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Cation Ordering in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PMN–PSN) Solid Solutions

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Cation Ordering in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PMN–PSN) Solid Solutions

Abstract

Extended thermal annealing treatments were used to modify the B-site cation order in the $(1 - x)\text{PMN} - x\text{PSN}$ perovskite system (where PMN is lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, and PSN is lead scandium niobate, $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$). Extensive 1:1 ordering could be induced in compositions with $x \geq 0.1$. The substitution of PSN into PMN produced a large increase in the thermal stability of the 1:1 ordered phase, with the maximum disordering temperature of $\sim 1360^\circ\text{C}$ being observed for the $x = 0.5$ composition. By monitoring the change in the degree of order with temperature, the order–disorder boundary for the PMN–PSN system was established and the transition temperature for pure PMN was estimated to be $\sim 950^\circ\text{C}$. The changes in stability across the system were consistent with the "random-site" description of the cation order. The change in enthalpy associated with the ordering was affected by the size difference of the two ordered cation sites and by the size and charge mismatch of the metal cations that occupy the random-site position.

Comments

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Extended thermal annealing treatments were used to modify the B-site cation order in the $(1 - x)\text{PMN}-x\text{PSN}$ perovskite system (where PMN is lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, and PSN is lead scandium niobate, $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$). Extensive 1:1 ordering could be induced in compositions with $x \geq 0.1$. The substitution of PSN into PMN produced a large increase in the thermal stability of the 1:1 ordered phase, with the maximum disordering temperature of $\sim 1360^\circ\text{C}$ being observed for the $x = 0.5$ composition. By monitoring the change in the degree of order with temperature, the order–disorder boundary for the PMN–PSN system was established and the transition temperature for pure PMN was estimated to be $\sim 950^\circ\text{C}$. The changes in stability across the system were consistent with the “random-site” description of the cation order. The change in enthalpy associated with the ordering was affected by the size difference of the two ordered cation sites and by the size and charge mismatch of the metal cations that occupy the random-site position.

I. Introduction

THE chemistry and stability of the B-site ordering and its relevance to the relaxor ferroelectric behavior of the lead magnesium niobate ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, PMN) family of perovskites has been the subject of considerable debate. For several years, the observation of a two-phase assemblage of nanosized 1:1 ordered domains and a disordered perovskite matrix in PMN was interpreted using the “space-charge” model.¹ In this model, the ordered doubled perovskite structure was claimed to be charge-imbalanced and to contain a 1:1 ratio of magnesium to niobium. However, recent experimental and theoretical studies of tantalate ($\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$, PMT) and niobate (PMN) members of the PMN family have provided convincing support for an alternate charge-balanced ordering scheme.^{2–11} For this model, the “random-site” structure, the β'' position in the 1:1 ordered $\text{Pb}(\beta'_{1/2}\beta''_{1/2})\text{O}_3$ phase is occupied solely by the “active” ferroelectric B-site cation (Nb or Ta), and the β' site is occupied by a random distribution of Mg cations and the remaining Nb/Ta cations. According to this model, the ordered structure of PMT, for example, can be represented as $\text{Pb}(\text{Mg}_{2/3}\text{Ta}_{1/3})_{1/2}\text{Ta}_{1/2}\text{O}_3$.

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The primary experimental support for the random-site model has come from new investigations of the ordered structures, and from the observation of extensive increases in the size of the chemical domains and the degree of ordering in samples equilibrated at elevated temperature.^{2–6,10,11} Additional support has been provided by calculations of the relative stabilities of different possible B-site ordering schemes.^{7–9} The preparation of large-chemical-domain PMN-type relaxors has also clarified the relationship between the crystal chemistry of the B-site ordering and the dielectric response. In contrast to the behavior of the lead scandium tantalate ($\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$, PST) and lead scandium niobate ($\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$, PSN) systems, the large-domain PMT systems retained their relaxor behavior.^{2,3,6} This result implied that the chemical randomness (and associated random fields) on the β' sublattice, and not the actual ordered domain size, is critical in mediating the ferroelectric coupling.

These new experimental studies also revealed that small concentrations of solid-solution additives have a large effect on the conditions required to promote chemical ordering and domain coarsening in PMN and PMT. For example, the addition of 5–10 mol% of lead zirconate (PbZrO_3) to PMT induced an order-of-magnitude increase in the size of the chemical domains after appropriate thermal annealing.² Although the crystal chemistries of niobate and tantalate members of the PMN family are quite similar, the stability of their chemical order was quite different. In PMT, the cation ordering is stable up to $\sim 1375^\circ\text{C}$; however, the absence of any increase in the order or domain size in pure PMN at any accessible temperature was proposed to result from a much lower order–disorder temperature, perhaps as low as 950°C .⁶ This suggestion was also supported by recent calculations of the stability of the ordering in these and other related perovskite systems.^{8,9}

In this paper, we investigate the cation ordering in the $(1 - x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $x\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PMN–PSN) solid-solution system. By examining the thermal stability of the cation order across the system, we provide evidence for an order–disorder temperature close to 950°C in PMN.

II. Experimental Methods

PMN–PSN ceramics were synthesized from high-purity (99.9%) oxides via a modified “columbite-type” route. Stoichiometric quantities of predried oxides of the B-site metals were mixed together 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 (YSZ) 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 in a closed platinum crucible, ball-milled for 3 h, and then reheated at 900°C for 3 h 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. For the higher-temperature annealing treatments, the ceramics were buried in a protective powder of the same composition.

X-ray diffractometry (XRD) (Model D-max B, Geigerflex, Rigaku Co., Tokyo, Japan) was used to determine the phase purity. The degree of order was monitored by scaling the integrated intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ supercell reflection (I_o) to that of the (001) subcell reflection of the perovskite subcell (I_{100}). The ordering parameter α was calculated from the scaled intensities, using the relation $\alpha^2 = (I_o/I_{100})_{\text{observed}} / (I_o/I_{100})_{\text{max}}$, where $(I_o/I_{100})_{\text{max}}$ is a value that is calculated assuming complete 1:1 B-site order within the random-site model. In this calculation, it was assumed that the Pb and O 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, operated at 120 kV; Philips, Eindhoven, The Netherlands). The TEM specimens were prepared by grinding, polishing, and dimpling thin sections of the ceramics. The final thinning to perforation was conducted via argon-ion milling (Model PIPS, at 5.5 kV and 20 mA; Gatan, Pleasanton, CA).

III. Results

As we have reported previously, experiments conducted for the purpose of enhancing the degree of ordering in pure PMN, by annealing samples at temperatures of ~900°–1350°C, were not successful.⁶ In all cases, the degree of ordering (~20 vol% in small (2–3 nm) domains) was essentially the same as that observed in as-sintered specimens. However, for the $(1-x)\text{PMN}-x\text{PSN}$ solid-solution system, the cation order was responsive to thermal treatment for compositions with $x \geq 0.1$. For most compositions, the as-sintered samples (1225°C, 1 h) exhibited very limited cation order; in all cases, longer-term annealing and/or slow-cooling treatments induced large increases in the degree of ordering. The intensity of the ordered peaks was typically maximized through a heat treatment for 3 h at 1250°C, followed by a slow cool at a rate of 10°C/h to 900°C. X-ray patterns of compositions across the system after this heat treatment are shown in Fig. 1. The variation in the intensity of the ordering reflections (plotted as $(I_o/I_{100})_{\text{observed}}$), relative to composition x , is shown in Fig. 2, along with the value of the order parameter α ($\alpha = [(I_o/I_{100})_{\text{observed}} / (I_o/I_{100})_{\text{max}}]^{1/2}$).

Examples of the microstructure of the slow-cooled specimens are shown in the dark-field TEM images in Fig. 3; these images were collected using the $(\frac{3}{2}, \frac{3}{2}, \frac{3}{2})$ supercell reflections. The grains consist of 1:1 ordered domains separated by narrow disordered boundaries. In agreement with the order parameter calculated from the XRD patterns, samples with $0.1 \leq x \leq 0.9$ show the highest levels of ordering and the largest chemical domain sizes, with the ordered regions in the $x = 0.5$ composition approaching ~200 nm in size.

The thermal stability of the cation order in each composition was examined by reannealing and quenching the well-ordered samples at temperatures up to 1375°C. Figure 4(a) shows an example of the X-ray data (for $x = 0.5$) collected from a well-ordered sample after the initial annealing and slow cooling, and after successive quenching treatments at different temperatures. The continuous change in the intensity of the supercell peaks, relative to increases in temperature, reflect the second-order character of the order–disorder transition. By extrapolating the scaled intensity to a zero value, the order–disorder temperature for each composition could be determined (see Fig. 4(b)). For the $x = 0.5$ composition, the transition temperature was 1376°C; the values for the other compositions are shown in Table I.

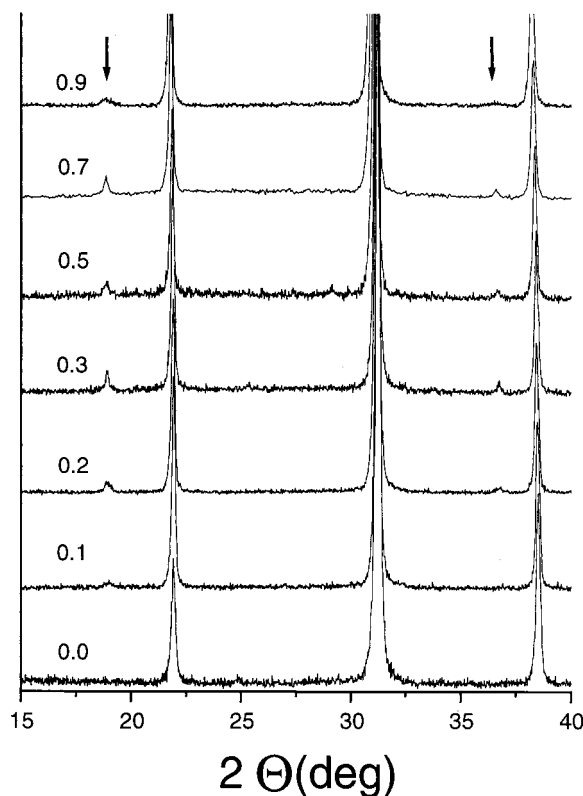


Fig. 1. XRD patterns of $(1-x)\text{PMN}-x\text{PSN}$ (x values shown in figure) after annealing at 1250°C for 3 h, followed by cooling at a rate of 10°C/h. Arrows indicate position of the ordering reflections.

To check the reversibility of the transitions and establish whether an equilibrium state was attained during the annealing treatments, the kinetics of the ordering process were examined by annealing and quenching disordered samples of each composition at temperatures up to 1375°C. Then, these data were compared with the results obtained from the annealing treatments of the ordered specimens. Data for the $x = 0.2$ composition are shown in Fig. 5. After 24 h of annealing at temperatures $\geq 1200^\circ\text{C}$, the degree of ordering is practically independent of the initial state of order in the sample. Moreover, for $T > 1250^\circ\text{C}$, equilibrium is attained after ~1.5 h. However, for $T < 1200^\circ\text{C}$ the degree of ordering observed after the ordered and disordered samples were annealed was quite different; the treatments for 24 h evidently were not sufficient to attain equilibrium in both types of samples. As expected, the kinetic limitations increased at even lower annealing temperatures, and, at $T < 1100^\circ\text{C}$, the order–disorder transformation was essentially suppressed by the inactivity on the B-site sublattice. By conducting similar experiments on compositions across the PMN–PSN system, we were able to delineate the order–disorder boundary; the resultant phase diagram is shown in Fig. 6. Extrapolation of the order–disorder boundary to pure PMN yields a transition temperature close to 950°C, a temperature that is clearly too low to allow the development of any significant long-range 1:1 chemical order.

To examine whether the domain size of the ordered samples could be modified by heat treatment, the microstructures of the specimens with the $x = 0.2$ composition after annealing for 3 h at 1250°C were compared with those after a treatment for 48 h at the same temperature. The microstructures of both samples are shown in Fig. 7. After either annealing, the samples were well-ordered and exhibited almost identical degrees of order. However, the microstructures of the samples were quite different. After the short anneal (Fig. 7(a)), the domains were relatively small, with a mean size of ~100 nm; the longer anneal promoted extensive domain coarsening and the irregularly shaped micrometer-sized ordered

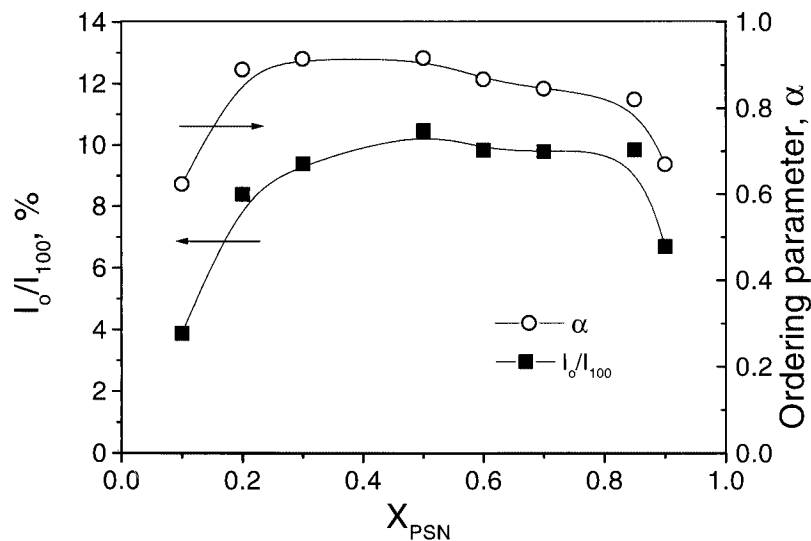


Fig. 2. Variation in the relative intensity of the ordering reflections (plotted as $(I_0/I_{100})_{\text{observed}}$) and ordering parameter (α), as a function of the PSN content.

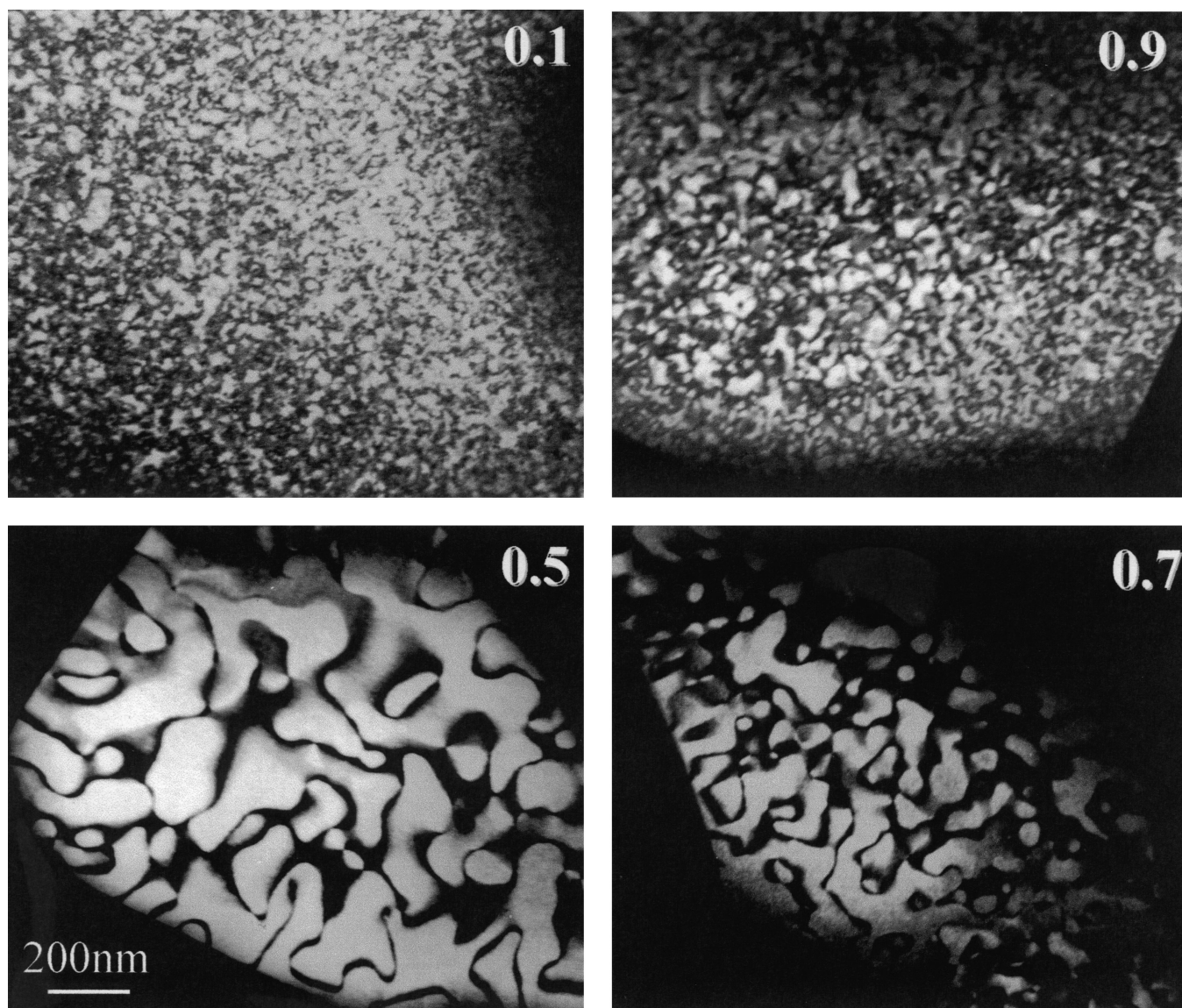


Fig. 3. Dark-field TEM images, collected using the $(\frac{3}{2}, \frac{3}{2}, \frac{3}{2})$ supercell reflection, of slow-cooled specimens of $(1-x)\text{PMN}-x\text{PSN}$; x values are shown on each micrograph.

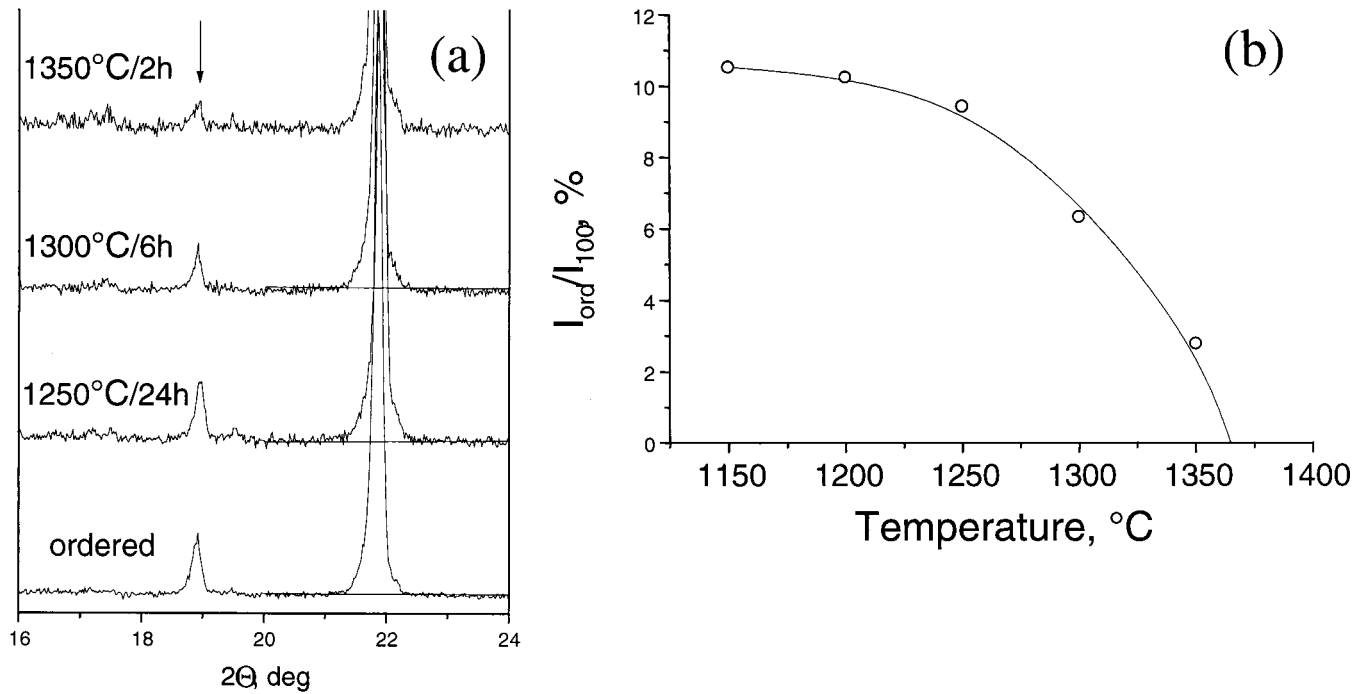


Fig. 4. (a) XRD patterns for $x = 0.5$ after annealing at different temperatures, followed by quenching (arrows indicate the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ordering reflection); (b) scaled $(I_{\text{ord}}/I_{100})_{\text{observed}}$ intensity for the XRD patterns in Fig. 4(a).

regions contained equiaxial domains 50–300 nm in size, enveloped by antiphase boundaries.

IV. Discussion

The data presented in Fig. 6 indicates that the introduction of scandium into PMN induces a large increase in the thermal stability of the cation order; for 10 mol% PSN, the order–disorder boundary is close to 1150°C. The maximum stability of the ordering occurs at $x = 0.5$, where the order–disorder temperature is $\sim 1365^\circ\text{C}$; this is also significantly higher than the reported temperature for the PSN end member (the experimental order–disorder transition temperature (T_{dis}) is 1210°C^{12}). Simple extrapolation of the boundary to pure PMN yields a transition close to 950°C , a temperature that, according to our ordering experiments, is too low for the B-site lattice to retain any reasonable “kinetic activity.” The lower degree of ordering observed in samples with $x = 0.1$ and 0.9 compositions is also consistent with their relatively low transition temperatures, which lead to a narrower window of kinetic activity during the slow-cooling and annealing treatments.

Additional information on the stability of the ordering and its relationship to the domain coarsening was obtained using simple thermodynamic models to describe the cation mixing on the B-site lattice. The enthalpic stability of the 1:1 ordered $\text{Pb}(\beta'_{1/2}\beta''_{1/2}\text{O}_3$

phases in the PMN–PSN system, and that of all other ordered mixed-metal perovskites, is derived from the valence difference of the β' and β'' sites and the difference in the average β' –O and β'' –O bond lengths. The substitution of PSN into PMN (where the effective replacement scheme is described as $x\text{Sc}^{3+} = (2x/3)\text{Mg}^{2+} + (x/3)\text{Nb}^{5+}$ on the β' site) does not change the average valence of the two ordered positions (which remain 3+ and 5+ for all values of x); however, the incorporation of the larger Sc cations onto the β' position ($r(\text{Sc}^{3+}) = 0.745 \text{ \AA}$, whereas $[\frac{2}{3}r(\text{Mg}^{2+}) + \frac{1}{3}r(\text{Nb}^{5+})] = 0.693 \text{ \AA}$) does increase their size difference. The random distribution of metal cations on the β' sublattice also introduces a significant configurational entropic contribution to the free energy of the random-site structure, which, as we have previously noted, can produce large changes in bulk stability.^{2,13}

Using a simplified approach in which the ordering reactions are assumed to be first-order transitions (which they are not), the enthalpy of ordering can be calculated using classical thermodynamic treatments. The composition of the 1:1 ordered $(1-x)\text{PMN}-x\text{PSN}$ random-site structure is given by $\text{Pb}[(\text{Mg}_{(2-2x)/3}\text{Nb}_{(1-x)/3}\text{Sc}_x)_{1/2}[\text{Nb}]_{1/2}\text{O}_3$ and the disordered perovskite by $\text{Pb}(\text{Mg}_{(1-x)/3}\text{Nb}_{(4-x)/6}\text{Sc}_{x/2})\text{O}_3$. The configurational entropy of the random-site structure (S_{RS}) can be calculated from

$$S_{\text{RS}} = -\frac{R}{2} \left\{ \left[\left(\frac{2-2x}{3} \right) \ln \left(\frac{2-2x}{3} \right) \right] + \left[\left(\frac{1-x}{3} \right) \ln \left(\frac{1-x}{3} \right) \right] + x \ln x \right\} \quad (1)$$

and the entropy of a fully disordered perovskite (S_{dis}) can be calculated from

$$S_{\text{dis}} = -R \left\{ \left[\left(\frac{1-x}{3} \right) \ln \left(\frac{1-x}{3} \right) \right] + \left[\left(\frac{4-x}{6} \right) \ln \left(\frac{4-x}{6} \right) \right] + \frac{x}{2} \ln \frac{x}{2} \right\} \quad (2)$$

Using this mixing model to calculate the entropy of ordering ($\Delta S_{\text{ord}} = S_{\text{RS}} - S_{\text{dis}}$), the enthalpy associated with the cation order

Table I. Thermodynamic Properties of the $(1-x)\text{PMN}-x\text{PSN}$ System

X_{PSN}	T_{dis} ($^\circ\text{C}$)	S_{dis} ($\text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$)	S_{RS} ($\text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$)	ΔS_{ord} ($\text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$)	ΔH_{ord} (J/mol)
0.0		5.30	2.65	-2.65	
0.1	1160	6.58	3.73	-2.85	-4084
0.2	1334	7.25	4.20	-3.05	-4904
0.3	1355	7.67	4.39	-3.28	-5340
0.5	1376	7.98	4.21	-3.77	-6217
0.85	1270	7.08	2.15	-4.93	-7607
1.0	1210 [†]	5.76	0.0	-5.76	-8542

[†]From Stenger and Burggraaf.¹²

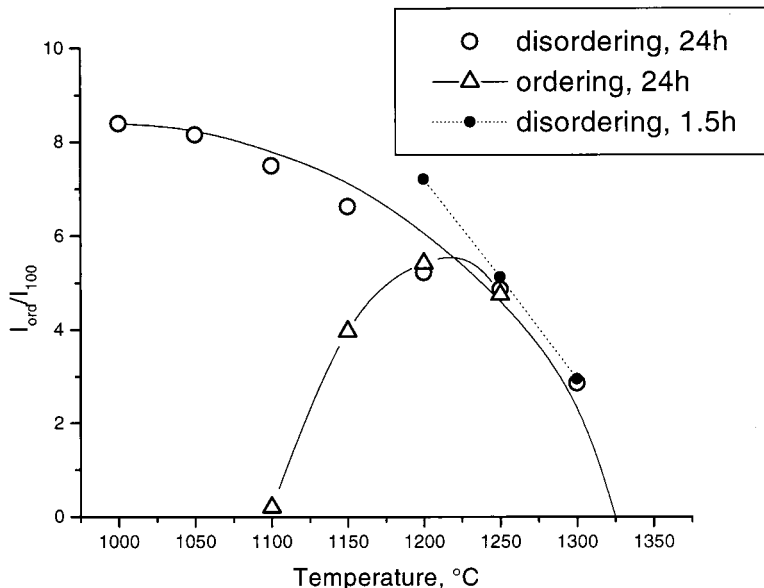


Fig. 5. Intensity of ordering reflections (plotted as $(I_{ord}/I_{100})_{observed}$) after annealing disordered and ordered $x = 0.2$ specimens at different temperatures.

(ΔH_{ord}) can be determined from the experimental order-disorder transition temperature (T_{dis}) by equating ΔH_{ord} and $T_{dis}\Delta S_{ord}$ (see Table I). The resultant enthalpies, plotted as a function of composition in Fig. 8, show an almost-linear variation across the system and range from an extrapolated value of -3835 J/mol for pure PMN to -8542 J/mol for PSN (Table I).

The thermodynamic calculations provide useful additional information on the crystal chemical stability of the system, although they rely on a classical first-order treatment of the disordering reactions. As mentioned previously, the incorporation of scandium onto the random-site position would be expected to stabilize the cation order by increasing the difference in the size of the β' and β'' sublattices. Although this expectation is supported by the increase in the enthalpy of ordering for increasing x , if the average size difference is the only factor that affects ΔH_{ord} , the magnitude of the increase is surprisingly large. However, for the random-site type of ordering, unfavorable “excess” contributions to ΔH_{ord} must result from the mixing of ions with different sizes and charges on the β' position. This excess contribution will be maximized for the ordered PMN end member where the β' position contains a 2:1

mixture of cations with the largest size and charge difference ($r(Mg^{2+}) = 0.72 \text{ \AA}$, $r(Nb^{5+}) = 0.64 \text{ \AA}$). When the increase in the size difference of the β' and β'' positions and the reduction in the charge/size mismatch on the β' sublattice are considered, the very large enhancement in ΔH_{ord} , relative to increasing x , seems

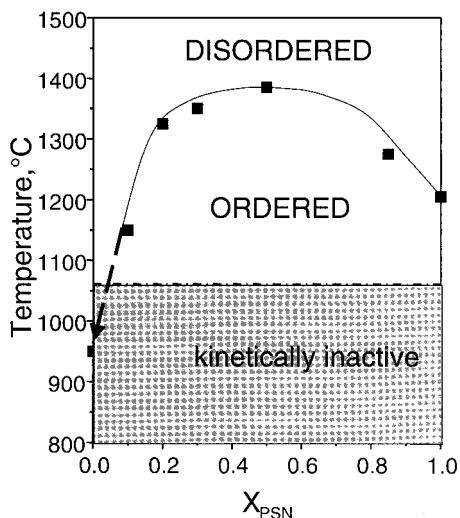


Fig. 6. Experimental order-disorder boundary for the PMN-PSN system. Arrow indicates extrapolated transition temperature for pure PMN. Shaded area represents the region where significant kinetic limitations to achieving order were observed.

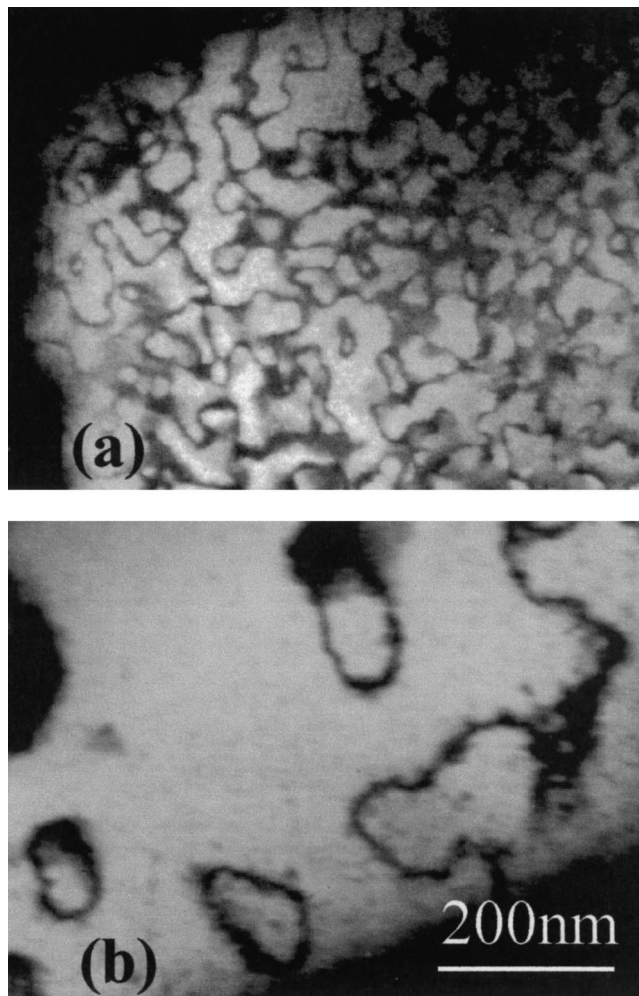


Fig. 7. Dark-field TEM micrographs of the $x = 0.2$ samples after annealing at 1250°C for (a) 3 h and (b) 48 h.

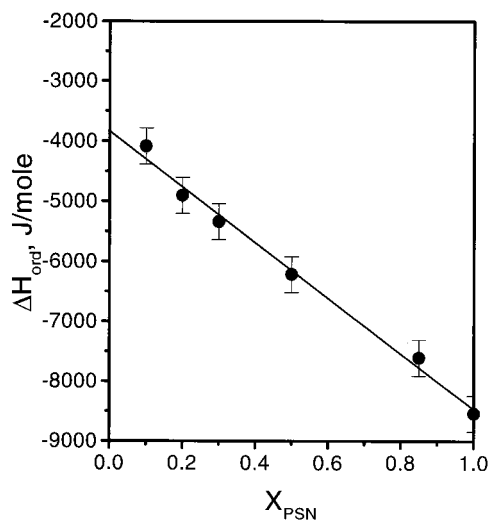


Fig. 8. Enthalpy of ordering (ΔH_{ord}), calculated using data in Table I (see text).

reasonable. The overall change in the free energy of the ordered 1:1 structure and the variation in the transition temperature, which is maximized at $x \approx 0.5$, is ultimately a compromise between the composition with the highest enthalpic stability (PSN) and the least-negative entropy of ordering (PMN).

Having established the changes in stability of the 1:1 ordering, we return to the issue of the variations in domain size that has been highlighted in Fig. 3. Although extensive ordering could be induced for compositions of $x = 0.1$ – 1.0 , the domain size in the annealed/slow-cooled samples shows a nonlinear variation, relative to x . The degree of domain coarsening after short-term annealing evidently parallels the trend in the energetics of the system, with the maximum domain size and stability occurring for $x = 0.5$. An increase in the stability of the cation order necessarily increases the excess energy of boundaries (antiphase boundaries, APBs) that separate different translational variants of the ordered structure and of the interfaces between ordered and disordered regions of the sample. Therefore, although kinetics clearly are very significant in permitting these systems to approach an equilibrated state, even for prolonged heat treatments, the effect of scandium on the domain coarsening can be rationalized in terms of the bulk stability and crystal-chemistry ideas proposed earlier.

The impact of the alterations in domain size and degree of ordering on the dielectric response of this system will be presented in a future publication.

V. Conclusions

Relatively low-level substitutions of lead scandium niobate (PSN) (10 mol%) are effective in stabilizing extensive 1:1 B-site chemical ordering in lead magnesium niobate (PMN). The maximum stability of the 1:1 order in PMN–PSN is observed at $x = 0.5$; by extrapolating the phase boundary, an order–disorder transition for PMN is predicted at temperatures of $\sim 950^\circ\text{C}$. The enthalpy change associated with the order–disorder reaction contains a favorable term that is related to the difference in the charge and size of the ordered sites, as well as an unfavorable contribution from the valence and size mismatch of the metal cations that occupy the β' random site. The alterations in the size of the ordered 1:1 chemical domains are consistent with the change in thermal stability and the window of kinetic activity for each composition.

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