Resonant X-ray Diffraction Search for Non-stoichiometric Chemically Ordered Domains in PMN

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Abstract. Lead Magnesium Niobate (PMN) displays a superstructure characterized by the presence of broad half-order diffraction peaks. The structure is known to involve chemical ordering between alternate B sites within small domains. It has been proposed that this might be due to small domains of Mg:Nb chemical ordering with full 1:1 stoichiometry. Such order is inconsistent with the bulk composition of $PbMg_{1/3}Nb_{2/3}O_3$ and would lead, moreover, to a net charge of $-\frac{1}{2}e$ per unit cell. In this work we report our resonant X-ray diffraction experiments designed to distinguish 1:1 from bulk-stoichiometric ordering.

CHEMICAL ORDERING OF PMN

Lead Magnesium Niobate (PMN) was first synthesized in 1958 [1] and is a prototypical relaxor ferroelectric material. It displays a characteristic superstructure identified by the presence of broad half-order diffraction peaks [2,3]. The structure is known to involve chemical ordering between alternate B sites, denoted B' and B". It was originally proposed that this chemical ordering was due to $Mg : Nb$ chemical ordering with full 1:1 stoichiometry [4], as shown in Figure 1. Such order is inconsistent with the bulk composition of $PbMg_{1/3}Nb_{2/3}O_3$ and would require the presence of compensating regions of opposite charge. An alternative "Random Layer" model was then proposed [5] that has pure Nb ions on the B" sites with a random mixture of Mg with $\frac{2}{3}$ average occupancy and Nb with $\frac{1}{3}$ average occupancy on the B' sites. This model, therefore, still allows partial chemical ordering while maintaining the overall stoichiometry of the bulk composition. Strong support for the Random Layer model in the analogous material, $PbMg_{1/3}Ta_{2/3}O_3$, comes from the observation [6] that high temperature annealing coarsens the domain size, but such evidence is so far lacking for PMN [7].

We previously carried out a detailed X-ray diffraction study of the structure of PMN and a series of single crystals grown with La doping [8]. X-ray crystal-

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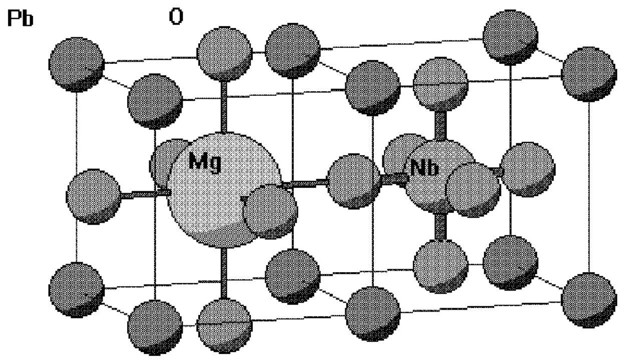

FIGURE 1. Two unit cells of the Perovskite structure of PMN showing the chemical-ordering model. The B-site marked Mg is referred to as the B' site while Nb ions are on the B" sites.

lography [9] is a powerful method for providing detailed information about small displacements in a crystal structure [10–12]. La substitution for Pb on the A-site of PMN leads to a slight contraction of the lattice parameter [13]. As previously found [5], La dramatically improves the chemical ordering, as indicated by the increased size of the ordered domains. For a series of La-doped PMN crystals, we measured structure factors for the half-order reflections and, by crystallographic analysis, established a trend in the oxygen displacements that parallels the lattice parameter changes [8]. Comparing the resulting $Nb-O$ and $Mg-O$ bondlengths with the sums of ionic radii, we showed that most of the changes occurred in the size of the B' site in the lattice, usually associated with Mg. The size of the B' ion was the same as for Mg^{++} in pure PMN, but reduced to a smaller value upon doping. The B' ion size for 10% La was appropriate for the $\frac{1}{3}:\frac{2}{3}$ $Nb:Mg$ ratio of the B' site in the Random Layer model. It was suggested, but by no means proven, that 1:1 ordering might exist in pure PMN, but might then switch over to Random-Layer ordering in the La-doped compounds. This crossover would nicely explain the dramatic enlargement of the chemical-ordering domain sizes with La-doping.

RESONANT X-RAY DIFFRACTION

Resonant x-ray diffraction exploits the energy-dependent terms in the atomic form factor, f, whose energy corrections are usually expressed as $f = f_0 + f'(E) + if''(E)$. $f'(E)$ is sharply peaked and negative when the energy, E, is near an X-ray absorption edge. $f''(E)$ has the form of a step function and accounts for the discontinuity in X-ray absorption characteristic of edges. In the case of Nb, the K edge is at $E = 18.968keV$, while f' has a maximum negative value of -13 electrons. Since f_0 for Nb is roughly 34 electrons for the measurements described here, this resonant contribution can lead to a significant change in the diffraction intensity.

In a crystal like PMN with multiple atomic sites in the unit cell, the structure factors of different Bragg reflections have different contributions from *Nb*, so the resonant effect will depend on which reflection is being studied. In centro-symmetric crystals like PMN, the phase of the scattering atoms is either zero or π. Using resonant techniques, it is possible to determine the relative phase of a given atom compared to the other scatterers. For example, evaluating the structure factor of the (001) peak gives

$$F_{001} = f_{Pb} - f_{O} - (\frac{2}{3} f_{Nb} + \frac{1}{3} f_{Mg}), \tag{1}$$

assuming random ordering of the B sites by *Nb* and *Mg* according to the bulk stoichiometry. By contrast, the (101) peak has a structure factor of

$$F_{101} = f_{Pb} - f_{O} + (\frac{2}{3} f_{Nb} + \frac{1}{3} f_{Mg}). \tag{2}$$

Since the photon energy in this experiment was near the *Nb* K-edge only, the non-resonant f_0 form factors for *Pb*, *Mg* and *O* can be used, but f_{Nb} must be given by the full resonant expression. At the momentum transfer of the (001) peak, f_{Nb} is approximately 37 electrons off-resonance and 24 electrons on-resonance [15], while f_{Pb} is 76 electrons, $f_{Mg} = 10$ and $f_O = 7$. For the (001) peak, the resonant contribution in equation (1) will cause $|F|$ to increase by making the difference between f_{Pb} and f_{Nb} greater. However, for the (101) peak in equation (2), the resonant contribution will decrease the amount of scattering because the *Pb* and *Nb* contributions are in phase. Also, the resonant contribution will have a greater effect on the (001) peak because the structure factor involves the difference between *Pb* and *Nb* instead of the sum, so its proportional contribution will be larger.

Our goal was to search for variations in net stoichiometry associated with the proposed *Nb*-deficient domains predicted by the space-charge model. Resonant X-ray measurements, as just described, allow a relatively direct measure of the *Nb* contribution to the diffraction feature under investigation. It would appear to be most useful to measure the half-order reflections which arise from the B':B" chemical ordering directly. Unfortunately, comparing the structure factor for the 1:1 ordering model,

$$F^{1:1}_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = f_{Nb} - f_{Mg}, \tag{3}$$

with that of the Random Layer model,

$$F^{RL}_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = f_{Nb} - (\frac{1}{3} f_{Nb} + \frac{2}{3} f_{Mg}), \tag{4}$$

shows that they differ only by a scale factor. The two models are, therefore, indistinguishable in a measurement of half-order intensities that does not have absolute intensity calibration.

We decided to measure near the bulk reflections instead. There, the Pb contribution to the structure factor can be used as a reference with which the changing, resonant Nb contribution can be compared. Since the scattering from the small chemically-ordered domains produces a broad peak of intensity at both integer-order and half-order positions, the contribution should be visible *in the wings* of the bulk reflections. To look for domains of $50\AA$ in size, this suggests an optimum reciprocal-space distance from the Bragg peaks in the range of $0.05 - 0.1$ reciprocal lattice units (RLU). All contributions near the (001) or (101) bulk peaks, whether Bragg or diffuse, that arise from material with bulk-stoichiometric composition will have resonant contributions given by equations (1) or (2) respectively. Any recorded deviation from these values must be due to variations of Nb stoichiometry.

EXPERIMENTAL METHOD

The measurements were made at beamline X16C of the National Synchrotron Light Source (NSLS). The sagittally-focussing, double Si(111) monochromator was tuned in the vicinity of $E = 18.968keV$, corresponding to the Nb K-edge. The sample was mounted on a Kappa diffractometer [14] programmed to execute "energy scans" at constant reciprocal-lattice coordinate. The resolution was defined by $2 \times 2mm$ slits in front of a scintillation detector. Energy scans were made at strategic points along radial reciprocal lattice directions passing through the (001) and (101) peaks. Even with the narrow slits, fluorescence was found to contribute a significant background which accounted for a large part of the observed increase in intensity above the edge. A combined fluorescence and absorption correction was made by measuring the intensity far away from a Bragg peak. The resonant effect (after corrections) resulted in either a peak in intensity for (001)-type peaks or a "valley" for (101)-type peaks in the energy scans, as predicted by equations (1) and (2).

Energy scans were made at various points in reciprocal space near the Bragg peak. The top panel of figure 2 shows the raw intensity measured in an energy scan through the Nb K-edge while sitting at (0.96, 0, 0.96) in the wing of the (101) Bragg peak. The fluorescence-correction measurement is shown in the middle panel of figure 2; this was taken by scanning at an off-peak position, (0.9, 0, 0.9), with the same counting time and slit settings. After the fluorescence counts are subtracted point-by-point from the diffraction signal counts, there still remains a step in the curve, due to the abrupt increase in crystal's absorption length upon crossing the Nb K-edge. The multiplicative absorption correction factor, derived from the residual edge jump, is also shown in the middle panel of figure 2.

After making both of these corrections, the resonant peak is clearly seen in the form of an intensity "valley" in the bottom panel of figure 2. The sense of the Nb contribution is positive or negative depending on the reflection. The example shown is negative, while the corrected peaks for scans near (001) were found to have positive resonant contributions. In each case, the *resonant fraction* was then

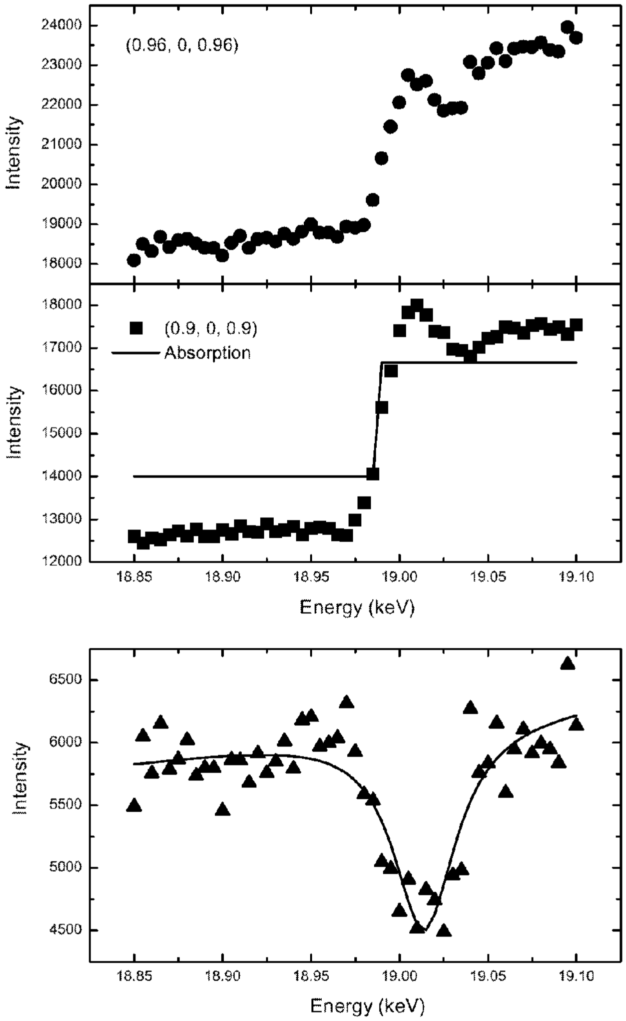

FIGURE 2. Illustration of our data collection procedure for resonant X-ray diffraction: (Top panel) Raw data collected by scanning energy while sitting on the slope of a Bragg peak at (0.96, 0, 0.96). (Middle panel) Fluorescence contribution measured far from Bragg peak, at (0.9, 0, 0.9) and the step absorption correction derived from it. (Bottom panel) Corrected data fitted to a fixed Lorentzian. The resonant fraction is determined by taking the Lorentzian height and dividing by the background level far away.

calculated by fitting the peak to a Lorentzian shape with fixed energy-position and width. The resonant fraction is obtained by taking the height divided by the "background" level far away from the resonance. The fixed Lorentzian width and position were determined independently by taking an average of several scans of half-order peaks where the shape of the Nb resonant contribution was more easily measured. For these superstructure peaks, the structure factor is given by equations (3) or (4), which are both simply proportional to $(f_{Nb} - f_{Mg})$, regardless of which model is used for the chemical ordering. In this way, we determined the Lorentzian width to be $41eV$, in agreement with known resonance data [15], and a value of -10 electrons for f' in our sample. This is slightly smaller than the bare atom value of -13 electrons [15], perhaps because of measurement energy-resolution and/or condensed-matter effects.

RESULTS AND DISCUSSION

The plots of resonant fraction *versus* Miller index at different reciprocal-space positions near the (001) and (101) peaks are shown in figures 3 and 4. The range of index chosen was restricted in the center by proximity of the Bragg peaks at (001) and (101) where the intensity became too strong, and where dynamical effects might distort the measurement. The index range was restricted on the outside by the rapidly falling intensity becoming dominated by the fluorescence effects (see figure 2). The range of momentum transfers explored covers roughly the region where the charge-ordered domains are expected to contribute.

The numerical values of resonant fraction obtained can be compared directly with the predicted values derived from the structure factors for the two models. A region of PMN with a local $Mg : Nb$ stoichiometry of 1:1 will have different structure factors from those given in equations (1) and (2):

$$F_{001}^{1:1} = f_{Pb} - f_O - (\frac{1}{2}f_{Nb} + \frac{1}{2}f_{Mg}) \tag{5}$$

$$F_{101}^{1:1} = f_{Pb} - f_O + (\frac{1}{2}f_{Nb} + \frac{1}{2}f_{Mg}) \tag{6}$$

For diffraction near bulk peaks, the chemically-ordered domains of the Random Layer (RL) model have the structure factors corresponding to the bulk stoichiometry, which are given by equations (1) and (2) directly. Inserting the values stated above for the form factors at the relevant momentum transfer magnitude, we obtain resonant fractions of 0.47 and 0.31 for the (001) peak for the RL and 1:1 models respectively and resonant fractions of -0.17 and -0.14 for the (101) peak for the RL and 1:1 models. These numbers could be compared with the observed values plotted in figures 3 and 4. However, it is unrealistic to use the free-atom value of $f'_{Nb} = -13$ in these calculations, when the value of $f'_{Nb} = -10$ was obtained experimentally, as mentioned above. The latter value gives reduced values for the

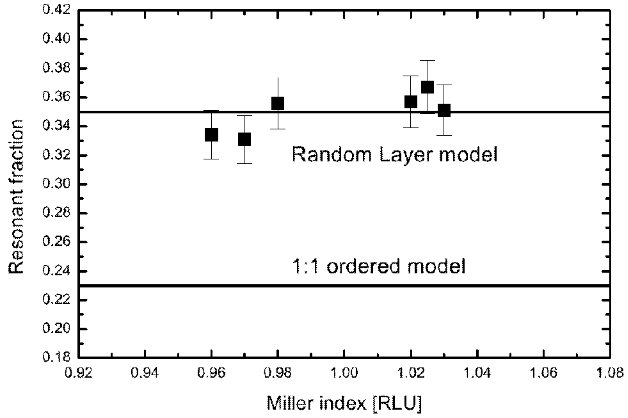

FIGURE 3. Resonant fraction measured at different points near the (001) Bragg peak. Predicted values for the two models with different *Nb* stoichiometries are indicated. These data appear to be more consistent with the Random Layer model.

resonant fractions: 0.35 and 0.23 for the (001) peak and −0.13 and −0.105 for the (101) peak for the RL and 1:1 models respectively. The revised numbers are plotted as horizontal lines in figures 3 and 4. It is more appropriate to compare the observed fractions with these numbers than with the free-atom numbers above. As can be seen, all our measurements are within reasonable error of these values.

No attempt has been made to account for all the other contributions of the parent crystal to the diffuse scattering near the Bragg peaks. These are notably: thermal diffuse scattering (TDS) from phonons [9], Huang scattering from point defects [16], crystal truncation rod (CTR) contributions from the external (or internal) surfaces [17] and the characteristic diffuse scattering from PMN's polar domains [10]. The important point here is that these will all lead to the resonant-fraction values appropriate for the bulk stoichiometry, unless of course they correspond to compositional rearrangements themselves. Conversely, any deviation of the resonant-fraction values must be associated with off-stoichiometric local regions in the structure on a length scale that is the inverse of the momentum transfer offset from the Bragg peak.

Our experiment thus did not establish any clear signature of off-stoichiometric local regions in pure PMN at the (reciprocal-space) locations we considered. Our search, therefore, did not find any evidence of space-charged domains. Although these results could be taken to support the random layer model in PMN, they are in fact inconclusive because there are many other contributions to the signal we examined. They are also inconclusive due to the relatively large error bars which resulted from both the difficulty of the measurement and the sensitivity that is required to see a small compositional change (from two- thirds to one-half) originating from the domains within the crystal, which also happen to be very small.

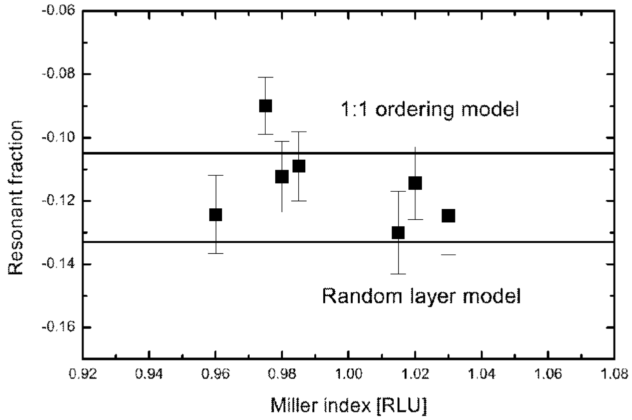

FIGURE 4. Resonant fraction measured at different points near the (101) Bragg peak. See caption of figure 3.

Because it is internally referenced, resonant X-ray diffraction is a very general and powerful method for seeking out stoichiometric variations in a complex material. For a known crystal structure, there is an exact prediction for the resonant contribution at a given point of reciprocal space. Any deviation from that value means that the chemical composition (relative to the element probed) is different from that expected. Careful measurements should be able to detect variations down to the percent level. To be more conclusive, our measurements could be extended to other parts of reciprocal space, for example very close to the Bragg peaks. More accurate data would certainly have helped in detecting small variations in stoichiometry. We have, nevertheless, demonstrated that resonant X-ray diffraction is a viable technique for detecting local variations in composition on a selectively chosen length-scale.

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