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

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Abstract. The Vienna Ab-initio Simulation Package (VASP) was used to perform fully relaxed, plane-wave pseudopotential calculations of formation energies ($\Delta E_{VASP}$) 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 $\Delta E_{VASP}$ were used to fit a cluster expansion Hamiltonian to verify that the no other superstructure is predicted to have lower energy than the lowest $\Delta E_{VASP}$, 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, $Pm3m$, to tetragonal, $P4_2/mnm$, 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\(_3\)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\textsuperscript{1+} and Bi\textsuperscript{3+} cations perpendicular 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 $(1 - X) \cdot NaTiO_3 + X \cdot BiTiO_3$, in Figures 2a and b. All calculations were performed with the Vienna *ab initio* simulation program (VASP) \cite{16} using ultrasoft Vanderbilt \cite{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\textsuperscript{1}; Bi 6s\textsuperscript{2}6p\textsuperscript{3}; Ti 4s\textsuperscript{2}3d\textsuperscript{2}; O 2p\textsuperscript{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\textsubscript{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\textsubscript{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\textsubscript{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 $\Delta E_{VASP}$ 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\textsubscript{CC} structure is *not only* the lowest energy configuration that was tried, GS\textsubscript{VASP}, it is also the predicted GS that one obtains by fitting a cluster expansion (CE) Hamiltonian \cite{19,20} to the set \{\$\Delta E_{VASP}\$\}, GS\textsubscript{CE}. The fitting was done as follows:

- Fit a CE to the set of formation energies \{\$\Delta E_{VASP}\$\}.
- Use the CE to predict a new GS\textsubscript{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 \Delta E_{VASP} for the 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}\}.

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 \textit{Pm}3\textit{m} to \textit{P4}_2/\text{mmc}. Octahedral tilting [18] in the \textit{a}−\textit{a}−\textit{c}+ system (Figures 3a-c) further reduces space group symmetry to the acentric monoclinic group \textit{P}11\textit{m} (\textit{c}-axis unique).

\begin{align*}
[0, 1/2, 0] \quad \text{AND} \quad [1/2, 0, 0] \quad \text{STACKING FAULTS}
\end{align*}

Disregarding octahedral tilting, the introduction of [0, 1/2, 0], or [1/2, 0, 0], stacking faults in every other (\textit{h},\textit{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\textsuperscript{th} 1:1 configuration in a brute force enumeration for the 2\times2\times4 supercell. Performing the VASP calculation, and allowing atomic positions to relax, leads to \textit{a}+\textit{a}+\textit{c}− octahedral tilting in the orthorhombic space group \textit{Pmm}2. The energy difference between 80_{628} and 40_{CC} is tiny (0.15 kJ/mol) \textsuperscript{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 \textit{a}- and \textit{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 \textit{a}- and \textit{b}-axis relaxations.

\textbf{DISCUSSION}

The VASP results (Figure 2b) clearly rule out NaCl-type ordering of Na\textsuperscript{1+} and Bi\textsuperscript{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\degree C at 5\degree C per hr, and TEM hot-stage measurements were made between 20\degree C and 600\degree C. The predicted 40_{CC} GS with \textit{a}−\textit{a}−\textit{c}+ octahedral tilting is consistent with the diffraction data of Soukhojak et al. [12], but the extremely

\textsuperscript{1} 0.15 kJ/mol is about three times the precision of VASP calculations.
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.

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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; \( \Delta E = 0.15 \text{ kJ/mol} \) relative to the \( 40_{CC} \) GS. Projections on: b) \([001]\); c) \([100]\), d) \([010]\).
REFERENCES