1:1 Ordered Domain Growth in Pb(Mg$_{1/3}$Ta$_{2/3}$)O$_3$–La(Mg$_{2/3}$Ta$_{1/3}$)O$_3$

Relaxor Ferroelectric Perovskites

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Single-phase perovskite solid solutions are formed across the entire (1 − x)Pb(Mg$_{1/3}$Ta$_{2/3}$)O$_3$−xLa(Mg$_{2/3}$Ta$_{1/3}$)O$_3$ (PLMT) pseudobinary system. Although as-sintered (1300°C, 3 h) samples with x ≤ 0.1 adopt a phase-separated, “PMN-type” microstructure comprising small (2–3 nm) ordered domains dispersed in a disordered matrix, extensive domain growth and complete order can be induced by extended thermal annealing (1300°C, 24 h). These observations, and the alterations in the thermal stability and domain size across the system, can be interpreted using a charge-balanced random site model for the cation order. No evidence is found to support the space-charge models currently used to describe the cation ordering and properties of the corresponding niobate systems.

I. Introduction

For several years it has been recognized that the relaxor properties of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN)-type perovskites are associated with localized inhomogeneities in the distribution of metal cations on the B-site sublattice.1–4 The structures of the as-sintered forms of all members of this lead-based 1:2 family of perovskites comprise small chemically ordered nanodomains dispersed in a disordered matrix.5–7 Diffraction studies have shown the periodicity of cation ordering within the nanodomains is not compatible with the overall 1:2 stoichiometry of the B-site cations.5–7 The appearance of additional reflections at (h ± 1/2, k ± 1/2) and (l ± 1/2) indicate that, within the domains, the cations adopt a 1:1 ordered Pb($^{9}$B$_{1/2}^{1/2}$)O$_3$ structure with a face-centered arrangement of two different B-site positions in a doubled perovskite cell. Until recently, the structure and chemistry of the ordered domains has been interpreted in terms of a compositionally segregated, space-charge model.6–11 According to this model, each of the two ordered B-site positions are occupied exclusively by a single type of cation. For PMN, the composition of the ordered domains predicted by this model is Pb(Mg$_{1/2}$Nb$_{1/2}$)O$_3$, with the excess charge being compensated by a positively charged, niobium-rich, disordered matrix. Clearly, for this model, any growth of domains would be inhibited by the local charge imbalance associated with compositional segregation.

Widespread acceptance of the space-charge model for PMN-type systems5–11 has been derived primarily from the apparent lack of any growth of nanosized domains during extended thermal annealing.6,9,12,13 However, additional support for the model has come from studies on the effect of the partial replacement of Pb$^{2+}$ by La$^{3+}$ on the A-site sublattice.8,9,14,15 In these, donor-doped P$_{1-x}$La$_x$(Mg$_{1-x}$La$_x$Nb$_{2/3}$)O$_3$ (PLMN) solid solutions, where the substitution of lanthanum was compensated by an increase in the overall Mg:Nb ratio, the intensity of the superlattice reflections and the size of the ordered domains were observed to increase dramatically with x.8,9,14,15 For example, in solid solutions of PLMN with x = 0.1, 0.2, and 0.3, domain size increased to ~200, >300, and 500 nm, respectively.9 The growth of domains has been claimed to result from a reduction in the charge imbalance in the 1:1 ordered regions, which were assumed to maintain a 1:1 distribution of magnesium and niobium, by the lanthanum donor cations.8,9,14,15

While it is clear that the incorporation of lanthanum and the formation of ordered domains with the composition (Pb$^{2+}$)$_{2/3}$La$_{(1/2)}$(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ ($\geq 0.1$) would reduce the excess charge, it should be noted that a large charge imbalance (e.g., 0.3+ per unit cell for x = 0.2) would still be present for all compositions except x = 0.5. In our opinion, the existence of such large charges in domains >300 nm does not seem reasonable. Furthermore, according to the space-charge model, all PLMN compositions with 0.0 ≤ x < 0.5 should contain a charge-compensating disordered matrix. With, perhaps, the exception of samples with x = 0.05, the presence of significant volumes of a disordered matrix is not apparent from the published micrographs of the microstructures of the PLMN system.8,9 This model also fails to find support from detailed X-ray studies that have been made of the PLMN system. The two-phase, compositionally segregated microstructure should produce very clear splittings of the perovskite subcell reflections; these are notably absent in the published X-ray data.14,15 An alternate interpretation for the 1:1 cation order, the so-called random site model, was initially proposed but subsequently rejected in the original microstructural studies of the PMN and PLMN systems.8,9 In this description of cation order, only one B$^{9}$ of the two cation positions in the Pb($^{9}$B$_{1/2}^{1/2}$)O$_3$ structure is assumed to be occupied by a single type of metal (Nb$^{5+}$), while the other B$^{9}$ contains a 2:1 random distribution of magnesium and niobium. For this model, where the 1:1 form of PMN can be represented as Pb(Mg$_{2/3}$Nb$_{1/3}$)O$_3$, the ordered domains are charge balanced and have the same overall chemistry as the bulk. For this type of cation order, domain coarsening would be expected, given that the phases were annealed under conditions where the sample was kinetically active and ordering was thermodynamically stable. The primary reason for the rejection of the random site model was the inert response of PMN to extended annealing.6,9,12,13 However, in recent studies of the corresponding tantalate relaxor Pb(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (PMT), which adopts the usual nanodomain plus disordered matrix structure after normal sintering, we have identified thermal conditions that promote domain coarsening.17 By treating these samples at temperatures significantly higher (1325°C) than those used in the studies of PMN (typically 850°–975°C), the degree of order and the domain size could be increased by ~70% and 10 nm, respectively.17 More significant changes were identified in PMT relaxors that contain small concentrations (5–10 mol%) of PbZrO$_3$. In this case, thermal annealing induced extensive coarsening, and fully 1:1 ordered samples were produced with domains approaching 200

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of the reflections originating from the doubled Pb(B1/2Bv1/2)O3 structure. The strength of these reflections (e.g., those highlighted at 2θ = 19° and 37° in Fig. 1) increased continuously up to x = 0.5 and then progressively decreased for x > 0.5. Direct observations of the ordering were made by TEM. In the as-sintered samples of pure PMT, diffuse supercell reflections were observed at (h ± 1/2, k ± 1/2, l ± 3/2), and the corresponding dark-field images revealed the usual phase-separated microstructure comprising ~2–3 nm 1:1 ordered domains dispersed in a metastable disordered matrix (Fig. 2(a)). A similar phase-separated morphology was maintained in as-sintered (1300°C, 3 h) samples of PLMT with x = 0.1 (Fig. 2(b)). However, again consistent with previous studies of the PLMN system, ordered domains in Pb0.9La0.1(Mg0.36Ta0.63)O3 were significantly larger (~50 nm) than those observed in pure as-sintered PMT.

To examine whether the microstructures of the as-sintered samples represented an equilibrated structural state, we heated green pellets of the PLMT solid solutions to 1300°C for different durations (3, 24, and 36 h) and reexamined them by XRD and TEM. The lower-angle region of the X-ray patterns of a sample with x = 0.1, Pb0.9La0.1(Mg0.36Ta0.63)O3, is shown after each heat treatment in Fig. 3. In this figure, it is clear that the diffuse supercell reflections exhibit a significant increase in intensity and decrease in width during the first 24 h of the annealing treatment. The change in the degree and correlation length of the cation order is even more evident in the dark-field micrograph in Fig. 4, which was collected from the sample after 24 h of annealing at 1300°C. From this image, it is evident that the phase-separated microstructure of the as-sintered ceramic is completely eliminated by additional thermal equilibration, and the size of the ordered domains now exceeds 500 nm. The changes in the ordering induced by additional annealing are not as significant for samples with higher concentrations of lanthanum. Very minor modifications are noted for x = 0.15, which forms an essentially fully ordered large domain microstructure after only 3 h at 1300°C, and complete ordering is achieved for x > 0.15 in the as-sintered form. The thermal stability of the PLMT phases is also probed through a limited number of quenching experiments. Previously we demonstrated that the upper limit of stability for the 1:1 order in PMT is ~1375°C.17 For samples of Pb0.9La0.1(Mg0.36Ta0.63)O3, the strong ordering reflections are unchanged by heat treatments at 1450°C, confirming that the substitution of lanthanum induces a large increase in the thermodynamic stability of the 1:1 ordered structure. The effect of the substitution of lanthanum on the dielectric properties of PMT was examined for an entire series of thermally equilibrated samples. Quite small levels of lanthanum were effective in eliminating the relaxor characteristics of PMT (see Fig. 5), and a transition from relaxor, to diffuse ferroelectric, to linear dielectric behavior was observed. These observations were in good agreement with those reported for the PLMN system.9

IV. Discussion

While our observations on the structures of the as-sintered forms of the PLMT solid solutions are similar to those reported previously for lanthanum-substituted PMN,8,9,14,15 our interpretation of their crystal chemistry and local chemistry are quite different. If the accepted space-charge models for PLMN are applied to PLMT, all compositions, with the exception of x = 0.5, should comprise a stable two-phase mixture of 1:1 ordered domains and a disordered matrix. While short anneal times can lead to this type of microstructure for low lanthanum compositions, our experiments clearly show that this is a metastable state, and extended thermal equilibration coarsens the 1:1 ordered domains and eliminates any residual disordered matrix. These results are entirely inconsistent with the predictions of the space-charge model.

Instead, we believe the changes in structure and stability of the cation ordering in the PLMT system can be understood in
terms of the charge-balanced random site models recently used to interpret the 1:1 structures of PMT–PZ relaxors and a series of barium-based dielectric systems.17–23 If this model is applied to the 1:1 Pb$_{1-x}$La$_x$(Mg$_{1-2x}$/3 Ta$_{1+x}$/3)O$_3$ structures of PLMT solid solutions with $x \approx 0.5$, one position ($\beta'$) is occupied by tantalum, and the second ($\beta''$) by a random distribution of magnesium and tantalum with stoichiometry (Mg$_{1-2x}$/3 Ta$_{1+x}$/3). Using this model, the enhancements in the stability of 1:1 order

Fig. 1. XRD patterns of Pb$_{1-x}$La$_x$(Mg$_{1-2x}$/3 Ta$_{1+x}$/3)O$_3$ solid solutions.

Fig. 2. TEM dark-field images of (a) pure PMT and (b) PLMT with $x = 0.1$. Images were collected using the (3/2,3/2,3/2) supercell reflection.

Fig. 3. XRD patterns of PLMT with $x = 0.1$ sintered at 1300°C for 3, 24, and 36 h.

Fig. 4. TEM dark-field image of PLMT $x = 0.1$, sintered at 1300°C for 24 h.
and the associated increase in the driving force for domain coarsening can be understood in terms of a systematic increase in the difference in the charge and size of the $\beta^+$ and $\beta^-$ cation positions as $x$ approaches 0.5. For example, using simple ionic radii and formal charges for $x = 0$ and 0.5, the two cation sites differ in size by 0.053 and 0.08 A and in charge by 2+ and 3+, respectively. A continuous change in the chemistry of the random site position, from (Mg$_{2/3}$Ta$_{1/3}$) for $x = 0$ to complete occupancy by magnesium for $x = 0.5$, also accounts for the systematic increase in the intensities of the supercell reflections observed for $0.0 \leq x \leq 0.5$.

On the lanthanum-rich side of the PLMT system, 1:1 ordering is retained for all compositions, including the LMT end member that has overall 2:1 Mg:Ta stoichiometry. Our studies indicate that these compositions are consistent with a compositionally segregated, space-charge model for the cation order. Instead, these results support the formation of a random site, cation-ordered arrangement on the B-site sublattice. With this model, ordered solid solutions with $0.0 \leq x \leq 0.5$ can be represented by Pb$_{1-x}$La$_x$(Mg$_{2/3}$Ta$_{1/3}$)$_{1/2}$O$_3$ and compositions with $0.5 \leq x \leq 1.0$ by Pb$_{1-x}$La$_x$(Mg$_{1/2}$Ta$_{4/3}$)$_{1/2}$O$_3$. The changes in the stability and coarsening of the 1:1 domains can be readily interpreted in terms of the size and charge difference of the two cation sites in the Pb$_{1-x}$La$_x$($\beta^+$)$_{1/2}$($\beta^-$)$_{1/2}$O$_3$ ordered structure.

V. Conclusions

The observation of fully ordered, single-phase microstructures in thermally equilibrated members of the Pb$_{1-x}$La$_x$- (Mg$_{2/3}$Ta$_{1/3}$)$_{1/2}$O$_3$ (PLMT) solid-solution system is not consistent with a compositionally segregated, space-charge model for the cation order. Instead, these results support the formation of a random site, cation-ordered arrangement on the B-site sublattice. With this model, ordered solid solutions with $0.0 \leq x \leq 0.5$ can be represented by Pb$_{1-x}$La$_x$(Mg$_{2/3}$Ta$_{1/3}$)$_{1/2}$O$_3$ and compositions with $0.5 \leq x \leq 1.0$ by Pb$_{1-x}$La$_x$(Mg$_{1/2}$Ta$_{4/3}$)$_{1/2}$O$_3$. The changes in the stability and coarsening of the 1:1 domains can be readily interpreted in terms of the size and charge difference of the two cation sites in the Pb$_{1-x}$La$_x$($\beta^+$)$_{1/2}$($\beta^-$)$_{1/2}$O$_3$ ordered structure.

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References