

Atomic-scale Dual-EELS/EDX Spectroscopy Applied to Rare-earth Oxide Superlattices

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Rare-earth nickelates are known to display complex electronic and magnetic behaviors owed to a very localized and sensitive Ni-site atomic and electronic structure. Specifically, in the wake of recent predictions that nickelates can achieve an electronic structure which mimics that of the high-temperature cuprate superconductors, much research has been focused on manipulating the energetic ordering of Ni d orbitals and 2D conduction in these heterostructures [1,2].

Toward this goal, the present work focuses on the experimental characterization of thin film nickelate superlattice structures, while highlighting critical results which can only be attained by employing the most recent and advanced spectrometers, detector designs, and software. Specifically, the superlattice in question consists of alternating layers of LaTiO₃ and LaNiO₃ sandwiched between a dull insulator, LaAlO₃. Using aberration-corrected scanning transmission electron microscopy (STEM)-based methods, properties such as interfacial sharpness, electron transfer, O presence, and local electronic structure can be probed at the atomic scale, and will be discussed at length. As both energy dispersive X-ray (EDX) and electronic energy loss (EEL) spectroscopies are required, a JEOL JEM-ARM300CF (operated at 160 kV), equipped with dual large-angle EDX silicon drift detectors (SDDs) and a Quantum Gatan imaging filter (GIF) was used; of note is the attainable 0.35 eV energy and 100 pm spatial resolution in spectroscopy mode. Simultaneous acquisition of both signals allows one to bypass the difficult high-energy EELS edges (La, Ni, and Al in this case), favoring a higher energy dispersion, thereby relying on EDX to identify the remaining elements. The higher energy dispersion also allows for detailed fine structure analysis of relevant energy loss edges (Ti L and O K). All of these elements are critical to the above analysis.

A subset of experimental results is presented in Figure 1 below. The repeated superlattice structure is barely visible in the annular dark field (ADF) STEM image, although with the simultaneous EELS/EDX acquisition of the Ni, Ti, and Al signals, the layers are easily identifiable. The color map was recorded on a similar area, and contains only EELS signals from Ni, Ti, Al, and La, demonstrating the large energy range possible with the Quantum GIF. Detailed EELS fine structure analysis will also be discussed in detail, specifically with regards to the O K and Ti L edges, as these can provide fingerprints to identify the local electronic structure, on a layer-by-layer (atomic) scale. The focus of the talk will remain not only on the aforementioned properties, but will also include details and parameters of the acquisitions to facilitate future characterization at this level.

References

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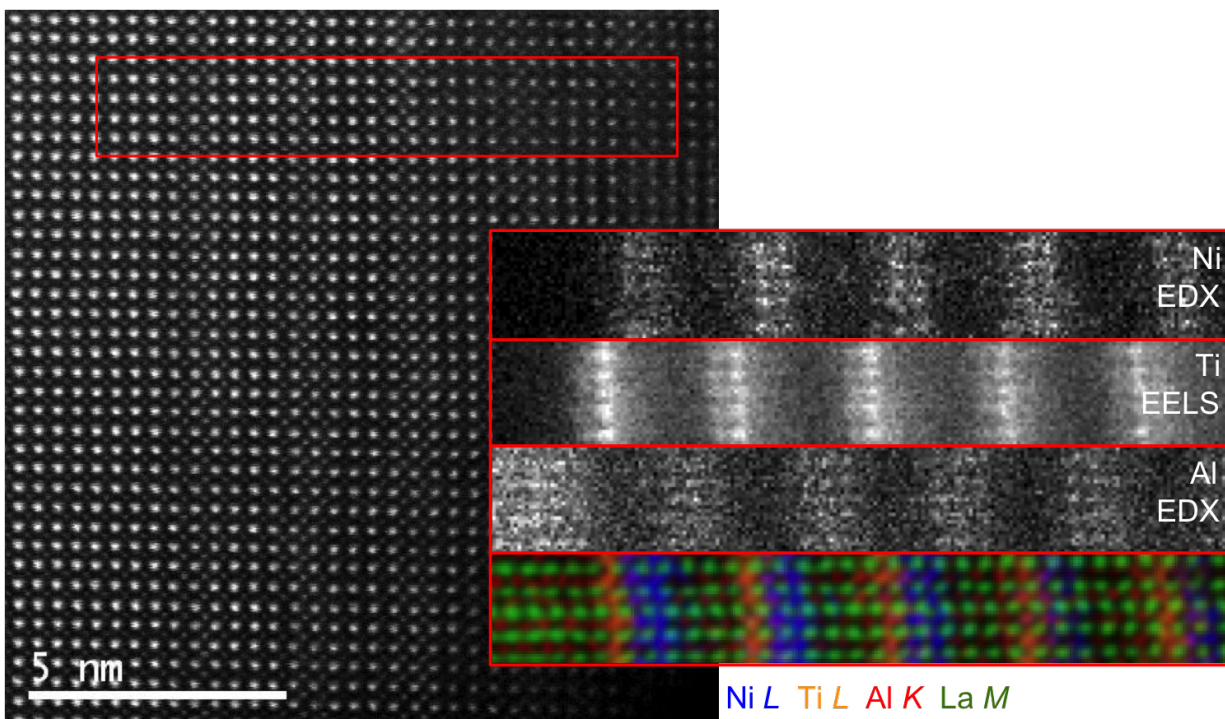


Figure 1: ADF STEM image spanning approximately five superlattice repeats in the horizontal (growth) direction, with various spectroscopic maps shown. The grayscale images resulted from a simultaneous EELS/EDX acquisition; with both the Ni and Al signals coming from EDX, and the Ti coming from EELS. The color map is from a similar region, but contains only EELS data, including Ni, Ti, Al, and La.