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Influence of Cation Order on the Dielectric Properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Pb(Sc_{1/2}Nb_{1/2})O_3$ (PMN-PSN) Relaxor Ferroelectrics

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Abstract
The effect of the B-site cation chemistry and ordering on the dielectric properties of solid solutions in the $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$Pb(Sc_{1/2}Nb_{1/2})O_3$ (PMN-PSN) perovskite system was examined in samples with $0.1 \leq x \leq 0.9$. Thermal annealing treatments were effective in inducing long-range B-site order in the samples within this compositional range. The well-ordered, large chemical domain ceramics exhibit relaxor behavior up to $x = \sim 0.5$; for higher values of x, normal ferroelectric behavior was observed. For $x \leq 0.5$ reductions in the chemical domain, size had no significant effect on the weak-field dielectric properties, but induced a transition to relaxor behavior for $x > \sim 0.6$. The disordered PSN-rich samples undergo a spontaneous zero-field relaxor to ferroelectric transition similar to that reported previously for PSN. The field-dependent properties of compositions lying closest to the relaxor to ferroelectric crossover exhibited the highest sensitivity to alterations in the chemical order. The properties of this system are consistent with a "random site" description of the 1:1 ordered $Pb(\beta'_{1/2}\,\beta_{1/2})O_3$ structure with $\beta' = (Mg_{(2\text{-}2x)/3}Nb_{(1\text{-}x)/3}Sc_x)$ and $\beta'' = Nb$.

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Influence of Cation Order on the Dielectric Properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Sc_{1/2}Nb_{1/2})O_3$ (PMN-PSN) Relaxor Ferroelectrics

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The effect of the B-site cation chemistry and ordering on the dielectric properties of solid solutions in the $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Sc_{1/2}Nb_{1/2})O_3$ (PMN-PSN) perovskite system was examined in samples with $0.1 \leq x \leq 0.9$. Thermal annealing treatments were effective in inducing long-range B-site order in the samples within this compositional range. The well-ordered, large chemical domain ceramics exhibit relaxor behavior up to $x = \sim 0.5$; for higher values of x, normal ferroelectric behavior was observed. For $x \leq 0.5$ reductions in the chemical domain, size had no significant effect on the weak-field dielectric properties, but induced a transition to relaxor behavior for $x > \sim 0.6$. The disordered PSN-rich samples undergo a spontaneous zero-field relaxor to ferroelectric transition similar to that reported previously for PSN. The field-dependent properties of compositions lying closest to the relaxor to ferroelectric crossover exhibited the highest sensitivity to alterations in the chemical order. The properties of this system are consistent with a "random site" description of the 1:1 ordered $Pb(\beta'_{1/2}\ \beta_{1/2})O_3$ structure with $\beta' = (Mg_{(2-2x)/3}Nb_{(1-x)/3}Sc_x)$ and $\beta'' = Nb$.

I. Introduction

The relationship between the B-site cation order and ferroelectric properties of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) family of perovskites has been extensively investigated.[1] For several years, it has been recognized that the relaxor behavior in these systems is related to localized inhomogenieties in the distribution of the metal cations on the B sublattice. Recent experimental and theoretical investigations of $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT) and PMN have provided convincing evidence that the order on the B-sites conforms to a "random site" model.[2–9] In this model, one of the cation positions (β) in the 1:1 ordered $Pb(\beta'_{1/2}\ \beta''_{1/2})O_3$ phases is occupied by a ferroelectrically active cation (niobium or tantalum), whereas the second contains a random mixture of active and inactive (magnesium) cations. Using thermal treatments to tailor the degree of cation order, alterations in the size of the chemically ordered domains in relaxors based on PMN and PMT were shown to have relatively little effect on the weak-field dielectric response.[4–8] This is quite different from the behavior of the $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) and $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) systems where alterations in the degree of order produce a transition from relaxor (disordered) to normal (ordered) ferroelectric behavior.[10] In this paper, we examine the response of the dielectric properties of a solid solution of PMN-PSN to alterations in the degree of chemical order.

Support for the random site model for the B-site order in PMN-type systems has come from new investigations of their ordered structures[2,3] and from the observation of extensive increases in the size of the chemical domains and degree of order in samples equilibrated at elevated temperature.[4–8] In a previous paper,[9] we reported that the chemical order in PMN was enhanced significantly by the substitution of relatively small (~10 mol%) concentrations of PSN. After slow-cooling or extended annealing, extensive order was observed in samples across the $(1-x)$PMN–(x)PSN solid solution system when $x \geq 0.1$. By monitoring the changes in the order as a function of temperature, the order-disorder boundary for the PMN–PSN system was established. The transition temperature for pure PMN was estimated to be ~950°C, and the highest transition, 1360°C, was observed for $x = 0.5$. The changes in stability across the system were consistent with the "random site" description of the cation order where sites in the $Pb(\beta'_{1/2}\ \beta_{1/2})O_3$ 1:1 ordered solid solution have $\beta' = (Mg_{(2-2x)/3}Nb_{(1-x)/3}Sc_x)$ and $\beta'' = Nb$. Because of their higher ordering temperatures, the degree of chemical order and chemical domain size in the $x \geq 0.1$ compositions could be modified extensively by thermal annealing.

Several studies have been made of the dielectric properties of the PSN and PMN end members. For PSN (and its tantalate counterpart, PST) it is well known that the formation of a 1:1 ordered structure is accompanied by a transition from a relaxor to normal ferroelectric response.[10] Because of its overall 1:1 B-site stoichiometry, in PSN, complete structural order is accompanied by complete chemical order with one cation position occupied by scandium and the other by niobium (or tantalum in PST). In contrast, for the PMN-type systems, the formation of a well-ordered 1:1 B-site structure does not produce any significant change in the weak-field dielectric response and relaxor behavior is observed regardless of the degree of order or the chemical domain size.[7,8] The difference can be attributed to the absence of complete chemical order in the 1:1 random site form of the PMN systems. Because of the overall 1:2 B-site stoichiometry, 1:1 structural order in PMN is accompanied only by chemical order on one cation position (β), and a random cation distribution is always retained on the second site (β′). For the PSN systems, lead vacancy formation has also been shown to induce additional variations in the dielectric behavior. In particular, disordered, vacancy-free compositions (prepared by annealing in a PbO-rich environment) were observed to undergo a spontaneous zero-field relaxor-to-normal ferroelectric transition at temperatures below the dielectric maximum.[11] This transition was suppressed in samples that contained small vacancy concentrations. Similar observations of a zero-field relaxor-to-normal ferroelectric transition have also been reported in the PMN-PT system for 10% PT.[12]

Because the two end members exhibit quite different responses to alterations in their chemical order, we were interested in examining at what point this system would exhibit a crossover from PMN-type to PSN-type behavior. We demonstrate that the weak-field dielectric properties of PMN-rich compositions ($x < 0.5$) retain their insensitivity to the chemical domain size and observe a transition to PSN-type behavior for higher values of x.

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*Member, American Ceramic Society.

II. Experimental Methods

PMN–PSN ceramics were synthesized from high-purity (99.9%) oxides via a modified "columbite-type" route.[13] Stoichiometric quantities of predried oxides of the B-site metals were mixed in an agate mortar for 10 min and then calcined at 1100°C for 6 h. The resultant calcine was ball-milled in a polyethylene jar for 3 h using yttria-stabilized zirconia balls and acetone as a milling medium. After drying and recalcining, the slurry at 1100°C for 12 h, stoichiometric amounts of lead oxide were added and mixed in an agate mortar. This mixture was precalcined at 750°C for 3 h, ball-milled for 3 h, and then reheated at 900°C for 3 h. All these treatments were conducted in a closed platinum crucible. After a final ball-milling for 10 h, pellets 4–5 mm thick and 10 mm in diameter were isostatically pressed at 600 MPa. Final sintering of the ceramics was conducted at a temperature of 1225°–1250°C for 1 h. During the sintering and subsequent high-temperature annealing treatments, the ceramics were buried in a protective powder of the same composition.

X-ray diffraction (XRD; Model D-max B, Geigerflex, Rigaku, Tokyo, Japan) was used to determine the phase purity. The degree of order was monitored by scaling the integrated intensity of the (1/2, 1/2, 1/2) supercell reflection, I_o, to the (001) subcell reflection of the perovskite subcell, I_{100}. The order parameter α was calculated from the scaled intensities from $\alpha^2 = (I_o/I_{100})_{observed}/(I_o/I_{100})_{max}$, where $(I_o/I_{100})_{max}$ is a value calculated assuming complete 1:1 order within the random site model. In this calculation, it was assumed that the lead and oxygen ions are not displaced from their ideal positions in the perovskite unit cell; however, it is recognized that these displacements do exist and will induce errors in our calculations of the subcell peak intensities.

The microstructures of the ceramics were characterized using transmission electron microscopy (TEM; Model 420 EX, Philips, Eindhoven, Netherlands) operated at 120 kV. The TEM specimens were prepared by grinding, polishing, and dimpling ceramic thin sections. The final thinning to perforation was conducted via argon-ion milling (5.5 kV and 20 mA, PIPS, Gatan, Pleasanton, CA).

Low-field dielectric measurements were performed using a high-precision LCR meter (HP 42824A, Agilent Technologies, Palo Alto, CA). The temperature-dependent measurements were made using an environmental chamber (Delta 9023, Delta Design, San Diego, CA). High-field polarization measurements used a ferroelectric test system (Model RT66, Radiant, Albuquerque, NM).

III. Results

The extensive degree of chemical order induced by slow-cooling the $(1-x)$PMN–(x)PSN samples is evident in the dark-field TEM images in Fig. 1 that were collected using the (3/2, 3/2, 3/2) supercell reflections. Details of the thermal conditions required to induce the order are provided elsewhere.[9] Although the microstructure of the $x = 0.1$, 0.5, 0.7, and 0.9 specimens all show evidence for high levels of chemical order (bright regions in Fig. 1), the size of the chemically ordered domains is clearly different in each sample. The largest ordered regions (~200 nm) are observed in $x = 0.5$, which was previously shown to also exhibit the highest order–disorder transition temperature. The variation in the domain size across the system also parallels the trend in the ordering temperatures discussed in the previous paper.[9]

The response of the dielectric properties to the alteration in bulk chemistry, degree of order, and chemical domain size was examined by collecting weak-field data from the well-ordered samples, and from specimens exhibiting minimal cation order. Data collected from the ordered ceramics, with the microstructures shown previously in Fig. 1, are shown in Fig. 2. For $x \leq 0.5$ the permittivity of the ordered samples exhibits diffuse and frequency-dependent behavior characteristic of a relaxor type response. However, for $x \geq 0.6$, the ordered compositions show a normal ferroelectric behavior and the dielectric properties are similar to those observed in the pure ordered PSN end member. It is important to note that the crossover from relaxor-to-normal behavior (between $x = 0.5$ and 0.6) shows no correlation to the size of the chemical domains in the ordered samples. The composition with the largest chemical domains ($x = 0.5$) is a relaxor, whereas

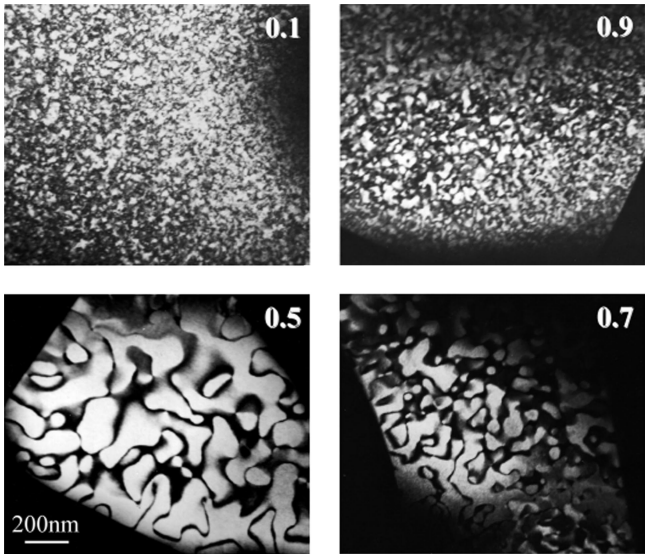

Fig. 1. Dark-field image collected from chemically ordered $(1 - x)$PMN–(x) PSN with (a) $x = 0.1$, (b) $x = 0.5$, (c) $x = 0.7$, and (d) $x = 0.9$.

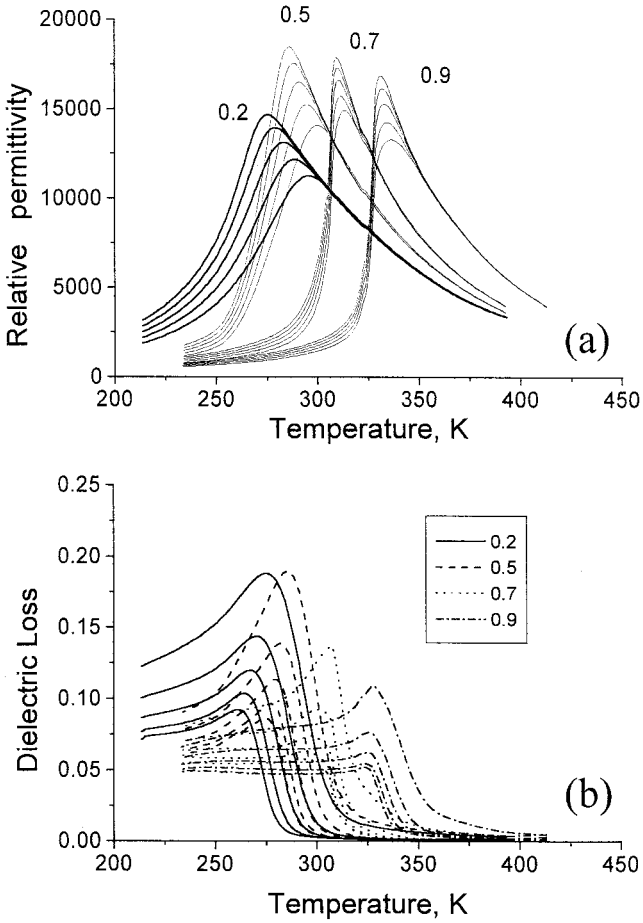

Fig. 2. (a) Real part of the permittivity, (b) dielectric loss for ordered samples of $(1 - x)$PMN–(x)PSN with $x = 0.2$, 0.5, 0.7, and 0.9. Frequencies correspond to 100 Hz, 1 kHz, 10kHz, 100 kHz, and 1MHz.

a composition with small domains ($x = 0.9$) has a normal ferroelectric response.

To examine the possible influence of lead-vacancies on the dielectric properties, which have been shown to induce relaxor-type behavior in PSN (and PST), the properties of the ordered samples were remeasured after a low-temperature anneal in a lead-rich atmosphere. The lead anneal did not produce any significant change in the dielectric properties. The absence of a correlation between the type of ferroelectric response, the chemical domain size, or the presence of lead vacancies suggests that the dielectric properties of the ordered ceramics in the PMN–PSN system are controlled by the chemistry of the ordered random-site structure, specifically by the composition of the β' site. This will be discussed later.

The dielectric properties of the disordered PMN-PSN ceramics are shown in Fig. 3. Compositions with $x < 0.5$, which exhibit relaxor behavior in their ordered forms, show very little change with the reduction in the degree of order. However, for $x > 0.5$ (normal ferroelectrics in their ordered forms), the reduction in the degree of ordering induces a transition to frequency-dependent, relaxor behavior. This change is accompanied by an increase in the magnitude of the permittivity and the temperature of the permittivity maximum (e.g., $\sim\Delta T = \sim 35°C$ for $x = 0.9$). The disordered PSN-rich samples also exhibit a discontinuity in the real part of the permittivity at temperatures just below the permittivity maximum (see Figs. 3 and 4). This type of discontinuity has also been observed in the disordered PSN end member and arises from a spontaneous zero-field, relaxor-to-normal ferroelectric phase transformation.[11]

Further evidence for the different behavior of the samples with $x \leq 0.5$ and $x > 0.5$ was obtained from measurements of

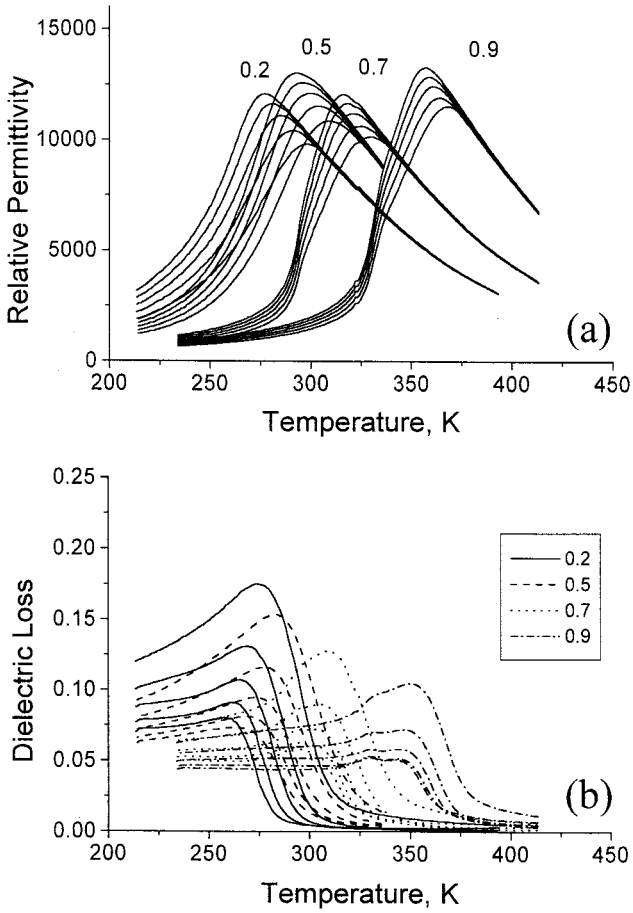

Fig. 3. (a) Real part of the permittivity, (b) dielectric loss for disordered samples of $(1 - x)$PMN–(x)PSN with $x = 0.2$, 0.5, 0.7, and 0.9. Frequencies correspond to 100 Hz, 1 kHz, 10kHz, 100 kHz, and 1MHz.

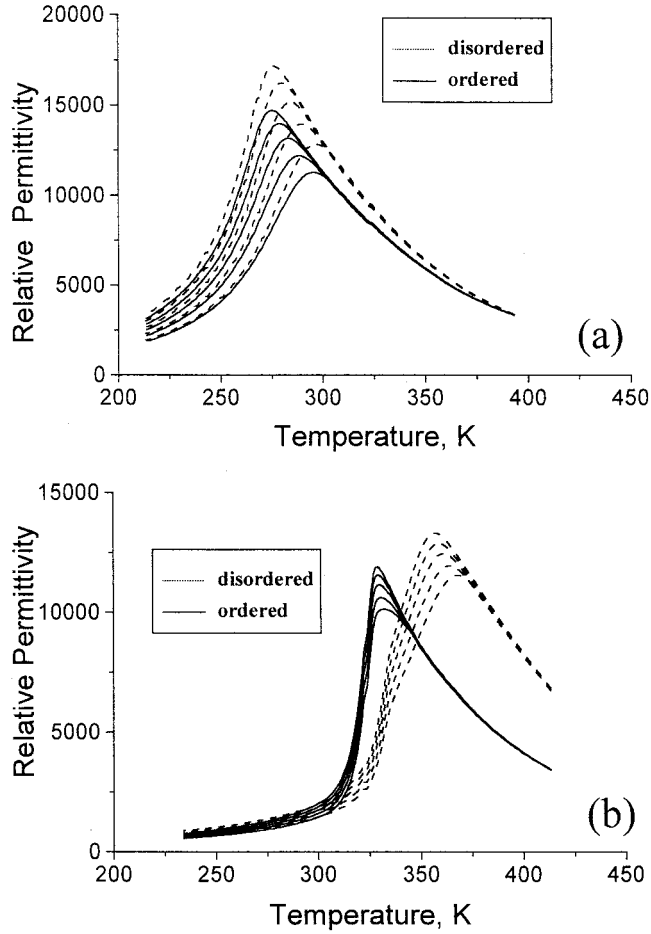

Fig. 4. Real part of the permittivity for disordered and ordered forms of (a) $x = 0.2$ and (b) $x = 0.9$.

the thermal hysteresis of the dielectric properties. A typical example of the data collected during thermal cycling (cooling followed by heating) for the PSN-rich compositions is shown in Fig. 5(b) for $x = 0.9$. The real part of the permittivity and the dielectric loss exhibit thermal hysteresis associated with the spontaneous relaxor-to-normal ferroelectric-phase transition. In contrast, similar experiments conducted on the PMN-rich compositions did not reveal any measurable hysteresis in the dielectric response for either the disordered or ordered samples (see Fig. 5(a) for $x = 0.2$) and the data collecting on heating and cooling were identical.

More detailed measurements were made on the $x = 0.5$ composition, which lies at the boundary between the relaxor and normal sides of the system. The very high order/disorder transition temperature for this composition ($T_{trans} = \sim 1360°C$) prevented preparation of ceramics with complete cation disorder; however, elevated temperature heat treatments could be used to prepare samples with differing order parameters (α). Although all the samples exhibited relaxor-type behavior, some hysteresis was observed (Fig. 6). The difference in the properties on cooling and heating were very small in the sample with a lower degree of ordering (Fig. 6(a), $\alpha = 0.76$), but increased with the degree of order (Fig. 6(b), $\alpha = 0.97$). Therefore, this composition at the relaxor to normal boundary combines features of the PMN-rich and disordered PSN-rich sides of the system.

The field-dependent properties of the solid solutions were also probed as a function of temperature. Fig. 7(a) shows the polarization loops recorded at different temperatures for a PMN-rich ordered composition with $x = 0.2$. The hysteresis loops are typical of those observed in relaxors and showed little dependence on the degree of order. The temperature dependence of the remanent

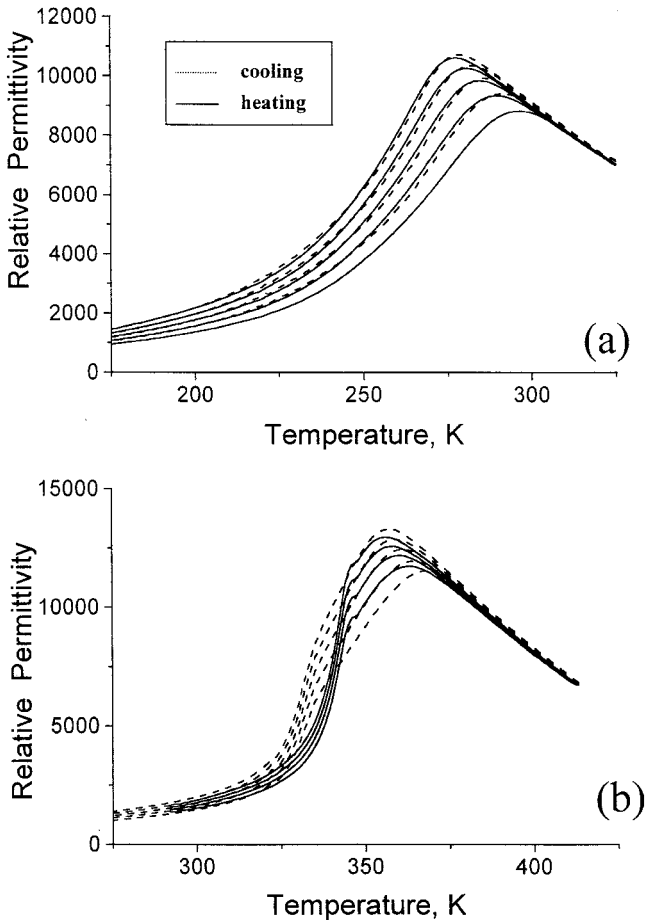

Fig. 5. Thermal hysteresis in the real part of the permittivity for disordered samples of (a) $x = 0.2$ and (b) $x = 0.9$.

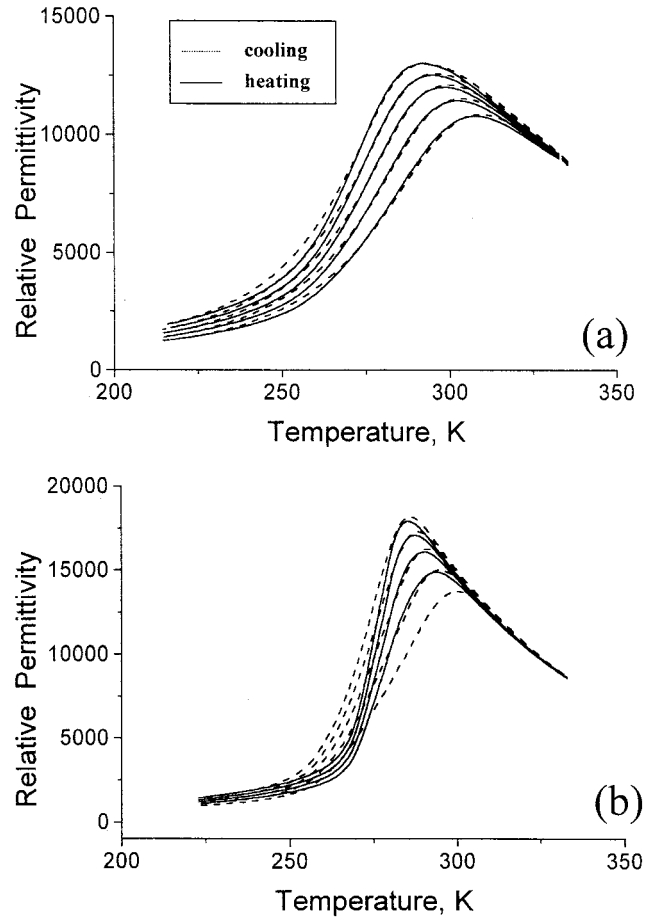

Fig. 6. Effect of the order parameter (α) on the thermal hysteresis of $x = 0.5$ for (a) $\alpha = 0.76$, (b) $\alpha = 0.97$.

polarization, determined from the measurements made during cooling, is shown in Fig. 8(a) for ordered and disordered forms of $x = 0.2$. The remanent polarization shows a broad dependence on temperature with the curve for the ordered sample being shifted to slightly higher temperatures. The field-dependent properties of the ordered and disordered PSN-rich samples (see Fig. 7(b) and 7(c)) for $x = 0.9$ are very similar to those previously reported for pure PSN. Below the dielectric maximum, the square hysteresis loops are typical of a normal ferroelectric with long-range dipole coupling. At temperatures close to the zero-field relaxor-to-normal transition, there is evidence for a double hysteresis loop associated with a coexistence of phases with long-range and nanopolar correlations. The dependence of the remanent polarization with temperature for $x = 0.9$ (Fig. 8(c)) reveals a relatively sharp transition from a ferroelectric to paraelectric state, although the transition is broader and shifted to higher temperature for the disordered sample. Consistent with its relaxor-type weak-field response, the disordered sample also shows evidence for nanopolar domain correlations above the transition temperature.

The largest differences between the field-dependent properties of the ordered and disordered forms of PMN-PSN were observed for $x = 0.5$, a sample that the weak-field dielectric data indicated was close to a relaxor-to-ferroelectric "crossover." The field-dependent properties are shown in Fig. 8(b) for samples with different order parameters. The remanent polarization for the well-ordered sample ($\alpha = 0.97$) increases over a very narrow range of temperature beginning just below T_{max} and is similar to the field-dependent behavior of a normal ferroelectric. However, the change in the partially disordered specimen is considerably broader and occurs over a range of ~80°C.

IV. Discussion

For PMN- and PSN-type relaxors, the degree of chemical order and chemical domain size has often been cited as being a critical factor in determining the nature of the ferroelectric response. In the $(1-x)$PMN–(x)PSN system the largest chemical domains and highest degree of chemical order is observed for $x = 0.5$, the weak-field properties of this sample exhibit frequency-dependent relaxor-type behavior. The smallest chemical domains occur for ordered samples with $x = 0.1$ and $x = 0.9$, the former also exhibits relaxor behavior but the latter is a normal ferroelectric. Clearly, the properties of this system are not simply related to the size of the 1:1 ordered domains, but respond to the changes in the chemistry of the 1:1 ordered structure—in particular to the composition of the random-site position. The two sides of the system also exhibit a different response to alterations in the degree of chemical order. On the PMN-rich side, relaxor behavior is observed in both the ordered and disordered forms of the samples. On the PSN-rich side, disordered samples are relaxors and ordered samples exhibit normal ferroelectric behavior. The disordered PSN-rich samples also exhibit a characteristic zero-field relaxor-to-normal ferroelectric-phase transformation at temperatures just below the dielectric maximum. The relaxor-to-normal ferroelectric "crossover" lies close to $x = 0.5$, this composition also exhibits the highest sensitivity of the field-dependent properties to the degree of chemical order.

The alterations in the dielectric response of the ordered samples across the system highlight the importance of the composition of the random-site position in mediating the ferroelectric transitions. In the $(1-x)$ PMN–(x) PSN solid-solution system, the random-site model predicts that one of the ordered positions (β'') in the Pb($\beta'_{1/2}$

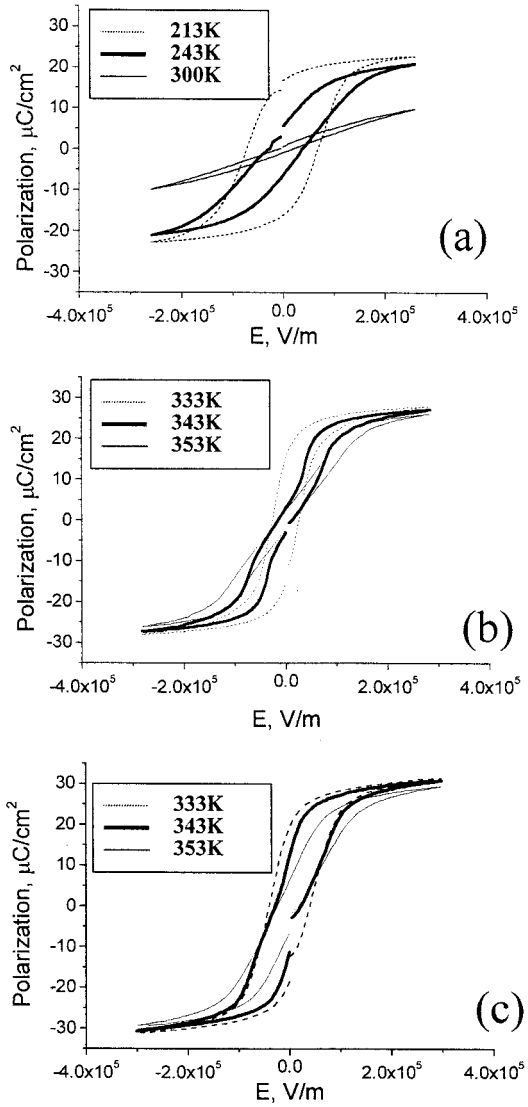

Fig. 7. Polarization loops at different temperatures for (a) $x = 0.2$ ordered, (b) $x = 0.9$ ordered, (c) $x = 0.9$ disordered.

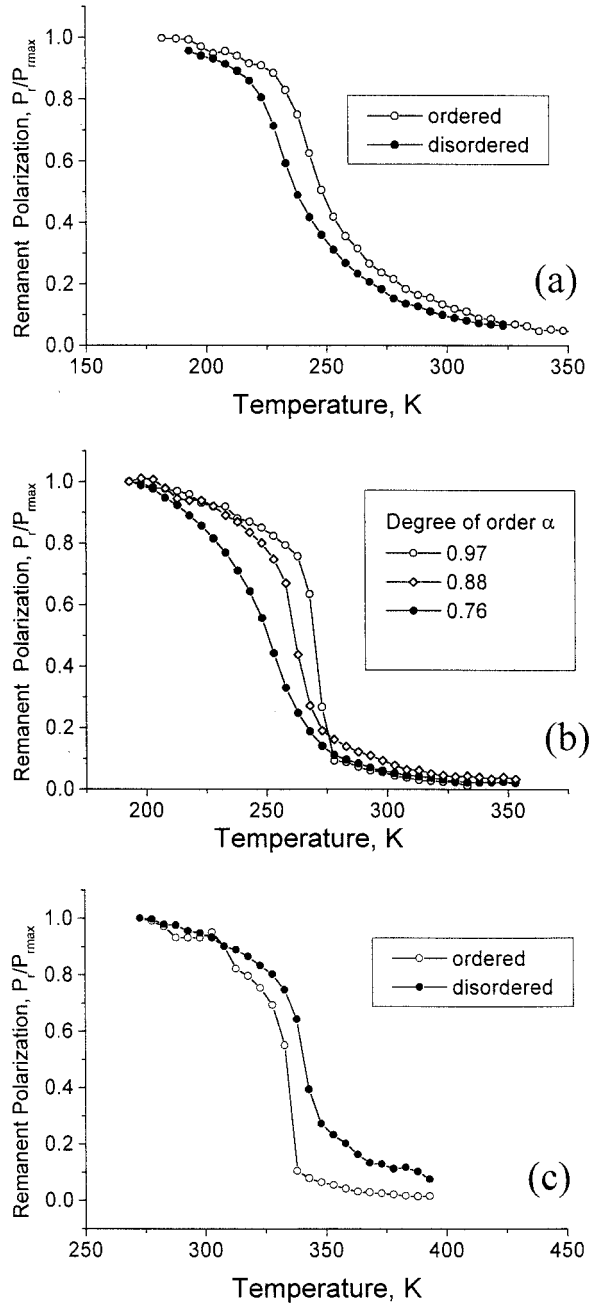

Fig. 8. Effect of ordering on the temperature dependence of the remanent polarization in (a) $x = 0.2$, (b) $x = 0.5$, (c) $x = 0.9$.

$\beta_{1/2})O_3$ structure is occupied solely by the "ferroelectrically" active niobium cations, but the other (β') contains a random distribution of active and inactive (magnesium and scandium) cations with a stoichiometry ($Mg_{(2-2x)/3}Nb_{(1-x)/3}Sc_x$). The ferroelectric interactions in these and other 1:1 ordered lead-based perovskites are thought to involve displacement and coupling of the lead, oxygen, and ferroelectrically active B-site ions along the <111> direction. Chen *et al.* have described how the relative sizes of the cations on the β' and β'' sublattice can influence the strength of the coupling.[14] When the β' position is occupied by a larger inactive cation (e.g., magnesium or scandium) and the β position by a smaller "active" cation (e.g., niobium), the intermediate oxygen anions will be displaced toward the β'' position. Chen has suggested that this anion displacement induces movement of the Pb^{2+} cation along <111> toward the β' position to form three shorter Pb-O-β' bonds and three longer Pb-O-β bonds and accommodate the lone-pair of electrons. This cooperative displacement mechanism can then provide for extended ferroelectric coupling. This mechanism can be extended to interpret the importance of the chemical disorder (and associated random fields) on the β' sublattice in mediating the ferroelectric transitions in the PMN-PSN system. Although the coupling described above can operate when the β' site is occupied by magnesium or scandium, it cannot be as effective when it contains niobium where the lead cation has identical cations as neighbors along the <111> direction. Therefore, the presence of randomly distributed niobium ions on the β' sublattice provides a mechanism for producing a distribution of different coupling lengths. Considering the coupling along one unique <111> direction for the 2:1 distribution of Mg:Nb on the β' site in PMN, on average one out of every three positions contain niobium and the mean correlation length (d) for [-β''-Pb-β'-Pb-β-] cooperative ferroelectric interactions (i.e., for $\beta' = Mg$) is $d = \sim 3$ nm. This value is close to the estimates of the average size of the nanopolar domains in these systems. Because the coupling lengths in the ordered random site structure are so short, on the PMN-side of the system, the actual size of the chemically ordered regions have no significant effect on the dielectric response or the polarization.

At higher values of x, when the concentration of active niobium cations (and also the charge mismatch of the cations) on the β' site is reduced and the mean correlation length (d) is increased. At a critical dilution limit, or critical correlation length, the concentration of niobium will be low enough to permit the barriers to

long-range coupling to be overcome and a transition to normal ferroelectric behavior can be expected. Under weak-field conditions in the PMN-PSN system, this transition occurs close to $x = 0.5$ (between 0.5 and 0.6). For $x = 0.5$, the composition of the random sublattice is ($Mg_{1/3}Nb_{1/6}Sc_{1/2}$) and on average one out of every six β' positions is occupied by niobium. Assuming that the coupling is terminated by each of these niobium cations, the mean <111> correlation length can again be estimated from the length of the Nb(β'')–Pb–Mg/Sc(β') sequences along the body diagonal. For $x = 0.5$ this average distance is $d = \sim 7.5$ nm, and for $x = 0.6$, $d = \sim 9$ nm.

Because the correlation lengths are much longer in the ordered samples on the PSN-rich side of the system, the size of the chemical domains and degree of chemical order now become important factors. In this case the coupling can be frustrated, and relaxor behavior induced by disordering the samples and reducing the size of the chemical domains below the critical correlation length.

The field-dependent properties of the PMN-PSN system also seem to fit into this description of the coupling. When the coupling length is close to the critical limit, the application of relatively small fields will be effective in overcoming the barriers to long-range coupling promoting normal ferroelectric behavior. The largest ordering-induced changes in the field-dependent properties were observed in the compositions lying close to the weak-field relaxor to ferroelectric crossover. For example in $x = 0.5$, an essentially fully ordered sample ($\alpha = 0.97$) undergoes a field-induced transition to a ferroelectric state, but a sample with a smaller domain size, lower degree of order ($\alpha = 0.76$) and shorter value of d retained its diffuse relaxor-type response.

The ferroelectric domain structures of the ordered forms of several compositions were examined by TEM. By examining images collected using the fundamental reflections of the perovskite structure and the supercell reflections from the cation order, it was possible to collect images of both the chemical and polar domain structures. However, we observed no direct correlation between the size and shape of the chemical and ferroelectric domains.

V. Summary and Conclusions

Frequency-dependent relaxor behavior is observed in both ordered and disordered forms of $(1-x)$PMN–(x)PSN solid solutions with $x \leq 0.5$. At higher levels of substitution, the dielectric response is dependent on the degree of order; disordered samples are relaxors and ordered samples exhibit normal ferroelectric behavior. A spontaneous relaxor-to-normal ferroelectric phase transformation is also observed in the disordered forms of the PSN-rich samples with $> \sim 60$ mol% PSN. The field-dependent properties of the compositions close to the crossover in behavior exhibit the highest sensitivity to alterations in the cation order. The properties of the system are consistent with the random site description of the 1:1 structural order.

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