Absence of phase separation in nano-chessboard super-lattices in A-site deficient Ca-stabilized $Nd_{2/3}TiO_3$

Feridoon Azough[1], Demie Kepaptsoglou[2], Quentin M. Ramasse[2], Bernhard Schaffer[2] and Robert Freer[1]

[1.]School of Materials, Materials Science Centre, University of Manchester, Manchester M1 7HS, United Kindgom.
[2.]SuperSTEM Laboratory, STFC Daresbury Campus, Keckwick Lane, Warrington WA4 4AD, United Kingdom.

A-site deficient perovskites form a class of functional oxides of particular interest because of their attractive properties, such as ionic conductivity [1], dielectric behaviour [2] and transport properties [3]. A number of these ceramics show 'cross-type' satellite reflections in their [001] diffraction patterns indicating the presence of a two-dimensional superstructure, that has been attributed to a micro domain model comprising of a system of periodically tilted oxygen octahedra [4]. Intriguingly several such compounds exhibit a peculiar contrast in their [001] High Resolution Transmission Electron Microscopy images (HRTEM), resembling a 'nano-chessboard'. The origin of this contrast has been the object of debate, with two main models put forward: the first is based on a chemical phase separation into 'chessboard' domains [5] and the second one attributes the origin of observed contrast to strain arising from a network of incommensurately tilted oxygen octahedra [6].

Here, we report on a nano-chessboard structure in the A-site deficient $Nd_{0.6}Ca_{0.1}\square_{0.3}TiO_3$ ceramic (where $\square$ denotes vacancies). Using Electron Energy Loss Spectroscopy (EELS) in the UltraSTEM 100 aberration corrected, dedicated Scanning Transmission Electron Microscope (STEM) , we demonstrate beyond any doubt that the observed nano-chessboard contrast (Figure 1) does not originate from chemical phase separation into nano-domains [7]. Instead, closer inspection of High Angle Annular Dark Field (HAADF) STEM images and atomically resolved electron energy loss spectroscopy (EELS) chemical maps in two orthogonal directions suggest that, in the Nd0.6Ca0.1□0.3TiO3 system, Ca predominantly occupies Nd-vacancy shared sites, creating locally a higher occupation of the site and thus promoting vacancy-cation ordering in both a and b lattice directions. These observations corroborate previous studies [6], which suggest that the observed contrast in electron micrographs is a result of strain originating in intricately-modulated octahedral tilting distortions of the O sub-lattice combined with local cation-vacancy pairing.

References:
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[8] We acknowledge the financial support of EPSRC through EP/H043462, EP/I036230 and R113738. The SuperSTEM Laboratory is the U.K. National Facility for Aberration-Corrected STEM, funded by the EPSRC.
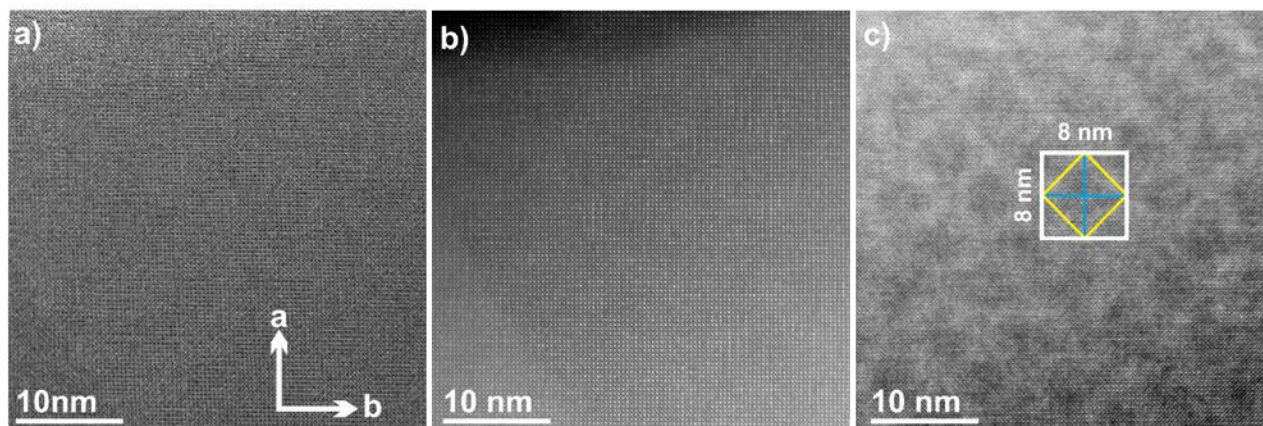

Figure 1. [001] STEM images (a) Bright Field, (b) High High Angle Annular Dark Field (HAADF) and (c) Medium Angle Annular Dark Field (MAADF) of the A-site deficient $Nd_{0.6}Ca_{0.1}\square_{0.3}TiO_3$ ceramic, showing a nanochessboard contrast. While the contrast is weak in the HAADF images it is significantly enhanced in the more strain-sensitive MAADF images.
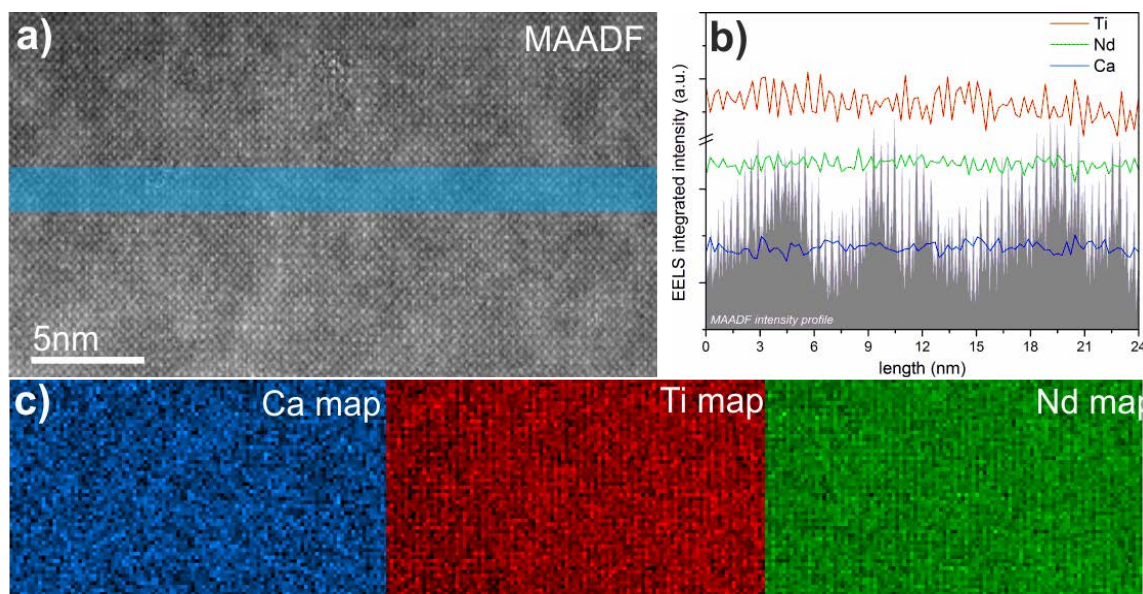

Figure 2. (a): MAADF STEM image of [001] the A-site deficient $Nd_{0.6}Ca_{0.1}\square_{0.3}TiO_3$ ceramic acquired during 2D EELS mapping. (b) MAADF intensity profile averaged over the blue the line indicated in (a) clearly the nano-chessboard intensity modulations. The integrated signals of the Ca $L_{2,3}$, Ti $L_{2,3}$ and Nd $M_{4,5}$ edges are also shown and by contrast show no appreciable modulations across the domains. (c) corresponding Ca $L_{2,3}$, Ti $L_{2,3}$ and Nd $M_{4,5}$ 2-D maps.