Determination of the ordered structures of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Ba(Mg_{1/3}Nb_{2/3})O_3$ by atomic-resolution Z-contrast imaging

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The atomic structure of ordered domains in $Ba(Mg_{1/3}Nb_{2/3})O_3$ and La-doped and undoped $Pb(Mg_{1/3}Nb_{2/3})O_3$ is studied by high-resolution Z-contrast imaging. The ordered domain structure in both doped and undoped $Pb(Mg_{1/3}Nb_{2/3})O_3$ is determined to be in agreement with the charge balanced random-layer model and inconsistent with the space-charge model. It is shown that La doping in $Pb(Mg_{1/3}Nb_{2/3})O_3$ enhances not only the domain size but also the degree of ordering. © *1998 American Institute of Physics.* [S0003-6951(98)00424-0]

Lead based cubic perovskites, $Pb(B^{I}_{1/3}B^{II}_{2/3})O_3$, are attractive relaxor ferroelectrics because of their high dielectric constants and high electrostrictive coefficients.[1–3] It is know that dielectric properties may be strongly influenced by localized order and disorder, which is common in these relaxor ferroelectrics.[2] Thus, to improve the dielectric properties it is important to understand the atomic structure of the ordered phases.

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is one of the lead based relaxor ferroelectrics. In this family, two models have been proposed for the ordered structure, the space-charge model and the charge balanced random-layer model.[4–8] Diffraction studies have revealed that the ordered domains in the PMN family present 1/2{111} superlattice reflections.[4] The doubling of the unit cell arises due to a 1:1 distribution of two different cation sites (B^{I} and B^{II}). Fig. 1(a) shows the projection of the supercell of the ordered domain along the [110] direction. The large black dots and crosses represent Pb and O columns, respectively. In the space-charge model, it is postulated that the B^{I} and B^{II} position in the 1:1 ordered structure are occupied exclusively by the Mg^{2+} and Nb^{5+} cations, respectively, in the form $Pb(Mg_{1/2}Nb_{1/2})O_3$. Consequently these ordered regions carry a net negative charge. For overall electroneutrality, an equal and oppositely charged, disordered, Nb^{5+} rich matrix is proposed. Due to the strong charge effects, ordered domains with this structure are expected to inhibit domain growth. Reports that ordered domains fail to grow after thermal treatment at 900 °C for 30 h[4,9] have supported the space-charge model.

An alternative model has been proposed for this material, the charge balanced random-layer model. Here, the B^{II} columns are exclusively occupied by Nb^{5+}, but the B^{I} columns contain a random distribution of Mg^{2+} and Nb^{5+} in a 2:1 ratio. The structural formula can be represented as $Pb((Mg_{2/3}Nb_{1/3})_{1/2}Nb_{1/2})O_3$. In this case, the ordered domains are microscopically charge balanced and would be expected to grow during thermal treatment. Recently the domain size and degree of ordering of the tantalate members of the PMN family, $Pb(Mg_{1/3}Ta_{2/3})O_3$, have been reported to increase by two orders of magnitude through annealing at 1325 °C.[10] It was suggested that the lack of growth reported previously is due to kinetic rather than thermodynamic constraints. However, no direct evidence of the atomic structure of the ordered phase has yet been reported.

High-resolution Z-contrast imaging is an ideal technique to determine directly the ordered structures in the PMN family. The Z-contrast image is incoherent, with intensity highly localized about the atomic column positions.[11–13] The image intensity is approximately proportional to the mean square atomic number (Z) in the columns. Thus, the occupation at the B^{I} site in the two models is directly distinguishable in a Z-contrast image taken along the [110] zone axis. If the space-charge model is correct, the intensity ratio between the B^{I} columns (Mg) and the B^{II} columns (Nb) is given by $Z^2(B^{I})/Z^2(B^{II})$, about 1/12, which implies that the B^{I} columns would have very little intensity. If the charge balanced random-layer model is correct, the intensity ratio is about 1/4, which implies that although the B^{I} columns would be weaker than the B^{II} columns, they should have significant intensity. In this letter, we report images that directly confirm the charge balanced random-layer model.

Specimens were prepared for electron microscopy by first mechanical polishing to ~100 μm, then dimpling the central portion of the specimens to ~10 μm. Samples were thinned to electron transparency using a 4 kV Ar ion beam at

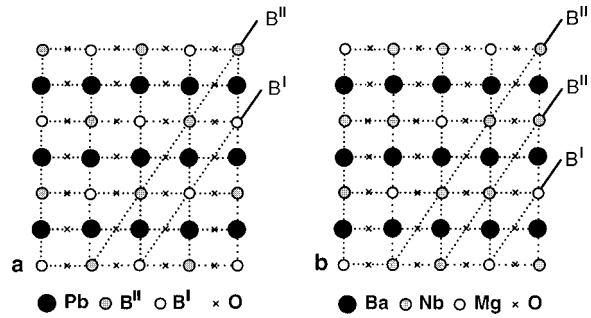

FIG. 1. Structure models proposed for (a) 1:1 ordered $Pb(Mg_{1/3}Nb_{2/3})O_3$ and (b) 1:2 ordered $Ba(Mg_{1/3}Nb_{2/3})O_3$, projected along the [110] zone axis.

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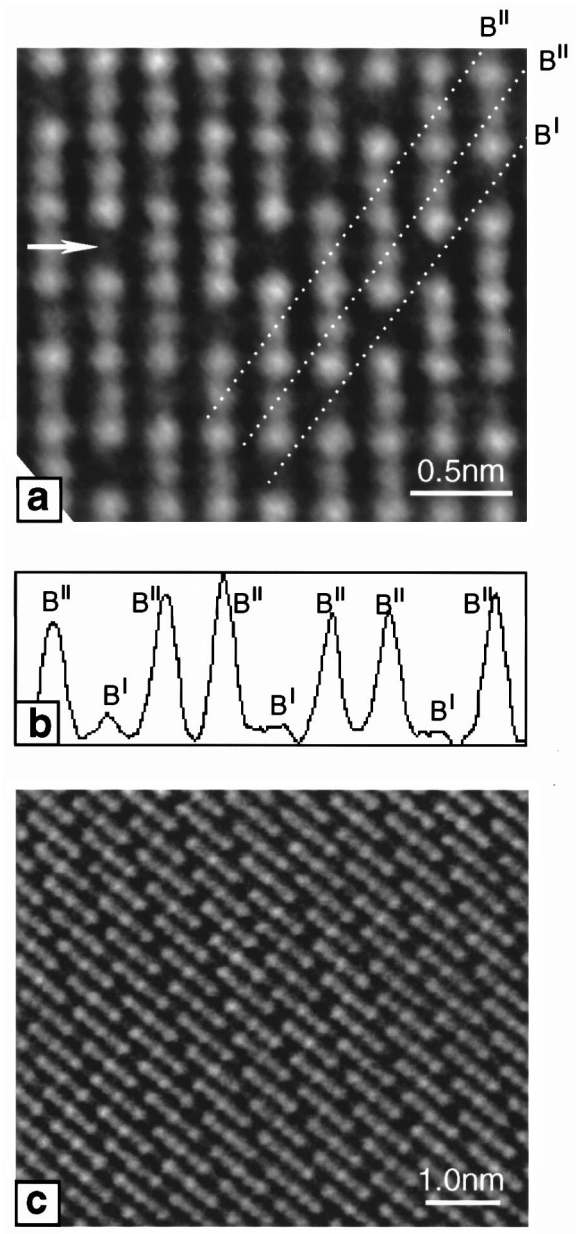

FIG. 2. (a) Atomic-resolution Z-contrast image of an ordered domain in $Ba(Mg_{1/3}Nb_{2/3})O_3$, (b) intensity profile along the arrowed plane showing weak intensity from the B^I sites, (c) lower magnification view showing extended 1:2 ordering.

13° inclination and then cleaned at lower voltage (1.5 kV). Finally, surface contamination was removed using a Fischione plasma cleaner. High-resolution imaging was performed using a VG Microscope HB603U STEM operating at 300 kV. Z-contrast images were formed by scanning a 1.26 Å probe across a specimen and recording the transmitted high angle scattering with an annular detector.

Because the ordered structure in $Ba(Mg_{1/3}Nb_{2/3})O_3$ is well known,[8,14] the Z-contrast image from an ordered domain is used as a reference to calibrate the intensity ratio. $Ba(Mg_{1/3}Nb_{2/3})O_3$ has the 1:2 ordered structure, with a tripled unit cell containing one B^I and two B^{II} planes. In the fully ordered domains, B^{II} and B^I columns are completely occupied by Nb and Mg, respectively, as shown in Fig. 1(b). A Z-contrast image of an ordered domain is shown in Fig. 2(a). The brightest spots correspond to Ba columns, the weaker spots correspond to the B^{II} columns (Nb). The B^{II} and B^I sublattices are indicated by dotted lines. Figure 2(b) shows an intensity profile measured along the plane indicated by an arrow, which contains both B^I and B^{II} columns. The two right-hand B^I columns (Mg) show very little intensity, consistent with the expected ratio of 1/12. The left-hand B^I site shows slightly greater intensity, implying some occupation by Nb. Figure 2(c) is a Z-contrast image with lower magnification showing that the 1:2 ordered structure is present over an extended region. The size of the ordered domains in $Ba(Mg_{1/3}Nb_{2/3})O_3$ is on the micron scale.

It is known that surface damage induced during sample preparation can cause a statistical fluctuation in the intensities of atomic columns measured from Z-contrast images. Since there is no ordering on the Ba sites, we used the intensities measured from the Ba sites to estimate the fluctuations caused by surface damage. We systematically measured the intensities from over 200 Ba sites. It is found that more than 90% of the sites have an intensity within $\pm 10\%$ of the mean value, and no site deviated by more than $\pm 15\%$. In the two models of the ordered structure, the expected intensity ratio between the B^{II} and B^I columns differs by more than 300%, so that clearly fluctuations due to the damaged surface layer will not affect our ability to distinguish the two models.

The ordered domains in undoped $Pb(Mg_{1/3}Nb_{2/3})O_3$ have a size of 2–5 nm, and are dispersed in a disordered matrix. However, La doping enhances the ordering in PMN, and the domain size in ordered 25% La-doped PMN grows to the micron scale.[4] Figure 3(a) shows a Z-contrast image from such a domain, with the B^{II} and B^I planes marked by dotted lines. The fully ordered 1:1 structure is clearly seen from the image, and from the intensity profile measured along the arrowed plane containing alternating B^I and B^{II} positions [Fig. 3(b)]. Clearly, the B^I columns show significant intensity. As demonstrated by the Z-contrast image of the $Ba(Mg_{1/3}Nb_{2/3})O_3$, if the B^I columns were fully occupied by Mg, they would show very low intensity. Since the ordered domain size is on the micron scale, this strong intensity cannot be due to overlapping domains, and can only be due to some occupation by Nb. The space-charge model is therefore inconsistent with the image, but the image intensities are consistent with the 1/4 ratio expected for the charge balanced random-layer model.

Although many regions showed intensity profiles similar to those in Fig. 3(b), indicative of complete ordering, occasional sites within the same domain showed significant variability of both B^I and B^{II} intensity. This implies that the degree of ordering can vary locally across the grain. It has been reported that La doping not only enhances domain size, but also the degree of ordering in PMN.[4] In order to prove this enhancement, 7% La-doped PMN was also investigated by high-resolution Z-contrast imaging. These images indeed showed a more variable image intensity, on both the B^I and B^{II} sites, as shown by the line trace in Fig. 3(c). This is direct evidence that La doping enhances the degree of ordering in PMN, and not just the domain size.

Fig. 4(a) shows a Z-contrast image from the undoped $Pb(Mg_{1/3}Nb_{2/3})O_3$. Z-contrast images were taken at the edge of the samples in order to minimize the overlap of domains through the sample thickness. A line trace through the ar-

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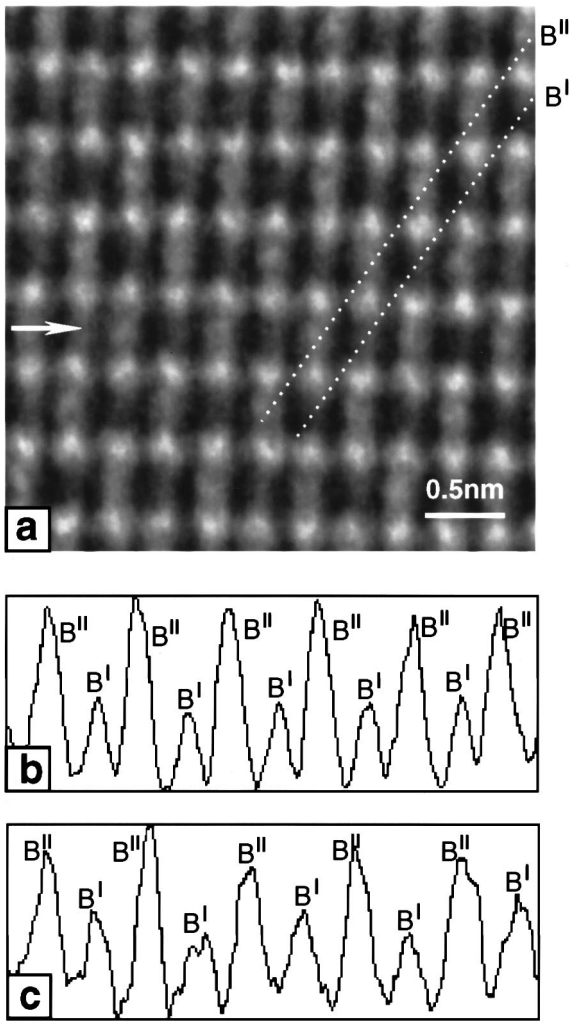

FIG. 3. (a) Z-contrast image of an ordered domain in 25% La-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$, (b) intensity profile along the arrowed plane, showing perfect ordering, (c) intensity profile from a single domain in 7% La-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$, showing reduced order.

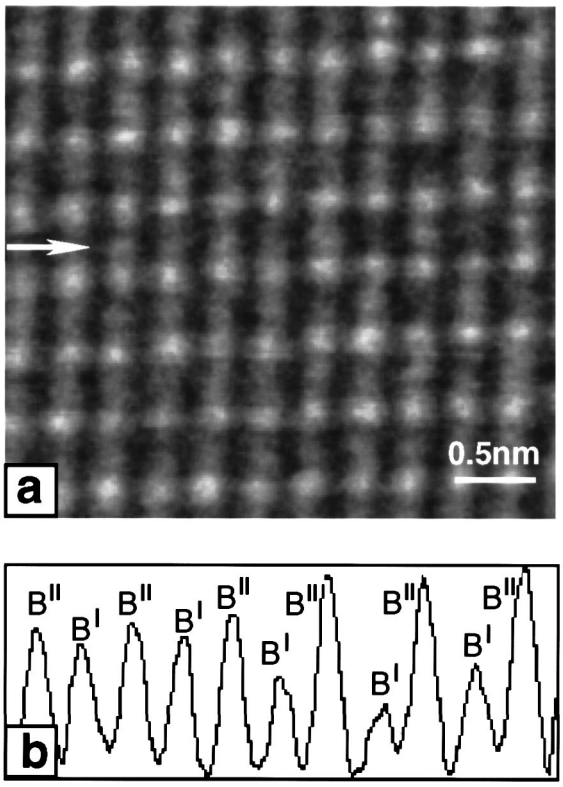

FIG. 4. (a) Z-contrast image of an ordered domain in undoped $Pb(Mg_{1/3}Nb_{2/3})O_3$, (b) intensity profile along the arrowed plane showing local fluctuations, with maximum order consistent with the charge balanced random-layer model.

rowed plane is shown in Fig. 4(b). Significant fluctuation is seen in the intensity of the B^I site, which may be due to overlap between the ordered domain and a disordered matrix, or partial ordering. However, during extensive examination of thin regions of the sample, the maximum intensity ratio was consistent with the 1/4 value expected for the charge balanced random-layer model. Never were intensity ratios found to be consistent with the 1/12 ratio expected for the space-charge model. We therefore conclude that undoped PMN takes the charge balanced random-layer model.

In conclusion, we report the first direct observations of the atomic structure of ordered domains in $Ba(Mg_{1/3}Nb_{2/3})O_3$ and La-doped and undoped $Pb(Mg_{1/3}Nb_{2/3})O_3$ by high-resolution Z-contrast imaging. The Z-contrast images are consistent with the charge balanced random-layer model of ordered PMN, though local fluctuations can exist. The space-charge model is clearly inconsistent with the image intensities. It is further proved that La doping enhances not only the domain size but also the degree of ordering.

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