Atomic-resolution mapping of phonon modes across Magnéli structures in thermoelectric (Al,Nb)-doped TiO2

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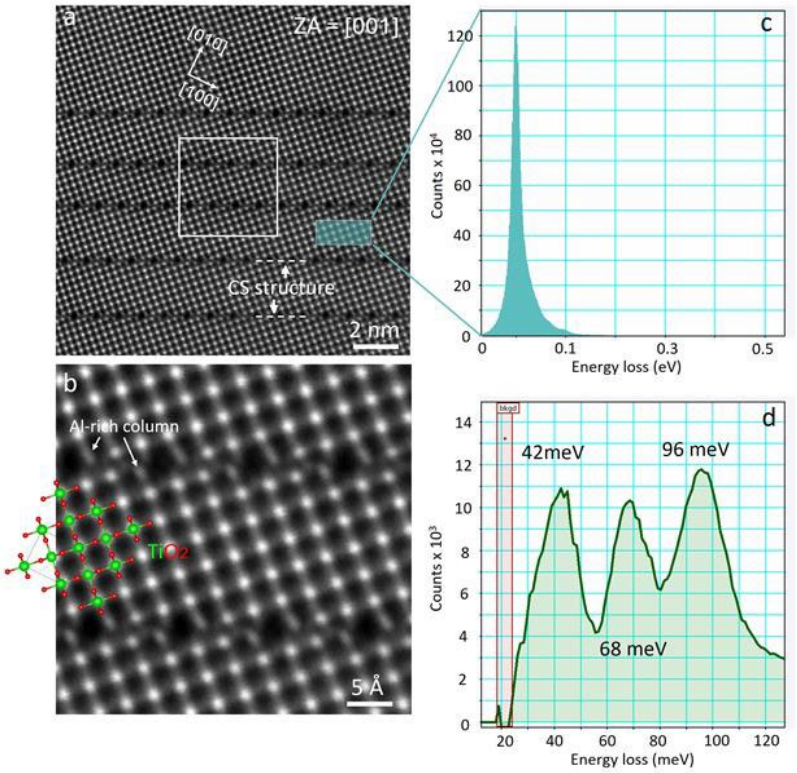
Background incl. aims
Phonons play a critical role in many physical properties of a materials including their thermal and electrical conductivities. Changes in normal phonon mode frequencies occur in the presence of defects. In thermoelectric materials (TE), such defect-induced localised modification of the vibrational response is widely used to tailor the thermal conductivity [1]. In previous work [2,3] it was shown that atomic-level defect engineering resulted in the enhancement of the TE performance of (Al,Nb)-doped TiO2. The introduction of crystallographic shear (CS) structures leads to the reduction of lattice thermal conductivity, which is believed to occur through enhanced phonon scattering. Therefore, it becomes important to measure the spatial distribution and dispersion of the localized vibrational response across the CS structure, in order to gain insight into the heat-conduction process. Recent advances in scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) have provided powerful and flexible tools to study phonons at high spatial resolution, down to single atom sensitivity [4]. In this work, we use STEM-EELS to probe the localised phonon response in CS structures at atomic resolution in the polar (Al,Nb)-doped TiO2.

Methods
EELS measurements were performed on a Nion UltraSTEM100MC 'Hermes' scanning transmission electron microscope, equipped with a Nion IRIS high energy resolution EELS spectrometer with a Dectris ELA direct electron detector. The acceleration voltage was 60 kV and the probe convergence semi angle was 31.5 mrad, resulting in a 1 Å probe size. The experimental optical geometry follows the conditions in Ref [4], in which the off-axis , or dark-field EELS (DF-EELS) geometry significantly reduces the contribution to the EELS signal of electrons having undergone delocalized dipole scattering, while promoting that of localized impact phonon scattering. This approach enables in principle single-atom sensitivity of phonon scattering.

Results
Fig. 1(a-b) shows a HAADF STEM image of the {120}-type CS structure in (Al,Nb)-doped TiO2 acquired along the [001] (rutile-equivalent) zone axis. The CS structure, which results in complex atomic lattice re-arrangements, is accompanied by the segregation of Al along the shear planes, with Al-rich columns preferentially occupying the Ti sites indicated by white arrows on Fig. 1b. Atomically resolved VEELS measurements performed across (Fig. 1(c-d)) reveal atomic scale variations localised at the CS structure boundaries. Changes in both the intensity and the frequency of the main modes are observed at the boundaries, with localised effects on the Al-rich columns. Results are discussed in context of the local structure and chemistry, determined at the same position through careful chemical mapping, while

phonon map simulations using the frequency-resolved frozen phonon multislice method [5] are used to rationalize the experimental findings.

Graphic:



Keywords:

vibrational EELS, phonon, thermoelectric materials

Reference:

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