

Atomic scale characterisation of A-site deficient thermoelectric perovskites using high spatial and energy resolution EELS

Kepaptsoglou, D.^{1,2}, Azough, F.³, Baran, J.⁴, Molinari, M.⁵, Mizoguchi, T.⁶, Parker, S.⁴, Freer, R.³ and Ramasse, Q.^{1,7}

¹ SuperSTEM, United Kingdom, ² University of York, United Kingdom, ³ University of Manchester, United Kingdom, ⁴ University of Bath, United Kingdom, ⁵ University of Huddersfield, United Kingdom, ⁶ University of Tokyo, Japan, ⁷ University of Leeds, United Kingdom

There are limited numbers of ceramic compositions suitable for high-temperature thermoelectric (TE) applications. [1] The most promising candidates include SrTiO₃ based perovskites, due to their high Seebeck coefficient and simple perovskite structure, which easily lends itself to doping and thus to tailoring of its electron- and thermal-transport properties [2]. However, one their main the drawbacks of is their high thermal conductivity, which has a strong temperature dependence. In the search for new oxides with low thermal conductivities, which could be used on their own as new materials or in conjunction with STO as binary systems, we have identified A-site deficient perovskites as systems with great potential in TE applications. Due to the presence of a large number of cation vacancies in their structure, they can exhibit different degrees of structural ordering, such as cation-vacancy ordering or oxygen octahedral tilting domain ordering. These structural features can significantly affect their electronic structure, by for instance introducing electronic states in the vicinity of the Fermi level, or reduce significantly lattice thermal conductivity. Here we use atomic-scale, high energy resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to inform theoretical predictions from density functional theory electronic band-structure calculations combined with the Boltzmann transport theory, to two promising TE oxide systems.

Firstly, this approach allows us to elucidate structure property relationships in a La_{1/3}NbO₃ ceramic that presents the highest vacancy content among the A-site-deficient perovskite family (whereby 2/3 of the A sites are vacant), a feature which may promote glasslike low thermal conductivity [3]. Atomically resolved imaging and EELS analysis reveals the presence of a layered structure in addition to A-site cation vacancy pairing along the $[\bar{1}\bar{1}1]$ and $[11\bar{1}]$ crystallographic directions. First-principles electronic structure calculations are used to link the temperature dependence of the Seebeck coefficient measured experimentally to the evolution of the density of states with temperature and indicate possible avenues for further optimization through electron doping and control of the A-site occupancies. Moreover, lattice thermal conductivity calculations give insights into the asymmetric dependence of the thermal conductivity on specific crystallographic directions of the material, which could be exploited via nanostructuring.

A similar combination of experimental analysis and theoretical validation was applied to a second A-site deficient perovskite system, based on the Nd_{2/3}TiO₃ double perovskite whose peculiar superstructure originates in part in an incommensurate cation vacancy ordering of the A-site [4]. Using atomically resolved monochromated core loss EELS measurements, acquired with an energy resolution better than 90 meV with a Nion UltraSTEM 100MC microscope, it is possible to map individual components of the Ti L_{2,3} and O K near edge fine structures (ELNES). First-principles multiplet calculations are used to explain subtle changes in the ELNES, and associate them predominantly with Coulombic interactions from the A-sites. Annular Bright Field Imaging can then correlate the presence of tilting domains in the TiO₆ sub lattice with these electronic structure changes observed by EELS.

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[5] SuperSTEM is the U.K. National Research Facility for Advanced Electron Microscopy funded by EPSRC

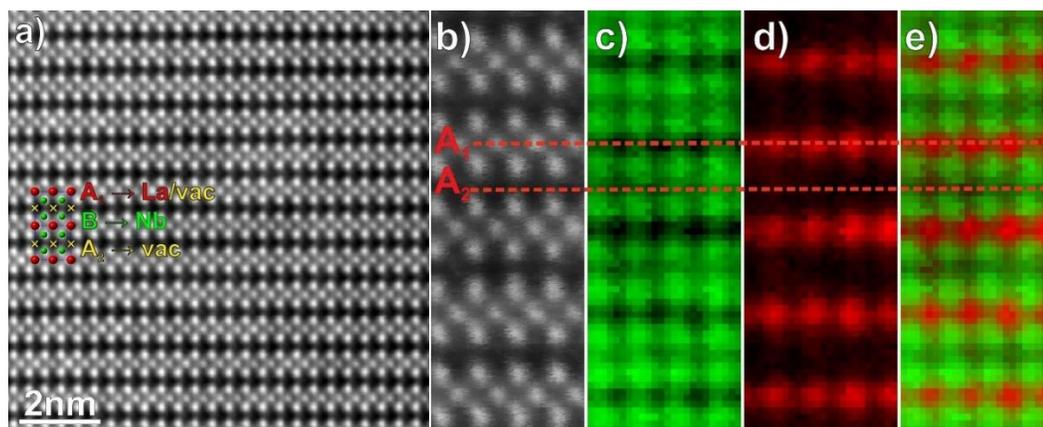


Figure 1. a) HAADF STEM survey image of $\text{La}_{1/3}\text{NbO}_3$ acquired along the [001] zone axis, and atomically resolved EELS maps; b) HAADF STEM, c,d) integrated EELS intensity map of the Nb $L_{2,3}$ and La $M_{4,5}$ edges, respectively and e) RGB overlay of (c) and (d).

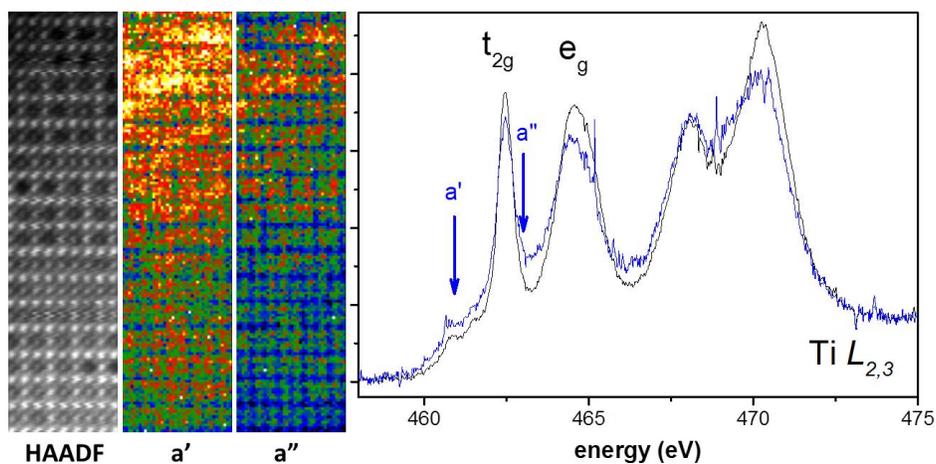


Figure 2. Monochromated core loss EELS maps of individual components a' and a'' of the Ti $L_{2,3}$ ELNES and relative intensity changes related to local electronic charge variations in the vacancy-rich area seen at the top of the HAADF image (left) recorded simultaneously with the EELS