Neutron Powder Diffraction of $(Nd_{7/12}Li_{1/4})TiO_3$ Nano-Checkerboard Superlattices

Beth S. Guiton,*,[†] Hui Wu,[‡] and Peter K. Davies*,[†]

Department of Materials Science and Engineering,
University of Pennsylvania, 3231 Walnut Street,
Philadelphia, Pennsylvania 19104, and NIST Center for
Neutron Research, 100 Bureau Drive, MS 6102
Gaithersburg, Maryland 20899

Received February 17, 2008
Revised Manuscript Received March 25, 2008

In a recent transmission electron microscopy (TEM) study of the neodymium lithium titanate perovskites in the series $(Nd_{2/3-x}Li_{3x})TiO_3$ ($0.047 < x < 0.151$), we described periodic A-site cation phase separation, resulting in images which resemble a checkerboard on the nanometer length scale (Figure 1).[1] The cation ordering which leads to phase separation occurs on several levels: first there is a well-known[2–5] primary cation order, resulting in perovskite A-site (001) layers fully occupied by Nd^{3+} cations alternating with layers occupied by a mixture of Nd^{3+} and Li^{+} cations and vacancies. Secondary ordering then occurs within the mixed A-site layers, on the nanometer length scale, to give a periodically arranged superlattice of nanodomains comprising a Li-rich phase, separated by a zig-zagging boundary region comprising a Nd-rich phase (Figure 2).[1] For the case of $x = 1/12$ (i.e., $(Nd_{7/12}Li_{1/4})TiO_3$) the compound phase separates into roughly half of each of the two end members, $(Nd_{1/2}Li_{1/2})TiO_3$ and $Nd_{2/3}TiO_3$, resulting in a $14a_p \times 28a_p \times 2a_p$ unit supercell (where the subscript p refers to the primitive aristotype). In addition to showing evidence for the arrangement of cations within this supercell we also postulated that the TiO_6 octahedral tilt system is of the Glazer[6] $a^-a^-c^0$ type and twinned periodically, dissecting the supercell into four quadrants. Here we present a complimentary neutron powder diffraction (NPD) study of the $(Nd_{7/12}Li_{1/4})TiO_3$ nano-checkerboard structure.

The main aim of this study was to demonstrate that the supercell model resulting from periodic phase separation is valid not only for those crystals included in the TEM study but for the entire bulk powder sample. In particular we intend to test the validity of our proposed periodically twinned tilt system. Finally, we present a preliminary temperature dependent NPD study, from room temperature to 900 °C.

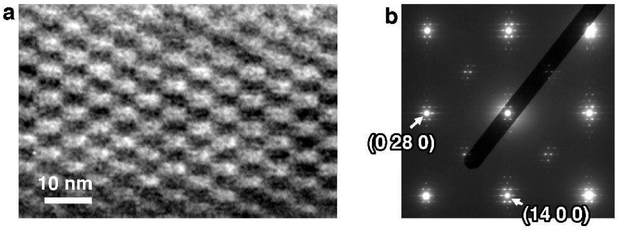

Figure 1. Checkerboard contrast. TEM image (a) and corresponding electron diffraction pattern (b) of a grain of $(Nd_{7/12}Li_{1/4})TiO_3$ taken with the electron beam parallel to [001]. Indexing reveals an overall $14a_p \times 28a_p \times 2a_p$ C-centered supercell, with underlying $2a_p \times 2a_p \times 2a_p$ C-centered unit cell.

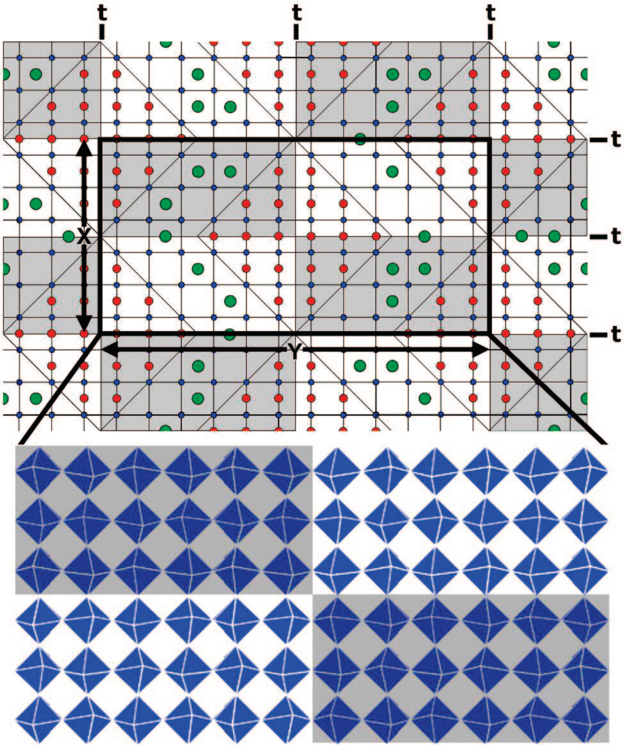

Figure 2. Schematic diagram of phase separation and the resulting checkerboard contrast. A smaller unit supercell than that observed experimentally (i.e., $6a_p \times 12a_p \times 2a_p$ rather than $14a_p \times 28a_p \times 2a_p$) is drawn for clarity. Top: Only cations in the alternate mixed layer are shown: Nd = green, Li = red, and Ti = blue. Phase separation into Li-rich square domains separated by Nd-rich zig-zagging boundaries leads to mirror planes in the strain field concurrent with octahedral tilt-system twin boundaries (labelled t). Bottom: Pattern of $a^-a^-c^0$ TiO_6 tilts for a single supercell. Shaded quadrants show twinned tilt variants.

The model supercell contains close to 4000 atoms (Supporting Information, Table 1), described by more than 1000 independent structural parameters, rendering it impossible to perform a meaningful Rietveld refinement with our current resources, as would be the usual course of action for the interpretation of NPD data. For this reason we present instead a qualitative comparison of the experimental data with simulations generated using the CrystalMaker software suite.

Figure 1 shows a low resolution TEM image of a $(Nd_{7/12}Li_{1/4})TiO_3$ crystal displaying checkerboard contrast, and the accompanying electron diffraction pattern. Satellites in the diffraction pattern indicate that the unit supercell for this crystal has dimensions of $14a_p \times 28a_p \times 2a_p$. We previously argued that this checkerboard pattern is indicative of periodic

---

* Corresponding authors. E-mail: davies@seas.upenn.edu (P.K.D.), guiton@seas.upenn.edu (B.S.G.).

[†] University of Pennsylvania.

[‡] National Institute of Standards and Technology.

(1) Guiton, B. S.; Davies, P. K. *Nat. Mater.* **2007**, *6*, 586.
(2) Rooksby, H. P.; White, E. A. D.; Langston, S. A. *J. Am. Ceram. Soc.* **1965**, *48*, 447.
(3) Iyer, P. N.; Smith, A. J. *Acta Crystallogr.* **1967**, *23*, 740.
(4) Abe, M.; Uchino, K. *Mater. Res. Bull.* **1974**, *9*, 147.
(5) Lee, H. J.; Park, H. M.; Oh, S. H.; Cho, Y. K.; Son, J. O.; Nahm, S. *Jpn. J. Appl. Phys* **2004**, *43*, 7592.
(6) Glazer, A. M. *Acta Crystallogr.* **1972**, *B28*, 3384.

10.1021/cm800473m CCC: $40.75

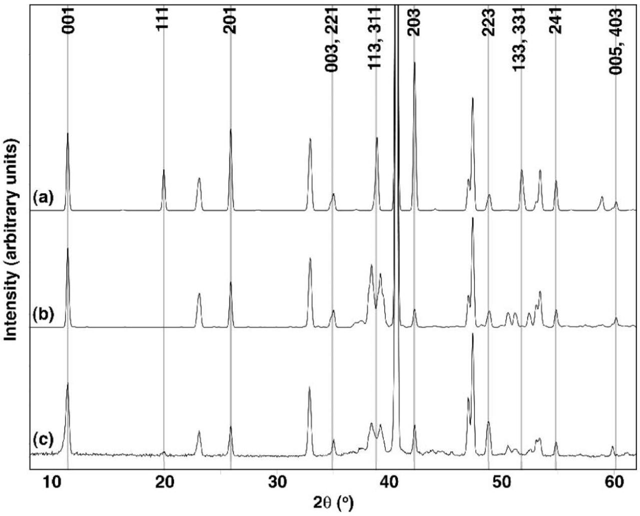

Figure 3. Comparison of simulated NPD patterns with experimental data. Indexing shown for X- and R-point peaks. (a) $(Nd_{7/12}Li_{1/4})TiO_3$ with 1:1 primary order along the c-direction (resulting in X-point peaks) and $a^-a^-c^0$ tilt system (resulting in R-point peaks). (b) $(Nd_{7/12}Li_{1/4})TiO_3$ periodically phase separated into 50% $[(Nd_{1/2}Li_{1/2})TiO_3]$−50% $[Nd_{2/3}TiO_3]$, on a $14a_p \times 28a_p \times 2a_p$ unit supercell. (c) NPD data obtained for $(Nd_{7/12}Li_{1/4})TiO_3$.

mirror planes in the strain field of the crystal and should therefore be echoed by a pattern of periodic twin boundaries in the TiO_6 octahedral tilt system;[1] this is indicated schematically in Figure 2. Since the TiO_6 tilt system is a feature of the oxygen anion positions in the perovskite network, it should be readily measurable using NPD.

Figure 3a shows a simulated NPD pattern of the non-phase-separated $(Nd_{7/12}Li_{1/4})TiO_3$ perovskite structure, parameters for which are given in Supporting Information, Table 2. The unit cell is described by a $\sqrt{2}a_p \times \sqrt{2}b_p \times 2c_p$ cell, where $a_p \approx b_p$ (=3.825 Å) and $a_p < c_p$ (= 3.855 Å). These parameters were determined from a Lebail refinement of the NPD data to be presented below. Pertinent structural features are (i) 1:1 primary ordering of the A-site cations along the c-direction to give layers of A-sites fully occupied by Nd^{3+} cations alternating with layers containing a statistical mixture of Nd^{3+}, Li^+, and vacancies; (ii) Li^+ cations cooperatively displaced to reside in one set of the 4-coordinate "bottleneck" sites (as described in the literature[7–10] and in ref 1) rather than the larger A-sites; (iii) a small antiferroelectric "pairing" of the Ti^{4+} cations, as described in ref 1; and (iv) Glazer tilt system $a^-a^-c^0$ or, equivalently, tilting of the TiO_6 octahedra around $[110]_p$, tilt angle 15.44°.

The $a^-a^-c^0$ tilt system was deduced as follows: In terms of the $2a_p \times 2a_p \times 2a_p$ unit cell generated by tilting, electron diffraction shows (Figure 1b) that the cell is C-centered; therefore, the tilt system must be either C- or F-centered. The tilt system has twin boundaries which lie on the (100) and (010) planes; therefore, the tilt axis cannot lie on one of these planes—this rules out an a^0 or b^0 tilt. The phase-separated supercell is also C-centered, and the (1/2 1/2 0) peak is always absent, which means that $(X + Y)/2$ is always odd ($(X + Y)/2 = 21$ for this composition); for these two statements to be simultaneously true there cannot be a tilt around the z-axis. From inspection of the Glazer[11] $2a_p \times 2a_p \times 2a_p$ unit cells this eliminates all but two systems: system (19), $a^0b^-c^-$ and system (20), $a^0b^-b^-$ or, equivalently, $a^-b^-c^0$ and $a^-a^-c^0$. Of these two Glazer predicts[11] $a_p = b_p$ only for the $a^-a^-c^0$ system; therefore, we conclude that this is the correct tilt system. It should be noted that Glazer also predicts $c_p < a_p$ for this system; 1:1 ordering along the c-direction can explain the expansion of c_p to give $c_p > a_p \approx b_p$ as found from Lebail refinement. It is of interest to note that this choice of tilt system is consistent both with calculations by Woodward[12,13] and also with the group theoretical analysis performed by Howard and co-workers,[14–16] where this tilt system is obtainable by a single continuous transition from the high temperature 1:1 primary ordered structure.

Peaks in the resulting powder pattern can be classified as one of three types. In terms of a $2a_p \times 2a_p \times 2a_p$ (i.e., C-centered) cell these are "even even even" (eee) or primitive perovskite peaks, "even even odd" (eeo) or X-point peaks, and "odd odd odd" (ooo) or R-point peaks, to use the terminology of Howard et al.[17,18] Primitive perovskite peaks (eee) are present with intensity ratios and splittings to reflect the lattice parameters. In particular this can be seen in the 1:2 ratio of the (004):(400) doublet at $2\theta \sim 47°$. X-point peaks (eeo) arise due to primary 1:1 cation ordering,[14,18] and R-point peaks (ooo) are indicative of out-of-phase octahedral tilts.[11] Note that no "even odd odd" or M-point peaks arise since this would require either in-phase tilting or R- and X-point ordering to occur in concert.[11,18,19]

Figure 3b shows a simulation of the same compound after undergoing periodic phase separation to give a $14a_p \times 28a_p \times 2a_p$ unit supercell (Supporting Information, Table 1). This structure differs from the one in Figure 3a in both its periodic distribution of cations and the periodic twinning of the tilt system. There are several notable differences in the resulting powder pattern: (i) (111) becomes systematically absent; (ii) (113) splits into a doublet of satellite reflections; (iii) (133) splits into a quartet of satellite reflections; and (iv) (224) (at ~59°) reduces to weak satellite reflections.

Shown for comparison in Figure 3c is our experimental NPD data. NPD data were collected at the NIST Center for Neutron Research using the BT-1 32 detector high-resolution neutron powder diffractometer with the Cu(311) monochromator at $\lambda = 1.5403(2)$Å. Data were collected over the 2θ range of 3−168° with a step size of 0.05°. It can be seen from inspection of the NPD data that all the features of the $14a_p \times 28a_p \times 2a_p$ unit supercell simulation are qualitatively

---

(7) Alonso, J. A.; Sanz, J.; Santamaria, J.; Leon, C.; Varez, A.; Fernandez-Diaz, M. T. *Angew. Chem., Int. Ed.* **2000**, *39*, 619.
(8) Sanz, J.; Alonso, J. A.; Varez, A.; Fernandez-Diaz, M. T. *J. Chem. Soc., Dalton Trans.* **2002**, 1406.
(9) Sommariva, M.; Catti, M. *Chem. Mater.* **2006**, *18*, 2411.
(10) Catti, M. *Chem. Mater.* **2007**, *19*, 3963.
(11) Glazer, A. M. *Acta Crystallogr.* **1975**, *A31*, 756.
(12) Woodward, P. M. *Acta Crystallogr.* **1997**, *B53*, 32.
(13) Woodward, P. M. *Acta Crystallogr.* **1997**, *B53*, 44.
(14) Howard, C. J.; Zhang, Z. *J. Phys.: Condens. Matter* **2003**, *15*, 4543.
(15) Howard, C. J.; Zhang, Z. *Acta Crystallogr.* **2004**, *B60*, 249.
(16) Howard, C. J.; Stokes, H. T. *Acta Crystallogr.* **2004**, *B60*, 674.
(17) Howard, C. J.; Knight, K. S.; Kennedy, B. J.; Kisi, E. H. *J. Phys.: Condens. Matter* **2000**, *12*, L677.
(18) Zhang, Z.; Howard, C. J.; Knight, K. S.; Lumpkin, G. *Acta Crystallogr.* **2006**, *B62*, 60.
(19) Woodward, D. I.; Reaney, I. M. *Acta Crystallogr.* **2005**, *B61*, 387.

well replicated. This is strong evidence that both our choice of tilt system and pattern of periodic twin boundaries are valid throughout the bulk powder sample. It should be noted that the (111) peak is not systematically absent from our data but greatly reduced in intensity from the prediction of the non-phase-separated compound; this suggests the presence of defects in the superlattice periodicity, which is consistent with the stacking faults previously observed in the TEM images. A quantitative refinement would need to be conducted to gain a more accurate measure of the tilt angle, which in our study was estimated by optimizing bond valences. This should help to correct discrepancies in the intensities of the R-point peaks and satellite clusters.

It is clear that though extremely informative about anion positions, NPD is not an ideal technique to make a detailed study of the cation positions in our sample. The NPD simulation predicted a number of very low angle cation-dependent reflections which we did not observe in a concurrent low angle NPD study. This is perhaps to be expected since not only were the simulated peaks weak due to negligable differences in scattering length densities between the domain and the boundary chemistries but the crystal grain sizes in our sample are not more than a single order of magnitude larger that the ordering itself which should lead to significant broadening of the peaks; this, added to the greatly reduced signal/noise ratios obtainable at low angle, would make observation of these peaks extremely difficult. Other cationic structural features which we do not probe in this study are (i) the extent to which the 1:1 order along the c-direction may or may not be perfect and (ii) possible displacements of the cations away from their ideal positions along the *z*-axis—our model deals purely two-dimensionally with cation positions within the (001) plane. These studies would perhaps be better served by single crystal diffraction or a combined neutron and synchrotron X-ray diffraction study.

Figure 4 shows a series of diffraction patterns collected from room temperature to 900 °C. The sample was sealed in a vanadium sample can under oxygen gas to prevent loss of lithium and oxygen and valence changes of titanium at high temperatures. The sample was allowed to equilibrate for 1 h at each temperature before data collection. The effects observed are not marked, primarily a weakening and broadening of low intensity reflections due to increased Debye−Waller factors and a shift to lower angles due to increased cell volume. A gradual reduction in the intensity of the R-point clusters is observed on heating, which could be indicative of a reduction in tilt angle as a tilt system phase transition is approached. It is somewhat surprising that no phase transitions are observed for the temperature range studied: structurally similar compounds commonly display one or more transitions.[14,18,20,21] We postulate that since the $a^-a^-c^0$ tilt system reflects the symmetry of the periodically phase-separated cations, this pattern of tilts and the corresponding periodic twins will be frozen in up to the cation phase-separation temperature.

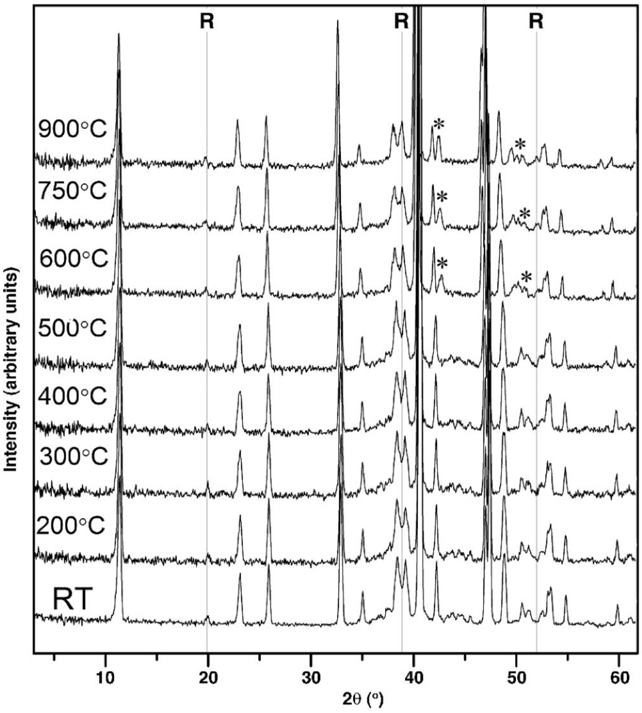

Figure 4. NPD of $(Nd_{7/12}Li_{1/4})TiO_3$ taken over a range of temperatures. The positions of the R-point peaks (ooo) for the room temperature pattern are indicated. Peaks labelled * are from the stainless steel connector used to mount the sample can on the sample stick at high temperature.

To summarize, NPD results suggest that refinement of the $(Nd_{7/12}Li_{1/4})TiO_3$ structure will require a $14a_p \times 28a_p \times 2a_p$ unit supercell. The existence of R-point (ooo) (and not M-point (eoo)) peaks and their splittings is consistent with Glazer tilt system $a^-a^-c^0$, twinned periodically on (100) with periodicity $7a_p$, and (010) with periodicity $14a_p$. No change in the octahedral tilt system (or its twinning) was detected up to 900 °C.

Acknowledgment. This study was supported by the International Center for Diffraction Data Ludo Frevel Crystallography Scholarship Award and by the National Science Foundation, under Grant DMR0704255 and by the MRSEC program under Award No. DMR05-20020.

Supporting Information Available: Crystallographic data for the structures simulated in Figure 3 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM800473M

---

(20) Kennedy, B. J.; Howard, C. J.; Kubota, Y.; Kato, K. *J. Solid State Chem.* **2004**, *177*, 4552.

(21) Zhang, Z.; Howard, C. J.; Kennedy, B. J.; Knight, K. S.; Zhou, Q. *J. Solid State Chem.* **2007**, *180*, 1846.