Detection of oxygen sub-lattice ordering in A-site deficient perovskites through monochromated core-loss EELS mapping

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Perovskite oxides are widely studied for a variety of applications, from thermoelectrics to fuel cells. Part of the attraction lies in the fact that perovskite ceramics are relatively easy to dope chemically over a wide range of compositions, resulting in various degrees of structural ordering [1]. As a consequence, the properties and functionalities of such materials can be readily tailored [2]. For instance in systems proposed for thermoelectric applications, the presence of superlattices, or domain boundaries vacancies can suppress the thermal conductivity due to increased phonon scattering [3,4]. Understanding therefore the mechanisms behind the formation of such types of ordering in ceramic systems is crucial for their implementation in engineering applications.

Here, we report on an A-site deficient perovskite system based on the Nd$_{2/3}$TiO$_3$ double perovskite. This system, a candidate for thermoelectric applications[5,6], has attracted significant attention due to the presence of a peculiar superstructure [7,8] originating in part in A-site cation vacancy ordering [9].

Using aberration corrected Scanning Transmission Electron Microscopy we investigate a series of Nd$_{2/3}$TiO$_3$ ceramics engineered to possess different degrees of A-site cation-vacancy ordering and as a result vastly different thermoelectric properties. Annular Bright Field Imaging (Figure 1a) of the [110] orientation, preformed in the Nion UltraSTEM 100™ reveals the presence of tilting domains in the TiO$_6$ sub lattice, dependent on the A-site occupancy. Furthermore, advanced image analysis of the electron micrographs was used to measure local distortions in the TiO$_6$ lattice (Figure 1b).

The presence of these octahedral distortions was further investigated by employing atomically resolved monochromated core loss Electron Energy Loss measurements, acquired with an energy resolution better than 0.100eV, using the Nion UltraSTEM 100MC™ instrument. With this approach it is not only possible to map individual components of the Ti L$_{2,3}$ near edge fine structure, but also fine local changes in the ELNES (Figure 2); subtle changes Ti L$_{2,3}$ pre-peak intensity – usually not discernible in conventional EELS measurements as well as changes in the Ti L$_3$ $e_g/t_g$ and $t_g$ L$_3$/L$_2$ intensity ratios all indicative of local TiO$_6$ distortions [10].

References:
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Figure 1. a) Annular Bright Field Image of a Nd$_{2/3}$TiO$_3$ ceramic acquired along the [110] zone axis, showing change in the TiO$_6$ octahedral ordering and b) the same image showing relative displacements of the O sub lattice positions.

Figure 2. Monochromated core loss EELS maps of individual components of the Ti L$_{2,3}$ ELNES and relative intensity changes indicating local distortions of the TiO$_6$ sublattice