Prediction of the $[Na_{1/2}Bi_{1/2}]TiO_3$ Ground State

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Published in Fundamental Physics of Ferroelectrics 2001,
AIP Conference Proceedings **582**, 82- (2001) Henry Krakauer Ed.

Abstract. The Vienna Ab-initio Simulation Package (VASP) was used to perform fully relaxed, planewave pseudopotential calculations of formation energies (ΔE_{VASP}) for a large number of ordered supercells in the perovskite based system $NaTiO_3 - BiTiO_3$, including 38 supercells with the $[Na_{1/2}Bi_{1/2}]TiO_3$ (NBT) composition. The ΔE_{VASP} were used to fit a cluster expansion Hamiltonian to verify that the no other superstructure is predicted to have lower energy than the lowest ΔE_{VASP}, which is a 40 atom supercell with space group symmetry $P11m$. Its chemical ordering is characterized by pseudocubic doubling of the cell constants, with alternating [100] rows of Na and Bi atoms in (hk0) planes plus alternating [010] rows in (hk$\frac{1}{2}$) planes. Chemical ordering alone reduces space group symmetry from cubic, $Pm\overline{3}m$, to tetragonal, $P4_2/mmc$, and octahedral tilting ($a^-a^-c^+$ system) further reduces it to monoclinic, $P11m$.

INTRODUCTION

Sodium bismuth titanate, $[Na_{1/2}Bi_{1/2}]TiO_3$ (NBT), has attracted much attention as a lead-free piezoceramic [1–14] with properties intermediate between those of $Pb(Zr_{1-x}Ti_x)O_3$-based materials and Pb-based relaxor ferroelectrics such as $Pb(Mg_{1/3}Nb_{2/3})O_3$. Many studies concentrated on temperature induced phase transitions (rhombohedral? $\rightarrow$ $530K$ $\rightarrow$ tetragonal; tetragonal $\rightarrow$ $783-813K$ $\rightarrow$ cubic) in samples of NBT, NBT-$BaTiO_3$, or NBT-$PbTiO_3$ [6,11,12]; subject to the implicit assumption that A-site cations were disordered [12–14]. Some studies [4,5,7,9–11] however, invoked chemical long-range-order (LRO) or short-range-order (SRO) to explain diffraction data [7,9–11] or Raman spectra [4,5]. In all of these latter studies [4,5,7,9,10] it was assumed that cation ordering was of NaCl-type, $Fm\overline{3}m$, (Figure 1a) although Chiang et al. [11] proposed a $Pm\overline{3}m$ structure as a possible ordering for a sample with composition

$[Na_{7.5/16}Bi_{7.5/16}Ba_{1/16}]TiO_3$ (Figure 1b).

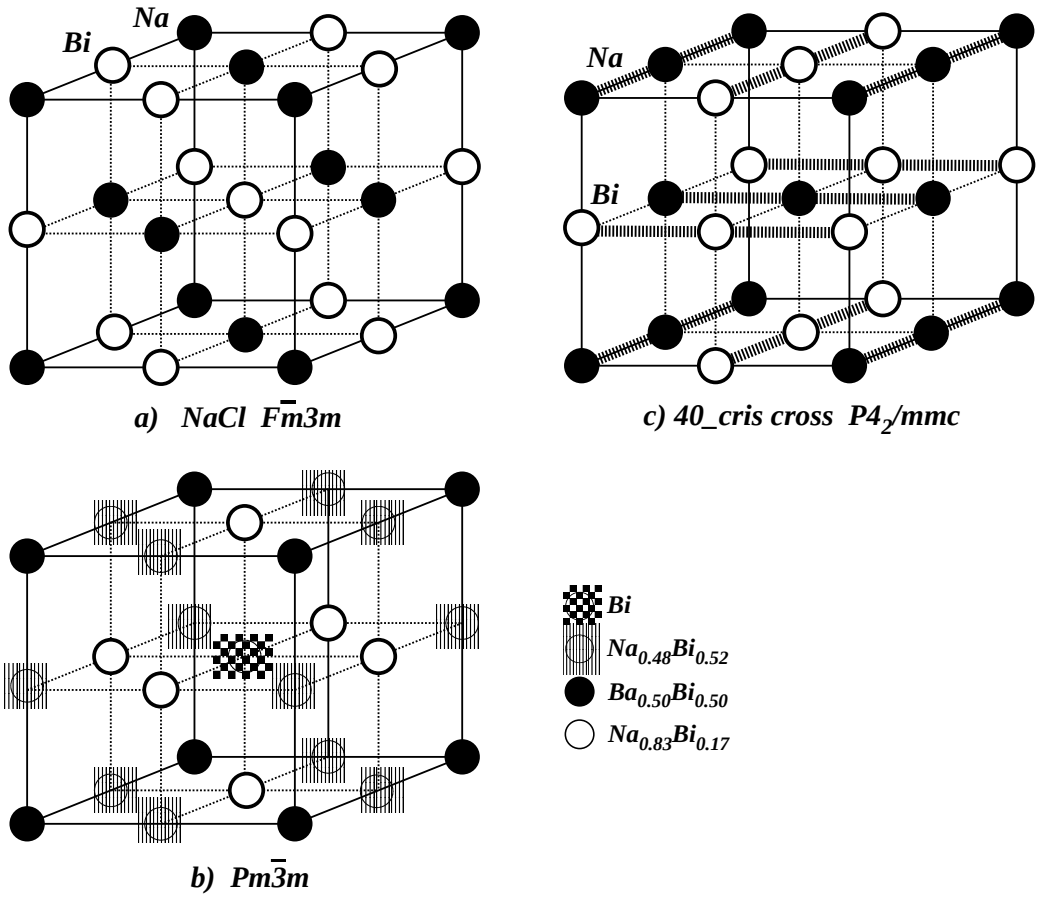

FIGURE 1. A-site patterns of chemical ordering: a) NaCl-type; b) A $Pm\bar{3}m$ partially ordered configuration proposed by Chiang et al. [11]; c) The predicted ground-state configuration 40_{CC}, $P4_2/mmc$.

It is reasonable to expect that the 1:1 mixture of Na^{1+} and Bi^{3+} in $[Na_{1/2}Bi_{1/2}]TiO_3$ would exhibit NaCl-type ordering, because NaCl is the ground-state (GS) structure for equal numbers of plus and minus charges on a simple cubic array of sites; and in NBT, Bi^{3+} and Na^{1+} have effective charges of +1 and -1 respectively, because the average A-site charge is +2. Also, the low-temperature ferroelectric phase has generally been described as rhombohedral [1,2,10] with $a^-a^-a^-$ octahedral tilting [18] which is, for example, the ferroelectric state for NaCl-ordered perovskites such as $Pb(Sc_{1/2}Ta_{1/2})O_3$ [15] in which ordering occurs on the B-sites. Soukhojak et al. [12], however, observed only $(h+\frac{1}{2}, k+\frac{1}{2}, 0)$ type superlattice reflections, not $(h+\frac{1}{2}, k+\frac{1}{2}, l+\frac{1}{2})$, and reported $a^0a^0c^+$ tilting which implies space group symmetry that is tetragonal or lower; and they found no evidence for NaCl-type LRO. The calculations discussed below clearly rule out NaCl-type LRO in the NBT GS, and predict instead that the GS is the 40_{CC} structure; a 40

atom supercell with "crisscross" (CC) rows of Na^{1+} and Bi^{3+} cations perpendiculat to [001] (Figure 1c).

TOTAL ENERGY CALCULATIONS

Total energies were calculated for 65 perovskite based superstructures in the system $NaTiO_3 - BiTiO_3$, including 38 supercells with the NBT composition; these results are plotted as formation energies, relative to mechanical mixtures of $(1-X) \circ NaTiO_3 \; + \; X \circ BiTiO_3$, in Figures 2a and b. All calculations were performed with the Vienna *ab initio* simulation program (VASP) [16] using ultrasoft Vanderbilt [17] 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: Na $3s^1$; Bi $6s^2 6p^3$; Ti $4s^2 3d^2$; 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: 8x8x8 within the Brillouin zone for ABO_3 pseudo primitive unit cells.

As seen in (Figure 2a) there is approximately linear variation of $\Delta E_{VASP}(X)$ between the calculated GS (40_{CC}) and the fictive end members $NaTiO_3$ and $BiTiO_3$. This trend reflects linear variation of the concentrations of electrons that are either: forced into the conduction band ($X<\frac{1}{2}$); or depleted from the valence band ($X>\frac{1}{2}$), as functions of composition. At the $X = \frac{1}{2}$, $[Na_{1/2}Bi_{1/2}]TiO_3$, composition (Figure 2b), it is clear that many superstructures have lower ΔE_{VASP} than the NaCl-type. Therefore, if cation ordering is present in the NBT samples used for experiments, it is clearly not LRO, or SRO, of the NaCl-type.

GROUND STATE SEARCH

The 40_{CC} structure is *not only* the lowest energy configuration that was tried, GS_{VASP}, it is also the predicted GS that one obtains by fitting a cluster expansion (CE) Hamiltonian [19,20] to the set $\{\Delta E_{VASP}\}$, GS_{CE}. The fitting was done as follows:

- Fit a CE to the set of fomnation energies $\{\Delta E_{VASP}\}$.
- Use the CE to predict a new GS_{CE}; by performing a brute force GS search on a 2x2x4 supercell (16 A-sites).

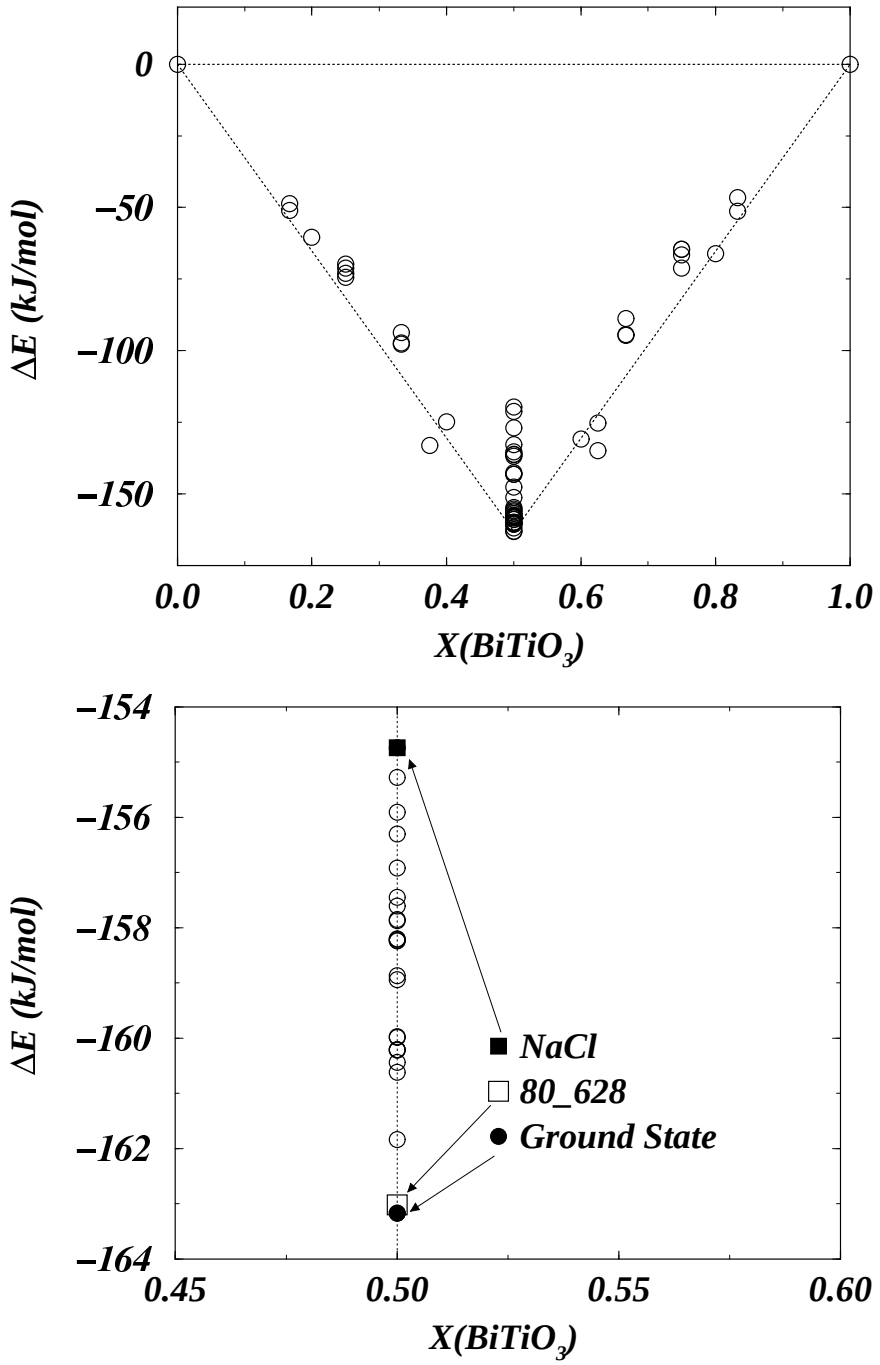

FIGURE 2. a) Formation energies per ABO_3 mol for supercells in the system $NaTiO_3 - BiTiO_3$. b) Formation energies near the 40_{CC} GS structure which is the predicted ground-state. Also marked are the formation energies for NaCl-type ordering (•) and the 80_{628} structure (□).

- If GS_{CE} is not an element of the set $\{\Delta E_{VASP}\}$, then calculate ΔE_{VASP} for the predicted GS.
- If GS_{CE} is the same as GS_{VASP} calculate ΔE_{VASP} for the lowest predicted excited states that are not elements of $\{\Delta E_{VASP}\}$.
- The last step was repeated three times, and did not lead to a new predicted GS; did not predict $GS_{CE} < GS_{VASP}$.

As noted above, chemical ordering in the 40_{CC} structure (Figure 1c) reduces its space group symmetry from $Pm\overline{3}m$ to $P4_2/mmc$. Octahedral tilting [18] in the $a^-a^-c^+$ system (Figures 3a-c) further reduces space group symmetry to the acentric monoclinic group $P11m$ (c-axis unique).

$[0, 1/2, 0]$ AND $[1/2, 0, 0]$ STACKING FAULTS

Disregarding octahedral tilting, the introduction of $[0, 1/2, 0]$, or $[1/2, 0, 0]$, stacking faults in every other (h,k,0) layer of the 40_{CC} GS structure leads to the 80_{628} structure (Figures 4a-d and 2b); called 80_{628} because there are 80 atoms in the supercell, and it is the 628'th 1:1 configuration in a brute force enumeration for the 2x2x4 supercell. Performing the VASP calculation, and allowing atomic positions to relax, leads to $a^+a^+c^-$ octahedral tilting in the orthorhombic space group $Pmm2$. The energy difference between 80_{628} and 40_{CC} is tiny (0.15 kJ/mol) [1] and 80_{628} is the lowest excited state shown in Figure 2b. This very small difference is expected because 80_{628} has identical (chemical) correlations [19] for all clusters within the pseudoprimitive unit cube. Such a small energy difference implies that cation ordering in 80_{628} is highly susceptible to $[0, 1/2, 0]$ and $[1/2, 0, 0]$ stacking faults. Note that in the relaxed structure a- and b-axes are symmetrically distinct, so one might expect different energies for $[0, 1/2, 0]$ and $[1/2, 0, 0]$ stacking faults; however, in terms of chemical ordering alone, $[0, 1/2, 0]$ and $[1/2, 0, 0]$ stacking faults are equivalent. It is only the tetragonal to monoclinic symmetry breaking associated with octahedral tilting that allows symmetrically distinct a- and b-axis relaxations.

DISCUSSION

The VASP results (Figure 2b) clearly rule out NaCl-type ordering of Na^{1+} and Bi^{3+} on A-sites, and the electron diffraction results of Soukhojak et al. [12] suggest that their samples exhibited no NaCl-type LRO, or SRO; their samples were cooled from 1350-800°C at 5°C per hr, and TEM hot-stage measurements were made between 20°C and 600°C. The predicted 40_{CC} GS with $a^-a^-c^+$ octahedral tilting is consistent with the diffraction data of Soukhojak et al. [12], but the extremely

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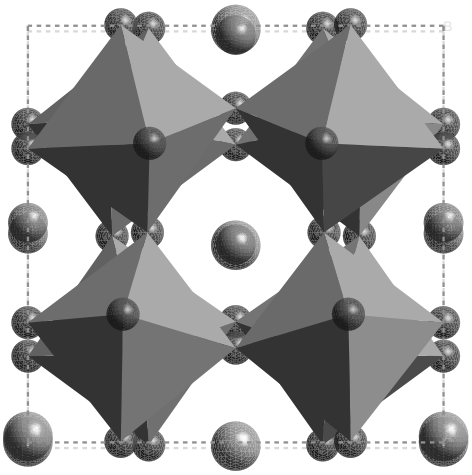
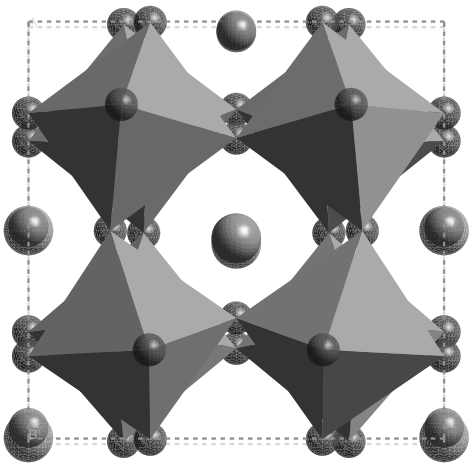
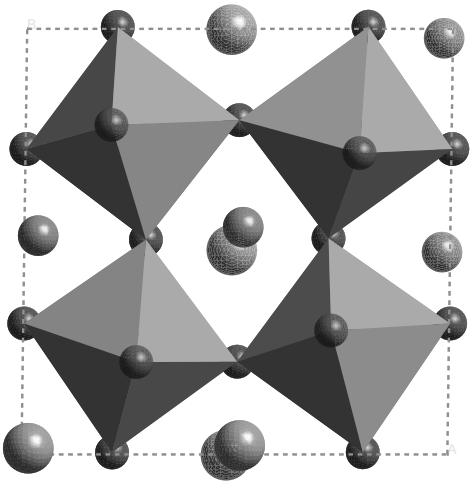
[1] 0.15 kJ/mol is about three times the precision of VASP calculations.



a) [100]



b) [010]



c) [001]

FIGURE 3. The monoclinic 40_{CC} structure, space group $P11m$ (c-axis unique), $a^-a^-c^+$ tilt system, projected on a) [001]; b) [010]; c) [100].

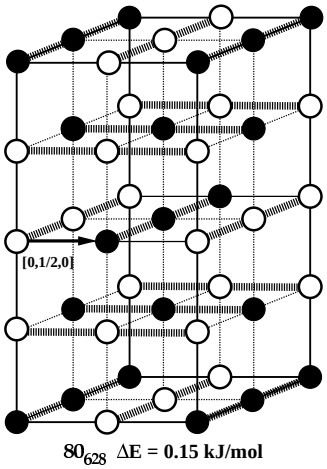
low energy difference between 40_{CC} and 80_{628} structures suggests that real samples probably have substantial disorder. Disordered samples are permissive of all tilting systems; so, the essential unanswered question is, does 40_{CC}-related LRO, or more likely SRO, influence observed octahedral tilting? Answering this question requires a reexamination of the diffraction data to see if 40_{CC}-related SRO is detectable.

CONCLUSIONS

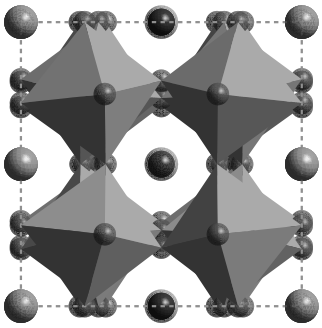
If A-site cation ordering occurs in NBT it is clearly not of the NaCl-type. The predicted GS is the 40_{CC} structure (Figures 1c, 3a-c). Because the stacking fault energy that relates the 40_{CC} and 80_{628} structures is so small, one expects the 40_{CC} structure to be highly susceptible to disorder. Therefore, if cation ordering has a significant effect on the observed properties of NBT it is most probably SRO related to the 40_{CC} structure.

ACKNOWLEDGEMENT

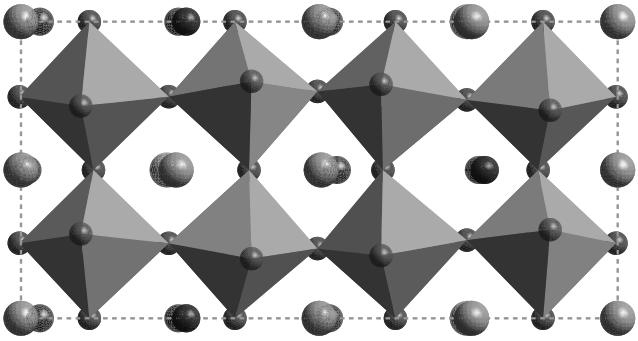
The authors thank Igor Levin for many helpful discussions about octahedral tilting.



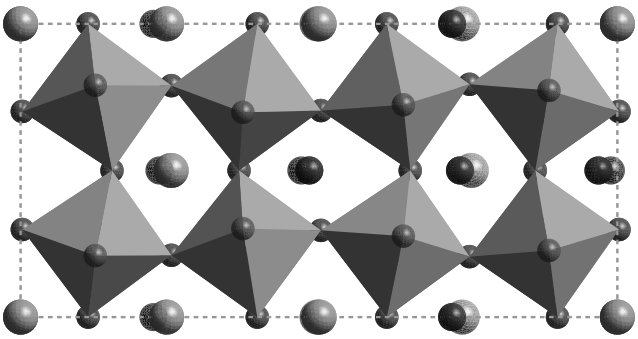
a)



b) [001]



c) [100]



d) [010]

FIGURE 4. The orthorhombic 80_{628} structure, space group $Pmm2$, tilt system $a^+a^+c^-$, which is related to the 40_{CC} structure by a [0,1/2,0] stacking fault; a) Chemical ordering configuration; ΔE =1.5 kJ/mol relative to the 40_{CC} GS. Projections on: b) [001]; c) [100], d) [010].

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