Z-Contrast Imaging of Ordered Structures in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$

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Z-CONTRAST IMAGING OF ORDERED STRUCTURES IN Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ AND Ba(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$

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Lead-based cubic perovskites such as Pb(B$_{1/3}^+$B$_{2/3}^{5+}$)$_3$O$_3$ (B$^{5+}$ = Mg, Co, Ni, Zn; B$^{2+}$ = Nb, Ta) are relaxor ferroelectrics. Localized order and disorder often occur in materials of this type. In the Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ (PMN) family, previous studies have proposed two models, space-charge and charge-balance models$^{1-4}$. In the first model, the ordered regions carry a net negative charge [Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$], while in the second model it does not carry a net charge [Pb((Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$)$_3$]. However, no direct evidence for these two models has appeared in the literature yet. In this paper we report the first direct observations of local ordering in undoped and La-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$, using high-resolution Z-contrast imaging.

Because the ordered structure in Ba(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ is well known, the Z-contrast image from an ordered domain is used as a reference for this study. Fig.1(a) shows the projection of the supercell of fully ordered Ba(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ along the [110] direction. The $\beta^1$ and $\beta^2$ sublattices are occupied by Mg$^{2+}$ and Nb$^{5+}$ respectively. Fig. 2(a) shows a Z-contrast image of an ordered domain. The measured intensity profile for the marked plane clearly shows the ordered structure of $\beta^1$(Mg), $\beta^2$(Nb) and $\beta^3$(Nb). In a fully ordered structure, the intensity ratio $Z^2(\beta^1)/Z^2(\beta^2)$ is about 1/17, which implies that the Mg columns are almost invisible. This is confirmed by the two right hand $\beta^1$ sites showing no detectable intensity. However, the two left hand $\beta^1$ sites show detectable intensity. This implies some occupation by Nb, indicating incomplete ordering in these columns.

In undoped PMN, it has been revealed that the ordered structure has a doubled unit cell along each cube direction. Fig. 1(b) shows the projected structure of the ordered cell along [110]. There are two distinct B-site cation sublattices ($\beta^1$ and $\beta^3$) seen as alternating {111} planes in this projection. The space-charge 1:1 model postulates that the $\beta^1$ and $\beta^3$ planes are each fully occupied by Mg and Nb respectively. The charge balance model suggests instead that the $\beta^1$ plane contains both Mg and Nb in the ratio 2:1. Thus, the space-charge model predicts a $Z^2(\beta^1)/Z^2(\beta^3)$ of about 1/17, as before, whereas the charge balance model predicts a ratio of about 1/4. Fig. 2(b) shows a Z-contrast image from 25% La-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$. The arrow indicates the plane consisting of alternating $\beta^1$ and $\beta^3$ columns. The intensity profile shows a strong intensity from the $\beta^1$ column. Since the domain size in this sample is on the micron scale, this strong intensity is not due to overlapping domains, but indicates occupation of this column by Nb. Fig. 2(c) shows a similar behavior in a 7% La-doped PMN, again with a large domain size. Fig. 2(d) shows a Z-contrast image from undoped PMN, again showing the presence of ordering, but now the domain size is on the nm scale, and we cannot exclude the possibility that the intensity of the $\beta^1$ columns arises from overlapping domains.

References
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Fig. 1 Projected structures of ordering models for (a) Ba(Mg_{1/3}Nb_{2/3})O_3 and (b) Pb(Mg_{1/3}Nb_{2/3})O_3 along the [110] zone axis.

Fig. 2 High-resolution Z-contrast image of (a) BMN, (b) 25% doped PbMN, (c) 7% La-doped PMN (d) undoped PMN. The intensity profiles were measured from the planes marked by arrows.