The Effect of Nearest Neighbor [Pb-O] Divacancy Pairs on the Ferroelectric-Relaxor Transition in Nano-Ordered $Pb(Sc_{1/2}Nb_{1/2})O_3$

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Molecular dynamics simulations were performed on a first-principles-based effective Hamiltonians for chemically short-range ordered $Pb(Sc_{1/2}Nb_{1/2})O_3$ with nearest neighbor [Pb-O] divacancy pairs. The divacancy-concentration ($X_{[Pb-O]}$) vs. temperature phase diagram was calculated, and it is topologically equivalent to the hydrostatic pressure (P) vs. temperature diagram: a ferroelectric ground-state phase at low $X_{[Pb-O]}$ (P); that transforms to a relaxor paraelectric phase at moderate $X_{[Pb-O]}$ (P); followed by a crossover to a normal paraelectric phase at high $X_{[Pb-O]}$ (P).

Keywords: PSN; Relaxor Ferroelectric; lead vacancies; oxygen vacancies; phase transitions; random fields

INTRODUCTION

Chemically disordered $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) exhibits a relaxor ferroelectric (RFE [1,2]) to normal ferroelectric (FE) transition; and Chu et al. [3] demonstrated that the addition of 1.7 atomic percent [Pb-O] divacancy pairs depresses the FE transition temperature (T_{FE}) of chemically disordered PSN from ≈373K to ≈338K. Chu et al. also reported similar and more complete results for isostructural $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) [4-6]. These results suggest that a sufficient concentration of divacancy pairs, $X_{[Pb-O]}$, will drive the system to a fully relaxor state, that has no FE ground-state phase. Introducing Pb-vacancies [7], or [Pb-O] divacancy pairs [8] increases the average strength of local ``random fields" $\langle \boldsymbol{h}_i \rangle$, (<...> indicates spatial statistical averaging) [9,10] that, at sufficient $X_{[Pb-O]}$ yield a fully relaxor state. Thus, $\langle \boldsymbol{h}_i \rangle$ can be regarded as a *nonordering* field [11] that tunes the proportions of RFE and FE character in the system.

Increasing hydrostatic pressure (P) drives chemically disordered PSN into a fully relaxor state [12] and the results of previous simulations by Tinte et al. [9] convincingly explain this as follows: 1) P has a negligible effect on $\langle \boldsymbol{h}_i \rangle$; 2) P smoothly and monotonically reduces FE well depths [13-15] and thus destabilizes the FE phase relative to the RFE state of the paraelectric (PE) phase; 3) Keeping $\langle \boldsymbol{h}_i \rangle$ constant while reducing FE well depth corresponds to an *indirect relative increase* in $\langle \boldsymbol{h}_i \rangle$. Because P *indirectly* increases $\langle \boldsymbol{h}_i \rangle$, it will only induce a FE-RFE

transition in a sample that has some RFE character even at P=0 (e.g. chemically disordered PSN). In a sample without significant $\langle \boldsymbol{h}_i \rangle$ (e.g. PSN with perfect chemical order) moderate pressure induces a FE-PE transition [16] without RFE character. Increasing $X_{[Pb\text{-}O]}$, *directly* increases $\langle \boldsymbol{h}_i \rangle$, and drives the system towards a FE-RFE transition, even if $\langle \boldsymbol{h}_i \rangle = 0$ initially (e.g. PSN with perfect chemical order has $\langle \boldsymbol{h}_i \rangle = 0$).

COMPUTATIONAL METHODS

Simulations were performed using the first-principle effective Hamiltonian, H_{eff}, which is described in detail in [10]; H_{eff} is an expansion of the potential energy of PSN in a Taylor series about a high-symmetry perovksite reference structure. It includes those degrees of freedom relevant to ferroelectric phase transitions:

$$H_{eff} = H(\{\boldsymbol{\xi}_i\}) + H(e_{\alpha\beta}) + H(\{\boldsymbol{\xi}_i\},\varepsilon_{\alpha\beta}) + PV + H(\{\boldsymbol{\xi}_i\}, \{\sigma_l\}, \{[Pb\text{-}O]\})$$

where $\boldsymbol{\xi}_i$ represents Pb-site centered local polar distortion variables; $e_{\alpha\beta}$ is the homogeneous strain term; $H(\{\boldsymbol{\xi}_i\},e_{\alpha\beta})$ is a strain coupling term; and PV the standard pressure-volume term. The first four terms are sufficient to model pressure-dependent phase transitions in a normal FE perovskite [17]. The fifth term, $H(\{\boldsymbol{\xi}_i\}, \{\sigma_l\}, \{[Pb\text{-}O]\})$, represents coupling between polar variables and "random" local fields, $\langle \boldsymbol{h}_i \rangle$ [10,18,19] from: 1) screened electric fields from the quenched distribution of Sc^{3+} and Nb^{5+} ions (σ_l); and 2) randomly distributed nearest neighbor (NN) Pb-O divacancy pairs, *[Pb-O]*.

Further details of the simulations used to calculate Figures 2 are given in: the review by Burton et al. [10]; the study of P-effects [9]; and the first-principles calculation of the dipole moment for a [Pb-O] NN divacancy pair in $PbTiO_3$ [8]. In Tinte et al [9] the simulation supercell contained 40x40x40 Pb-site local mode variables in a ``nano-ordered" chemical configuration of 20 ordered 800-site clusters, in a percolating random matrix which (for accounting purposes only) was subdivided into 60 disordered clusters. The same simulation cell is used here, except that $(40^3)X_{[Pb\text{-}O]}$ randomly selected local mode variables are replaced by dipole moments corresponding to NN [Pb-O] divacancy pairs. This treatment is distinct from Bellaiche et al. [7] which considered [Pb]-vacancies without charge-compensating [O]-vacancies; presumably the real system has both [Pb]- and [O]-vacancies as reported by Chu et al. [3].

RESULTS AND DISCUSSION

The simulations predict a significantly steeper slope for the FE-RFE transition than is observed experimentally. A possible explanation is that the populations of second- and possibly farther-neighbor divacancy pairs are significant, and that a realistic representation would include local electric fields induced by [Pb]- and [O]-vacancies and by closely bound [Pb-O] divacancy pairs. In fact, Vienna abinitio simulation package with projector aumented wave potentials and a generalized gradient approximation for the exchange/correlation potential [20] calculations for NN and next-NN (NNN) [Pb-O] divacancy pairs in a 2x2x2 supercell (40 atoms for PSN; 38 atoms with a divacancy) indicate that NNN divacancies are actually $\approx$0.016 eV lower in energy than NN divacancies (Fig. 1; Table 1).

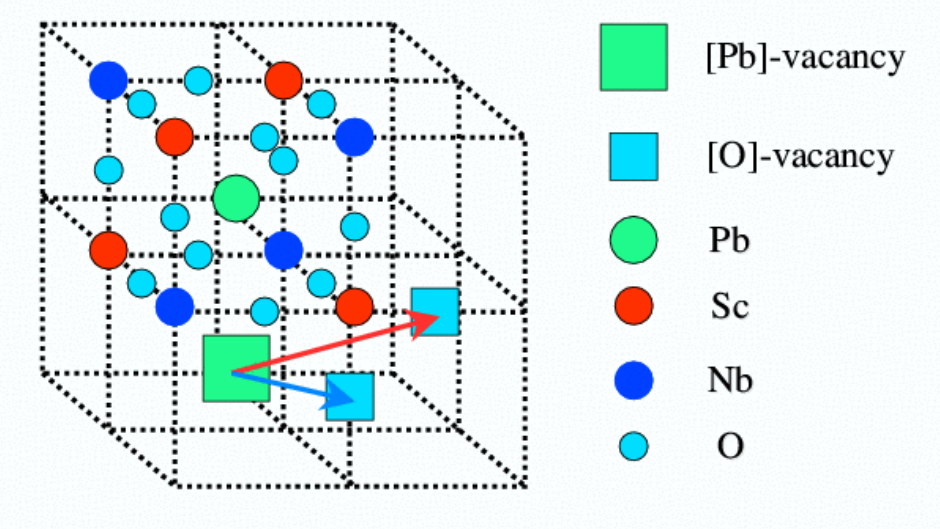

Figure 1: Representation of the 2x2x2 perovskite supercell for chemically ordered $Pb_8(Sc_4Nb_4)O_{24}$ and the $Pb_7(Sc_4Nb_4)O_{23}$ supercells with nearest- and next-nearest neighbor divacancy pairs. Atoms are only shown in 1/8 of the supercell.

There are two plausible relations from which to estimate formation energies for the NN and NNN divacancy pairs:

1. $\Delta E_f = E(Pb_7Sc_4Nb_4O_{23}) + E(\alpha\text{-}PbO) - E(Pb_8Sc_4Nb_4O_{24})$.

2. $\Delta E_f = E(Pb_7Sc_4Nb_4O_{23}) - (7/8)E(Pb_8Sc_4Nb_4O_{24}) - (1/2)E(ScNbO_4)$

Initial structures for *α-PbO* and Wolframite-structure $ScNbO_4$ were taken from [21] and [22] respectively (the $CdWO_4$ structure in their Table II). Munkhorst-Pack k-point meshes were used: 10x10x8 *α-PbO;* 6x6x6 $ScNbO_4$; 4x4x4 for $Pb_8Sc_4Nb_4O_{24}$ and $Pb_7Sc_4Nb_4O_{23}$ supercells. All calculations were done with an energy cuttoff of 500 eV, and all were fully relaxed. The (very similar) results from both are listed in Table 1 with corresponding volumes of formation, ΔV_f.

Table 1: Formation energies and formation volumes of nearest- and next-nearest-neighbor [Pb-O] divacancy pairs in a chemically ordered $Pb_8Sc_4Nb_4O_{24}$ supercell.

	Relation 1		*Relation 2*	
System	ΔE_f *(eV)*	ΔV_f *(A³)*	ΔE_f *(eV)*	ΔV_f *(A³)*
NN [Pb-O] divacancy	*1.54*	*37.6*	*1.51*	*43.6*
NNN [Pb-O] divacancy	*1.40*	*34.9*	*1.38*	*40.8*

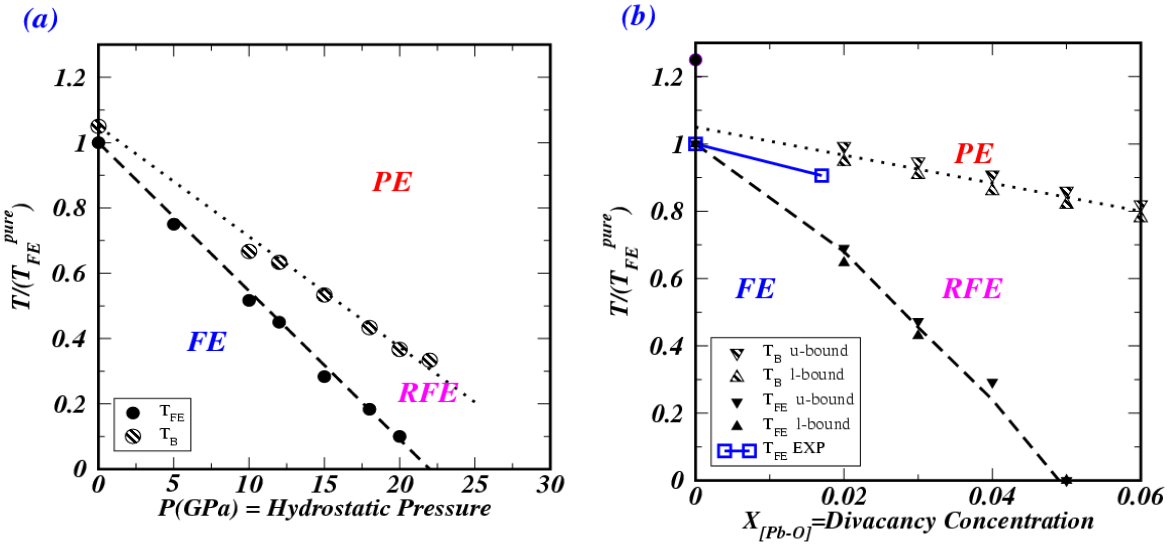

Figure 2: Predicted PSN phase diagrams: (a) pressure vs. reduced temperature [9]; (b) [Pb-O] divacancy concentration vs. reduced temperature. Dashed lines indicate ferroelectric-relaxor transitions. Dotted lines indicate Burns temperatures, T_B [23]. Triangles indicate upper- and lower-bounds, u- and l- respectively. The diagrams are topologically equivalent because both P and $X_{[Pb-O]}$ tune the delicate balance between FE well depth (increasing P reduces well depths) and the spatial average strength of the ``random fields," $\langle h_i \rangle$, that promote the relaxor state.

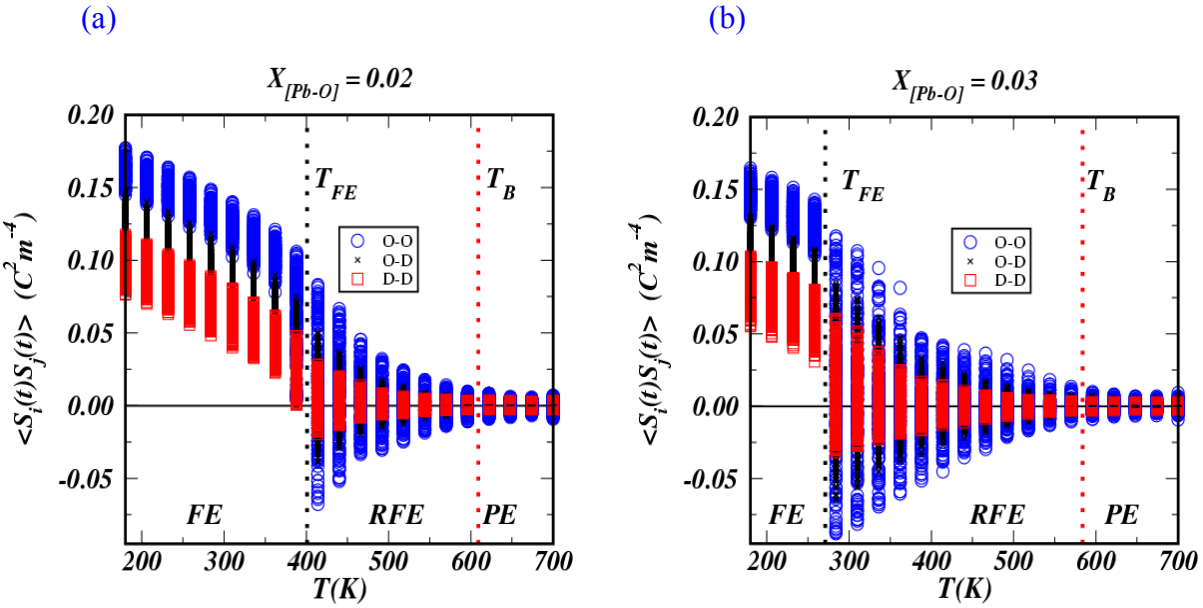

Figure 3: Predicted cluster-cluster spin products for a nano-ordered system with (a) $X_{[Pb-O]} = 0.02$ and (b) $X_{[Pb-O]} = 0.03$. Vertical lines indicate T_{FE} and T_B, the ferroelectric transition temperature and the Burns temperature [20], respectively. Increasing $X_{[Pb-O]}$ increases the relaxor interval and, drives the ferroelectric-relaxor transition to lower temperature.

The results presented in Table 1 indicate that our NN divacancy approximation is an oversimplification, because ΔE_f(NN) > ΔE_f(NNN). Thus, a realistic treatment would at least include about equal concentrations of NN- and NNN-divacancies, and probably isolated [Pb] and [O] vacancies as well, with the precise distribution depending on temperature. That said, there is no obvious reason to believe that a more realistic model for the vacancy distribution would yield qualitatively different results.

Calculated P vs. T/T_{FE} and $X_{[Pb\text{-}O]}$ vs. T/T_{FE} diagrams are plotted in Figs. 2a and 2b, respectively. Dashed lines indicate FE-RFE transitions, and dotted lines indicate Burns temperatures, T_B [20]. Qualitatively, the only apparent (small) difference between Figures 2a and 2b is that the RFE-FE transition in Fig. 2a is approximately linear, while in Fig. 2b it exhibits slight negative curvature.

As in the P-dependent simulations, cluster-cluster spin products were calculated for 800-site clusters (Figs. 3): O-O are the products between average spins on two chemically ordered clusters; O-D are products between one chemically ordered and one chemically disordered cluster; and D-D the products between two chemically disordered clusters. These results are analogous to those from P-dependent simulations, in that they exhibit the same hierarchy of correlations: O-O > O-D > D-D. Also, as $X_{[Pb\text{-}O]}$, and therefore $\langle h_i \rangle$, is increased, the RFE-state region grows, mostly at the expense of the FE-phase.

CONCLUSIONS

Directly increasing local "random fields", $\langle h_i \rangle$, by increasing $X_{[Pb\text{-}O]}$, enlarges the RFE-state region and ultimately drives the system into a fully relaxor state. This progression mirrors the phenomenology of PSN under increasing hydrostatic pressure. The essential difference is that $X_{[Pb\text{-}O]}$ *directly* increases $\langle h_i \rangle$, whereas increasing pressure makes FE well depths shallower, which corresponds to an thus *indirect* increase in $\langle h_i \rangle$, relative to FE well depth.

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