

Large Scale Simulations of Ferroelectricity in $PbSc_{1/2}Nb_{1/2}O_3$ B.P. Burton¹, U. Waghmare² and E. Cockayne¹¹NIST; 1 Bureau Dr.; Gaithersburg, MD 20814, USA²JTheoretical Sciences Unit, JNCASR, Jakkur, Bangalore, 560 064, INDIA

Subject Categories: Category1, Category2, etc.

Abstract

Local electrostatic fields caused by B-site disorder in $A(B_{1/2}^{3+}B_{1/2}^{5+})O_3$ and $A(B_{1/3}^{2+}B_{2/3}^{5+})O_3$ perovskites are calculated in a nearest neighbor approximation to model *distributions* of Pb-displacements in $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). First principles based cluster expansion Hamiltonian models were used to calculate cation configurations, in PSN and PMN, in which local, "random," fields are a major cause of Pb-displacements.

Introduction

Relaxor ferroelectrics (RFE) [1, 2] are technologically important materials with extraordinary characteristic dielectric properties. Specifically, Vogel-Fulcher [3] temperature (T) and frequency (ω) dependence of the dielectric constant, $\epsilon(T, \omega)$; which is not observed in conventional ferroelectrics (FE)[4]. In a RFE, $\epsilon(T, \omega)$ exhibits a broad peak that is associated with nontrivial dispersion over more than 10 decades of frequencies; clearly indicating processes that occur at several time-scales. The phrase "diffuse phase transition" is often used describe RFE, but it should be noted that a genuine phase transition does not occur in the absence of an applied electric field, \vec{E} .

Fluctuations of the chemical long-range order (LRO) parameter (η) on a scale of ~ 10 nm[1] define nano-scale[5] heterogeneities with intense random fields (RF)[6, 7]. Coupling between these RF and FE degrees of freedom (DOF) are thought to generate nano polar regions (NPR) with collective dipole moments. Elucidating the correlations between chemical LRO, or short-range order (SRO), and NPR is a central problem in studies of RFE.

Chemical order-disorder on the B-sites of $A(B_{1/2}^{3+}B_{1/2}^{5+})O_3$ and $A(B_{1/3}^{2+}B_{2/3}^{5+})O_3$ perovskites creates local "random" electric fields, \vec{h} that cause Pb-displacements, \vec{d}_{Pb} , and therefore RFE-properties. Quian and Bursil [7] derived a nearest neighbor (nn) approximation for \vec{h} in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and applied it in a two-dimensional Potts-model simulation. A three-dimensional version of this nn approximation is

used below to analyse *distributions* of \vec{h} , and average \vec{d}_{Pb} (\bar{d}_{Pb}) in $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) and PMN [8, 9, 10, 11, 12, 13].

A range of phenomena have been attributed to Pb-displacements in RFE: Based on neutron scattering data, Vakhrushev and Okuneva [11] reported Pb-displacements, R_{max} , in PMN that followed the trend $R_{max}(T)$ ($T - 635$) R_{max} is plotted as an order parameter that continuously goes to zero at the Burns temperature $T_{Burns} \approx 635K$.

Pb-vacancies, presumably Pb-O vacancy pairs, are another source of random fields that dramatically affect RFE properties. As demonstrated experimentally, [?, ?, ?] 1 – 5% Pb-vacancies in chemically disordered PSN, or $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST), cause significant changes in $\epsilon(T, \omega)$: the $\epsilon(T)$ peak is broadened, and the temperature at which it is maximized, T_{max} , shifts to lower-T; both the magnitude and frequency-dispersion of $\epsilon(T, \omega)$ are enhanced. i.e. RFE properties are enhanced.

Presented below are discussions of simple models for chemical-disorder induced RF, and the results of large scale (40^3 unit cells) simulations [14] that track $\vec{d}_{Pb}(T)$.

Random Fields in the Nearest Neighbor Approximation

As discussed by Quian and Bursil [7] one can approximate the local "random" field on a Pb-atom that is caused by B-site disorder, \vec{h} as shown in Figure 1.

The average charge on a B-site is assumed to be +4, and the effective charges on B-sites that are occupied by Nb^{5+} , Sc^{3+} and Mg^{2+} are therefore +1, -1, and -2 respectively. With B-sites indexed as in Figure 1 \vec{h} and its components h_x , h_y and h_z are:

$$\begin{aligned} \vec{h} &= \langle h_x, h_y, h_z \rangle & (1) \\ h_x &= 2(k + l + o + p - i - j - m - n) \\ h_y &= 2(i + l + m + p - j - k - n - o) \\ h_z &= 2(i + j + k + l - m - n - o - p) \end{aligned}$$

where i,j,...p take values +1, -1, and -2 for B-sites occupied by Nb^{5+} , Sc^{3+} and Mg^{2+} , respectively. To first order (nn-approximation) the *distribution* of "random"

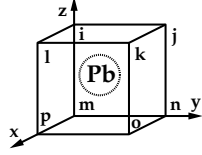


Figure 1: Indexing of B-sites that are nearest neighbors to an A-site that is occupied by a Pb^{2+} -ion.

fields at A-sites, that is caused by B-site cation disorder is relatively simple: of the $2^8 = 256$ possible configurations on the eight nn B-sites that surround each A-site (Fig. 1) only 22 are symmetrically distinct; these 22 configurations exhibit only seven distinct magnitudes for $|\vec{h}|$; and \vec{h} points in only five crystallographically distinct directions, $\langle 0,0,0 \rangle$, $\langle 0,0,1 \rangle$, $\langle 1,1,0 \rangle$, $\langle 1,1,3 \rangle$, $\langle 1,1,1 \rangle$. Values of \vec{h} , in the nn-approximation, are listed in Table for PSN and PMN stoichiometries ($1.5\vec{h}_{PSN} = \vec{h}_{PMN}$, owing to the different effective charges).

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Local fields at A-sites that have symmetrically distinct nearest neighbor B-site coordination cubes.

Configuration, Fig. 1 $i, j, k, l, m, n, o, p^\dagger$	$^\ddagger M_{256}$	$ \vec{h} $ PSN*	$ \vec{h} $ PMN	Crystallographic Direction
-,-,-,-,-,-,-,-	1	0	0	$\langle 0,0,0 \rangle$
-,-,-,-,-,-,-,+	8	6.93	10.39	$\langle 1,1,1 \rangle$
-,-,-,-,-,-,+,+	12	11.31	16.97	$\langle 1,1,0 \rangle$
-,-,-,-,-,+,-,+	12	8.00	12.00	$\langle 0,0,1 \rangle$
-,+,-,-,-,-,-,+	4	0	0	$\langle 0,0,0 \rangle$
-,-,-,-,-,+,,+,+	24	13.27	19.90	$\langle 1,1,3 \rangle$
-,-,+,-,-,-,+,-,+	8	6.93	10.39	$\langle 1,1,1 \rangle$
-,+,-,-,-,-,-,+,,+	24	6.93	10.39	$\langle 1,1,1 \rangle$
-,-,-,-,-,+,+,+,+	6	16.00	24.00	$\langle 0,0,1 \rangle$
-,+,-,+,-,+,-,+,-	2	0	0	$\langle 0,0,0 \rangle$
-,+,-,+,-,+,-,+	6	0	0	$\langle 0,0,0 \rangle$
-,-,+,-,-,-,+,,+,+	8	13.86	20.78	$\langle 1,1,1 \rangle$
-,-,-,+,-,+,,+,+,+	24	8.00	12.00	$\langle 0,0,1 \rangle$
+,-,-,-,-,-,+,,+,+	24	11.31	16.97	$\langle 1,1,0 \rangle$
+,-,+,-,-,-,+,,+,+	24	6.93	10.39	$\langle 1,1,1 \rangle$
+,+,-,-,-,-,+,,+,+	8	6.93	10.39	$\langle 1,1,1 \rangle$
+,+,+,-,-,-,+,,+,+	24	13.27	19.90	$\langle 1,1,3 \rangle$
+,-,+,-,-,-,+,,+,+	4	0	0	$\langle 0,0,0 \rangle$
+,+,+,-,-,-,+,,+,+	12	8.00	12.00	$\langle 0,0,1 \rangle$
+,+,+,-,-,-,+,,+,+	12	11.31	16.97	$\langle 1,1,0 \rangle$
+,+,+,-,-,-,+,,+,+	8	6.93	10.39	$\langle 1,1,1 \rangle$
+,+,+,-,-,-,+,,+,+	1	0	0	$\langle 0,0,0 \rangle$

† In column one: -1 implies Sc^{3+} , or Mg^{2+} ; $+1$ implies Nb^{5+} .

‡ Multiplicity (degeneracy) per 256 possible configurations.

* \vec{h} is in normalized units of the form $4\pi\epsilon_0\epsilon_\infty | \langle r_{Pb-B} \rangle \cdot |\vec{h}|$.

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