Correlations between nanoscale chemical and polar order in relaxor ferroelectrics and the lengthscale for polar nanoregions

Benjamin Paul Burton,¹ Eric Cockayne,¹ and Umesh V. Waghmare²

¹Ceramics Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology Gaithersburg,

Maryland 20899-8520, USA

²J. Nehru Theoretical Sciences Unit, JNCASR, Jakkur, Bangalore, 560 064, India

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Molecular-dynamics simulations of a first-principles Hamiltonian for the model relaxor ferroelectric $Pb(Sc_{1/2}Nb_{1/2})O_3$ were used to determine the nature of correlations between chemical and polar short-range order. Relative to chemically disordered regions (CDRs), chemically ordered regions (CORs) exhibit enhanced polarization, and polarization fluctuations at all temperatures. Magnitudes of pairwise cluster-cluster polarization correlations follow the trend COR-COR, COR-CDR, CDR-CDR correlations. This result implies that the characteristic lengthscale for polar nanoregions is the same as for chemical short-range order.

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I. INTRODUCTION

Perovskite-based $A(B_{1/2}B'_{1/2})O_3$ and $A(B_{1/3}B'_{2/3})O_3$ relaxor ferroelectrics (RFEs),^{1,2} such as Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) and Pb(Sc_{1/2}Nb_{1/2})O₃ (PSN), are technologically important transducer-actuator materials with extraordinary dielectric and electromechanical properties. They also exhibit fundamentally interesting Vogel-Fulcher³ temperature (T) and frequency (ω) dependence of their dielectric constant, $\epsilon(T, \omega)$, that is not observed in conventional ferroelectrics (FEs) or antiferroelectrics (AFs).⁴ In RFEs, $\epsilon(T, \omega)$ exhibits a broad peak that is associated with ω dispersion, 1 Hz $\leq \omega$ \leq 1 GHz, which clearly indicates relaxation processes at multiple time scales. While the oxymoronic phrase "diffuse phase transition" (DPT) is often used to describe RFEs, they are distinct from other FEs with a DPT, such as $Pb(Fe_{1/2}Nb_{1/2})O_3$, whose dielectric response does not have Vogel-Fulcher form.⁵ The maximum temperature for an RFE is called the Burns temperature, T_{Burns} , and below T_{Burns} index of refraction data deviate from a Curie-Weiss trend. The minimum temperature is either a point of transition to a FE phase, as in PSN, or a glassy freezing point T_f , as in PMN.⁶ Some reserve the term RFE for systems such as PMN that have a T_f at low $T.^6$

Fluctuations of the chemical short-range order (SRO) on a lengthscale of $\approx 2-6 \text{ nm}^{7-9}$ (5–15 unit cells) define nanoscale¹⁰ heterogeneities with disordered local fields (\vec{h}_i , iindexes a crystallographic site) that are often called random fields (RFs).^{11,12} Coupling between \vec{h}_i and FE degrees of freedom is thought to generate polar nanoregions (PNRs) with collective dipole moments,^{13,14} and PNRs are deemed essential to the ferroglass freezing that is observed in PMN.⁶ Elucidating the relationship(s) between chemical SRO, and PNRs, and their respective lengthscales, is a long-standing and central problem in RFE studies. In 1983, Burns and Dacol¹³ suggested that polar clusters would be "…several unit cells in size…" whereas in 2003, Blinc *et al.*⁶ describe them as "…smaller than 500 Å…" an uncertainty range of ≈ 1.5 orders of magnitude. The simulations described below link atomistic firstprinciples calculations to mesoscopic models, such as the spherical random bond random-field model (SRBRFM).¹⁵ A realistic microstructure [PSN,⁸ PMN (Refs. 7 and 9)] is modeled and analyzed by directly calculating polarizations and dielectric susceptibilities for nanoscale chemically ordered regions (CORs) in a percolating disordered matrix (PDM) of chemically disordered regions (CDRs). Simulations allow a complete *spatial* accounting and analysis of correlations between chemical and polar ordering which has not been achieved experimentally, and therefore an analysis of the characteristic PNR lengthscale.

A. Previous simulations

Simulations were performed for PSN rather than PMN because the PSN cation ordered ground state is known, and this simplifies derivation and fitting of the first-principles effective Hamiltonian (Refs. 16-19 and references therein). Previous PSN simulations¹⁹⁻²¹ share some common predictions. Consistent with experiment: (i) a first-order $Pm\bar{3}m \rightleftharpoons R3m$ transition to a FE ground state $(R3m;a_0)$ =4.080 Å, α =89.89° at room temperature²²), in both the chemically ordered and disordered states; (ii) some broadening of $\epsilon(T)$ in the disordered state; (iii) *apparently* contrary to experiment,⁸ they all predict that the chemically ordered phase has a higher FE-transition temperature than the chemically disordered phase, $T_{FE}(Ord) > T_{FE}(Dis)$. This result is surprising because in isostructural $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) the observed order of transitions is $T_{FE}(\text{Ord}) > T_{FE}(\text{Dis})$,²³ and one expects the RF in a chemically disordered crystal to depress T_{FE} , as in PST. The unexpected T_{FE} (Ord) $< T_{FE}$ (Dis) result in PSN is partially explained by greater Nb and/or Sc displacements in PSN, relative to Ta and/or Sc displacements in PST. An effective Hamiltonian simulation that describes PSN ferroelectricity in terms of both Pb and Nb modes²¹ reduces the difference between $T_{FE}(Ord)$ and T_{FE} (Dis), but does not reverse their order. Most likely, however, the $T_{FE}(\text{Ord}) < T_{FE}(\text{Dis})$ result is a sample preparation



FIG. 1. (Color online) A (110) plane through the simulation box representing the projected local field (arbitrary units) at each Pb site in the plane. Chemically ordered regions (approximately circular) have small approximately homogeneous fields, and chemically disordered regions have larger more varied and disordered local fields.

problem: long annealing times are required to achieve a high degree of chemical order, and this promotes Pb loss, which depresses T_{FE} and yields a more diffuse dielectric peak, as in the Perrin *et al.* "PSN-85" sample.⁸

B. Local fields $\vec{h_i}$

Chemical order-disorder on the *B*-sites of $A(B_{1/2}^{3+}B_{1/2}^{\prime5+})O_3$ and $A(B_{1/3}^{2+}B_{2/3}^{\prime5+})O_3$ perovskites creates local fields $\vec{h_i}$ that induce Pb displacements which presumably cause, or at least contribute to, RFE properties. Quian and Bursil¹² derived a nearest-neighbor (NN) approximation for $\vec{h_i}$ in Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) and applied it in a twodimensional Potts-model simulation. A similar threedimensional model is used here, but the $\vec{h_i}$ (Fig. 1) are calculated from an electrostatic point-charge model for the whole 40³ *B*-site configuration, rather than NN *B*-sites only.

II. SIMULATION

Molecular-dynamics (MD) simulations were performed on a first-principles effective Hamiltonian model¹⁹ for PSN in a 40³ unit-cell simulation box. Local-field terms were combined with an effective Hamiltonian model for a normal FE,^{16–18} in which all atomic displacements are projected onto a subspace of low-energy FE distortions, via Pb-centered polar variables. For PSN this model predicts, T_{FE} (Ord) $> T_{FE}$ (Dis) in *apparent* contradiction to experiment, noted above, but it includes the essential ingredients for a generic RFE model with which to study nanoscale correlations between chemical and polar ordering.

The chemical and therefore h_i microstructure of the simulation box consists of 20 CORs in a PDM of 60 CDRs. Each COR, and each CDR, contains 800 Pb sites in a convex approximately spherical shape. Figure 1 is a (110) cross section through the simulation box, in which arrows represent \vec{h}_i . The CORs have relatively low and homogeneous \vec{h}_i ,



FIG. 2. (Color online) A snapshot of local mode polarizations at $T=600 \text{ K} \approx T_{FE}$. More highly correlated (dark gray, blue) regions are chemically ordered and the more disordered matrix (light gray, red) is chemically disordered.

roughly circular projections in Fig. 1. The CDRs that make up the PDM have larger more varied $\vec{h_i}$. In PSN with perfect chemical long-range order, $\vec{h_i}=0$ at all Pb sites, and when *B*-site disorder is introduced, a distribution of $\vec{h_i}$ develops.²⁴ In a NN approximation,¹² $\vec{h_i}=0$ at most Pb sites inside the COR.

III. RESULTS

Figure 2 shows a snapshot of simulated local polarization vectors at $T=600 \text{ K} \approx T_{FE}$. In the COR local polarizations are more highly correlated and more uniform in magnitude. In the PDM there is more disorder with respect to both magnitude and direction because of pinning by local fields. In a movie made from 96 such snapshots, one can clearly see that local polarizations in the COR rotate more freely and in a more mutually correlated way than those in the PDM which are often pinned by local fields.

Figure 3 plots average COR and CDR polarizations,



FIG. 3. (Color online) Average polarizations per unit-cell for 800 unit cell clusters, as functions of temperature.



FIG. 4. (Color online) Polarization fluctuations in chemically ordered and disordered clusters. Lines are for individual ordered clusters.

 $|\langle S_i(t) \rangle|$, as functions of *T*: subscript i=O indexes a COR, i = D indexes a CDR, and *t* is the MD time step. Time averaging is over at least 800 MD snapshots with 100 MD time steps between snapshots (80 000 MD steps \approx 70). Clearly, the CORs exhibit significantly enhanced FE order over the full *T* range, and enhanced polarization *fluctuations* ε_i

$$\varepsilon_i(T) \equiv \langle \vec{S}_i(t) \cdot \vec{S}_i(t) \rangle - \langle \vec{S}_i(t) \rangle \langle \vec{S}_i(t) \rangle, \qquad (3.1)$$

plotted as functions of *T* in Fig. 4: $\varepsilon_i(T) \approx$ a local, intracluster, dielectric constant. Maxima for $\varepsilon_O(T)$ curves are two to four times greater than those for $\varepsilon_D(T)$. The $\varepsilon_O(T)$ maxima occur over a wider range of temperatures, and the normalized widths of $\varepsilon_O(T)$ curves are significantly greater than those for $\varepsilon_D(T)$. Polarizations and their fluctuations are greatly reduced in CDRs because $\langle \vec{h}_i \rangle$ is large (... \Rightarrow statistical average) and the local fields hinder cooperative, highly correlated rotations in the CDR. Thus the CORs are nanoscale regions of enhanced polarization and susceptibility, i.e., PNRs, or components of multi-COR PNRs.

The prediction of a $Pm\bar{3}m \Rightarrow R3m$ FE phase transition is evident in Fig. 5 which plots T-dependent dot products of cluster moments, $\langle S_i(t) \cdot S_i(t) \rangle$. Solid and dashed lines in Fig. 5 connect averages over subsets of the 80 clusters: COR-COR, COR-CDR, and CDR-CDR. Clearly, the model predicts a FE transition with $T_{FE} \approx 600$ K. Below T_{FE} , all three populations $[\langle \tilde{S}_{O}(t) \cdot \tilde{S}_{O'}(t) \rangle, \langle \tilde{S}_{O}(t) \cdot \tilde{S}_{D}(t) \rangle, \text{ and } \langle \tilde{S}_{D}(t) \cdot \tilde{S}_{D'}(t) \rangle]$ have averages greater than zero which indicates a FE transition throughout the system. Superficially, this contradicts nuclear magnetic resonance studies of a "20-25 %" chemically ordered PSN single crystal by Laguta et al.²⁵ which indicates that FE long-range order is clearly stronger in CORs than in CDRs, but according to Laguta et al. FE longrange order is only established in the COR. However, Laguta et al. also say, "...that even in the disordered parts of the crystal, local polarization acquires a projection along the direction of spontaneous polarization," which is tantamount to



FIG. 5. (Color online) Cluster-polarization dot products as functions of temperature: *O-O* indicate products between moments of two chemically ordered clusters, $|\langle \vec{S}_O(t) \cdot \vec{S}_{O'}(t) \rangle|$; *O-D* for products between chemically ordered and disordered clusters, $|\langle \vec{S}_O(t) \cdot \vec{S}_D(t) \rangle|$; *D-D* are for two disordered clusters, $|\langle \vec{S}_D(t) \cdot \vec{S}_{D'}(t) \rangle|$. Solid lines link average products.

acknowledging FE long-range order in the CDR as well. Furthermore, Perrin *et al.*⁸ report a first-order FE transition in *chemically disordered* PSN. Thus simulations and experiments agree.

The length scale for cluster-cluster separations d_{ij} that is sampled in these simulations is $3 \leq d_{ij} \leq 14$ nm (*i* and *j* index O=COR or D=CDR clusters). At this scale, there is no clear d_{ij} dependence in cluster-cluster correlations ξ_{ij} ,

$$\xi_{ij} \equiv \langle \tilde{S}_i(t) \cdot \tilde{S}_j(t) \rangle - \langle \tilde{S}_i(t) \rangle \langle \tilde{S}_j(t) \rangle, \qquad (3.2)$$

except perhaps for $d_{ij} \leq 6$ nm, Fig. 6, which appears to rule out multi-COR PNRs. Apparently random, d_{ij} -independent distributions of $\xi_{OO'}$, ξ_{OD} , and $\xi_{DD'}$ above T_{FE} [Figs. 6(b) and 6(c)] strongly suggest random-bond-type interactions, as postulated in the SRBRFM.¹⁵

IV. DISCUSSION AND CONCLUSIONS

The predicted hierarchy of cluster-cluster correlations

$$|\xi_{OO'}| > |\xi_{OD}| > |\xi_{DD'}|,$$
 (4.1)

implies the spatial mapping COR \approx PNR because, at T_{FE} $< T < T_{Burns}$, all the strong correlations are between CORs, but none are so strong as to imply multi-COR PNRs, or there would be significant $d_{i,j}$ dependence. A simulation value for T_{Burns} was not determined, but experimentally,⁸ T_{Burns} $\approx 1.1T_{FE}$ for PSN, consistent with enhanced simulation values for $\varepsilon_O(T)$ above T_{FE} . Therefore the characteristic length scale for chemical short-range order is the same as the characteristic length scale for the PNR. The essential picture is of CORs as islands of normal ordered PSN in a PDM that has reduced FE activity owing to its high $\langle \vec{h}_i \rangle$. The CORs \approx PNRs do not grow in the temperature range $T_{freezing} < T$ $< T_{Burns}$ because of pinning by local fields, that are mostly in



FIG. 6. (Color online) Isothermal pairwise cluster-cluster correlations as functions of intercluster separation d_{ij} : (a) $T < T_{FE}$, 550 K;(b) $T \approx T_{FE} \approx 600$ K;(c) $T > T_{FE}$, 650 K. The magnitudes of pairwise correlations exhibit the hierarchy: $|\langle \vec{S}_O(t) \cdot \vec{S}_{O'}(t) \rangle| > |\langle \vec{S}_O(t) \cdot \vec{S}_D(t) \rangle| > |\langle \vec{S}_O(t) \cdot \vec{S}_D(t) \rangle|$ > $|\langle \vec{S}_D(t) \cdot \vec{S}_{D'}(t) \rangle|$. All figures plotted at the same scale.

the CDR/PDM. This picture was confirmed, with respect to pinned PNR growth, by Jeong *et al.*,²⁶ who fit a two-phase (rhombohedral + cubic) model to their neutron pair distribution function analysis of PMN. For $T_{freezing} < T < T_{Burns}$ their Fig. 3 shows an initial growth in the "volume fraction of PNR" (rhombohedral phase) just below T_{Burns} , followed by an ≈ 250 K interval (300 < T < 600) in which the "volume fraction of PNR" is *constant* within experimental error; i.e. the PNRs that form at T_{Burns} and just below, do not grow until $T \approx T_{freezing}$.

The pairwise cluster-cluster correlation hierarchy also supports the idea that PNR-PNR interactions are essentially as postulated in the SRBRFM: *effective* PNR-PNR \approx COR-COR interactions, $J_{ij} \approx J_{OO'}$, are random; PNR-PDM \approx COR-CDR interactions ($\approx J_{OD}$; $|J_{OD}| < |J_{OO'}|$) are significantly weaker than PNR-PNR interactions.

An important difference between the simulations and the SRBRFM is that simulations include the interactions that drive FE ordering *within* the COR and PDM: nominally J and J', respectively. In principle, J and J' could be included in SRBRFM calculations, but in practice this was not done.¹⁵ In simulations, J approximately represents the coarse-grained *effective* FE interaction in chemically ordered PSN, and J'

< J is the analogous interaction in the PDM, which is weakened relative to J by the higher $\langle \vec{h}_i \rangle$ in the PDM.

Interactions J and J' are significantly stronger in $A(B_{1/2}B'_{1/2})O_3$ systems, hence PSN exhibits a FE transition even in the chemically disordered state. In $A(B_{1/3}B'_{2/3})O_3$ systems such as PMN, however, J and J' are inherently weaker because of enhanced $\langle \vec{h}_i \rangle$ in both CORs and CDRs: to a first approximation, \vec{h}_i in $A(B_{1/3}B'_{2/3})O_3$ systems are ≈ 1.5 stronger²⁴ owing to the larger difference in ionic charges, $Mg^{2+}+Nb^{5+}$ in PMN vs $Sc^{3+}+Nb^{5+}$ in PSN; and $A(B_{1/3}B'_{2/3})O_3$ stoichiometry is incompatible with a chemically ordered state in which all $\vec{h}_i \approx 0$, as in PSN. There is clearly a very delicate balance between systems that exhibit glassy freezing and those that exhibit a FE transition. For example, to a first approximation, \vec{h}_i in PMN are equal to \vec{h}_i in Pb(Zn_{1/3}Nb_{2/3})O_3 (PZN), but PZN exhibits a FE transition rather than glassy freezing.²⁷

Therefore the SRBRFM is a better approximation for $A(B_{1/3}B'_{2/3})O_3$ systems, such as PMN, which has ferroglass low-*T* states, than it is for $A(B_{1/2}B'_{1/2})O_3$ systems, such as PSN, which exhibits FE transitions.

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