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Gradient chemical order in the relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

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Abstract

Here, we apply aberration-corrected scanning transmission electron microscopy to quantify chemical ordering in the relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN). We find that contrary to the prevailing model of a binary distribution of chemically ordered regions within a disordered matrix, the degree of ordering smoothly varies within an ordered domain and approaches a minimum at anti-phase boundaries. These results provide direct insight into the nature of cation ordering in this important prototypical relaxor material.

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Gradient chemical order in the relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

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Here, we apply aberration-corrected scanning transmission electron microscopy to quantify chemical ordering in the relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN). We find that contrary to the prevailing model of a binary distribution of chemically ordered regions within a disordered matrix, the degree of ordering smoothly varies within an ordered domain and approaches a minimum at anti-phase boundaries. These results provide direct insight into the nature of cation ordering in this important prototypical relaxor material. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5016561>

Relaxors are a unique class of materials that demonstrate a frequency-dependent dielectric permittivity with a broad maximum.¹ Exhibiting high dielectric constants, low hysteresis, and large electromechanical strains, relaxors are important technological materials commonly used for the fabrication of actuators, transducers, and sensors.² Relaxor ferroelectricity in Pb-based compounds has traditionally been attributed to polar nanoregions (PNRs), a feature distinguishing them from classical ferroelectrics.³ PNRs are hypothesized to be on the order of nanometers in size and have been observed to form upon cooling through the characteristic Burns temperature, T_B , which is ~ 620 K for $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN).⁴ The PNRs are highly responsive to externally applied fields and have been shown to contribute the majority of the piezoelectric and dielectric response in several relaxor ferroelectrics.⁵

Pb-based relaxors are characteristically non-isovalent since the cations on at least one of the sub-lattice positions have different valence states, an example being Mg^{2+} and Nb^{5+} in PMN. The resulting local charge fluctuations on the cation sub-lattice are thought to generate random fields that perturb long range ferroelectricity and lead to the formation of PNRs.⁶ Although PNRs are commonly associated with relaxor behavior, a number of recent studies have suggested alternative models.^{7–10} Despite extensive studies, the origin of relaxor ferroelectricity remains a topic of debate.¹¹

The picture of nanoscale polar structures in relaxors induced by local fields is complicated by the observation of chemically ordered regions (CORs) that are found in most Pb based relaxors.¹² The local structure of relaxors has largely been probed using diffraction-based techniques.^{13–19} From these studies, the CORs in PMN have been found to adopt a double perovskite structure with two distinct B-cation (Mg/Nb) sub-lattices, which forms at ~ 1223 K in PMN.²⁰ Denoted by β' and β'' , these sub-lattices were originally thought to be fully occupied by Mg^{2+} or Nb^{5+} , respectively. This ordering scheme, however, is not charge balanced, and a surrounding space charge region containing a high concentration of Nb^{5+} is then required to negate the residual COR charge.²¹ The lack of evidence for this

concomitant chemical segregation has led this “space charge” model to be discarded.^{22–24}

Subsequent studies pointed to a different model of chemical ordering in Pb-based relaxors where local charge neutrality is maintained by random mixing of Nb and Mg on β' at a ratio of 2:1, while β'' contains only Nb.²⁵ This prevailing model of the CORs in PMN describes them as discrete, “charge balanced” ordered domains coexisting within a disordered matrix. The details of B-cation ordering within these domains and throughout the material are, however, largely unknown. This is a critical gap because the local Mg^{2+} and Nb^{5+} distributions and their statistical randomness on the β sub-lattices are responsible for frustrating the long range polarization while allowing the local organization of dipole moments into PNRs.²⁶ The direct measurement of the local chemical arrangement is thus important for understanding the origin and stabilization of the local fields that are proposed to govern relaxor behavior.

In this letter, we present direct, real-space characterization of chemical ordering in the prototypical relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. Utilizing aberration-corrected scanning transmission electron microscopy (STEM) and atomic number sensitive high angle annular dark-field imaging (HAADF), we identify the spatial distribution of CORs and anti-phase boundaries between them. Furthermore, we develop a metric to quantify and probe the spatial distribution of chemical ordering. We pair image simulations with experiment to interpret these results in the context of different structural models. With this approach, we show that the conventional model of discrete ordered regions within a disordered matrix is incompatible with our observations.

PMN single crystals for this study were grown by the high-temperature flux method. In this process, raw oxide materials including high purity Pb_3O_4 and MgNb_2O_6 were weighed according to the nominal composition with excess Pb_3O_4 or $\text{Pb}_3\text{O}_4/\text{B}_2\text{O}_3$ as a flux. The mixed powders were loaded into a platinum crucible, which was sealed in an alumina crucible to minimize the PbO evaporation at elevated temperatures. The assembly was then placed in a muffle resistance heating furnace and heated to 1473–1523 K with the dwell time of several hours to homogenize the melt. The crystallization process was driven by slowly cooling (0.5–1.0 K/h) the solution from the bottom of the crucible. After the growth process, the furnace was cooled

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to room temperature at 50–100 K/h, and then, the as-grown crystals were etched out with nitric acid.²⁷

Samples for electron microscopy were prepared by wedge polishing combined with low energy, low temperature argon ion milling.²⁸ A thin layer of carbon was deposited on the samples to reduce charging by the electron beam. A probe-corrected FEI Titan G2 S/TEM equipped with an extreme Schottky field emission gun and operated at 200 kV was used for STEM imaging. The beam current was 20 pA with a convergence semi-angle of 19.6 mrad. The annular dark-field inner collection semi-angle was 77 mrad. Images were acquired and processed by the revolving STEM (RevSTEM) method.²⁹ Each RevSTEM dataset consisted of 40 image frames of size 1024×1024 pixels with a 90° rotation between each successive frame. The sample thickness was determined using position averaged convergent beam electron diffraction.³⁰ Image analysis and quantification were carried out using custom MATLAB scripts. The multislice method was used to simulate STEM images, with parameters matching experiment.³¹ Thermal diffuse scattering was modeled using the frozen phonon approach³² with Debye-Waller factors from Ref. 33.

While previous characterization studies have largely relied on diffraction methods and dark-field imaging techniques to estimate the phase fraction of CORs and the degree of cation ordering, HAADF STEM provides a local sampling of the structure with atom column intensities that are sensitive to the type and number of elements present. Imaging PMN along $\langle 110 \rangle$, for example, enables the direct identification of the atom columns containing Pb/O from the β sub-lattices containing Mg/Nb as in Fig. 1(a). Close inspection of the Mg/Nb atom columns reveals significant intensity variation within these β sub-lattice atom columns. As expected from the doubled-perovskite structure, bright and dim Mg/Nb atom columns alternate on $\{111\}$ planes. To explore local chemical variation, we map the Mg/Nb atom column intensities normalized to their mean as in Fig. 1(b). The Mg/Nb atom columns exhibit an intensity standard deviation $\sim 2.5\times$ larger than that of the Pb/O atom columns, which is consistent with previous work.^{25,34} Furthermore, diffuse scattering in electron diffraction patterns indicates the presence of short range order as presented in Fig. S1 of the [supplementary material](#).

To separate the Mg/Nb sub-lattice positions into β^I and β^{II} , the six nearest neighbor sites surrounding each Pb/O atom column are considered. The set of three atom columns with the lower mean intensity are classified as β^I positions (Mg rich), while those with the higher mean are classified as β^{II} (Nb rich). Because the classification scheme is applied

with respect to every Pb/O atom column, each Mg/Nb β classification is determined six times. In cases where the classification changes from one Pb/O atom column to the next, the Mg/Nb β sub-lattice is marked as indeterminate.

An example of the β classification scheme is shown in Fig. 1(c). This map highlights distinct regions of chemical order where β^I (cyan) and β^{II} (magenta) alternate on $\{111\}$ planes, which is in agreement with a double perovskite. On average, 60% of the Mg/Nb atom columns are distinguished as belonging to either the β^I or β^{II} sub-lattice. Furthermore, the indeterminate atom columns (green) are found to separate neighboring CORs and define anti-phase boundaries (APBs) where the β classification flips across the boundary. Across 10 HAADF STEM images from samples of similar thickness, all distinct CORs are separated by APBs. The average diameter of the CORs is 4.8 ± 1.2 nm as determined from 10 images, approximating CORs as circular. This is consistent with previous estimates of ~ 2 –6 nm.^{17,18} Instances of larger CORs (diameters in excess of 10 nm) are also found and likely the result of two individual, but in-phase, ordered regions merging after nucleation.

Further examination of the β sub-lattice atom column intensities in the CORs reveals that the chemical order is not uniform within each COR, as can be observed in Fig. 1(b). To quantify the degree of local order, we define an order metric as the standard deviation (σ) of Mg/Nb atom column intensities surrounding each Pb/O atom column normalized to their mean. This metric is justified by noting that ordering results in significant chemical variation between the β^I and β^{II} sites, which in turn results in larger intensity variation. Using the charge-balanced model, for example, β^I atom columns contain 67% Mg on average and are thus relatively dim while β^{II} atom columns contain only Nb and are thus bright. Alternatively, if the Mg/Nb atom columns contain roughly the same composition (disordered), the intensities are nearly the same, and the order metric is near zero.

Across all regions analyzed, the order metric is found to smoothly decrease from the center of the CORs towards the APBs as in Fig. 2(a). The observed behavior strongly suggests a continuum of order, rather than the conventional model that considers an abrupt transition between a COR and the disordered matrix.^{26,35} Further evidence for a continuum of order is presented in Fig. 2(b), where the intensities for the β^I and β^{II} positions are considered within the specified order metric ranges. The largest intensity difference between the β positions occurs where the order metric is the largest. While the intensity difference between the two sub-

FIG. 1. (a) A representative HAADF-STEM image of the $\langle 110 \rangle$ zone axis with the inset highlighting a schematic of the Mg/Nb and Pb/O atom columns. (b) Normalized intensity of each Mg/Nb atom column with substantial variation due to chemical order. (c) Classification of β sub-lattices indicating the β^I (cyan), β^{II} (magenta), and indeterminate (green) atom columns. The inset highlights that anti-phase boundaries are found between CORs.

FIG. 2. (a) The order metric distribution overlaid on a HAADF-STEM image. (b) The average β' (cyan) and β'' (magenta) normalized atom column intensities for specified order metric ranges. Error bars represent the standard deviation.

lattices decreases with decreasing order metric, it does not go to zero. This further supports the observation that some degree of ordering persists up to at least the APBs.

For a quantitative comparison to ordering models, STEM image simulations serve as a benchmark^{36,37} and are presented in comparison to a typical COR from experiment in Fig. 3(a) where the order metric is 0.19 ± 0.07 . Each simulation is based on an 8 nm thick sample to match experiment where the β sub-lattices are assigned a specific site occupancy and filled with the corresponding fractions of Nb and Mg using a random binomial distribution.

Simulated images of a completely ordered “space charge” slab can serve as an order metric normalization factor. This is justified as this model is the most ordered scenario where the β' and β'' sub-lattices are either purely Mg or Nb and hence the largest intensity difference between the two sub-lattices. As evident from Fig. 3(b), the “space charge” order metric is uniformly much higher than experiment. For completeness, we also consider a full 8 nm slab consisting of the “charge balanced” model, Fig. 3(c). The average normalized order metric in that case is 0.65 ± 0.08 , which is also far greater than observed in experiment.

CORs embedded within a disordered matrix are also considered and approximate the prevailing model of PMN.²⁵ Specifically, we consider 4 nm spherical CORs surrounded by a disordered matrix. For a “space charge” COR, Fig. 3(d), the order metric is significantly reduced (0.49 ± 0.11) but is still inconsistent with experiment. Furthermore, even for an embedded “charge balanced” COR [Fig. 3(e)], the degree of ordering remains notably larger (0.34 ± 0.09) than experiment. Therefore, both the “space charge” and “charge balanced” models are incongruous with experiment.

Building from our observation of gradients in the order metric observed with aberration-corrected STEM, we consider instead that the degree of ordering allowed the linear variation across a COR, as a first order approximation. That is, a function of distance, r , away from the center of a COR with a radius, r_o , the β' and β'' Mg site occupancies are then given by $\beta' = 0.667 - 0.333(r/r_o)$ and $\beta'' = 0.333(r/r_o)$. It is important to emphasize that charge neutrality is maintained locally in this model. For $r > r_o$, the remaining Mg/Nb atoms, which would correspond to an APB, are assumed to be distributed randomly at the charge balanced ratio. The mathematical model used for each COR configuration is presented in the [supplementary material](#). Simulations of this structure, Fig. 3(f), show that the order metric is excellent agreement with experiment (0.22 ± 0.08). Furthermore, the maximum order metric from simulations is 0.39, which is consistent with a maximum of 0.37 in experiment. Further, a gradual decrease in the order metric from its maximum value is observed, which is also consistent with experiment.

For a more thorough comparison, ten additional CORs from experiment were quantified and compared with simulations of 2–6 nm CORs adopting the various models. The order metric analysis is summarized in Fig. 4. First, the “space charge” simulations show a linearly increasing order metric with the increasing COR size, which is far greater than experiment in almost all cases. Likewise, the order metrics for the “charge balanced” CORs remain larger than those from comparable experimental datasets. Finally, order metrics for the gradient-ordering model remain approximately the same regardless of the COR size. This is in excellent agreement with experiment, where the order metric mean and standard deviation are nearly independent of the COR size.

The simulations in Fig. 4 also offer insights into the variation of the order metric which are seen in experiment, e.g., Fig. 2(a). In each case, the simulated COR is smaller than the 8 nm sample thickness, as measured in the experiment. For the “space charge” and “charge balanced” models, the average predicted order metrics are inconsistent with experiment [Fig. 2(a)] for all but the smallest CORs. Regardless of the depth and size, the *maximum* order metric is consistently about 0.3–0.35 and only in agreement with the proposed gradient-ordering model.

The observed COR gradient ordering is likely connected to the high density of energetically unfavorable APBs. Because there is limited diffusion near the order/disorder transition of PMN (<1173 K), the APB boundary area to COR volume ratio cannot be reduced through coarsening.³⁵ Instead, as we have observed, the local degree of ordering can spatially vary and decrease towards the APBs to the

FIG. 3. Order metrics from (a) representative COR from experiment, (b) “space charge” slab, (c) “charge balanced” slab, (d) embedded “space charge” COR, (e) embedded “charge balanced” COR, and (f) embedded COR with ordering gradient. Each COR is 4 nm in diameter with a disordered APB at the top and bottom of the model structure.

point where β^I and β^{II} are indistinguishable.³⁸ Therefore, the APBs are disordered to increase boundary entropy, which minimizes the boundary free energy.^{39,40} This disorder can be viewed to “wet” the CORs throughout the material.

The proposed mechanism shares many similarities with order/disorder transformations observed in some face centered cubic metal alloys.^{41,42} In that case as well, disordering initiates at the APBs and also exhibits a non-abrupt ordering transition.⁴³ Beyond PMN, the relaxor ferroelectric lead scandium tantalate (PST) exhibits significant discrepancy between the concentration of ordered phase fraction determined from dark-field TEM and XRD. Previous studies provided indirect evidence that there is significantly more ordering that would be suggested by conventional TEM.⁴⁰ These results also have important implications for the origin of relaxor ferroelectricity. Specifically, the random fields introduced by chemical disorder are thought to play a critical

role in forming the PNRs that introduce the diffuse relaxor behavior.⁴⁴ Since cation order is more prevalent than expected, the observations are important to incorporate into modeling. For example, a recent study has proposed a multi-domain relaxor structure that describes polar structures as being in a slush-like state where static and dynamic domains coexist.⁷ With the emergence of alternative models describing relaxor behavior, the influence of local chemistry must be taken into account^{45,46} to provide the necessary quantitative assessment of chemical ordering.

In summary, we have shown that previously proposed chemical ordering models for PMN do not agree with direct observations from atomic resolution HAADF STEM imaging. In contrast to the prevailing model, the degree of ordering gradually decreases up to APBs, which are found to exist between CORs. Moreover, the chemical disorder is maximized at the APBs, where it serves to reduce the boundary energy. This interpretation is validated through a combination of experiment and simulations, which establishes the existence of chemical order gradients in the relaxor PMN. These results thus provide a starting point to connect relaxor behavior with the interplay of local chemistry and structure.

See [supplementary material](#) for electron diffraction patterns showing diffuse scattering and mathematical descriptions of the models used to generate the structures for STEM image simulations.

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FIG. 4. The average order metric as a function of embedded COR size. The horizontal lines represent the mean order metric (solid) $\pm$ one standard deviation (dashed lines) obtained from 10 experimental regions with the same dimensions as the simulations.

North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI).

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