Influence of annealing on *B*-site order and dielectric properties of $(0.4)Pb(In_{1/2}Nb_{1/2})O_3:(0.6)Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxor ceramics

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(Received 10 May 2006; accepted 15 September 2006; published online 5 December 2006)

The structural long-range *B*-site ordered domains and dielectric properties of the as-sintered and postannealed ceramics $(0.4)Pb(In_{1/2}Nb_{1/2})O_3:(0.6)Pb(Mg_{1/3}Nb_{2/3})O_3$ have been characterized. Transmission electron microscopy studies show an increase in the size of the ordered domains following annealing. In the low-field dielectric measurements, the longer the annealing time, the narrower is the diffuse phase transition. A high-temperature dielectric anomaly at low frequency in the as-sintered sample significantly weakens following postannealing. The annealed samples retained their exceptionally slim ferroelectric hysteresis loops. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2374934]

Pb-based complex perovskites with a general formula of $Pb(B'_xB''_{1-x})O_3$ are an important class of oxides because of their outstanding dielectric, electromechanical, and electro-optical properties.[1,2] Phase transitions and ferroelectric properties of most Pb-based complex perovskites are influenced by the degree of 1:1 long-range order (LRO), as exemplified by $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST).[3] The influence of order-disorder on the properties of $Pb(B'_xB''_{1-x})O_3$ perovskites have been extensively studied.[4–9] $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) has a very low degree of LRO,[5] which is controlled by the driving forces originating from differences in size and charge between the B-site cations. Also, the degree of LRO is modified by cation substitutions only.[10] The high-energy electronic configurations of the disordered states are stabilized by the hybridization of Pb 6*s* and O 2*p* states.[11] The size of short-range ordered domains is less than 10 nm.[12] Unlike PMN, LRO can be modified by heat treatment in $Pb(In_{1/2}Nb_{1/2})O_3$ (PIN). Highly ordered PIN is antiferroelectric below the transition temperature, but becomes a relaxor when disordered or incompletely ordered.[13] By mixing an antiferroelectric or relaxor PIN with PMN, a relaxor solid solution $(x)PIN:(1-x)PMN$ is formed. In the as-sintered ceramic form, the dielectric, electromechanical phase transition, ferroelectric hysteresis characteristics, and LRO domain size are composition dependent.[14–17] Here, we report the influence of annealing on the *B*-site LRO and on the dielectric properties of 0.4PIN:0.6PMN ceramics.

0.4PIN:0.6PMN ceramics were fabricated by the two-step solid state reaction method.[17] Following sintering, two of the samples were annealed at 1050 °C for 12 and 36 h and one sample remained in the as-sintered form. Images of the LRO domains were recorded at room temperature using dark-field (DF) imaging in a JEOL-2011 transmission electron microscope (TEM) operated at 200 kV. The relative permittivity (ε_r) and loss tangent ($\tan\delta$) of the silver-coated samples were measured at different frequencies and temperatures using an impedance analyzer (HP4194A) and a computer-controlled oven (Delta Design Delta-9023). The ferroelectric hysteresis loops of the ceramics were measured at room temperature using a Sawyer-Tower circuit.[18]

In (0.4)PIN:(0.6)PMN, TEM has revealed superstructure reflections as well as their corresponding domains of LRO, which were not detected in x-ray profiles. DF images of LRO domains in the as-sintered and the two annealed samples were recorded using the superstructure reflection 1/2 1/2 1/2 along a ⟨110⟩ zone axis (Fig. 1). In the as-sintered sample [Fig. 1(a)] the size of the ordered domains ranges from 10 to 50 nm across, larger than the domains observed in PMN (<10 nm).[12] The domains in the proximity of grain boundaries are larger than those away from grain boundaries.

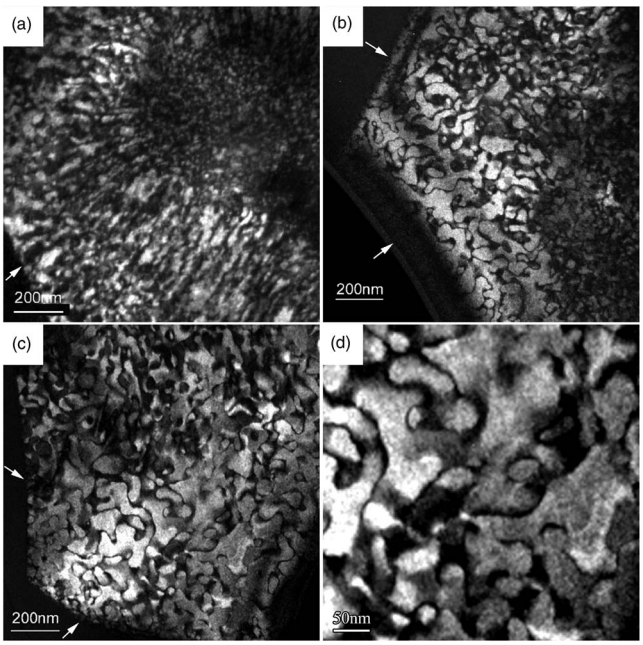

FIG. 1. Dark-field images of the 1:1 LRO domains in 0.4PIN:0.6PMN ceramics: (a) as-sintered, (b) 12 h annealed, and (c) 36 h annealed samples. Grain boundaries are indicated by white arrows. (d) Enlarged image of distinctively sharp antiphase boundaries in the 36 h annealed ceramic.

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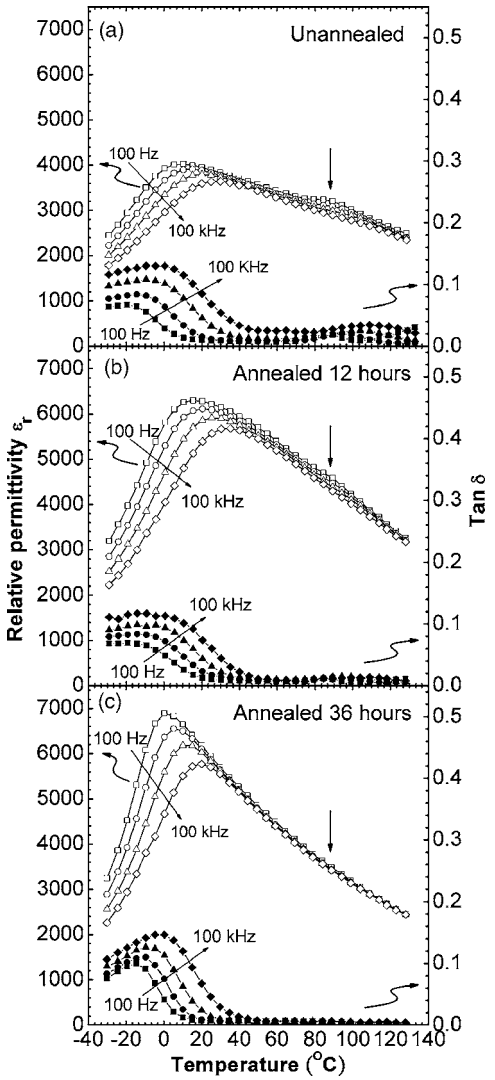

FIG. 2. ε_r and tan δ of 0.4PIN:0.6PMN ceramics: (a) as-sintered, (b) 12 h annealed, and (c) 36 h annealed samples. The high-temperature dielectric anomaly (90 °C), indicated by an arrow, occurs at low frequencies in the as-sintered sample.

This kind of spatial preferential ordering is very common in many order-disorder complex perovskite ceramics, e.g., in PST.[19] In the sample annealed for 12 h, the LRO domains were ~30–150 nm across [Fig. 1(b)]. The increase in domain size is more apparent away from grain boundaries. Preferential ordering in the annealed sample is apparent near the grain boundary, similar to the as-sintered sample. The extended thermal annealing for 36 h yields further increase in the size of the ordered domains, which range from 50 to 200 nm across [Fig. 1(c)]. The size distribution in the 36 h annealed sample is more uniform. Distinctive antiphase boundaries also develop throughout the grain, indicating the onset of an intermediate degree of LRO [Fig. 1(d)]. These observations show that the degree of LRO in 0.4PIN:0.6PMN ceramics can be modified by heat treatment similar to the end member PIN.

Figure 2 shows ε_r and tan δ of the as-sintered and the two annealed samples measured at the frequencies ranging from 100 Hz to 100 kHz and temperatures from −30 to 130 °C. A summary of the dielectric properties of the ceramics is given in Table I. All the three samples exhibit a typical relaxor behavior characterized by (i) frequency dispersions in both temperature-dependent ε_r and tan δ near $T_{\max}$, and (ii) maximum values of ε_r ($\varepsilon_{\max}$) and tan δ measured at an identical frequency do not occur at the same temperature. The value of $\varepsilon_{\max}$ increases with increasing annealing time. The loss tangent at 100 kHz remains at ~0.12 in all the three samples.

A broad diffuse phase transition is observed in the as-sintered sample [Fig. 2(a)], but the sample subjected to longer annealing time displays narrower diffuse transition [Figs. 2(b) and 2(c)]. In order to quantitatively characterize the temperature-dependent dielectric response, the Curie-Weiss temperatures (T_0) of the samples were obtained by extrapolating the reciprocal relative permittivity ($1/\varepsilon_r$) as a function of temperature at 100 Hz. Both T_0 and ΔT_M ($T_{\max} - T_0$) decrease with increasing annealing time, inducing a decrease in the dispersion in the ε_r versus temperature curve. The width of the diffuse phase transition in a relaxor can also be described by the diffuseness constant (δ) derived from the modified Curie-Weiss law, $1/\varepsilon - 1/\varepsilon_{\max} = (T - T_{\max})^{\gamma}/(2\varepsilon_{\max}\delta^{\gamma})$. The empirical exponent γ gives the quantitative information on the nature of the transition. The denominator is the modified Curie-Weiss constant.[20] The value of γ located between 1.0 and 2.0 indicates that the phase transition lies between a normal and a relaxor ferroelectric. In 0.4PIN:0.6PMN ceramics, δ decreases with increasing annealing time. However, strong frequency dispersions are noted in the temperature-dependent dielectric responses of both the as-sintered and annealed samples:—an indication that the samples are relaxors. The value of γ at 1.5, which fluctuates only slightly with annealing in these ceramics, is in contradiction with the value of γ in most Pb-based relaxor complex perovskites in which variations in γ and $T_{\max}$ normally decrease with annealing.[3,7] All the measured γ values for these ceramics are lower compared to PMN (γ=1.64).[20] The lower value of γ combined with the decrease in ΔT_M is in agreement with the observation of reduced dispersion in the ε_r versus temperature curves recorded for these ceramics.

A dielectric anomaly is observed above $T_{\max}$ in the as-sintered and the 12 h annealed samples, especially at low frequencies as indicated by arrows in Fig. 2. The temperature

TABLE I. Summary of both low- and high-field dielectric properties of the 0.4PIN:0.6PMN ceramics. The average error for γ values is about 3%.

Annealing time (h)	$\varepsilon_{\max}$	$T_{\max}$ (°C)	T_o (°C)	ΔT_M (°C)	γ_1	γ_2	γ (average)	δ (°C)	C' ($\times 10^5$)	P_r (μC/cm^2)	E_c (kV/cm)	$D_{\max}$ (μC/cm^2)
0	4025	10.3	−236.6	246.9	1.38	1.43	1.41	95.0	38.55	1.08	1.20	21.70
12	6314	12.8	−105.9	118.7	1.57	1.54	1.55	71.0	92.95	0.11	0.21	19.84
36	6909	1.5	−18.4	19.9	1.48	1.52	1.50	54.7	42.40	0.08	0.15	15.85

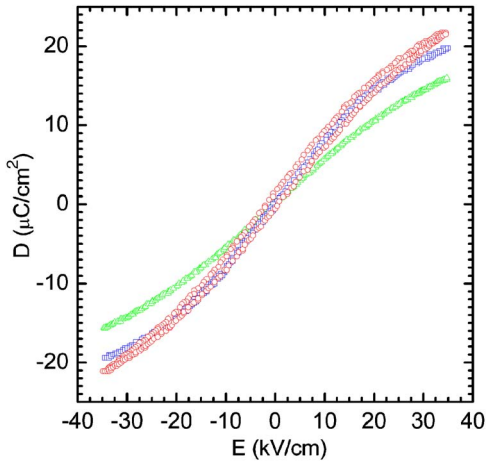

FIG. 3. (Color online) Ferroelectric hysteresis loops of the as-sintered (red), 12 h (blue), and 36 h (green) annealed 0.4PIN:0.6PMN ceramics.

of such anomalies (T_{HT}) is stable at 90 °C and does not change after annealing. The small dielectric peak is reduced as frequency increases, subsequently disappearing at 100 kHz. This anomaly is diminished by annealing and completely disappears in the 36 h annealed sample. It can be deduced that the degree of LRO significantly influences the high-temperature dielectric anomaly. In fact, the high-temperature dielectric anomalies have also been observed in other compositions of the as-sintered PIN:PMN ceramic series.[17] The measured T_{HT} is very close to the temperatures reported for PIN crystals at 95 °C (Ref. 21) and 116 °C (Refs. 22 and 23). In these studies, the influence of the impurity ions from the flux may have significant contribution to the dielectric responses and structural phase transitions. In these ceramics, the high-temperature dielectric anomaly might arise from the transition between spontaneous relaxor and ferroelectric transition. Similar characteristics have been already observed in several ferroelectrics/relaxors, such as PST, $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN), and some irradiated P(VDF-TrFE) copolymers.[24–27] It is suggested that the relaxor to ferroelectric transition in these materials is caused by defects or chemical heterogeneities, which does occur in (x)PIN:$(1-x)$PMN ceramics. The compositional fluctuation inhibits the formation of macroscopic ferroelectric domains to establish a normal ferroelectric behavior and also causes dielectric relaxation. In the previous studies of (x)PIN:$(1-x)$PMN, such high-temperature dielectric anomaly has not been clearly observed.[14–16] It is concluded that the fabrication methods and conditions could considerably influence the degree of 1:1 LRO and consequently the properties.

Figure 3 shows the ferroelectric hysteresis loops of the as-sintered and the two annealed samples measured at room temperature. The hysteresis loop of the as-sintered sample is very slim compared to many relaxors. We have also found that the hysteresis loops become slimmer with increasing annealing time. In the 36 h annealed sample (green trace in Fig. 3), the behavior is similar to a nonlinear lossless dielectric rather than a ferroelectric/relaxor. Typically, the B-site cations have gained sufficient kinetic energy by annealing to migrate to their favorite sites in order to minimize the configurational entropy, causing the size of the 1:1 LRO domains to increase. Consequently, the long-range ferroelectric domains grow to a submicron/micron size near the transition temperature.[5,7] A wide open and fairly square hysteresis loop is assumed in the annealed samples similar to most of the annealed order-disorder perovskite ferroelectrics/relaxors. In this study, it is proposed that the electric-field induced polarization could be suppressed by the antiparallel dipoles. These dipoles are highly likely to exist in (x)PIN:$(1-x)$PMN since the end member PIN can be either an antiferroelectric or relaxor. The macroscopic (anti)ferroelectric domain configuration and its crystallographic details in the annealed (x)PIN:$(1-x)$PMN need further investigations.

In summary, the influence of the cation order on dielectric properties of 0.4PIN:0.6PMN was studied. The characteristics of diffuse phase transitions and dielectric responses (low and high fields) of the ceramics are highly influenced by the degree of 1:1 LRO, which is controlled by annealing. It is interesting that slimmer hysteresis loops lead to lower P_r and E_c in the ceramics with higher degree of LRO. Extended measurements such as high-temperature *P-E* loop or TEM studies of nanodomain to microdomain switching would be necessary to prove high-temperature dielectric anomaly.

This work is supported by the Centre for Smart Materials of The Hong Kong Polytechnic University. One of authors (C.W.T.) is grateful for the financial support by Grant No. B-Q891.

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