Direct observation of the formation of polar nanoregions in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ using neutron pair distribution function analysis

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Using neutron pair distribution function (PDF) analysis over the temperature range from 1000 K to 15 K, we demonstrate the existence of local polarization and the formation of medium-range, polar nanoregions (PNRs) with local rhombohedral order in a prototypical relaxor ferroelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. We estimate the volume fraction of the PNRs as a function of temperature and show that this fraction steadily increases from 0% to a maximum of ~30% as the temperature decreases from 650 K to 15 K. Below T~200 K the PNRs start to overlap as their volume fraction reaches the percolation threshold. We propose that percolating PNRs and their concomitant overlap play a significant role in the relaxor behavior of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$.

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Relaxor ferroelectrics, such as lead magnesium niobate Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), have been widely applied due to their high, relatively temperature-independent, permittivities. Relaxors are characterized by a frequency dispersion in their maximum permittivity temperature ($T_M$ ~285 K in PMN), with no macroscopic phase transition into a ferroelectric state at $T_M$. These behaviors are fundamentally different from those of normal ferroelectrics and are similar to spin-glasses. It is now believed that local polarization, resulting from structural and chemical disorder, plays a crucial role in relaxor behavior. Several models have been proposed to explain the nature of the interactions between these local polarizations and the mechanism for relaxor behavior. These models include superparamagnetic and dipole glasses, as well as random field interactions. The microscopic mechanism behind relaxor ferroelectricity is, however, not fully understood, and is still controversial due to its high degree of complexity.

In this Letter, we report the temperature evolution of the local and medium-range crystal structure of PMN from 1000 K to 15 K using neutron pair distribution function (PDF) analysis. We present evidence for both local atomic displacements (local polarization) and for medium-range (~5 Å - 50 Å) ordering, called polar nanoregions (PNRs). These medium-range correlations are modeled using rhombohedral symmetry, enabling for the first time an estimate of the temperature dependence of the volume fraction of the PNRs. This fraction increases with decreasing temperature, reaching the three dimensional percolation threshold below T~200 K, where the PNRs start to overlap. We discuss the implications of these findings on the dielectric properties of PMN.

Evidence for the existence of local polarization in PMN below $T_d$ ~620 K, known as the Burns temperature, was deduced from optical and strain measurements and atomic pair distribution function (PDF) analysis. Nb K-edge EXAFS measurements on PMN suggested a displacement of Nb ions with respect to their oxygen octahedra by about 0.1 Å from room temperature down to 4.5 K. Pb K-edge EXAFS measurements indicated strong static disorder on the Pb sites, but provided no detailed information about static Pb displacements. This is in contrast to neutron PDF measurements on PMN which clearly showed that the Pb ions are off-center with respect to the O$_{12}$ cage by as much as 0.5 Å. Our measurements were performed on the NPDF instrument at the Los Alamos Neutron Science Center (LANSCE). Powder diffraction patterns were corrected for background, absorption and multiple scattering, and normalized using a vanadium spectrum to ob-
tain the total scattering structure function \( S(Q) \), using the PDFgetN program. The PDF \( G(r) \) is obtained from \( S(Q) \) via the Fourier transform shown in Eq. 1,

\[
G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^{Q_{max}} Q[S(Q) - 1] \sin Q r dQ,
\]

where \( \rho(r) \) and \( \rho_0 \) are the atomic number and average number densities, respectively. Since \( S(Q) \) includes both Bragg and diffuse scattering, the resultant PDF provides short-, medium-, and long-range structural information. This technique has been used to study local atomic structures and correlated atomic motions of atom pairs in many materials.

Below room temperature (Fig. 1 (b)) the experimental PDFs reveal more interesting structure. First, the Mg/Nb-O peak around 2.02 Å splits into two peaks, suggesting local Mg/Nb displacements along the (111) direction. Note that this peak shows almost no temperature dependence between 250 K and 15 K, consistent with Nb K-edge EXAFS measurements. In general, PDF peaks become sharper with decreasing temperature due to decreasing thermal motion. Thus, this unusual temperature dependence indicates an increasing distribution of static Mg/Nb displacements with decreasing temperature. Second, the Pb-O peak around 2.85 Å splits into three peaks at \( \sim 2.45 \), 2.85, and 3.33 Å. Third, the Pb-Mg/Nb peak around 3.5 Å splits into two Pb-Mg/Nb bonds at \( \sim 3.33 \) and 3.64 Å mostly due to the displacement of Pb ions. Thus, the peak around 3.3 Å has both Pb-O and Pb-Mg/Nb components. The splitting of the Pb-O and Pb-Mg/Nb peaks below room temperature suggests that the Pb ions may locally shift mostly along (100) or (111) directions. Interestingly, the peak around 4.05 Å (lattice constant of PMN) is well defined; thus, the overall cubic symmetry is maintained although the local cubic symmetry is not.

We now address the medium-range correlations (PNRs) between these local atomic displacements. Fig. 2 (a) shows the PDF spectra from 1000 K to 15 K in the \( r \)-range up to 16 Å, and Fig. 2 (b) shows the temperature dependence of the peak intensities in the doublet between 8.0 Å < \( r < 9.8 \) Å. Here both peaks have contributions from almost all possible ionic pairs. The solid line is the calculated temperature dependence of the peak height using the average Pb, Mg/Nb, and O thermal parameters from Bonneau et al., which are reproduced in the inset. Note the strong deviation of the data below...
We modeled the PNRs using rhombohedral symmetry (R-model: space group R3m), wherein the Pb, Mg/Nb and oxygen octahedra are displaced along the (111) directions, assuming rigid oxygen octahedra. Similar models of rhombohedral correlations with (111) atomic displacements \cite{21,22,23} and non-collinear (100) displacements that average to rhombohedral symmetry \cite{24} have been proposed in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} and Pb(Sc\textsubscript{1/2}Ta\textsubscript{1/2})O\textsubscript{3}, respectively. Attempts to model our data using displacements of orthorhombic symmetry (with the atoms and oxygen octahedra displaced along (110) directions with the same magnitudes as in the rhombohedral model) were unsuccessful, with some PDF peaks being too strong and others too weak.

In Fig. 2 (c) we compare the R-model PDF with the experimental PDF at 650 K. For the R-model PDF calculation the thermal parameters were taken from Bonneau et al. \cite{21}, and the following atomic positions were used, determined to best simulate the differences between low temperature PDFs and the PDF at 650 K: Pb (-0.0392, -0.0392, -0.0392), Mg/Nb (0.5062, 0.5062, 0.5062) and O (0.5308, 0.5308, 0.0308).

The PDF peaks of the R-phase are quite distinct from those of the paraelectric cubic phase. In fact, the relative intensities of the PDF peaks in the R-phase and in the paraelectric cubic phase resemble the low-temperature and high-temperature end members shown in Fig. 2 (a), respectively. Therefore, if we assume that PNRs are dispersed as “islands” in the paraelectric cubic lattice \cite{21} growing in size and volume fraction with decreasing temperature, we expect that features of the R-model PDF will become more evident with decreasing temperature. This is exactly what we observe in the experimental PDFs shown in Fig. 2 (a).

The volume fraction of the PNRs was estimated using a simple model PDF: $G_m = \alpha(T)G_R + (1-\alpha(T))G_C$, where $G_R$ and $G_C$ are model PDFs for the rhombohedral and paraelectric phases. $\alpha(T)$ is the volume fraction of the rhombohedral phase. (d) The volume fraction increases with decreasing temperature, reaching 30% at 15 K. The inset shows the correlation length of local polarization as a function of the temperature (taken from Xu et al. \cite{21}).

The volume fraction of PNRs at T~250 K, an indication of PNRs, as we now show.

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electric cubic and rhombohedral PDFs at a given temperature, \( \alpha(T) \) was adjusted to obtain the best match to the corresponding experimental PDF. Figures 3 (a-c) show these comparisons at 500 K, 250 K, and 50 K in the r-range up to \( r=16 \) Å. Considering the simplicity of the model PDF calculations, the overall agreement at various temperatures is very good.

In Fig. 3(d) we show the temperature dependence of \( \alpha(T) \), along with the correlation length of local polarization determined by Xu et al. using neutron elastic diffuse scattering \[27\], shown in the inset. The volume fraction steadily increases with decreasing temperature, reaching \( \sim 30\% \) at 15 K. The correlation length \( \xi \) of local polarization increases from \( \xi \sim 15 \) Å to \( \xi \sim 60 \) Å. Note that around \( T \sim 200 \) K, where the correlation length drastically increases, \( \alpha(T) \) reaches the percolation threshold \( P_c \sim 28\% \) for spherical objects in three dimensions \[27\]. This implies that the PNRs start to overlap with each other below \( T \sim 200 \) K. This correlates well with the abrupt increase in the correlation length of local polarization to \( \xi \sim 50 - 60 \) Å, determined independently.

Neutron scattering measurements by Wakimoto et al. \[25\] suggest that locally, each PNR maintains a stable spontaneous polarization below \( T \sim 220 \) K where the correlation length is about \( \sim 50 - 60 \) Å. Further growth of these large PNRs (beyond \( \sim 60 \) Å) may be hindered by electric and elastic energy barriers, which are proportional to the size of the PNR. In an applied electric field, however, the polarizations in the separate PNRs are aligned, and the separate PNRs form a macro polar domain. Once the macro polar domain is formed, the dipoles in the domain do not randomly orient even after the electric field is turned off.

This picture helps to explain some basic behavior found in PMN, such as hysteresis in the field-induced polarization \[20\], the field-induced rhombohedral phase transition below \( 220 \) K \[20\] and the anomaly in the dielectric permittivity near \( 212 \) K upon field heating after transition below \( 220 \) K \[30\] and the anomaly in the dipolarization \[29\], the field-induced rhombohedral phase found in PMN, such as hysteresis in the field-induced dipoles in the domain do not randomly orient even after the macro polar domain is formed, the polarization increases from \( \sim 15 \) Å to \( \sim 60 \) Å. Note that around \( T \sim 200 \) K, where the correlation length drastically increases, \( \alpha(T) \) reaches the percolation threshold \( P_c \sim 28\% \) for spherical objects in three dimensions \[27\]. This implies that the PNRs start to overlap with each other below \( T \sim 200 \) K. This correlates well with the abrupt increase in the correlation length of local polarization to \( \xi \sim 50 - 60 \) Å, determined independently.

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