

Absence of phase separation in nano-chessboard super-lattices in A-site deficient Ca-stabilized $\text{Nd}_{2/3}\text{TiO}_3$

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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 $\text{Nd}_{0.6}\text{Ca}_{0.1}\square_{0.3}\text{TiO}_3$ 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 $\text{Nd}_{0.6}\text{Ca}_{0.1}\square_{0.3}\text{TiO}_3$ 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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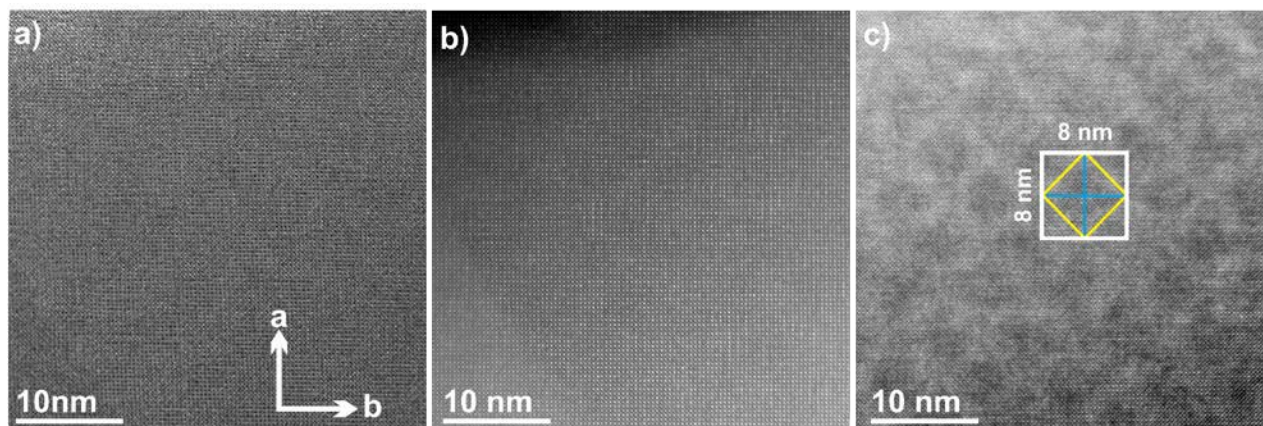


Figure 1. [001] STEM images (a) Bright Field, (b) High High Angle Annular Dark Field (HAADF) and (c) Medium Angle Annular Dark Field (MAADF) of the A-site deficient $\text{Nd}_{0.6}\text{Ca}_{0.1}\square_{0.3}\text{TiO}_3$ ceramic, showing a nano-chessboard contrast. While the contrast is weak in the HAADF images it is significantly enhanced in the more strain-sensitive MAADF images.

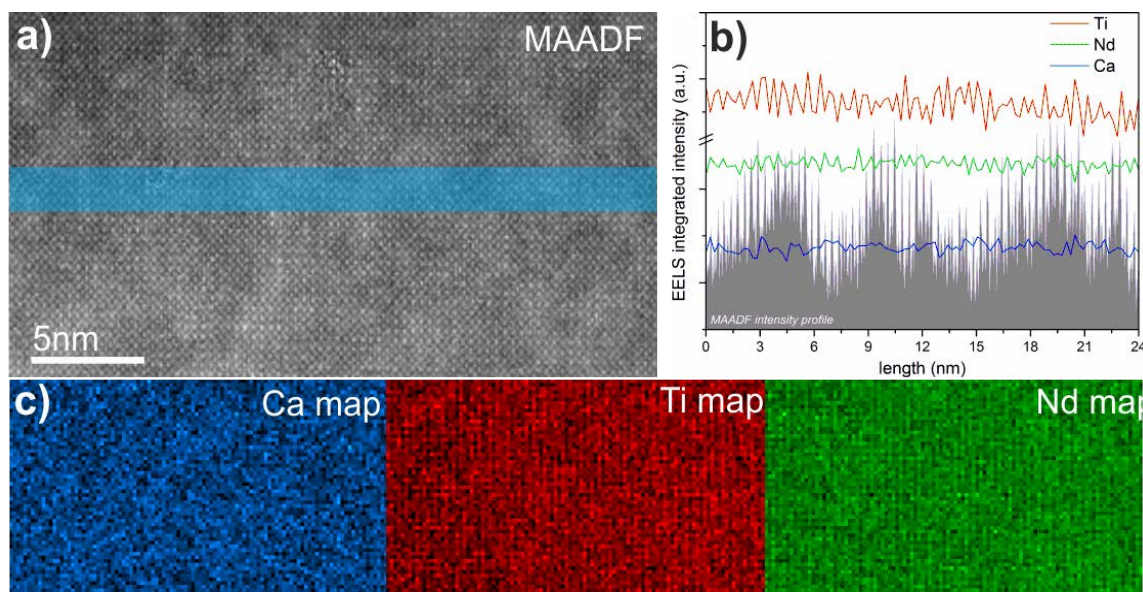


Figure 2. (a): MAADF STEM image of [001] the A-site deficient $\text{Nd}_{0.6}\text{Ca}_{0.1}\square_{0.3}\text{TiO}_3$ ceramic acquired during 2D EELS mapping. (b) MAADF intensity profile averaged over the blue the line indicated in (a) clearly the nano-chessboard intensity modulations. The integrated 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.