

# Unexpected Ground State Structures in Relaxor Ferroelectrics

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## Abstract

Cluster expansion Hamiltonians derived from pseudopotential total energies were used to predict ground-state (GS) cation configurations for some  $A(B_{1/2}^{3+}B_{1/2}^{\prime 5+})O_3$ ,  $A(B_{1/3}^{2+}B_{2/3}^{\prime 5+})O_3$ , and  $[A_{1/2}^{1+}A_{1/2}^{\prime 3+}]BO_3$  perovskites. Predicted GS structures for  $Pb(Mg_{1/3}Nb_{2/3})O_3$  (PMN),  $Pb(Mg_{1/3}Ta_{2/3})O_3$ ,  $[Na_{1/2}Bi_{1/2}]TiO_3$ , and  $[K_{1/2}Bi_{1/2}]TiO_3$  differ from those predicted by a purely ionic model. Monte Carlo simulation of cation order-disorder phenomena in PMN predicts the transition sequence:  $[001]_{NCC'} \rightarrow 1:1 \rightarrow Disordered$ .

Keywords: perovskites, relaxor ferroelectrics, cation ordering, ground states.

## INTRODUCTION

Computational studies of cation ordering energetics in some  $A(B, B')O_3$  and  $[A, A']BO_3$  perovskites predict unexpected ground-state (GS) structures for  $Pb(Mg_{1/3}Nb_{2/3})O_3$  (PMN),  $Pb(Mg_{1/3}Ta_{2/3})O_3$  (PMT),  $[Na_{1/2}Bi_{1/2}]TiO_3$  (NBT) and  $[K_{1/2}Bi_{1/2}]TiO_3$  (KBT); but the expected NaCl-type GS for  $Pb(Sc_{1/2}Nb_{1/2})O_3$  (PSN) and  $Pb(Sc_{1/2}Ta_{1/2})O_3$  (PST). Here, "unexpected" is used for GSs that are different from those predicted by a purely ionic model, which are: A 2:1 layer sequence perpendicular to  $[111]_{cubic}$  for  $A(B_{1/3}^{2+}B_{2/3}^{\prime 5+})O_3$  perovskites e.g. PMN or PMT; NaCl-type ordering on the A-sites for  $[A_{1/2}^{1+}A_{1/2}^{\prime 3+}]BO_3$  perovskites e.g. NBT or KBT; NaCl-type ordering on B-sites for  $A(B_{1/2}^{3+}B_{1/2}^{\prime 5+})O_3$  perovskites e.g. PSN or PST. As discussed in previous papers [1, 2, 3], unexpected GS structures in PMN and PMT can be rationalized as a consequence of interplay between long-range ionic and short-range (Pb-O) interactions which determine the the configurational contribution to the total energy ( $\Delta E_c$ ). Specifically,  $Pb^{2+}$  ions are attracted to underbonded oxygens, e.g. those between two  $Mg^{2+}$  ions. This Pb- underbonded oxygen interaction stabilizes configurations that have high ionic contributions to  $\Delta E_c$ . In PMN and PMT, the short-range Pb-O interactions are sufficient to stabilize unexpected GS structures, but in PSN and PST the ionic contribution dominates and the observed GS is the expected NaCl-type. In NBT [7] and KBT, all oxygens occupy sites between two  $Ti^{4+}$  ions, but the configurations of  $Bi^{3+}$  and  $Na^{1+}$ , or  $K^{1+}$ , create under- and overbonded oxygens which interact with  $Bi^{3+}$  ions in an analogous way.

# TOTAL ENERGY CALCULATIONS

Total energies were calculated for many perovskite based superstructures, and the results are plotted as formation energies ( $\Delta E$ ) in Figures 1 and 3 where  $\Delta E$  is plotted relative to fictive end members such as. For example the mechanical mixture  $(1-X) \circ PbNbO_3 + X \circ PbMgO_3$  is the reference state for PMN, and similarly for the other systems. All calculations were performed with the Vienna *ab initio* simulation program (VASP)[8] using ultrasoft Vanderbilt[9] type plane-wave pseudopotentials with a local density approximation for exchange and correlation energies. Electronic degrees of freedom were optimized with a conjugate gradient algorithm, and both cell constant and ionic positions were fully relaxed. Valence electron configurations for the pseudopotentials are: *Pb*  $5d^{10}6p^26s^2$ ; *Mg*  $2p^63s^2$ ; *Nb*  $4p^65s4d^4$ ; *Ta*  $5d^36s^2$ ; *Sc*  $3p^63d4s^2$ ; *Na*  $3s^1$ ; *Bi*  $6s^26p^3$ ; *Ti*  $4s^23d^2$ ; *O*  $2p^6$ . An energy cutoff of 395.7 eV was used, in the "high precision" option which guarantees that *absolute* energies are converged to within a few meV (a few tenths of kJ/mol; mol =  $ABO_3$ ). To promote cancellation of errors, all of the calculations for low-energy structures were performed with equivalent K-point meshes: 6x6x6 within the Brillouin zone for  $ABO_3$  pseudo primitive unit cells for PMN and PMT; 8x8x8 for PSN, PST, NBT and KBT.

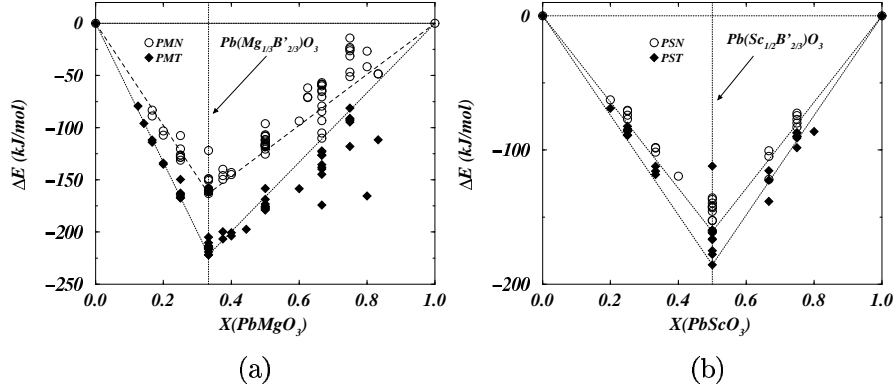


Figure 1: Formation energies for (a) PMN and PMT; (b) PSN and PST .

## GROUND STATES

Reported GS structures are *not only* the lowest energy configurations for which VASP calculations were tried,  $GS_{VASP}$ , they are also the predicted GSs that one obtains by fitting cluster expansion (CE) Hamiltonians [10, 11] to the sets  $\{\Delta E_{VASP}\}$ ,  $GS_{CE}$ . The fitting was done as follows:

- Fit a CE to the set of formation energies  $\{\Delta E_{VASP}\}$ .

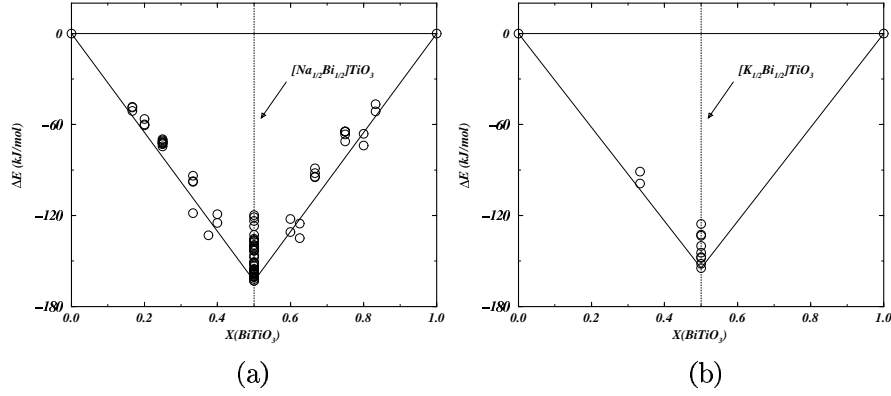


Figure 2: Formation energies for: a) NBT; b) KBT.

- Use the CE to predict a new  $GS_{CE}$ ; by performing a brute force GS search on a large supercell.
- If  $GS_{CE}$  is not an element of the set  $\{\Delta E_{VASP}\}$ , then calculate  $\Delta E_{VASP}$  for the newly predicted GS.
- If  $GS_{CE}$  is the same as  $GS_{VASP}$  calculate  $\Delta E_{VASP}$  for the lowest predicted excited states that are not elements of  $\{\Delta E_{VASP}\}$ .
- Repeat the last step three times, and see if it leads to a new predicted GS.

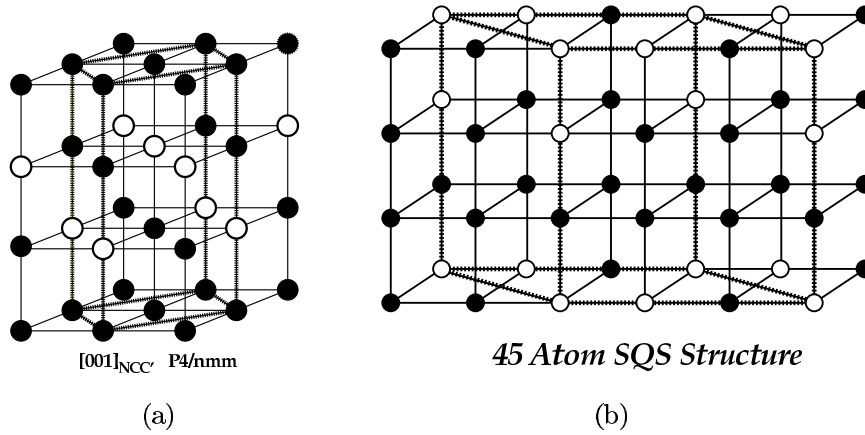


Figure 3: Predicted Ground-State B-site cation configurations for: (a) PMN, the  $[001]_{NCC'}$  structure in which Nb-layers perpendicular to  $[001]$  alternate with chessboard ordered double layer blocks; (b) PMT, the special quasi-random structure, SQS.

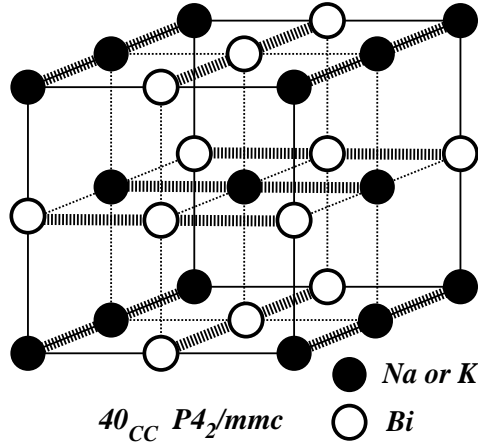


Figure 4: Predicted Ground-State A-site cation configuration for NBT and KBT.

Pseudocubic B-site cation configurations of the predicted GS structures for PMN and PMT are shown in Figures 3a and 3b respectively. The  $[001]_N CC'$  structure [2] is not so surprising because it is also the GS predicted by a slightly modified ionic model [5]. The predicted PMT GS is thoroughly surprising however, because it is also the structure chosen by Wu et al.[6] as a special quasi-random structure (SQS) [4] because its chemical correlations are so close to those of a random distribution of B-site cations. The pseudocubic A-site configuration of the GS structure predicted for NBT and KBT, the  $40_{CC}$  ( $40_{CrissCross}$  Figure 4.

## FINITE TEMPERATURE CALCULATIONS

The CE Hamiltonians used for GS analysis can also be used for finite temperature (T) Monte Carlo (MC) simulations of cation ordering. For example, a CE fit to the formation energies for PMN were used to generate the results shown in Figure 5. These results indicate a sequence of transitions, with increasing (reduced) temperature,  $\tau$ : for  $\tau \leq 20$  the predicted GS (Fig. 3a; solid line) is most stable; for  $25 \leq \tau \leq 35$  a 1:1 ( $Fm\bar{3}m$  bold dotted line); at  $35 \leq \tau$  the system is disordered. The fine dotted line that remains near zero is the order parameter for the expected ( $P\bar{3}m1$ ) GS which is never stable. This predicted transition sequence:

$$[001]_N CC' \rightarrow 1:1 \rightarrow Disordered$$

is entirely consistent with experimental work on PMN [12, 13, 14] and PMT [15], which clearly demonstrate that 1:1 ordered phases are stable in

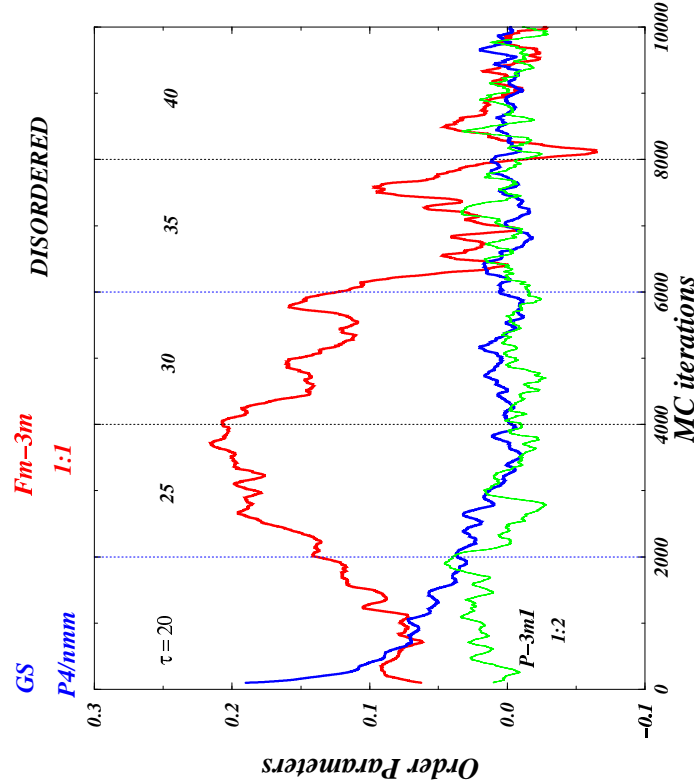


Figure 5: Temperature dependent order parameters for three different ordered phases with PMN composition,  $Pb(Mg_{1/3}Nb_{2/3})O_3$ : At low T the predicted GS,  $[001]_{NCC'}$ , is most stable; at intermediate T, a 1:1 phase is predicted; at high T, the system is disordered.

$PMN_{0.9}PSN_{0.1}$ [14] and PMT[15]. The 1:1 phases described in these studies are referred to as conforming to the "random site model" in which one B-site is occupied primarily by Nb while the other is  $\sim Mg_{2/3}Nb_{1/3}$ . Note that the presence of the disordered site ( $\sim Mg_{2/3}Nb_{1/3}$ ) implies the existence of some lower-T GS phase which minimizes total energy through further B-site ordering.

## CONCLUSIONS

Unexpected GS structures, different from those predicted by a purely ionic model, are predicted for the systems PMN, PMT, NBT and KBT. This deviation from ionic GS structures results from competition between long-range coulomb interactions and short-range Pb-O or Bi-O interactions. In PSN and PST the Pb-O interaction is not strong enough to compete and long-range coulomb in-

teractions dictate the GS structure. A MC simulation of cation ordering in PMN predicts the transition sequence:  $[001]_{NCC'} \rightarrow 1 : 1 \rightarrow \textit{Disordered}$ , consistent with experimental[12, 13, 14].

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