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Citation: *Journal of Applied Physics* **104**, 094105 (2008); doi: 10.1063/1.3009319

View online: <http://dx.doi.org/10.1063/1.3009319>

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Field-induced intermediate orthorhombic phase in (110)-cut $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.70}\text{Ti}_{0.30}\text{O}_3$ single crystal

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(Received 21 July 2008; accepted 14 September 2008; published online 6 November 2008)

Phase transformations of (110)-cut $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.70}\text{Ti}_{0.30}\text{O}_3$ single crystal before and after an electric (E)-field poling have been investigated by means of dielectric permittivity, polarization current, hysteresis loop, and *in situ* x-ray diffraction as a function of temperature. An R - T - C transition sequence was observed in the unpoled sample upon zero-field heating. R , T , and C are rhombohedral, tetragonal, and cubic phases, respectively. After a prior E -field poling, the crystal underwent an R - O (R)- T - C phase sequence with significant responses in polarization current. O (R) represents that the minor R phase coexists in the orthorhombic matrix. The dielectric permittivities with and without a prior poling were found to follow the Curie-Weiss equation, $\epsilon' = C/(T - T_0)$, above the Burns temperature 505 K with the same constants $C = 1.43 \times 10^5$ K and $T_0 = 462$ K.

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I. INTRODUCTION

Nanostructures or polar nanoregions (PNRs) have been considered as the most important feature in relaxor FEs because they play an important role in FE and piezoelectric properties. Nuclear-magnetic-resonance study of the prototype relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) showed two components in the crystal matrix, i.e., isotropic spherical glass matrix and anisotropic FE nanoclusters.^{1,2} The FE polar nanostructures, which can respond to an external E field, embed in the single-dipole-glass matrix, which does not respond appreciably to an E field.² This indicates that PMN is an incipient FE. The incipient FE nature was also found in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMN-PT) crystals in which a “hidden” intermediate phase can be enhanced by a prior poling.³

Structural twins are often expected in ferroelastic crystals to accommodate the spontaneous lattice distortion. A nanotwin diffraction theory^{4,5} shows that tetragonal (T) nanotwins of $\{101\}$ twin plane can mimic monoclinic (M) M_C phase, and rhombohedral (R) nanotwins of $\{001\}$ and $\{110\}$ twin planes can mimic monoclinic M_A and M_B phases, respectively. Since the nanodomain size is much smaller than the coherent length of x-ray radiation, diffracted waves from nanodomains can coherently superimpose.⁵ Nanotwins of T phase have been observed by transmission electron microscopy in (001) PMN-33%PT, which appears to be M_C phase in polarized light microscopy.⁶

Structural differences between the outer layer (10–50 μm) and the interior have been observed in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PZN-PT) and PMN-PT crystals.^{7–10} PMN-10%PT and PMN-20%PT transform to a so-called phase X instead of R phase below T_C .⁸ R phase was observed in both the outer layer and interior in PMN-27%PT.

These results suggest that the ground state of PMN-PT crystal interior prefers the X phase for small Ti content and becomes R phase as Ti content increases.

For piezoelectric performance, an E -field poling is usually employed before application. However, how an E -field poling affects nanostructure, FE polarization, and phase thermal stability still lacks consistent understanding in relaxor FE crystals, especially for the (110) oriented crystals near the morphotropic phase boundary. An additional intermediate phase was often seen upon zero-field heating after a prior E -field poling.¹¹ From the dielectric result of the (110) PMN-33%PT crystal, an R - O - T - C phase transition was suggested upon heating after a prior poling ($E < 4$ kV/cm) along $[110]$.¹² An E -field-induced R - O transition was proposed for $E > 5$ kV/cm at room temperature.¹² From the polarization result, an E -field-induced transformation from (111) R to (110) O phase through M_B -type M distortion was proposed for a (110) PMN-30%PT crystal.¹³ According to the eighth-order Devonshire theory,¹⁴ R - O , O - T , and R - T are all first-order transitions. From domain observation of (110) PMN-26%PT crystal, some R phase domains (possibly $[1\bar{1}\bar{1}]$, $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}\bar{1}\bar{1}]$) were enhanced for $E > E_C$ (≈ 3 kV/cm) along $[110]$, and an R / M - M - C transition sequence was proposed for both unpoled and poled crystals upon zero-field heating.¹⁵ In addition, the $[110]$ O domain was not observed during poling along $[110]$ at field strength up to 45 kV/cm, and instead a single homogeneous R phase was evidenced at room temperature.¹⁵

II. EXPERIMENTAL PROCEDURE

The PMN-30%PT crystal was grown using a modified Bridgman method. A Wayne Kerr Analyzer PMA3260A was used to obtain the real part ϵ' of dielectric permittivity. The sample was cut perpendicular to the $\langle 110 \rangle$ direction and its basal surfaces were sputtered with gold electrodes. Three

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FIG. 1. (Color online) (a) ZFH dielectric permittivity ϵ'_{ZFH} and ZFH polarization current density J_{ZFH} (with the scale at right vertical axis), (b) PP-ZFH dielectric permittivity ϵ'_{PP-ZFH} , and (c) PP-ZFH polarization current density J_{PP-ZFH} . The $1/\epsilon'$ [inset of (a)] from ZFH and ZFC processes and ϵ'_{ZFH} after PP-ZFH were taken at $f=10$ kHz.

processes were used in dielectric measurements. The first two are called “zero-field-heated” (ZFH) and “zero-field-cooled” (ZFC), in which the data were taken upon heating and cooling without an E field. In “prior-poled before zero-field-heated” (PP-ZFH), the sample was poled at room temperature with a dc $E=5$ kV/cm along $[110]$, then ZFH was performed without an E field. The piezoelectric resonance was seen in the PP-ZFH dielectric spectra for $f \geq 100$ kHz.

Two processes were used in the polarization current measurements by using a Keithley 6517A electrometer without applying voltage. The first one is called ZFH current density denoted by J_{ZFH} in Fig. 1(a), in which the current was taken upon zero-field heating without a prior poling. Note the small scale compared with Fig. 1(c), because the J_{ZFH} current comes from the small difference in positively and negatively randomly oriented domains. In PP-ZFH polarization current denoted by J_{PP-ZFH} in Fig. 1(c), the sample was poled at room temperature with a dc $E=5$ kV/cm along $[110]$, after which the polarization current was measured upon zero-field heating. Hysteresis loops were taken by us-

ing a Sawyer–Tower circuit at $f=46$ Hz and the sample thickness is 0.4 mm. A Janis CCS-450 cold head was used with a Lakeshore 340 controller for temperature-dependent measurements.

A Rigaku Model MultiFlex x-ray diffractometer (XRD) with $\text{Cu K}\alpha_1$ and $\text{Cu K}\alpha_2$ radiations was used for *in situ* symmetry study of the unit cell. The intensity ratio between $\text{K}\alpha_1$ and $\text{K}\alpha_2$ radiations is about 2:1.¹⁶ To avoid surface stress caused by polishing, thin gold films (thickness ≈ 30 nm) were deposited on the basal surfaces and were kept on the sample after poling. The x-ray penetration depth is expected to be less than $10 \mu\text{m}$.⁷ The XRD spectra were fitted by using the sum of Gaussian and Lorentzian terms. According to Refs. 8 and 9, both the outer layer and interior of PMN-xPT ($x \geq 27\%$) crystals have the same structure. Therefore, the XRD study in the PMN-30%PT crystal can present the interior structure.¹⁷

The XRD 2θ -reflection and d spacing obey the Bragg’s law $2d_{hkl} \sin \theta_{hkl} = n\lambda$. The d values for the six T domain types are $1/d^2 = (h^2 + k^2)/a_T^2 + (l^2/c_T^2)$, where (h, k, l) and (a_T, b_T, c_T) are crystallographic orientation and lattice parameters, respectively. The six T domain types have two d spacings from the (110) reflections, i.e., $1/d^2 = 2/a_T^2$ from two domain types and $1/d^2 = 1/a_T^2 + 1/c_T^2$ from four domain types.¹⁶ For the eight R domain types, two d spacings from four domain types each are expected from the (110) reflections according to the relation $1/d^2 = [(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)] / [a_R^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)]$.¹⁶ The unit cell of FE orthorhombic (O) domains seen in FE perovskite is canted at 45° to the C cell and has lattice constants $a_O \approx b_O \approx \sqrt{2}a_{\text{cub}}$ and $c_O \approx a_{\text{cub}}$.¹⁸ The 12 O domain types have three d spacings from the (110) reflections, i.e., $1/d^2 = 4/a_O^2$ from two domain types, $1/d^2 = 4/b_O^2$ from two domain types, and $1/d^2 = 1/a_O^2 + 1/b_O^2 + 1/c_O^2$ from eight domain types. These d spacings are based on the relation $1/d^2 = (h^2/a_O^2) + (k^2/b_O^2) + (l^2/c_O^2)$,¹⁶ where for the (110)-cut and O unit cell we have $(h = \pm 2, k = 0, l = \pm 1)$, $(h = 0, k = \pm 2, l = 0)$, or $(h = \pm 1, k = \pm 1, l = \pm 1)$ with the $\pm$ signs all independent.

III. RESULTS AND DISCUSSION

Figure 1 shows (a) ZFH dielectric permittivity ϵ'_{ZFH} and polarization current density J_{ZFH} , (b) PP-ZFH dielectric permittivity ϵ'_{PP-ZFH} , and (c) polarization current density J_{PP-ZFH} . The dielectric maxima (associated with frequency dispersion) and corresponding temperatures ($T_m \approx 410$ K) are nearly the same in both ZFH and PP-ZFH. The ϵ'_{ZFH} exhibits a step-up anomaly near 378 K and a steep-rise shoulder near 403 K followed by a frequency dispersion. These anomalies correlate with two wide-range thermal hystereses in the regions of 300–380 K and 380–403 K [inset of Fig. 1(a)], implying two first-order phase transitions. Two upward spikes seen in J_{ZFH} also confirm two first-order transitions near 378 and 403 K. These J_{ZFH} current responses mainly associate with spontaneous polarization P_S , i.e., $J_{ZFH} = -\partial P_S / \partial t$.

The ϵ'_{PP-ZFH} exhibits three sharp anomalies near 363, 372, and 405 K below $T_m \approx 410$ K. The J_{PP-ZFH} shows three

upward spikes, which are consistent with three anomalies in ε'_{PP-ZFH} and signify three first-order phase transitions. The J_{PP-ZFH} mainly associates with decay of the E -field-induced polarization P_{ind} , i.e., $J_{PP-ZFH} = -\partial P_{ind} / \partial t$.

It is important to note that $\varepsilon'_{PP-ZFH} \cong 4000$ is higher than $\varepsilon'_{ZFH} \cong 2600$ at room temperature for $f=10$ kHz. This increase indicates that the prior poling along $[110]$ must enhance some degree of FE order, probably R phase that has polarization rotation under the weak $[110]$ measuring field and so has relatively high permittivity compared with the ε'_{ZFH} . This order enhances the degree to which a different type of order, perhaps O phases, can suddenly arise at 363 K. At and above 363 K, these O domains have little tendency to rotate in the weak $[110]$ measuring field, and so have lower permittivity as observed in Fig. 1. In addition, the dielectric dispersion was depressed after a prior poling until $T_{re} = 405$ K, where the dielectric dispersion reappears completely [Fig. 1(b)], associated with a strong response in J_{PP-ZFH} . Here we define T_{re} as the temperature above which the dielectric dispersion recovers upon zero-field heating after a prior poling at room temperature.

Both ε'_{ZFH} and ε'_{PP-ZFH} were found to follow the Curie–Weiss equation, $\varepsilon' = C / (T - T_0)$, above 505 K, below which there is noticeable deviation from the Curie–Weiss law. The dashed lines in Figs. 1(a) and 1(b) are fittings with the same Curie–Weiss constants $C = 1.43 \times 10^5$ K and $T_0 = 462$ K. We consider 505 K to be the Burns temperature (T_B), below which dipole glass attenuate dielectric response and polar nanoclusters begin to develop.¹⁹ The weaker dielectric response of dipole glass causes deviation from the Curie–Weiss law and the polar nanocluster dynamics is responsible for the frequency dispersion.²⁰ Note that the Burns temperature of the prototype PMN crystal appears in the region of 600–650 K, below which nanoclusters are formed in the quenched short-range-ordered regions.^{19,21} The ZFC dielectric permittivity measured after the PP-ZFH process [Fig. 1(b)] shows the same behavior as seen in ε'_{ZFC} [the inset of Fig. 1(a)] and has the same Burns temperature. This indicates that the E -field-induced polarized state can be erased by thermal annealing.

Figure 2 shows temperature-dependent hysteresis loops. The coercive field (E_C) is about 3.2 kV/cm at room temperature. As shown in Fig. 3, E_C and remanent polarization (P_r), respectively, exhibit a local minimum and a steep decline near 363 K. As temperature increases, E_C reaches a local maximum and P_r shows a change of slope near 370 K. As indicated by the green lines in Fig. 2(e), the hysteresis loop at 370 K exhibits two possible spontaneous polarizations with values of about 18 and 25 $\mu\text{C}/\text{cm}^2$, suggesting a coexistence of two FE states. This indicates a first-order phase transition and is consistent with anomalies observed in ε'_{PP-ZFH} and J_{PP-ZFH} near 370 K. The polarization appears to retain some finite magnitude even above $T_m \cong 410$ K as seen commonly in disordered materials, but this could result from a field-induced transition or from the finite measuring frequency. The temperature-dependent behavior of FE polarization is consistent with dielectric anomalies in ε'_{PP-ZFH} . Three positive current responses [Fig. 1(c)] near 363, 370, and 405 K can be explained by the negative slopes of polarization in

FIG. 2. (Color online) Temperature-dependent hysteresis loops upon heating.

the corresponding temperature regions [Fig. 3], i.e., $J_{PP-ZFH} = -(\partial P_{ind} / \partial T)(\partial T / \partial t)$. Here, T is temperature, t is time, and $\partial T / \partial t$ is positive upon heating.

The ZFH (220) XRD spectra are given in Fig. 4. At 298 K, there are two d spacings, which correspond to $d_{220} = [a_R^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)]^{1/2} / [8 \sin^2 \alpha + 8(\cos^2 \alpha$

FIG. 3. (Color online) Temperature-dependent remanent polarization (P_r) and coercive field (E_C) upon heating. The vertical dotted lines indicate three transitions temperatures correlated with anomalies observed in ε'_{PP-ZFH} and J_{PP-ZFH} .

FIG. 4. (Color online) ZFH (220) XRD spectra. The solid and dashed lines correlate with the $K\alpha_1$ and $K\alpha_2$ radiations, respectively. The red solid line is the sum of fitting curves.

$-\cos \alpha)^{1/2}$ and $d_{220} = [a_R^2(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)]^{1/2} / [8\sin^2 \alpha - 8(\cos^2 \alpha - \cos \alpha)]^{1/2}$ from different oriented R domain types.¹⁶ The R phase at room temperature has been confirmed from the earlier results of (111) and (001) PMN-30%PT crystals.^{22,23} The ratio of spontaneous polarizations $P_S \cong 23.7 \mu\text{C}/\text{cm}^2$ and $P_S \cong 27.5 \mu\text{C}/\text{cm}^2$ [Fig. 5] taken respectively along [110] and [111] suggests an R phase. The ratio between 23.7 and $27.5 \mu\text{C}/\text{cm}^2$ is about 0.86 and is reasonably consistent with the projection fraction $\sqrt{2}/3$ of the [111] R polarization on the [110] axis.

From (220) $K\alpha_1$ reflections, the lattice constant a_R and α angle of R phase at room temperature were calculated to be $a_R = 4.023 \text{ \AA}$ and $\alpha = 89.883^\circ$, which are consistent with $a_R = 4.027 \text{ \AA}$ and $\alpha = 89.906^\circ$ obtained from the (111) PMN-30%PT crystal.²² As temperature increases [Figs. 4(b)–4(d) and 6(a)], the two different d spacings of R phase gradually approach each other and then shift to two lower d spacings discontinuously near 378 K, indicating a first-order phase transition. This is consistent with the anomalies seen in ϵ'_{ZFH} and J_{ZFH} near 378 K [Fig. 1(a)]. Figure 6(a) shows the temperature-dependent d spacing obtained from the (220) reflections of $K\alpha_1$ radiation.

Upon further heating, these two d spacings approach

FIG. 5. (Color online) Hysteresis loops obtained from (110) and (111) PMN-30%PT crystals (with the same thickness of 0.3 mm) at room temperature.

each other and then join together at 403 K [Fig. 6(a)]. Note that two d spacings are expected for the six T domain types from the (220) reflections, i.e., $d_{220} = a_T/2\sqrt{2}$ and $d_{202} = [4/a_T^2 + 4/c_T^2]^{-1/2}$.¹⁶ The phase transition near 378 K is R - T , because the α angle of R unit cell moves toward 90° near 378 K [Fig. 6(b)]. Above 403 K [Fig. 6], the crystal enters into the cubic phase and its d spacing gradually rises due to thermal expansion. The first-order T - C transition near 403 K is consistent with anomalies observed in ϵ'_{ZFH} and J_{ZFH} [Fig. 1(a)]. Above 403 K the dielectric dispersion becomes more apparent and then gradually vanishes as the Burns temperature $T_B = 505 \text{ K}$ is approached. Figure 6(b) gives the tem-

FIG. 6. (Color online) Temperature-dependent (a) d spacing and (b) lattice parameter obtained from the ZFH (220) XRD. The solid-line background is ϵ'_{ZFH} . The dotted lines indicate transition temperatures.

FIG. 7. (Color online) PP-ZFH (220) XRD spectra. The solid and dashed lines correlate with the $K\alpha_1$ and $K\alpha_2$ radiations, respectively.

perature dependences of lattice parameters obtained in the ZFH process. In brief, the (110) unpoled PMN-30%PT crystal undergoes an R - T - C transition sequence near 378 and 403 K upon zero-field heating. Note that the T - C transition at 403 K does not occur at dielectric maximum temperature $T_m \cong 410$ K. This shifting is commonly seen in disordered FE materials and results from the diffuse transition with frequency relaxation.

PP-ZFH (220) XRD spectra and temperature-dependent d spacing after a prior poling at $E=5.0$ kV/cm along $[110]$ are given in Figs. 7 and 8. At room temperature, the (220) XRD shows a single peak, which most likely corresponds to the (220) reflection of the only two R phase domain types ($[111]$ and $[11\bar{1}]$) with polarization components along the poling direction, due to disappearance of the other six R domain types by the prior poling along $[110]$. The minimum E field to induce this single R peak is about 2 kV/cm, which is smaller than $E_C \cong 3.2$ kV/cm. As temperature rises [Figs. 7(b) and 8], PP-ZFH (220) XRD spectra exhibit a three-peak splitting near 358 K, indicating a possible first-order R - O phase transition.

To interpret which XRD peaks correspond to which phases and domains, we consider both the peak locations and

FIG. 8. (Color online) Temperature-dependent (a) d spacing and (b) lattice parameter obtained from the PP-ZFH (220) XRD. The solid-line background is ϵ'_{PP-ZFH} . The dotted lines indicate transition temperatures.

the idea that as crystal phase changes with increasing temperature, the favored new domains will be those with polarizations most closely aligned with the polarizations of the domains in the old phase. This idea predicts that the $[111]$ and $[11\bar{1}]$ R domains will transform to $[110]$, $[101]$, $[011]$, $[10\bar{1}]$, and $[01\bar{1}]$ O domains because these require the smallest polarization rotation angle (θ) of 35.3° . The $[110]$ domain gives the smallest θ and the other four give the intermediate θ of the three θ values possible for O domains.¹⁶

This assignment of angles to domains is based on the fact that the FE perovskite structures tend to stretch in the polarization direction. Specifically, if the O domain is stretched in the direction of polarization ($\mathbf{P}$) (call this direction a) and compressed in the b direction so that $a > \sqrt{2}c$ and $c < b < \sqrt{2}c$, then two domains will give maximum d and minimum θ , two will give minimum d and maximum θ , and the other eight will give intermediate d and θ values. Based on this assumption about stretching, we can attribute the left-hand peak at 358, 363, and 368 K to the O domain with $\mathbf{P}$ along $[110]$ and the right-hand peak at these temperatures to the other four O domains, i.e., $[101]$, $[011]$, $[10\bar{1}]$, and $[01\bar{1}]$. The intermediate peak at these temperatures aligns with the R peak at 298 K, so we assume that this peak corresponds to a dominant R phase at 358 K and a minority R phase at 363 K and 368 K. This reduction in R phase explains why the significant drop in ϵ'_{PP-ZFH} [Fig. 1(b)] and the discontinuity in J_{PP-ZFH} [Fig. 1(c)] appear at 363 K, where the R - $O(R)$ phase transition takes place.

Note that at 368 K the $[110]$ O peak is by far the dominant one. This fact, together with the minimum-angle-change

idea, explains why at 373 K there is only one T peak after the O - T transition, presumably from domains with $\mathbf{P}$ along $[100]$ and $[010]$. The polarization rotation angle from $[110]$ to $[100]$ or $[010]$ is 45° , whereas the angle from $[110]$ to $[001]$ or $[00\bar{1}]$ is 90° , so such a larger rotation during the O - T phase transition seems much less likely.

Is the phase that is intermediate between R and T for PP-ZFH possibly monoclinic? It is possible because the M_A phase has its a_m and b_m axes oriented, respectively, along the pseudocubic $[1\bar{1}0]$ and $[110]$ directions with the c_m axis along the pseudocubic $[00]$ direction.²⁴ In other words, the M_A phase has lattice constants $a_m \cong b_m \sqrt{2} a_{\text{cub}}$ and $c_m \cong a_{\text{cub}}$. An argument against this possibility is that for PP-ZFH the left-hand peaks at 358, 363, and 368 K are well to the left of any R and T peaks. For this (110) crystal, given the tendency to stretch along the polarization direction, the $[110]$ O -domain polarization perpendicular to the crystal faces should give the smallest possible θ . For an M phase with $\mathbf{P}$ in a substantially different direction, one would expect a smaller shift in angle away from the R and T values.

As temperature increases [Fig. 8], three different d spacings merge together near 370 K, which indicates a first-order transition and is consistent with the intermediate anomaly in $\epsilon'_{\text{PP-ZFH}}$ [Fig. 1(b)] and the second spike in $J_{\text{PP-ZFH}}$ [Fig. 1(c)]. The structure between 370 and 403 K is T phase for the following reasons. First, the single (220) reflection peak from the T phase is due to the prior poling along $[110]$ that eventually, by the process described above, can enhance $[100]$ and $[010]$ T domains, which give the same d spacing.¹⁶ Second, the d spacing of the PP-ZFH (220) reflection near 373 K is consistent with the upper d spacing of ZFH (220) reflections in the region of 380–403 K [Fig. 6]. Thus, the transition near 370 K should be O - T , which is of first order according to the eighth-order Devonshire theory.¹⁴ This can explain why an obvious discontinuity appears in $\epsilon'_{\text{PP-ZFH}}$ and $J_{\text{PP-ZFH}}$ near 370 K [Fig. 1].

Upon further heating [Figs. 7 and 8], the d spacing exhibits a sudden drop near 405 K and then gradually rises upon heating, suggesting a first-order T - C phase transition. This first-order T - C transition was confirmed by the steep rise in $\epsilon'_{\text{PP-ZFH}}$ and discontinuous response in $J_{\text{PP-ZFH}}$ at 405 K. Above 405 K the dielectric dispersion reestablishes completely and then gradually disappears as the Burns temperature $T_B=505$ K is approached, just as for ZFH. Figure 8 gives the temperature dependences of d spacings and lattice parameters for various phases in the PP-ZFH process. For calculations of lattice parameters of the O phase, the following equations have been used: $d_L = a_O/4 = (c_O/2\sqrt{2}) + \Delta x$ (largest d), $d_S = b_O/4 = (c_O/2\sqrt{2}) - \Delta x$ (smallest d), and $c_O = (a_O/\sqrt{2} + b_O/\sqrt{2})/2$. Here Δx indicates a small distortion from the conventional unit cell of the O phase, i.e., $a_O \cong b_O \cong \sqrt{2} c_{\text{cub}}$ and $c_O \cong c_{\text{cub}}$. In brief, the (110) poled PMN-30%PT crystal has an R - $O(R)$ - T - C transition sequence near 355, 370, and 405 K, respectively, upon zero-field heating.

IV. CONCLUSIONS

The (110) unpoled PMN-30%PT crystal has an R - T - C phase sequence upon zero-field heating. After a prior poling

at $E=5.0$ kV/cm, an extra intermediate O phase was induced and the crystal underwent an R - $O(R)$ - T - C phase sequence upon zero-field heating. $\epsilon'_{\text{PP-ZFH}}$ was obviously enhanced after a prior poling along $[110]$. $\epsilon'_{\text{PP-ZFH}}$ shows a reentry of frequency dispersion at $T_{\text{re}}=405$ K, associated with the development of polar nanostructures. Both ϵ'_{ZFH} and $\epsilon'_{\text{PP-ZFH}}$ follow the Curie-Weiss equation, $\epsilon' = C/(T - T_0)$, with the same constants $C = 1.43 \times 10^5$ K and $T_0 = 462$ K above the Burns temperature $T_B = 505$ K.

The R - $O(R)$ - T - C phase sequence in the PP-ZFH process is essentially consistent with the R - O - T - C phase sequence proposed for the (110) poled PMN-30%PT¹¹ and PMN-33%PT¹² crystals from the zero-field heating dielectric results. However, $R(R_{\text{NT}})$ - $T(T_{\text{NT}})$ - C and R - M_A - T - C transition sequences were proposed respectively for the (001) and (111) poled PMN-30%PT crystals upon zero-field heating.^{22,23} R_{NT} and T_{NT} are R and T nanotwins, respectively.²³ These results suggest that the intermediate phase induced by a prior E -field poling is sensitive to crystallographic orientation.

ACKNOWLEDGMENTS

This work was supported by National Science Council of Taiwan Grant No. 96-2112-M-030-001.

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