Computational Study of Real Space Local Structure and Diffuse Scattering in a Relaxor

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Relaxor ferroelectrics are attractive materials due to a strong piezoelectric effect, a high permittivity value over a broad temperature range, and a unique dielectric response with strong frequency dispersion with the diffuse phase transitions.[1-3] Currently, the relaxor phase transitions are described by the widely-accepted polar nanoregions (PNR) in a matrix model. At the Burns temperatures (T_b) above the Curie-Weiss temperatures (T_c), spherical polar nanoregions (PNRs) appear in a non-polar matrix and the material undergoes a phase transition from the paraelectric phase to the dynamic relaxor phase. As the temperature is lowered further, the size of PNRs and interactions between PNRs grow and strengthen, and the local distortions appear at the intermediate temperature (T^*). When the system is cooled down to T_f, the growth of PNRs stops and their dynamics freeze as the system undergoes a transition from the dynamic relaxor phase to the frozen relaxor phase.

Investigations of local structure play a crucial role in understanding how the important properties of relaxors arise from their composition. While the real space local structure motifs are poorly understood due to the complexity of relaxor materials, experimental diffuse scattering (DS) studies have clear demonstrated that relaxor behavior is related to the appearance of local disorder in the ionic displacements. Recent diffuse scattering studies have questioned the PNR model[4] and the DS intensity patterns are reported in $Pb(Zr,Ti)O_3$ near T_c.[5]

In this work, we study how local Pb dipoles give rise to the observed DS patterns using bond-valence (BV) model molecular dynamics simulations of a 46656-atom supercell of the $0.75PbMg_{1/3}Nb_{2/3}O_3$-$0.25PbTiO_3$ (PMN-PT) relaxor ferroelectric with the random site rocksalt *B*-site cation arrangement.[6,7]

Our computational DS results reproduce the butterfly shape and exhibit a similar trend to the experimental results on cooling (Figure 1). We find that the magnitude of local displacements directly influences the extent of the DS pattern. To analyze the local structure, we examine the Pb displacement angle autocorrelation and the angles between the local time averaged Pb off-center displacements. We find that the time-averaged Pb displacement autocorrelation angle is small but greater than zero. This indicates that even in the the Pb dipoles are not frozen but rather rotate slowly. At low temperature, the angles between the local Pb dipoles are small up to Pb-Pb separation of 30-40Å, and increase dramatically to approximately70 degrees for larger Pb-Pb separation (Figure 2). This indicates that the frozen phase is a multidomain state with 71 degree domain walls separating small 3~nm sized ferroelectric like domains. The domain walls are centered on Pb atom with several Mg neighbors; such atoms display fast dynamics even in the frozen phase. Simulations of the DS pattern with model structures shows that it is this multidomain structure that gives rise to the butterfly shape observed in diffuse scattering. Thus, the butterfly shape is a signature of the formation of the multidomain state. Using an analogy with water,[8] the dynamic phase can be thought of as hydrogen-bonded liquid water while the frozen phase is consists of small ferroelectric regions separated by domain walls with fast dynamics analogous to a slushy mixture of ice and water.

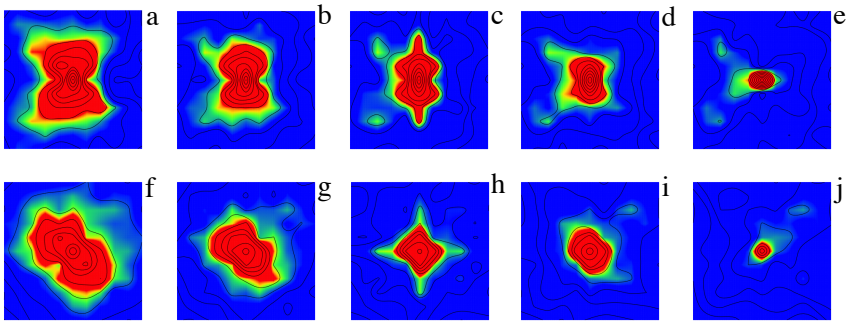

Figure 1 Diffuse scattering intensity on (*hk0*) plane. The intensities around *(100)* at 100K (a), 300K (b), 400K (c), 500K (d), and 600K (e) in upper panel. In lower panel, the intensities around *(110)* at 100K (f), 300K (g), 400K (h), 500K (i), and 600K (j).

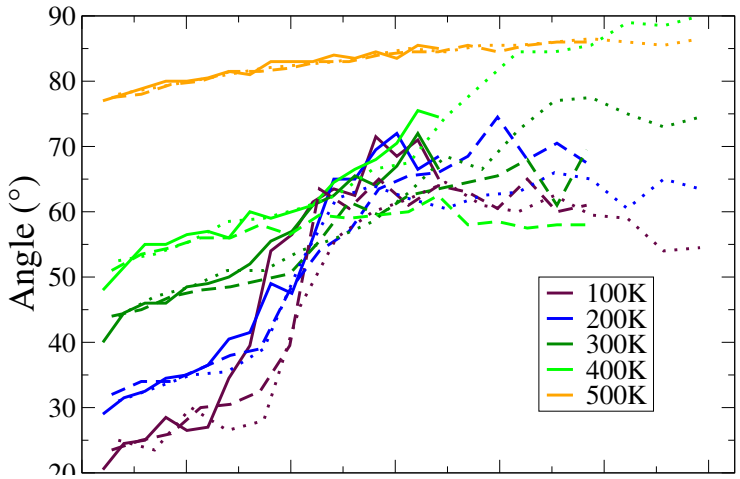

Figure 2 The peak height positions of the time-averaged angle correlations as a function of Pb atoms distance with various temperature. The solid lines are for *n00*, dashed line for *nn0*, and dotted lines for *nnn*.

In conclusion, the computational DS patterns exhibit evidence of local distortions around T^* similar to the experimental observations. The butterfly shape arises from the "slush" multidomain structure of the relaxor phase. One significant consequence of the slush structure is the extremely high non-180 degrees domain wall density, which is favorable for large piezoelectric response. Thus our results show how local structure gives origin to the diffuse scattering, phase transitions and the ultra-high piezoelectric response of relaxor materials.

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