–6BT and BNT–7BT, isothermal phase transition is also expected, but with increasingly long relaxation time since they are away from the long-range order state and in the fully frozen glass region. For BNT–6BT, only a very weak isothermal transition signal appeared after isothermal holding at room temperature for one month, while for BNT–7BT, no obvious isothermal transition signal was found for the same isothermal period. This indicates that isothermal phase transition takes much longer to complete for these two compositions, and also explains various transition results for BNT–6BT and BNT–7BT because transition in these compositions is strongly history dependent and isothermal phase transition upon heating can occur if they are placed at room temperature for enough time (room temperature is in their crossover region).

4. Conclusion

In summary, we used DMA, combined with DSC and permittivity measurements to characterize the T–R transition in BNT–xBT. It is found that the T–R transition is affected by the high-temperature strain glass transition, which leads to peculiar transition behaviors around the MPB. The crossover region caused by the interaction between the T–R structure transition and the strain glass transition produces a metastable glass phase which transforms to the long-range order phase under isothermal conditions.

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