Quenching-induced circumvention of integrated aging effect of relaxor lead lanthanum zirconate titanate and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$

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Quenching-induced circumvention of integrated aging effect of relaxor lead lanthanum zirconate titanate and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3

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The effect of quenching on the dielectric properties of ceramic $\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.98}\text{O}_3$ (PLZT 8/65/35) and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -6 mol. % BaTiO_3 (BNT-6BT) was investigated after annealing at a wide range of temperatures. The dielectric permittivity showed that the magnitude and shape profile of the permittivity were significantly affected by the quenching process in comparison to furnace-cooled specimens. We propose that the changes originate from a circumvention of integrated aging that takes place during cooling process. A comparison between PLZT 8/65/35 and BNT-6BT allowed us to conclude that two different types of polar nanoregions exist in BNT-6BT and the transition between them peaks at around 300 °C. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4788932>]

Since the terminology relaxor was introduced in 1987,¹ extensive research over the relaxor materials of practical importance, such as $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)_{1-4/x}\text{O}_3$ (PLZT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT), has been conducted to understand the underlying mechanisms.^{2,3} While most studies so far have been confined to lead-containing materials, attention to $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT)-based lead-free relaxors has been increasing significantly since the recent environmental regulations such as RoHS/WEEE by the European Union were enforced.⁴⁻⁶

It is generally agreed that the commonly referred relaxor features are largely attributed to the existence of polar nanoregions (PNRs).² Although various characterization techniques have been used to investigate the behaviors of PNRs, the underlying mechanism of their behavior below temperatures of maximum dielectric constant is still not fully understood.⁷ One of the important phenomena related to this temperature regime is the aging of relaxor ferroelectrics, which refers to the degradation in dielectric permittivity with time.⁸ Apart from the practical implications,⁹ the aging behavior of relaxor ferroelectrics is of special interest because it has been known to be directly related to the physics of the freezing of PNRs at low temperatures.¹⁰ Given this, Pan *et al.*¹¹ proposed that a “hardening” of inhomogeneously distributed long-range ordered regions is responsible for the aging in PMN-PT, while Colla *et al.*¹² considered spin-glass and thermal chaos effect as the origin of aging. However, it was later demonstrated that the aging effect is not solely confined to the temperatures near the freezing temperature that is known to match the depolarization temperature,^{6,13} but is also notable even above the maximum dielectric temperatures of the usual frequency range of kilohertz.^{14,15} So far, none of the proposed mechanisms clearly underpins all the observed aging-related phenomena in relaxor ferroelectrics yet.

In this work, the ceramic samples were annealed at a wide range of temperatures covering all the temperature

regimes of importance so far studied in the literature. A focused attention was paid to the influence of quenching on the changes in the frequency-dispersive regime in the dielectric spectra of both materials. Based on the results, we propose a perspective on the aging process of relaxor ferroelectrics, which describes the thermal evolution of PNRs in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -6 mol. % BaTiO_3 (BNT-6BT).¹⁶

The same set of ceramic samples with those reported in Ref. 16 was employed for a systematic quenching experiments. Based on our preliminary study showing that thermal annealing of electroded samples, especially at >300 °C, results in an alteration of ceramic properties due to an extensive diffusion of the electrode materials into the ceramic body, unelectroded $\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.98}\text{O}_3$ (PLZT 8/65/35) and BNT-6BT samples were heated at 5 °C/min up to 400 °C and annealed for 30 min to remove memory of the low-temperature state. Afterwards, the samples were cooled down in the furnace from 400 °C to 60, 150, 200, 300, 600 °C (for PLZT) and 100, 200, 300, 400, 500, and 600 °C (for BNT-6BT), respectively. The samples were annealed at the desired temperature for 30 min and then water-quenched to ambient temperature. Immediately after quenching, the samples were sputtered with Pt-electrodes, and their permittivity was measured. For reference, the as-sintered samples were also annealed at 400 °C for 30 min, furnace-cooled to room temperature, and sputtered with Pt-electrodes. For proper comparison of the different sets of materials, the first dielectric data points were taken for all the samples in about an hour after quenching treatment, the same conditions were also used for as-sintered samples. Complex dielectric permittivity ($\epsilon' - i\epsilon''$) was measured by an impedance analyzer (HP 4284A) equipped with a temperature-controllable furnace. Data points of capacitance and dissipation factor were recorded at every 2 °C from RT to 500 °C at a constant heating rate of 2 °C/min. Four measurement frequencies of 100 Hz, 1 kHz, 10 kHz, and 100 kHz were selected. For both PLZT 8/65/35 and BNT-6BT, the position of the dielectric maximum was determined by the inflection point in the imaginary part.¹³

Figure 1(a) shows the changes in the dielectric permittivity of PLZT 8/65/35 for two different quenching temperatures.

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FIG. 1. (a) Dielectric permittivity at 1 kHz of PLZT 8/65/35 samples as-sintered, quenched from 60 °C (q60) and quenched from 300 °C (q300). (b) The difference in permittivity between quenched and as-sintered PLZT 8/65/35 samples.

When quenched from 60 °C (q60), which is below the dielectric maximum T_m at 1 kHz but above the freezing temperature T_f (~ 34 °C¹⁶), the permittivity values below the quenching temperature increase notably, leading to the appearance of a shoulder near the quenching temperature. A similar change is also induced in the imaginary part of the dielectric permittivity (ϵ''). This increase in the permittivity below 60 °C is also evident in Fig. 1(b), where the difference in permittivity between as-sintered and quenched samples is compared. The shoulder near 60 °C (peak A of q60) indicates that there is an increase in permittivity at temperatures below the quenching temperature. In addition to the appearance of the shoulder near 60 °C, it is interesting to note that there is a slight depression of permittivity near 75 °C and an increase in permittivity above 75 °C (peak B of q60). The changes indicate that the quenching process also affects the dielectric response of the material at temperatures even above the quenching temperature.

Previous studies on the canonical relaxor ferroelectrics, such as PMN-PT¹¹ and PLZT,¹⁷ suggested that a significant amount of time may be required for the consequence of aging to be discerned. This could be partly due to relatively low temperature, i.e., limited thermal energy, where the aging experiments were usually practiced and partly due to a weak correlation among the defect dipoles in action. However, as well-known in the case of acceptor-doped $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics, where aging is unavoidable without quenching treatment,¹⁸ a degree of aging could be discerned even during furnace cooling procedures *albeit* small in extent depending on the type and density of defect dipoles existing in the system. In this sense, it is considered that the whole cooling process is subject to a continuous aging process, causing the resultant dielectric permittivity signal to be affected by the aging process integrated over the entire temperatures during cooling. Due to this integrated aging process, some portions of the PNRs become continuously reoriented along a certain direction during cooling, which leads to a systematic loss in the magnitude of dielectric permittivity. By quenching from a certain temperature, e.g., 60 °C, pending aging process below the quenching temperature is skipped; therefore, the aging-related degradation in the dielectric permittivity is circumvented. This is well-supported by the fact that the dielectric permittivity below the quenching temperature is evidently increased. The same tendency is observed for the sample quenched from other temperatures between T_m and T_f , which is consistent with the previously known single-stage and multiple-stage aging processes in the literature.^{8,10,12,14,15}

When quenched from 300 °C, which is much higher than T_m (92 °C at 1 kHz), the total permittivity increases considerably without any splitting in the permittivity, as seen in Figs. 1(a) and 1(b) (q300). This increase in the total permittivity can be rationalized by two effects. First, the quenching temperature of 300 °C is so high that the entire integrated aging effect could be circumvented. In this case, an increase in the magnitude of permittivity over the entire temperature range should be visible. Second, quenching from 300 °C may also affect the size distribution and number density of the PNRs leading to an overall increase in the magnitude of permittivity.

Figure 2(a) compares the peak position with the frequency dependence of the maximum permittivity of PLZT 8/65/35 at different quenching temperatures. It reveals that the peak position is shifted to higher temperatures when quenched from 60 °C, and this shift is most significant at lower frequencies. When quenched from 150 °C and above, the peak position is only slightly shifted to higher temperatures and, finally, no visible change is denoted when quenched from 300 °C and above. On the other hand, the comparison of the maximum value of permittivity in Fig. 2(b) suggests that the consequence of quenching from the temperatures, where frequency dispersion is negligibly small, is the decrease in permittivity due to the reduced number density of PNRs in the quenched samples.

Many features in common with PLZT 8/65/35 are evident in BNT-6BT quenched from different temperatures displayed in Fig. 3(a). When quenched from 100 °C that is below the local maxima of the first anomaly (Throughout the text, the notion, first and second anomaly, is designated by its appearance during heating.) but above T_f of ~ 83 °C,¹⁶ an enhanced shoulder appears at around 100 °C in the permittivity curve (q100). This increase in permittivity can also be clearly observed in the difference in permittivity as shown in Fig. 3(b), where an increase in permittivity at around 100 °C can be discerned (peak A of q100). As proposed in PLZT 8/65/35, the changes in the permittivity can also be explained by the suppressed integrated aging process below 100 °C with the quenching treatment. As well, a depression in permittivity between 100 and 300 °C and an increase in permittivity at 300 °C and above are apparent, although the depression in BNT-6BT q100 is much more significant than that in PLZT q60.

Apart from the similarities, a unique feature of BNT-6BT is revealed. A splitting in the permittivity is induced when the material is quenched from 300 °C, as shown in Figs. 3(a) and 3(b) (q300). It is noticed that this splitting is

FIG. 2. (a) Peak position of maximum dielectric permittivity of PLZT 8/65/35 samples quenched from different temperatures. (b) Magnitude of maximum dielectric permittivity of PLZT 8/65/35 samples quenched from different temperatures. For both figures, the first data points are from the as-sintered samples.

not reasonably explained by the elimination of integrated aging effect resulting from a finite cooling rate in that this temperature is far above the local maxima of the first anomaly. This implies that the splitting in the permittivity may have its origin on the presence of another type of PNRs. In addition, the fact that the magnitude of the first anomaly is lowered by the quenching treatment strongly implies that the number density of PNRs responsible for the first anomaly is decreased, indicating that a phase transition between two different types of PNRs exists somewhere between the two anomalies. This finding conforms well to the model,¹⁶ which states that the entire permittivity shape profile of BNT-6BT consists of the presence of low-temperature PNRs (LT-PNRs) and high-temperature PNRs (HT-PNRs) bridged by a phase transition.

When quenched from 500 °C (above the local maxima of the first anomaly¹⁶), the total magnitude of permittivity increases with the absolute permittivity value around the shoulder at about 200 °C (q_{500} in Figs. 3(a) and 3(b)) being more pronounced, causing the existing two dielectric anomalies to be less distinctive. Given that the system was quenched from 500 °C that is much higher than the transitional temperature region of LT-PNRs and HT-PNRs,¹⁶ HT-PNRs could be mainly responsible for this relaxation.

Figure 4(a) compares the local maxima of the first anomaly of BNT-6BT for different quenching temperatures with frequency dependence. It reveals that the position of the local maxima is shifted to lower temperatures when quenched from 100 °C and then shifted to higher temperatures when the quenching temperatures are increased above 100 °C. Comparison of Figs. 2(a) and 4(a) demonstrates a couple of discrepancies between BNT-6BT and PLZT 8/65/35. First, there is an increase in $T_{\max}$ for PLZT 8/65/35 quenched from 60 °C (PLZT q60), while a decrease in the temperature of local

maxima for BNT-6BT quenched from 100 °C (BNT-6BT q100) is observed. A phenomenological difference is that PLZT q60 undergoes a splitting in permittivity where the $T_{\max}$ (peak B in Fig. 1(b)) is shifted to higher temperatures, while BNT-6BT q100 has no splitting in permittivity. This implies that the local maxima for BNT-6BT q100 (peak A in Fig. 3(b)) are similar to the peak A of PLZT q60 in Fig. 1(b). Second, when quenched from temperatures above T_m , the peak position of PLZT 8/65/35 is shifted to higher temperatures reaching a maximum value when quenched from 300 °C, while the local maxima of the first anomaly of BNT-6BT keep being shifted to higher temperatures.

In Fig. 4(b), it is found that the total magnitude of the first anomaly is depressed when quenched from 100 °C and is enhanced when quenched from higher temperatures. The increase in permittivity when quenched from 200 °C can be attributed to the extinction of integrated aging process of the LT-PNRs. Above 300 °C, HT-PNRs contribute to the increasing permittivity at temperatures up to 500 °C. When quenched from 600 °C, the total magnitude of the permittivity decreases, which may be due to the decrease in HT-PNRs in number at 600 °C than at 500 °C. By comparing Fig. 2(b) with Fig. 4(b), discrepancy is found for PLZT q60 and BNT-6BT q100, which can be attributed to the absence of peak splitting in BNT-6BT q100 as we have discussed previously. Another feature of Fig. 4(b) is that the frequency dependence of BNT-6BT undergoes a reversion with a cross point at 300 °C (marked by an arrow in Fig. 4(b)), while in Fig. 2(b), the frequency dependence of PLZT 8/65/35 remains consistent through the whole temperature range. This reversion of frequency dependence in BNT-6BT suggests a transition in the nature of PNRs at that temperature.

Although the traditional view and previous studies define the aging of relaxor materials as the loss of

FIG. 3. (a) Dielectric permittivity at 1 kHz of BNT-6BT samples as-sintered, quenched from 100 °C (q100), from 300 °C (q300), and from 500 °C (q500). (b) The difference in permittivity between quenched and as-sintered BNT-6BT samples.

FIG. 4. (a) Peak position of the first dielectric anomaly of BNT-6BT samples quenched from different temperatures. (b) Magnitude of the first dielectric anomaly of BNT-6BT samples quenched from different temperatures. For both figures, the first data points are from the as-sintered samples.

permittivity after annealing at a certain temperature for a sufficiently long time (e.g., 24 h or longer), in this work, we introduce the concept that aging process also takes place in small time scales (e.g., during furnace cooling). The cooling process at low temperatures can be well defined as an integrated aging process, which occurs continuously during cooling process. However, like any other time-dependent process, this integrated aging process was shown to be circumvented by rapid cooling. The quenching experiments on both PLZT 8/65/35 and BNT-6BT suggest that the integrated aging process may be a common feature for relaxor ferroelectrics and be prevented partially or completely by quenching from higher temperatures, which results in enhancement in the magnitude of dielectric permittivity. This work suggests that the quenching technique could be a promising method for further investigation of the aging effect and other thermal behaviors in relaxor ferroelectrics.

In addition, an insight into the nature of the relaxor behavior of BNT-6BT was gained. The thermal behavior in both the first anomaly of BNT-6BT and the anomaly of PLZT 8/65/35 showed a strong similarity, which suggests that the first anomaly in BNT-6BT should be attributed mostly to the relaxation of a single type of PNRs, i.e., LT-PNRs. Second, both the splitting in the permittivity curve and the existence of relaxation due to HT-PNRs evidenced by quenching from 300 °C and above strongly suggest that two PNRs should coexist in BNT-6BT and a phase transition between LT-PNRs and HT-PNRs should take place at around 300 °C.

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