The effect of different tetravalent octahedral-site substitutions (M$^{4+}$ = Zr, Tb, and Ce) on the stability of the 1:1 chemically
directed ordered phase in Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ (PMN) relaxor ferroelec-
trics were investigated using X-ray diffractometry and trans-
mission electron microscopy. In their as-sintered form, all
the samples adopted a phase-separated microstructure that consis-
ted of nanosized 1:1 ordered domains dispersed in a disor-
dered matrix. However, after annealing at 1250°C for 24 h, a
fully 1:1 ordered microstructure with large domains (>100
nm) was stabilized in 10 mol%-terbium-doped PMN. No
ordered-domain coarsening was observed in pure or
zirconium-doped PMN, which indicated that the size of the
solid-solution additives was critical to stimulating the growth
and stability of the 1:1 order. The observation of complete 1:1
order in the terbium-doped system supports the “random-site”
model description of the Pb(b$_{10}$b$_{12}$)O$_3$ structure. This model
also can be used to explain the insensitivity of the diffuse
frequency-dependent dielectric properties to the size of the
chemically ordered domains.

I. Introduction

Lead-based 1:2 perovskites with the general formula Pb(b$_{10}$b$_{12}$)O$_3$ (B$^{4+}$ = Zn, Mg, or Ni; B$^{5+}$ = Nb or Ta) exhibit
relaxor ferroelectric properties, which are characterized by a broad
and frequency-dependent relative permittivity maximum ($\varepsilon_r$) among the many different compositions, Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ (PMN) relaxors have been investigated extensively,
because of their high relative permittivity and large electrostrictive
coefficients, for technological applications such as multilayered
ceramic capacitors, actuators, and electro-optic devices.

It is generally accepted that the relaxor properties of PMN are
associated with local inhomogeneities in the distributions of the Mg
and Nb cations on the B-site sublattice. The as-sintered forms of the
PMN family of relaxors adopt a structure that contains nanosized 1:1 ordered domains that are dispersed in a disordered
matrix. Within the domains, the B-site metals adopt a doubled
perovskite, Pb(b$_{10}$b$_{12}$)O$_3$-type, “1:1” structure with a face-
centered arrangement of two different (b$^+$ and b$^-$) cation positions.
Until recently, the crystal chemistry of the ordered
nanodomains has been widely interpreted in terms of a composi-
tionally segregated “space-charge” model. In this model, the
b$^+$ and b$^-$ octahedral sites are assumed to be exclusively occupied
by B$^{4+}$ and B$^{5+}$ cations, respectively, and the negatively charged
domains are claimed to be compensated by an oppositely charged
B$^{5+}$-rich disordered matrix. The primary experimental support for
this model originates from the absence of any coarsening of the
domains when PMN samples are subjected to extended low-
temperature thermal treatments, and from the observation of an
increase in the domain size in the “donor-doped” Pb$_{1-x}$La$_x$(Mg$_{1/3}$+x/3Nb$_{2/3}$-x/3)O$_3$ (PLMN) solid-solution sys-
tem.

In a series of recent investigations, we demonstrated that
extensive modifications of the cation order can be induced in tantalate relaxors that are based on Pb(Mg$_{1/3}$Ta$_{2/3}$)$_3$O$_3$ (PMT),
using thermal treatments in the temperature range of 1250°C–
1350°C. In its as-sintered form (1225°C, 1 h), the microstruc-
ture of PMT was typical of the PMN-type systems and contained
≈20 vol% of 2–3 nm ordered domains dispersed in a disordered
matrix. However, after a subsequent annealing at 1325°C, the
degree of ordering and the domain size increased to >70 vol% and
≈10 nm, respectively. Additional experiments revealed that the
structure modification could be achieved only in a relatively
narrow window of kinetic activity and thermodynamic stability.
For pure PMT, the samples were kinetically inactive at tempera-
tures below ≈1250°C; above ≈1375°C, they transformed to a
fully disordered perovskite.

The modification of the cation order in PMT was extremely
sensitive to the bulk chemistry of the octahedral sites, and PMT
relaxors that contained 5–25 mol% of PbZrO$_3$ (PZ) adopted a
large-domain, fully 1:1 ordered state after thermal equilibration at
a temperature of 1325°C. The observation of extensive changes in
the domain size and the formation of completely 1:1 ordered
structures in the PMT–PZ system conflict with the predictions of
the space-charge model. Instead, these results support a charge-
balanced “random-site” model for the cation order that had been
previously suggested and dismissed as a possible alternate explana-
tion for the ordering in PMN. In this model, only one (b$^+$) of the
two cation positions in 1:1 ordered PMT is occupied by a single
type of metal ion (Ta$^{5+}$), whereas the other (b$^-)$ contains a random
2:1 distribution of Mg and Ta cations.

Confirmation of the random-site model was obtained from a
structure refinement of a large-domain, fully 1:1 ordered PMT–
10 mol%-PZ relaxor. For this sample, the b$^+$ position was almost
exclusively populated (90%) by Ta ions, whereas the b$^-$ sublattice
contained a random distribution of Mg, Zr, and the remaining Ta
cations. The incorporation of Zr ions onto the b$^-$ site and the
accompanying increase in the size difference of the b$^+$ and b$^-$
positions induce a significant increase in the thermodynamic
stability of the 1:1 order that was still present in PMT–10-
mol%-PZ samples that were quenched from 1450°C (manuscript
in preparation). The localized disorder on the b$^-$ sublattice also
seems to have a critical role in frustrating the long-range ferro-
electric coupling in the PMT–PZ relaxors that retained their
diffuse frequency-dependent dielectric response, regardless of the
size of the 1:1 chemical domains.

Studies of the cation ordering in donor-doped
Pb$_{1-x}$La$_x$(Mg$_{1/3}$+x/3Ta$_{2/3}$-x/3)O$_3$ (PLMT) solid solutions provided
additional support for the random-site model. In this case, heat
treatments at 1300°C for 24 h yielded completely 1:1 ordered
samples for all values of x. The absence of any residual disordered matrix precluded the formation of a compositionally segregated charge imbalanced structure, and the crystal chemical features of the PLMT solid solutions could be modeled using a random-site structure with the formula $\text{Pb}_1-x\text{La}_x[(\text{Mg}_{2+x-z}\text{Ta}_{1-z})\text{P}_{1-x/2}\text{Ta}_{x/2}]\text{O}_{3} (0.0 \leq x \leq 0.5)$.

Although thermally induced structure modification has yet to be reported for the corresponding PMN-based systems, recent studies of the niobate relaxors question the validity of the space-charge model and suggest that the cation order in PMN should also be interpreted using the random-site description.\textsuperscript{16-18} For example, analyses of the composition of the $\beta'$ and $\beta''$ sites in PMN and PLMN via high-resolution Z-contrast imaging were in excellent agreement with the charge-balanced random-site model and confirmed the results of a previous high-resolution TEM study.\textsuperscript{16,17} Furthermore, small-angle resonant X-ray scattering measurements on PMN showed no evidence for compositional segregation between the ordered domains and the disordered matrix.\textsuperscript{19} However, the question remains as to whether the cation order in the niobates can be altered by thermal treatment.

Several efforts have been made to coarsen the nanodomains in PMN by annealing samples for extended periods at temperatures $\approx 950^\circ C$.\textsuperscript{5,8,11} At these temperatures, the structure was inert and the degree of order and domain size were unchanged. Following the observation that higher temperatures were required to increase the ordering in PMT, we investigated the response of PMN to annealing treatments as high as 1400°C. In agreement with the previous studies, no evidence was observed for any increase in the degree of order. Because the changes in the cation order in PMT were enhanced in the PMT–PZ solid-solution system, we also investigated the effect of a series of tetravalent-cation substitutions ($\text{Zr}^{4+}$, $\text{Ce}^{4+}$, and $\text{Yb}^{3+}$) on the ordering in PMN. These studies are the subject of this paper.

PMN-based ceramics were synthesized from high-purity (>99.9%) oxides via a modified “columbite-type” route.\textsuperscript{19} 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 balls and acetone as a milling medium. The slurry was dried and recalcined at 1100°C for 12 h. Then, 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°C–1250°C for 1 h.

X-ray diffractometry (XRD) (Model D-max B, Rigaku Co., Tokyo, Japan) was used to determine the phase purity, and the lattice parameters were calculated via the least-squares method, using data that were collected with an internal silicon standard. The microstructures of the ceramics were characterized via transmission electron microscopy (TEM) (Model 4000 EX, KEOL, Tokyo, Japan, operated at 400 kV). The TEM thin foils were prepared by grinding the ceramic pellets to a thickness of ~20 μm and polishing both sides with 5, 3, 1, and 0.25 μm alumina powder. Then, copper support grids were placed on the thin sections and the final thinning to perforation was conducted via argon-ion milling (5.5 kV and 6 mA, Model 600 dual ion mill, Gatan, Pleasanton, CA).

The dielectric properties of the ceramics were investigated as a function of frequency using a high-precision impedance–capacitance–resistance (LCR) meter (Model 42824A, Hewlett-Packard, Palo Alto, CA). During the measurements, the samples were placed in an environmental chamber (Model Delta 9023, Delta Design, San Diego, CA) and the measurement temperature was monitored using a copper-constantan thermocouple (T-type) that was placed next to the sample.

### III. Results

Our previous experiments indicated that the stability and growth of the 1:1 ordered phases in $\text{Pb(Mg}_{1-x}\text{Ta}_{1-x})\text{O}_3$ (PMT)\textsuperscript{12,13} and $\text{Ba(Mg}_{1-x}\text{Nb}_{2/3})\text{O}_3$ (BMN)\textsuperscript{20} could be enhanced by small amounts (≥5 mol%) of zirconium. Therefore, a series of compositions in the $(1-x)\text{PMN}-x\text{PZ}$ solid-solution system were subjected to a variety of thermal treatments in an attempt to coarsen the nano-sized ordered domains that were observed in the as-sintered ceramics. These experiments, which included slow cooling from high temperatures and thermal annealing at a fixed temperature, failed to record any appreciable domain growth in the temperature range of 900°C–1325°C. Work on the barium-based perovskites demonstrated that additional stabilization of the 1:1 ordering could be induced by introducing larger-sized, tetravalent B-site substituents;\textsuperscript{21} therefore, we also explored the phase stability of solid solutions of PMN with $\text{PbCeO}_3$ and $\text{PbTbO}_3$. In contrast to the barium-based systems, the substitution of Ce$^{4+}$ ions (0.87 Å) into PMN promoted the formation of nonperovskite phases and no significant range of solid solubility of $\text{PbCeO}_3$ was observed. However, perovskite PMN samples with partial substitutions of $\text{Ta}^{4+}$ ions, with an octahedral ionic radius (0.76 Å) between that of Zr and Ce ions, could be formed and were explored for ≤10 mol% of $\text{PbTbO}_3$.

The X-ray pattern that was collected from an as-sintered (1225°C, 1 h) sample of PMN–10 mol% $\text{PbTbO}_3$ is shown in Fig. I. The major peaks in this pattern, and also in those collected from a 5 mol% $\text{PbTbO}_3$ sample, correspond to the formation of a perovskite solid solution; minor reflections are observed from small concentrations of $\text{TbNbO}_4$ impurities. This trivalent impurity phase also was identified via TEM and was characterized by a high density of planar defects that originated from a ferroelastic domain structure. Least-squares refinement of the reflections from the primary perovskite phase indicated a small increase in the cell parameter—0.4048(2) and 0.4056(4) nm for 5

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Fig. I. Powder XRD patterns of PMN–10 mol% Tb after sintering at 1225°C for 1 h (pattern “A”) and after a subsequent annealing at 1250°C for 24 h (pattern “B”).
and 10 mol% of terbium, respectively—with increasing Tb substitution. Only very weak and broad reflections that originated from the 1:1 ordering could be discerned in the X-ray patterns of the as-sintered samples (see, for example, the \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) reflection at \(2\theta = 19^\circ\) in pattern “A” in Fig. 1). Direct evidence for the nanolevel order was obtained from dark-field TEM images that were collected using the \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) superlattice reflections. In this image (Fig. 2(A)), the 1:1 order is confined to domains \(\sim3\)–10 nm in size that are dispersed in a disordered matrix.

To investigate whether the ordering in the terbium-based system could be altered by longer thermal treatment, the 5 mol% sample was re-annealed at 1225°C for 48 h. The X-ray patterns of this heat-treated sample showed evidence for some degree of domain growth through a strengthening and sharpening of the supercell reflections in the X-ray patterns. The increase in the degree of order was even more evident after samples that contained 10 mol% Tb were annealed at 1250°C for 24 h. For this composition, the thermal treatment produced a large increase in the intensity and a decrease in the width of the reflections associated with the 1:1 cation order (see pattern “B” in Fig. 1). The corresponding dark-field image (Fig. 2(B)) confirmed the X-ray evidence and indicates that the structure is completely 1:1 ordered in domains \(>100\) nm in size.

The effect of Tb substitution on the dielectric properties of the PMN ceramics was examined as function of frequency and temperature (Fig. 3). With increasing levels of terbium, the temperature of \(\varepsilon'_r, \text{max}\) shifts slightly toward lower temperature and the magnitude of the relative permittivity decreases sharply, approaching 2800 and 1500 for 5 and 10 mol% Tb, respectively.

Our studies show that the response of the cation ordering to high-temperature treatment in pure and substituted PMN can be quite different to that of the corresponding PMT systems. Although modifications of the order can be achieved in PMT and its solid solutions with PbZrO\(_3\), in the PMN–PZ system, the nanolevel, short-range ordered structure of the as-sintered ceramics did not coarsen after extended thermal treatments. However, extensive changes in the cation order in PMN could be induced by introducing larger-sized Tb-cation substituents. This discussion begins by considering the valence state and location of the Tb cations in the PMN solid solutions; it then considers the nature of the cation distributions in the 1:1 ordered structure and finally compares and contrasts the response of the tantalate and niobate relaxors to the thermal annealing treatments.

Because Tb ions can adopt a stable 3+ and 4+ valence state in oxide compounds, it could be argued that one possible scheme for the substitution of PbTbO\(_4\) into PMN involves the partial replacement of Pb\(^{2+}\) ions by Tb\(^{3+}\) ions on the A-site sublattice. If that was the case, it could be further claimed that the increase in the degree of 1:1 ordering induced by Tb ions is similar to the well-known enhancement of the chemical order in the doped, A-site substituted, La-PMN or La-PMT systems.\(^{3,14,22}\) For this mechanism of substitution, the significantly smaller ionic radius of Tb\(^{3+}\), compared to Pb\(^{2+}\), should produce a decrease in the volume of the perovskite subcell, an expectation that is not supported by the experimental observation of an increase in the subcell volume with increasing terbium content. However, the increase in cell volume is consistent with a mechanism in which Tb\(^{4+}\) ions (octahedral ionic radius of \(0.76\) Å) replaces the smaller Mg\(^{2+}\) and Nb\(^{5+}\) cations (average octahedral radius for \(\frac{1}{3}\)Mg\(^{2+}\) + \(\frac{2}{3}\)Nb\(^{5+}\) is 0.67 Å) on the B-site sublattice. On the basis of this evidence, we suggest that the primary mechanism of chemical substitution involves the incorporation of Tb\(^{4+}\) ions onto the octahedral sites, and that the small fraction of the Tb content that assumes a trivalent state does so primarily in the form of the observed second phase, TbNbO\(_4\).

**Fig. 2.** Centered dark-field TEM images of pure PMN–10 mol% Tb (A) after sintering at 1225°C for 1 h and (B) after subsequent annealing at 1250°C for 24 h. The corresponding [110] electron diffraction pattern is shown in the inset in each figure.

**Fig. 3.** Temperature and frequency dependence of the real part of the dielectric permittivity and the dielectric loss of as-sintered PMN–5 mol% Tb, as-sintered PMN–10 mol% Tb, and PMN–10 mol% Tb after annealing at 1250°C for 24 h.

\((\varepsilon'_r, \text{max} \approx 15\,000\) for PMN). The typical, frequency-dependent response of the real and imaginary parts of the dielectric permittivity was observed in the small domains in the as-sintered ceramics and in the large domains in the heat-treated samples. The increase in the 1:1 order induced a very small decrease (\(-7°C\)) in the temperature of \(\varepsilon'_r, \text{max}\) and an \(\sim30\)% increase in the magnitude of the relative permittivity (Fig. 3).

**IV. Discussion**
Regardless of the distribution of the Tb cations in the structure, it is difficult to reconcile the observation of a completely 1:1 ordered microstructure in the 24-h-annealed PMN–10 mol% Tb samples within the framework of the space-charge model. For that model, the excess charge within the ordered domains must be compensated by a disordered matrix of equal and opposite charge. The annealed, Tb-doped PMN samples do not contain a disordered matrix; therefore, the structure of the single-phase ordered sample can only be interpreted using a single-phase charge-balanced model. We believe that this observation, in addition to the experimental results that have recently appeared on the 1:1 order in other closely related systems (PMT–PZ, 12,13 PLMT, 14 PMN, 16–18 BMN, 20,23 Ba(Mg0.3Ti0.7)O3, 21,24 Ba(Zn1/3Ta2/3)O3, 25,26 and Ba(Zn0.7Nb0.3)O3 27) and theoretical calculations of the cation distributions in the 1:1 ordered 2 perovskite systems, 28 provide convincing support for the random-site description of PMN-based relaxors. Following the argument given previously for the site occupancy of Tb, we propose that, for the 1:1 ordered form of PMN–10 mol% Tb, the structure is best described by the formula Pb(Mg0.6Nb0.2Tb0.2)1/2(Nb)1/2O3, where the β’ position is occupied by Nb and the β site is occupied by a random distribution of Mg, Tb, and the remaining Na cations.

The investigations of the formation of 1:1 ordered structures in the closely related Ba1/2Ti1/2O3–BaM1/2O3 (M = Ti, Sn, Zr, or Ce) perovskite systems showed that the stability of the random-site structure is strongly correlated to the size of the M+4+ substituent, with the larger cations imparting additional stability through an increase in the size difference of the β’ and β’’ positions. 21 The behavior of the PMN and PMT-substituted systems can be interpreted using similar arguments; however, to explain the different response of pure PMN and PMT to thermal annealing, the covalency of the Ta and Nb cations also must be considered. We have observed that pure PMN resists any structure modification, regardless of the heat treatment; this observation is consistent with previous reports in the literature. Furthermore, although PZ is effective in promoting extensive ordered-domain growth in PMT, it has little or no effect on PMN. It is our opinion that the thermodynamic transformation from 1:1 order to “complete” disorder in PMN occurs at a temperature that is too low (perhaps <800°C) to permit any growth of the cation-ordered domains beyond that usually observed (2–3 nm). We also propose that the nanolevel order that is observed in PMN may reflect the quenched, short-range ordered structure of the high-temperature “disordered” phase. This conclusion would imply that PMN samples that have been quenched from progressively higher temperatures should, in fact, show a decrease in the degree of cation order. A lower order–disorder transition temperature for PMN, compared to that of PMT (where Tdisorder ∼ 1375°C), is entirely consistent with the behavior of other niobate and tantalate perovskites (e.g., PbSc1/2Ta1/2O3 (Tdisorder ∼ 1200°C), 29 PbSc1/2Ta1/2O3 (Tdisorder ∼ 1500°C), 30 Ba(Zn1/3Nb2/3)O3 (Tdisorder ∼ 1325°C), 37 and Ba(Zn1/3Ta2/3)O3 (Tdisorder > 1650°C)) 11) and results from a reduction in the coulombic driving force for order by the higher covalency/polarizability of the Nb cation.

The continued absence of any significant change in the cation order in heat-treated PMN–PZ samples suggests that any reduction of the free energy of the 1:1 ordered phase by Zr ions is insufficient to increase its stability field to “kinetically active” temperatures. Apparently, this result can be achieved by introducing a larger-sized cation substituent (such as Tb) where the ordered phase is stable at temperatures that are high enough to permit the samples to adopt a completely 1:1 ordered state. We note that further confirmation of the critical role of the substituent size on the stability of the 1:1 order in PMN has been observed in the PMN–PbSc1/2Nb1/2O3 system (manuscript in preparation). For this system, small levels of Sc3+ ions (with an ionic radius (0.745 Å), similar to that of Tb4+ ions) also were effective in stabilizing a fully ordered 1:1 structure after extended annealing.

Characterization of the dielectric properties of Tb-doped PMN indicate that the relaxor characteristics of the large-domain, fully 1:1 ordered ceramics are very similar to those of the assintered samples. This observation again highlights the importance of the disordered distribution of the different ions on the β’ positions of the 1:1 ordered structure in frustrating the long-range ferroelectric coupling of Pb and Nb(Ta) cations. 22 The retention of relaxor behavior also reinforces our previous claims that, for the 1:2 type lead perovskites, the degree of 1:1 order or the size of the chemical domains is not of critical importance in producing a relaxor response.

V. Conclusions

Large-domain, fully 1:1 ordered microstructures were stabilized after annealing Pb(Mg0.53Nb0.47)O3 (PMN) ceramics that contained 10 mol% Pb5TbO3 at 1250°C for 24 h. The observation of complete 1:1 order and the absence of any residual disordered perovskite matrix is not consistent with the predictions of the space-charge model; instead, it supports a random-site description for the chemical order on the B-site sublattice. No domain coarsening was observed in pure PMN or in solid solutions of PMN with PbZrO3, which suggests that the larger size of the Tb cations may be a critical factor in increasing the thermodynamic stability of the 1:1 order to kinetically active temperatures. Alterations in the ordering in PMN–10 mol% Tb did not have a significant effect on the dielectric relaxor response, which seems to be associated with the localized disorder on the β’ positions of the random-site structure.

References


L. Chai, M. A. Akbas, and P. K. Davies; unpublished work.