TEM and XPS Evidences of O/F Ordering in NbO_2F

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NbO_2F is a member of a relatively small group of $MO_{3-x}F_x$ (M = Nb, Ta, Ti, Mo, W) oxyfluorides with the cubic ReO_3 structure type. They have been of interest in recent years as host compounds for Li-insertion in battery electrolytes [1] and also because of a pressure-induced phase transition from cubic (*Pm*3*m*) to rhombohedral (*R*3*c*) [2]. The average structure consists of corner-sharing $M(O,F)_6$ octahedra, as in undistorted ABO_3 perovskite, with the A sites being empty. Oxyfluorides are reported to exhibit a statistical distribution of O and F, generally attributed to their similar ionic radii (1.35 and 1.285Å, respectively). Bond-length/bond-strength calculations, however, suggest there should be a strong driving force for ordering. Evidence for a one-dimensional O/F ordered columns along ⟨*001*⟩, but with no lateral correlation from one column to the next have already been recognized from transmission electron diffraction [4]. In the present work, coupled HRTEM and electron diffraction revealed the presence of characteristic transverse planes of diffuse intensity running through G±⟨*hk*⅓⟩* regions (*i.e.* existence of O/F-ordering), and XPS confirmed the existence of two distinct atomic positions for O and F and just one for Nb. These data are consistent with three-dimensional O/F ordering within NbO_2F structure.

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