

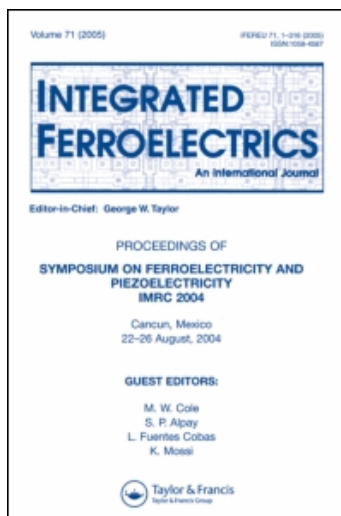
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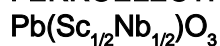


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THE EFFECT OF NEAREST NEIGHBOR [PbO] DIVACANCY PAIRS ON THE FERROELECTRIC-RELAXOR TRANSITION IN NANO-ORDERED



B.P. BURTON^a; SILVIA TINTE^a; ERIC COCKAYNE^a; U.V. WAGHMARE^b

^a Ceramics Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA ^b J. Nehru Theoretical Sciences Unit, JNCASR, Jakkur, Bangalore, India

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The Effect of Nearest Neighbor [Pb–O] Divacancy Pairs on the Ferroelectric-Relaxor Transition in Nano-Ordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$

B. P. Burton,^{1,*} Silvia Tinte,¹ Eric Cockayne,¹ and U. V. Waghmare²

¹Ceramics Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-8520, USA

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

ABSTRACT

Molecular dynamics simulations were performed on a first-principles-based effective Hamiltonians for chemically short-range ordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ with nearest neighbor [Pb–O] divacancy pairs. The divacancy-concentration ($X_{[\text{Pb}-\text{O}]}$) 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 $X_{[\text{Pb}-\text{O}]}$ (P); that transforms to a relaxor paraelectric phase at moderate $X_{[\text{Pb}-\text{O}]}$ (P); followed by a crossover to a normal paraelectric phase at high $X_{[\text{Pb}-\text{O}]}$ (P).

Keywords: PSN, relaxor ferroelectric, lead vacancies, oxygen vacancies, phase transitions, random fields

INTRODUCTION

Chemically disordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (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 ~ 373 K to ~ 338 K. Chu et al. also reported similar and more complete results for isostructural $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST) [4–6]. These results suggest that a sufficient concentration of divacancy pairs, $X_{[\text{Pb}-\text{O}]}$, 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] (Fig. 1) increases the average

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*Corresponding author. E-mail: benjamin.burton@nist.gov

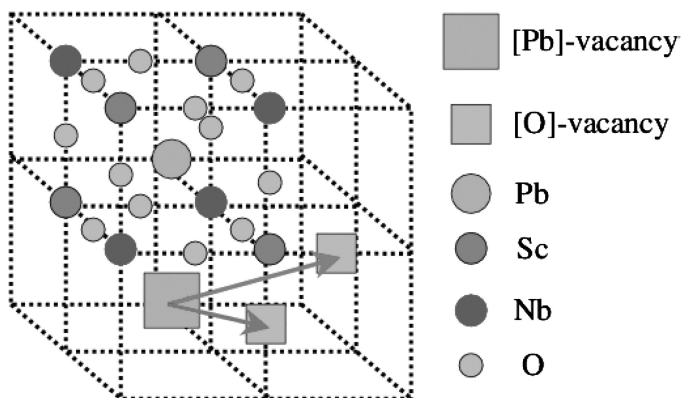


Figure 1. Representation of the $2 \times 2 \times 2$ perovskite supercell for chemically ordered $\text{Pb}_8(\text{Sc}_4\text{Nb}_4)\text{O}_{24}$ and the $\text{Pb}_7(\text{Sc}_4\text{Nb}_4)\text{O}_{23}$ supercells with nearest- and next-nearest neighbor divacancy pairs. Atoms are only shown in $1/8$ of the supercell. (See Color Plate V)

strength of local “random fields” $\langle \mathbf{h}_i \rangle$, ($\langle \dots \rangle$ indicates spatial statistical averaging) [9,10] that, at sufficient $X_{[\text{Pb}-\text{O}]}$ yield a fully relaxor state. Thus, $\langle \mathbf{h}_i \rangle$ can be regarded as a *nonordering* field [11] that tunes the proportions of RFE and FE character in the system.

Increasing hydrostatic pressure (P, Fig. 2a) 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 $\langle \mathbf{h}_i \rangle$; 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 $\langle \mathbf{h}_i \rangle$ constant while reducing FE well depth corresponds to an *indirect relative increase* in $\langle \mathbf{h}_i \rangle$. Because P *indirectly* increases $\langle \mathbf{h}_i \rangle$, 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 $\langle \mathbf{h}_i \rangle$ (e.g. PSN with perfect chemical order) moderate pressure induces a FE-PE transition [16] without RFE character. Increasing $X_{[\text{Pb}-\text{O}]}$, *directly* increases $\langle \mathbf{h}_i \rangle$, and drives the system towards a FE-RFE transition, even if $\langle \mathbf{h}_i \rangle = 0$ initially (e.g. PSN with perfect chemical order has $\langle \mathbf{h}_i \rangle = 0$).

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 perovskite reference

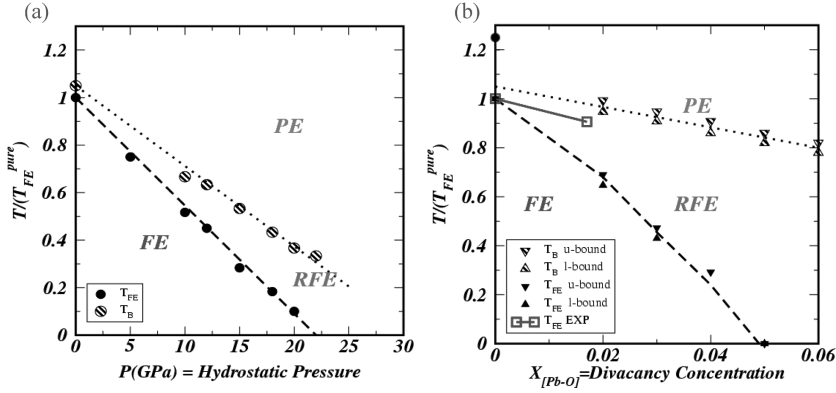


Figure 2. Predicted PSN phase diagrams: (a) pressure vs. reduced temperature [9]; (b) [Pb—O] divacancy concentration vs. reduced temperature. Dashed lines indicate ferroelectric-relaxor transitions. Dotted lines indicate Burns temperatures, T_B [23]. Triangles indicate upper- and lower-bounds, u- and 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. (See Color Plate VI)

structure. It includes those degrees of freedom relevant to ferroelectric phase transitions:

$$H_{eff} = H(\{\mathbf{X}_i\}) + H(e_{\mathcal{Q}}) + \sum_i \mathbf{X}_i \cdot \mathbf{e}_{\mathcal{Q}} + PV + H(\{\mathbf{X}_i\}, \{\mathbf{f}_i\}, \{[Pb-O]\} \mathcal{Q}),$$

where \mathbf{X}_i represents Pb-site centered local polar distortion variables; $e_{\mathcal{Q}}$ is the homogeneous strain term; $H(\{\mathbf{X}_i\}, e_{\mathcal{Q}} \mathcal{Q})$ 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, $H(\{\mathbf{X}_i\}, \{\mathbf{f}_i\}, \{[Pb-O]\} \mathcal{Q})$, represents coupling between polar variables and “random” local fields, $\langle h_i \rangle$ [10,18,19] from: 1) screened electric fields from the quenched distribution of Sc³⁺ and Nb⁵⁺ ions (\mathbf{f}_i); and 2) randomly distributed nearest neighbor (NN) Pb—O divacancy pairs, $[Pb-O]$.

Further details of the simulations used to calculate Fig. 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 PbTiO₃ [8]. In Tinte et al. [9] the simulation supercell contained $40 \times 40 \times 40$ 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 $(40^3)X_{[Pb-O]}$ randomly selected local mode variables are replaced by dipole moments corresponding to NN [Pb—O] divacancy pairs. This

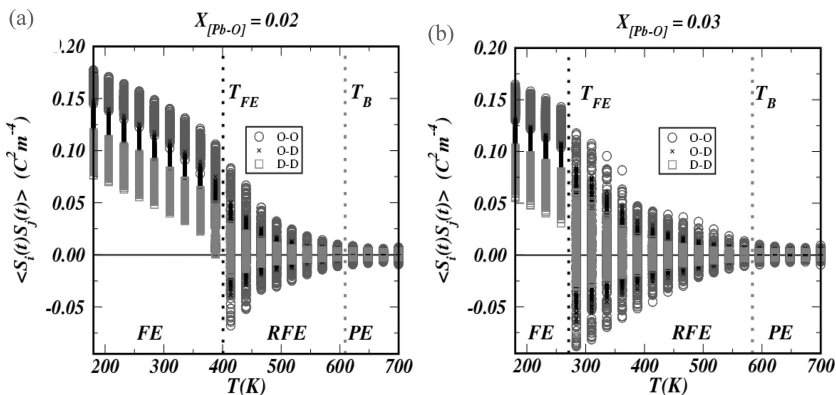


Figure 3. Predicted cluster-cluster spin products for a nano-ordered system with (a) $X_{[\text{Pb-O}]} = 0.02$ and (b) $X_{[\text{Pb-O}]} = 0.03$. Vertical lines indicate T_{FE} and T_{B} , the ferroelectric transition temperature and the Burns temperature [20], respectively. Increasing $X_{[\text{Pb-O}]}$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

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 augmented 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 $2 \times 2 \times 2$ supercell (40 atoms for PSN; 38 atoms with a divacancy) indicate that NNN divacancies are actually ~ 0.016 eV lower in energy than NN divacancies (Fig. 1; Table 1).

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

1. $\mathbb{E}_f = E(\text{Pb}_7\text{Sc}_4\text{Nb}_4\text{O}_{23}) + E(\mathcal{D}\text{-PbO}) - E(\text{Pb}_8\text{Sc}_4\text{Nb}_4\text{O}_{24})$.
2. $\mathbb{E}_f = E(\text{Pb}_7\text{Sc}_4\text{Nb}_4\text{O}_{23}) - (7/8)E(\text{Pb}_8\text{Sc}_4\text{Nb}_4\text{O}_{24}) - (1/2)E(\text{ScNbO}_4)$

Initial structures for \mathcal{D} -PbO and Wolframite-structure ScNbO_4 were taken from [21] and [22] respectively (the CdWO_4 structure in their Table II).

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 (Å ³)	ΔE_f (eV)	ΔV_f (Å ³)
NN [Pb-O] divacancy	1.54	37.6	1.51	43.6
NNN [Pb-O] divacancy	1.40	34.9	1.38	40.8

Munkhorst-Pack k-point meshes were used: $10 \times 10 \times 8$ \mathcal{S} -PbO; $6 \times 6 \times 6$ ScNbO₄; $4 \times 4 \times 4$ for Pb₈Sc₄Nb₄O₂₄ and Pb₇Sc₄Nb₄O₂₃ supercells. All calculations were done with an energy cutoff of 500 eV, and all were fully relaxed. The (very similar) results from both are listed in Table 1 with corresponding volumes of formation, $\mathcal{P}V_f$.

The results presented in Table 1 indicate that our NN divacancy approximation is an oversimplification, because $\mathcal{P}E_f(\text{NN}) > \mathcal{P}E_f(\text{NNN})$. 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-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-O], and therefore $\langle \mathbf{h}_i \rangle$, is increased, the RFE-state region grows, mostly at the expense of the FE-phase.

CONCLUSIONS

Directly increasing local “random fields”, $\langle \mathbf{h}_i \rangle$, by increasing X_[Pb-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 $X_{[\text{Pb}-\text{O}]}$ *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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