Study of near-edge structures of $SrO(SrTiO_3)_n$ Ruddlesden-Popper films using EELS in the TEM and simulations

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Perovskite-layered compounds of the composition $SrO(SrTiO_3)_n$ have attracted great attention not only due to their layered structure, but also due to several application-relevant properties. Of particular interest are the thermoelectricity, electronic conductivity and photocatalysis, which can be tailored by doping with transition metal or rare earth elements [1,2].

The present study focuses on interpreting electron energy-loss near-edge fine structures (ELNES) of $SrO(SrTiO_3)_n$ ($n=1, \infty$) Ruddlesden-Popper (RP) phases by comparison with first principles electronic structure and real space multiple scattering calculations. For that, O-K and Ti-$L_{2,3}$ ELNES have been collected in a monochromated transmission electron microscope of thin RP films prepared by chemical solution deposition on $SrTiO_3$ (001) substrate [3]. Selected area electron diffraction patterns reveal film areas consisting of monocrystalline RP n=1 phase. The chemical solution method has the potential to enable a low-cost, large-scale fabrication of thin layered perovskite films.

Fig. 1 compares the experimental O-K ELNES of $SrTiO_3$ and RP n=1 with the projected densities of unoccupied states (DOS) above the Fermi level calculated using the density functional theory based FPLO 7 code [4]. The peaks within the first 10eV from the edge onset can be understood in the DOS picture, since they correspond to electron transitions into empty O 2p states. Here, the spectrum of RP n=1 displays a characteristic maximum at about 4eV above the edge onset, which will be discussed in terms of the atomic sites in the crystal structure. In general, with increasing energy distance to the edge onset the appropriateness of the band structure model decreases, whereas that of the multiple scattering approach increases. This will be studied by means of calculations performed with the program FEFF 8.4 [5].

Owing to the high energy resolution the crystal field components of the Ti-L_3 and Ti-L_2 white-lines could be resolved (Fig. 2): Each of the Ti-L_3 and Ti-L_2 edges is split into two peaks originating from the t_{2g} and e_g levels of the Ti 3d electronic band. Again, a significant difference between $SrTiO_3$ and RP n=1 occurs: For RP n=1 the t_{2g} and e_g peaks have smaller widths than for $SrTiO_3$ which can be explained by the tetragonal symmetry of the RP crystal structure. Consequently, O-K and Ti-$L_{2,3}$ ELNES are suitable for identifying RP phases at the nanometer scale, especially in case of widespread crystallite orientations difficult to bring into zone axis.

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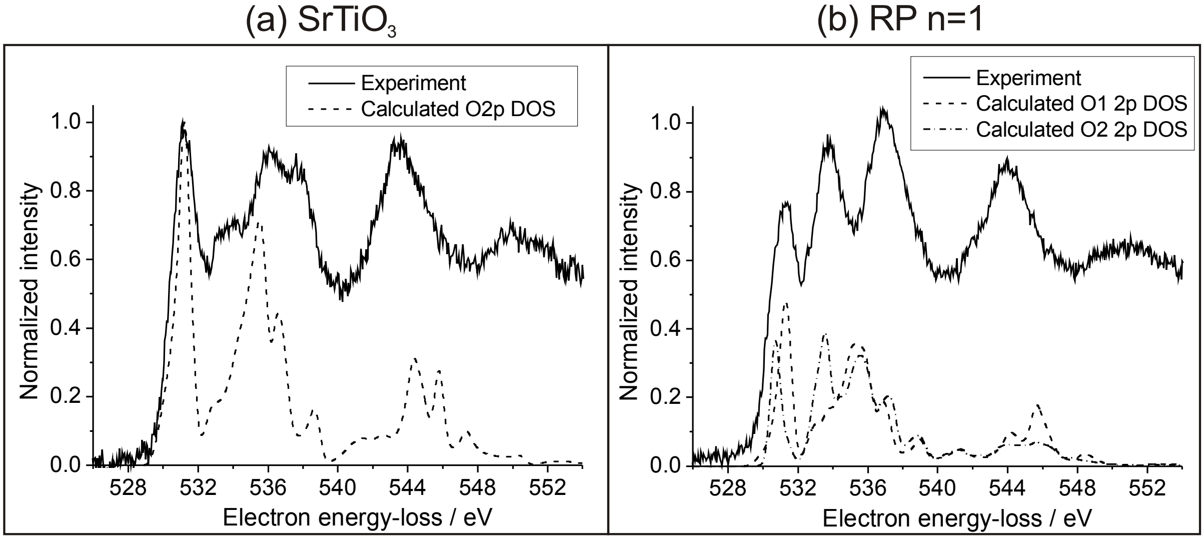

Figure 1. Experimental O-K ELNES compared to calculated projected O 2p DOS, convoluted with a Gaussian (FWHM=0.5eV) (a) for $SrTiO_3$ and (b) for RP n=1. O1 and O2 denote the oxygen sites in the RP n=1 structure. The spectra have been shifted in energy such that the position of the first peak of experiment and calculation coincide, respectively.

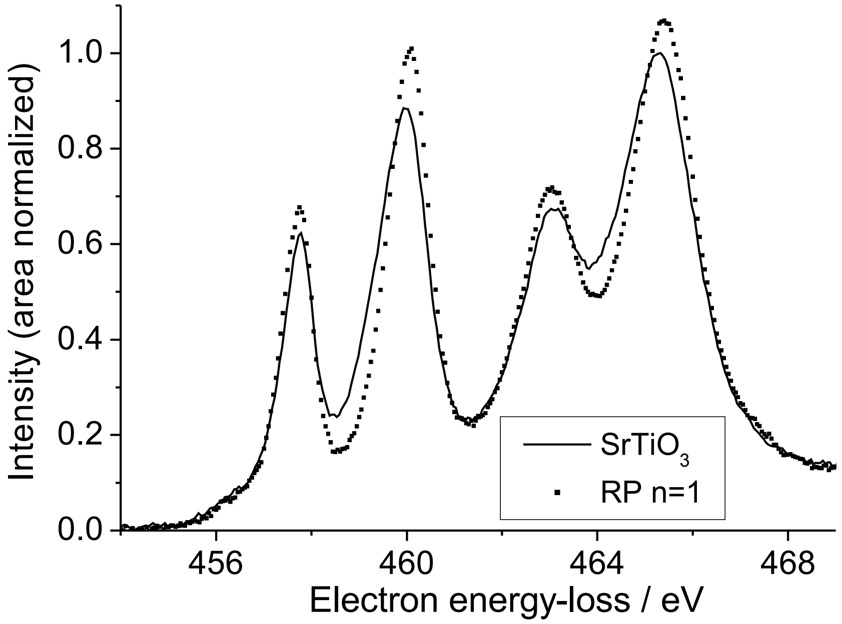

Figure 2. Experimental Ti-$L_{2,3}$ ELNES: $SrTiO_3$ versus RP n=1.

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