Thin Films and Coatings

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Perspectives on $Li_{3x}Nd_{2/3-x}TiO_3$ – a complex perovskite material with nano-chessboard contrast in TEM

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An important problem in materials science and crystallography is the question about the occupation of the lattice if different atomic species compete for the same sites. Whether long- or short-range order is established amongst atomic species that are hosted by the same type of crystalline lattice sites, or whether a material decomposes into two phases, is essentially ruled by the chemical nature and the size difference of the atoms. Complexity is added if additional effects need to be encountered. This is exemplified in complex perovskite materials where tilting distortions of the oxygen octahedra and polar cation displacements can occur. The interplay of such effects can lead to remarkable structural features which in the case of $Li_{3x}Nd_{2/3-x}TiO_3$ are manifested in a striking nano-chessboard contrast in TEM images. However, the fact that this chessboard pattern does not unambiguously relate to the structural nature of the material is revealed by a gradually changing pattern contrast, from chessboard to a diamond-type pattern, when the imaging conditions or the sample thickness is varied, see Fig. 1.

We employed electron microscopy, X-ray and neutron diffraction in order to revisit the structure of $Li_{3x}Nd_{2/3-x}TiO_3$ and to reveal the true nature of the chessboard contrast in TEM images. While the pattern contrast in coherently formed TEM images strongly depends on the sample thickness and the objective focus, STEM images of thicker sample areas reveal an invariant diamond pattern. It was argued that the reason for the diamond pattern observable in so-called *Z*-contrast STEM images lies in an ordered phase separation into a Li-rich and a Li-depleted phase [1]. However, our STEM investigation show that this intuitive contrast interpretation of the *Z*-contrast STEM images is inadequate as the pattern contrast diminishes with increasing scattering angle, i.e. while the pattern contrast is most visible in incoherently formed bright-field (BF) and annular dark-field (ADF) STEM images, there is only a very faint pattern contrast observable under strong *Z*-contrast conditions in high-angle annular dark-field (HAADF) STEM, see Fig. 2. The dependence of the pattern contrast on the detection angle reveals that the true source of the residual pattern contrast in the supposedly *Z*-contrast images lies in the channelling conditions given by the local strain.

Electron diffraction provides a complementary method to tackle the intriguing structure of $Li_{3x}Nd_{2/3-x}TiO_3$ and reveals a basic perovskite lattice (p) whose main reflections are decorated by satellites. In addition, a set of weak reflections near $½½0_p$-positions can be observed which are out of phase with respect to the satellites. These “forbidden” sets of reflections and the satellites provide indication that a domain structure is present. Based on earlier work by Labeau *et al.* [2] on $ThNb_4O_{12}$, García-Martín *et al.* [3] proposed that similar to $ThNb_4O_{12}$ a quasiperiodic microdomain structure is responsible for the diffraction behaviour. The domains are supposed to be formed by twin boundaries which separate areas wherein the pattern of tilted TiO_6 octahedra is uniform.

Powder synchrotron X-ray (ID31, ESRF) and neutron diffraction (D2B, ILL) in combination with the TEM data allowed for a complete quantitative structure solution of the (3+2)-dimensional incommensurately modulated $Li_{0.15}Nd_{0.617}TiO_3$ structure. Unlike the model of García-Martín *et al.* [3] or any other previously suggested model, Rietveld refinement revealed that the primary modulation is related to rectangular domains with a quasiperiodic two-dimensional perturbation of the in-phase tilting pattern of the TiO_6 octahedra around the *c*-axis [4]. The refinement undoubtedly demonstrated the absence of the compositional modulation and the earlier proposed phase separation. Moreover, contrary to the phase separation model [1], our (3+2)-dimensional model of $Nd_{0.617}Li_{0.15}TiO_3$, whose domain structure is merely due to displacive modulations with a primary contribution of the frustrated TiO_6 octahedra tilting, reproduces the experimental electron diffraction pattern (see Fig. 3), the varying pattern contrast in TEM images as well as the residual channelling contrast in BF and ADF STEM.

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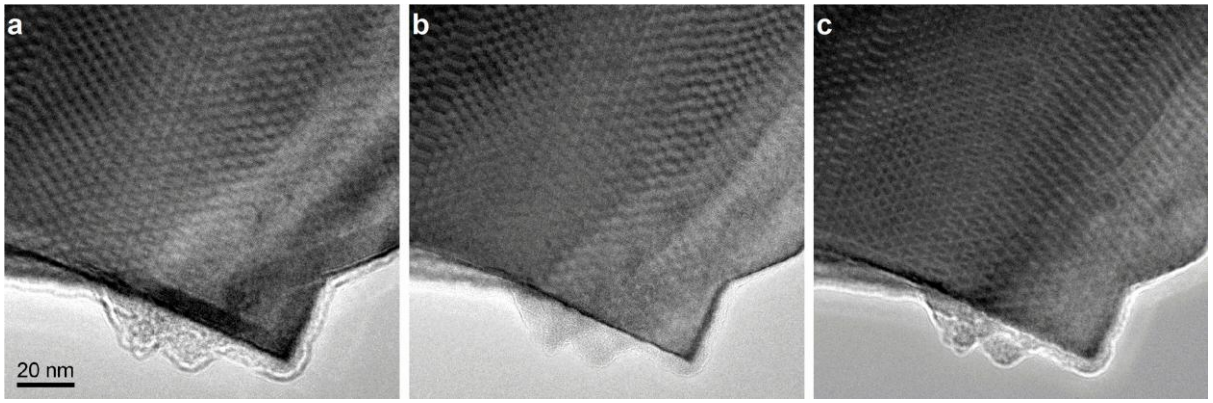

Figure 1. Dependence of the "chessboard" pattern on the imaging conditions of $Nd_{0.617}Li_{0.15}TiO_3$ in $[001]_p$ zone-axis orientation. The nominal defocus in (a), (b) and (c) is +1000 nm, +100 nm and -900 nm. The pattern contrast strongly depends on the local diffraction conditions (sample tilt), on the sample thickness and on the imaging conditions (defocus).

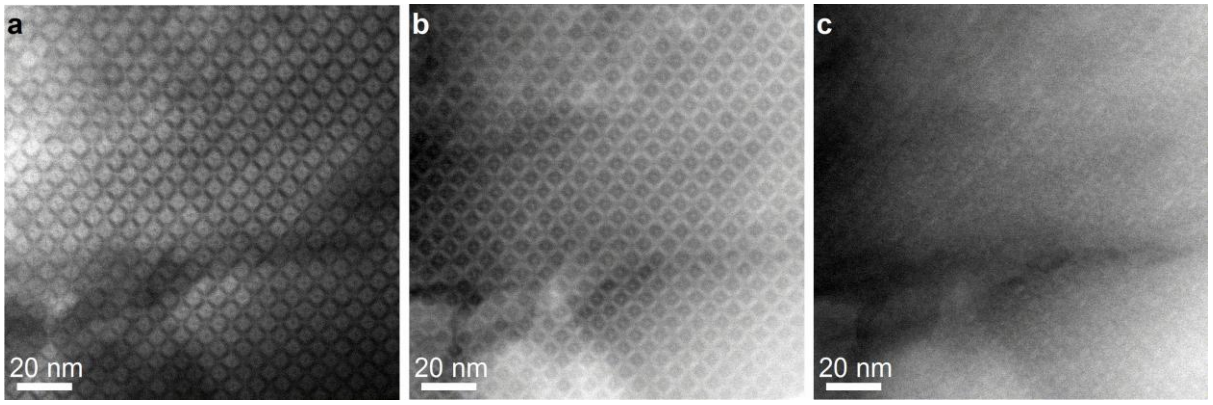

Figure 2. BF (a), ADF (b) and HAADF STEM (c) images of $Nd_{0.547}Li_{0.36}TiO_3$ in $[001]_p$ zone-axis orientation. The inner detection angles for the HAADF and the ADF STEM images are 100 and 35 mrad, respectively. As the contrast of the diamond pattern disappears with increasing dark-field detection angle, the pattern cannot be due to a compositional variation. STEM: 200 kV, semi-convergence angle: 10.8 mrad.

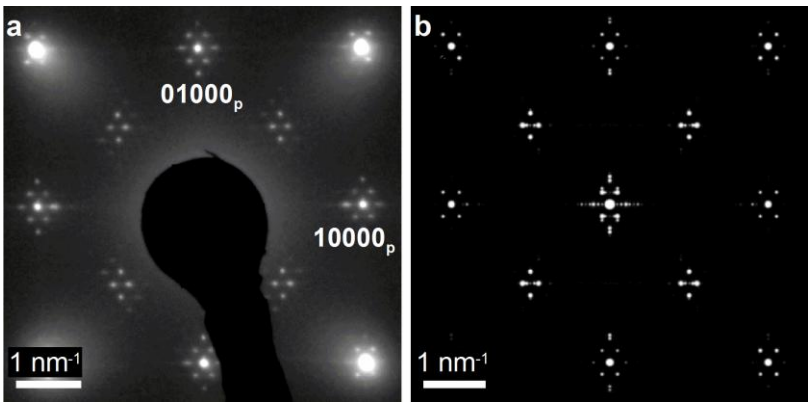

Figure 3. Experimental (a) and simulated (b) electron diffraction pattern of $Nd_{0.617}Li_{0.15}TiO_3$ in [00100] zone-axis orientation. The simulated ED pattern is based on a $40a_p x 40a_p x 2a_p$ commensurate approximant of the (3+2) dimensional quasiperiodic domain structure. The speckling along the vertical and horizontal directions in the center is due to the finite size of the approximant.