Anomalous synchrotron x-ray scattering studies of local fluctuations in a $Pb(Nb_{2/3}Mg_{1/3})O_3$ single crystal

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Introduction

Lead magnesium niobate $Pb(Nb_{2/3}Mg_{1/3})O_3$ (PMN) is a relaxor ferroelectric with dielectric constant >30,000 near T_m = 270 K [1, 2]. Temperature dependence of the dielectric constant is diffuse and very sensitive to the frequency of the applied electric field. Although the dielectric constant of PMN shows a maximum at T_m = 270 K, it has been inferred from x-ray and neutron scattering experiments that PMN doesn't show any noticeable macroscopic structural phase transition in the temperature range 15–600 K [3]. Instead, it was proposed that the system undergoes a transition into a glass-like state at the so-called freezing temperature, T_f = 200–230 K [4]. Importance of the local disorder and different kinds of local fluctuations (chemical and dipolar) in PMN and other related relaxors were demonstrated to be intimately related to the relaxor ferroelectric behavior. Correlation of these fluctuations is responsible for formation of different nanoregions, which may be studied through the associated superlattice reflections they produce [5, 6]. The focus of this work is to investigate the behavior of these nanodomains as a function of temperature and x-ray energy, leading to an improved understanding of the microstructure and the underlying physical principles responsible for the relaxor ferroelectric behavior.

Methods and Materials

Measurements were performed on the UNI-CAT undulator beamline (sector 33-ID) at the Advanced Photon Source (APS), Argonne National Laboratory. The energy of the incoming x-rays was tuned near Pb L_{III} edge (13.055 keV) for anomalous scattering measurements (Figure 1).

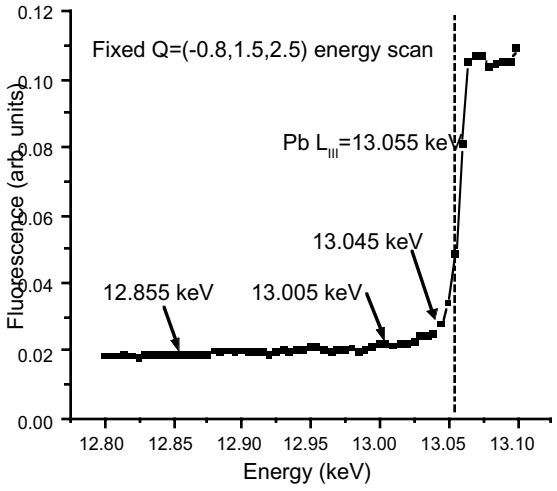

Figure 1: Energy dependence of the fluorescence from PMN.

Three values of the energies were chosen: 13.045 keV, 13.005 keV, and 12.855 keV, to emphasize the contribution of Pb to the superlattice peaks. Figure 1 depicts energy dependence of the fluorescence from the PMN. White beam from the undulator was monochromized by a double-crystal Si monochromator and focussed with two mirrors. Mirrors also serve as high-order harmonic rejection devices. The energy was calibrated with a standard Pb foil in the transmission mode, then checked with the actual sample. A scintillation detector was used to detect the diffracted beam. The size of the beam in the diffraction plane of the conventional four-circle Huber diffractometer was about 0.2 mm at the sample position. All measurements were performed with constant monitor counts. Displex cryostat has been used for low-temperature measurements in the range of 15–300 K. Measurements were done during heating of the sample from 15 K to room temperature. Size of the PMN single crystal was 3 x 3 x 1 mm^3 with a surface normal oriented in the [001] direction. Full width half maximum (FWHM) for 003 broad Bragg reflection is 0.003 reduced reciprocal lattice units (r. l. u.) for L direction scan. Resolution in reciprocal space is better than 0.001 r. l. u. along the H, K, and L directions.

Results

Two types of nanoregions exist in PMN: a) chemically ordered nanodomains and b) polar nanodomains, due to correlated ionic displacements. Each type of nanodomain gives rise to superlattice reflections at different positions in the reciprocal space. Reflections on the body-centered positions are called F spots and reflections on the face-centered positions are called α spots [7]. Temperature dependence of the F spots is weaker than that of the α spots. Intensity at the position of the α spots gradually decreases and reaches a constant value above T_f = 200 K (Figure 2).

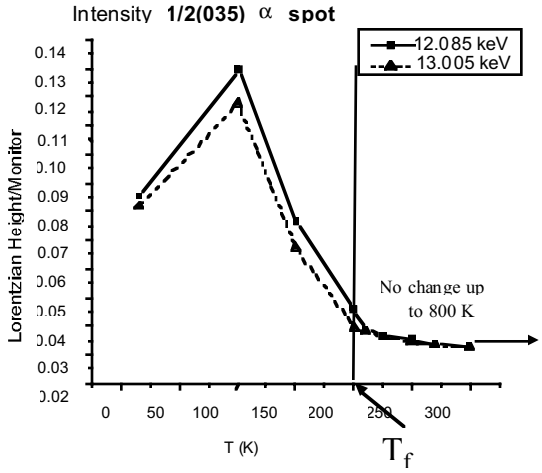

Figure 2: Intensity of the 1/2(035) α spot.

The 1/2(135) F spot shows about 20% reduction in intensity from 15 K to room temperature with a noticeable cusp near T_f (Figure 3). Detailed analysis revealed that α peaks vanish above T_f (Figures 2 and 4), and the remaining intensity is from soft $<110>_T$ phonon mode. FWHM of the F spots is temperature independent over the whole temperature range (Figure 3, inset). Small dependence on the energy of the x-rays tuned near Pb L_{III} edge is attributed to the contribution from correlated Pb atomic displacements (Figures 2 and 3).

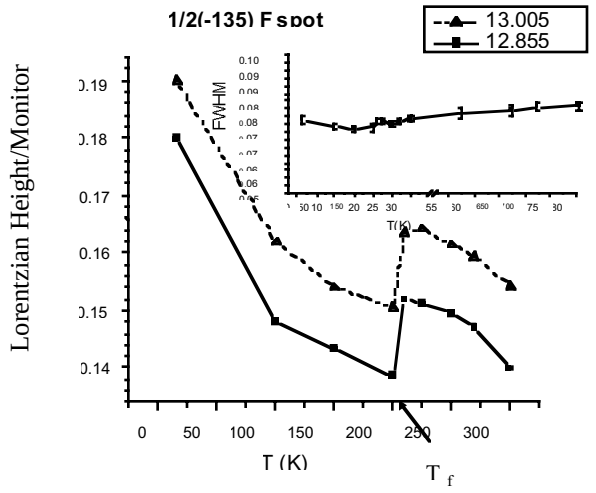

Figure 3: Intensity of the 1/2(135) F spot. Inset shows width of the peak over the 15–800 K temperature range.

Discussion

From the temperature dependence of the α superlattice peak profile (Figures 2 and 4) corresponding to polar regions, we found the freezing temperature (T_f) of the correlated atomic displacements near 200 K. Decrease in the intensity of the α superlattice peaks is accompanied by reduction of the thermal diffuse scattering corresponding to the soft $<110>_T$ mode (Figure 4 inset). This suggests the importance of the phonon coupling with the origin of the α spots. Structure factor calculations suggest two types of correlated oxygen octahedra rotations in PMN: 1) in phase and 2) out of phase. These two types of rotations displace Pb atoms in two different ways, which were modeled in this work and the results are in good agreement with the experimental observations. In-phase BO_6 rotations, coupled with corresponding displacements, contribute to the intensity of the α spots below T_f. Out-of-phase rotations, coupled with a different Pb displacement pattern, contribute to the F spots. We attribute the increase in the α spot intensity on cooling below T_f to the increased angle of the rotations due to freezing of the corresponding zone boundary phonon mode and due to the increased magnitude of coupled antiparallel Pb displacements. From the disappearance of the α spots on heating we suggest that there is no contribution from Pb displacements to the intensity of the α spots above T_f. Independence of the intensity above T_f measured at the position of the α spot from the x-ray energy tuned near Pb L_{III} absorption edge further supports this fact (Figure 2). Tendency for the whole crystal to order may compete with displacements caused by oxygen octahedra rotations below T_f. Instead, the system is subdivided into randomly oriented frozen nanoregions of the polar phase [1–3]. Appearance of the α spots below T_f is related to the competing antiparallel Pb displacements caused by oxygen octahedra rotations. Chemical disorder of the Nb^{5+} and Mg^{2+} ions is believed to play an important role in preventing the crystal from establishing polar long-range order. In contrast, chemically ordered nanodomains, which give rise to F superlattice peaks, exhibited isotropic shape and temperature-independent size. This leads us to believe that chemically ordered regions might be different and independent from the polar regions. Cusp in the temperature dependence of 1/2(135) F spot near T_f might be related to the change in competition between antiparallel Pb displacements caused by in-phase and out-of-phase oxygen octahedra rotations.

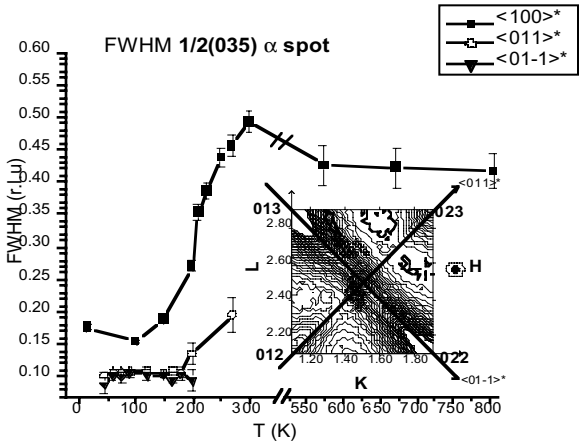

Figure 4: Width of the 1/2(035) α spot in different directions. Inset shows (100)* plane scan of the α spot with strong diffuse scattering in [10-1] direction.

Understanding the underlying microstructure is important for the explanation of the physical properties of this material. Interactions between different local fluctuations are believed to be responsible for unusual relaxor ferroelectric properties.

Acknowledgments

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