Nanocheckerboard Modulations in (NaNd)(MgW)O$_6$

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Abstract
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Nanocheckerboard modulations in (NaNd)(MgW)O$_6$

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Data is presented for a complex structural and compositional modulation in the perovskite (NaNd)(MgW)O$_6$. This modulation creates a large 14$a_p$ x 14$a_p$ x 2$a_p$ supercell ($a_p$ $\approx$ 3.9 Å is the lattice parameter of the cubic perovskite aristotype) containing ordered regions with doubled (110) d-spacings in the a-b plane separated by two-dimensional periodic antiphase boundaries and accompanied by a nanocheckerboard pattern. Faint periodic modulations in Z-contrast images suggest an associated periodic variation in composition. The presence of a sodium rich impurity implies the composition of the stable perovskite is nonstoichiometric. © 2010 American Institute of Physics. [doi:10.1063/1.3490637]

Cation order/disorder transitions play a major role in adjusting the crystal structure, phase stability, and properties of many ABO$_3$ complex oxide perovskites. Compared to the numerous examples of B-site ordered perovskites, structures involving the ordering of two different cations on the A-site are relatively rare. In the few known examples the order involves a (001) layering of the A$'$ and A$''$ cations.$^{1,2}$ The ordered A-site (A$'$A$''$)BO$_3$ perovskites have received increased attention following the observation of unusual periodic nanoscale phase separation in solid solutions of the lithium ion conducting (Nd$_{2/3}$Li$_{1/3}$)$_2$TiO$_4$ system.$^3$ The tunable superlattice consists of diamondlike domains of the Li-rich end-member (NdLiTi$_2$O$_6$) separated by Li-free regions of Nd$_{4/3}$Ti$_2$O$_6$. The phase separation leads to a nanocheckerboard strain pattern observed in high-resolution transmission electron microscopy (HRTEM) images. Periodic phase separated morphologies were also observed in Mn-, Cr-, and Al-substituted (Nd$_{3/2}$Li$_{1/2}$)$_2$TiO$_4$ solid solutions.$^4$

Recently examples of compositional modulation were observed in Li-free perovskites. For (NaLa)(MgW)O$_6$ the modulation occurs in one dimension leading to a striped pattern of light and dark regions with a repeat distance of 12$a_p$; compositional analyses indicated separation into Na-rich [(NaLa)(MgW)O$_6$] and Na-deficient [La$_{1/3}$(MgW)O$_6$] phases.$^5$ HRTEM images of (KLa)(MnW)O$_6$ provided evidence for checkerboard type modulations in another A$'$/A$^{3+}$ mixed A-site system.$^6$

This paper focuses on the perovskite (NaNd)(MgW)O$_6$, one of several (A$'$A$''$)(B$'$B$''$)O$_6$ perovskites with both A- and B-site ordering.$^7$ The B-site cations adopt an ordered “rocksalt-type” arrangement with an alternation of Mg$^{2+}$ and W$^{6+}$; the A-site cations (Na$^+$,Nd$^{3+}$) adopt the usual (001) layering with c=2$a_p$ (see Fig. 1). Samples of (NaNd)(MgW)O$_6$ were synthesized using standard ceramic methods from stoichiometric mixtures of dried Na$_2$CO$_3$, Nd$_2$O$_3$, MgO and WO$_3$ starting materials. After an initial calcine at 900 °C (3 h) all subsequent firings were conducted on pelleted samples buried in “sacrificial” powders of the same composition to minimize any loss of sodium. Equilibrium, as gauged by the absence of any changes in the powder x-ray diffraction (PXRD) patterns, was reached after repeated grinding and heating at 1100 °C (12 h) and 1150 °C (12 h). The final samples were reheated to 1050 °C for 6 h and cooled to room temperature at 0.1 °C/min. The phase composition was characterized by a laboratory x-ray diffractometer (Rigaku GiegerFlex D/Max-B) and by synchrotron PXRD from data collected at Argonne National Laboratory with $\lambda$=0.41225 Å. TEM analysis was conducted on a JEOL 2010F TEM/scanning transmission electron microscope (STEM) operating at 197 kV; Z-contrast images were obtained using a high-angle annular detector (54.9 mrad) in dark field STEM operating mode.

Figure 2 shows an HRTEM image and accompanying selected-area electron diffraction (SAED) pattern of (NaNd)(MgW)O$_6$ collected with the electron beam oriented along [001]. The sharp, well-defined satellites grouped around the primary perovskite reflections indicate the presence of a highly ordered superstructure with modulations along the g$_{100}$ and g$_{010}$ directions. The spacing of the satellites corresponds to a 14$a_p$ x 14$a_p$ supercell ($\approx$5.46 x 5.46 nm) within the a-b plane. In the thicker regions of the grain the image is dominated by contrast from a check-

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FIG. 1. Crystal structure of the double perovskite (NaNd)(MgW)O$_6$. The light octahedra, MgO$_6$, the darker WO$_6$. Na$^+$ and Nd$^{3+}$ are represented by the light and dark spheres, respectively.
erboard arrangement of darker and lighter squares with edges along [100] and [010]. Although the size of the squares shows some variation, typically they correspond to 7a_p × 7a_p. The checkerboard patterns show remarkable perfection and persist across the entire grain (see Fig. 3). The morphology of the patterns for (NaNd)(MgW)O_6 is quite different to those reported for its La counterpart, which comprise dark and light linear stripes of width 6a_p.

In the thinner regions of the grain, upper right region of Fig. 2(a), the lattice image reveals a periodic arrangement of approximately square nanodomains with edges parallel to (110) and (110). Within the domains additional fringes corresponding to a doubled (110) plane d-spacing (highlighted as white cross-hatching) are evident along both (110) directions. The image also reveals an antiphase relationship between the doubled (110) spacings in adjacent domains. The antiphase boundaries (APB’s) are orthogonal to each other, parallel to the {110} planes, and separated by 7(110)a_p. The resultant C-centered supercell has a 14a_p × 14a_p repeat. The signature of this modulation is also evident in the diffraction patterns [Fig. 2(b)], which contain four especially pronounced satellite reflections centered around the (h/2 k/2 0) positions. The width of the APB’s is difficult to fully quantify but appears to be limited to one or two perovskite unit cells. The doubled (110) fringes and periodic arrangement of APB’s is very similar to the features reported for the phase-separated (Nd_{2/3-λ}Li_{3λ})TiO_3 system. Although not mentioned in the previous study, we note the doubling of (110) and formation of APB’s can also be discerned in the HRTEM images of (NaLa)(MgW)O_6 [see Fig. 4(c), Ref. 5].

To simplify the image-contrast mechanisms, the grains were investigated using high-angle annular dark field STEM (Z-contrast imaging). The Z-contrast image in Fig. 4, collected along [001], shows a faint nanoscale compositional modulation with lighter and darker regions. The observation of this contrast implies the structural modulation in (NaNd)(MgW)O_6 is accompanied by a periodic variation in composition.

The checkerboard modulations and domain structures in (NaNd)(MgW)O_6 strongly resemble the phase-separated structures reported for the (Nd_{2/3-λ}Li_{3λ})TiO_3 system. They also share several similarities to the striped patterns observed in (NaNd)(MgW)O_6 which were argued to result from an ordered phase separation of Na-rich, (NaLa)(MgW)O_6, and Na-deficient, La_{4/3}(MgW)O_6, end member phases. The nanoscale structures in both of those systems also involve a periodic twinning of the a”a”c”0 (Glazer notation) octahedral tilt system, the same tilt system reported for (NaNd)(MgW)O_6. With these similarities it is tempting to conclude the modulations reported here for (NaNd)(MgW)O_6 involve periodic phase separation into (NaNd)(MgW)O_6 domains separated by Na-deficient regions of Nd_{4/3}(MgW)O_6. However, if this model is correct the actual composition of the grains would have to deviate from a 1:1 Na:Nd stoichiometry.

For (NaLa)(MgW)O_6 local fluctuations in composition and/or Na-loss during the synthesis were suggested as possible sources for the nonstoichiometric phase separated structures. However, local variations in composition are unlikely to explain the structures of the (NaNd)(MgW)O_6 system as the formation and periodicity of the modulations patterns was not a localized phenomenon and encompassed the entire grain of every crystal imaged along [001] as seen in Fig. 3.

While sodium loss during the synthesis is possible, our preparations used sacrificial powders, a technique that is usually highly effective in suppressing component volatility. The previous preparations of (NaLa)(MgW)O_6 and related compounds incorporated excess Na into the starting stoichiometry to compensate for potential volatilization and typically contained residual Na impurities, (e.g., Na_2WO_4). Even though our starting compositions were based on a stoichiometric...
metric ratio of Na:Nd:Mg:W, we also noticed the PXRD patterns of (NaNd)(MgW)O₆, with Pattern orientation anomalies observed due to the doubled periodicity along the [001] direction. The resultant doublet supercell in the space group P2₁/m, with: a = 5.4750 Å, b = 5.4868 Å, c = 7.8622 Å, β = 90.11°, comprises of ordered domains with a doubled periodicity along the b-axis. The observation of an excess Na phase confirms the effectiveness of our synthetic method in suppressing volatility; however, it also suggests the composition of the stable end-member is not (NaNd)(MgW)O₆, but is Na (and perhaps W) deficient.

In summary, the structure of (NaNd)(MgW)O₆ is comprised of ordered domains with a doubled periodicity along both (110) directions in the a-b plane. Neighboring domains have an antiphase relationship and are separated by twodimensional periodic APB's parallel to the (110) planes with a 7(110)ₐₕ repeat. The resultant C-centered supercell in the a-b plane has a 14ₐₕ × 14ₐₕ (~5.46 × 5.46 Å) periodicity. The formation of the ordered APB structure is accompanied by a checkerboard strain contrast throughout the grains. The observation of excess Na (and W) impurity phases in samples with a bulk 1:1:1:1 Na:Nd:Mg:W ratio suggests the modulated structure is nonstoichiometric, most likely from a different local chemistry in the regions close to the APB. Understanding the origin of the doubled (110) spacing of the APB's parallel to the (Nd₂/₃₋ₓLiₓ)TiO₃ system will require additional study. The formation of periodic antiphase domains with a similar doubled (110) contrast in the (Nd₂/₃₋ₓLiₓ)TiO₃ system was associated with the ordering of cation displacements in the TiO₆ octahedra. It is possible that the W could be responsible for the modulations in (NaNd)(MgW)O₆, though periodic twinning of the octahedral tilt system is also important in these systems.}

It is clear that the 001 ordering of A-site cations in (NaNd)(MgW)O₆ and other A⁺⁺/A⁺⁺⁺ perovskites introduces some type of instability that produces a complex structural and compositional modulation. For the (Nd₂/₃₋ₓLiₓ)TiO₃, system, alterations in the bulk composition of the solid solution changed the width of the interdomain boundary regions and enabled the relaxation of the phase-separated checkerboard structures. The possible formation of similar tunable structures based on (NaNd)(MgW)O₆ will require clarification of the composition of the “second-phase” APB regions.

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