NbO$_2$F is a member of a relatively small group of \(\text{MO}_3\cdot\text{Fx}\) (\(\text{M} = \text{Nb, Ta, Ti, Mo, W}\)) 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 (\(\text{Pm}\overline{3}m\)) to rhombohedral (\(\text{R}\overline{3}c\)) \[2\]. The average structure consists of corner-sharing \(\text{M}(\text{O,F})_6\) octahedra, as in undistorted \(\text{ABO}_3\) perovskite, with the \(\text{A}\) 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 1.285\,\text{Å}, 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 \(\langle 001\rangle\), 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 \(G \pm \langle hk\rangle^*\) 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$_2$F structure.


Keywords: O/F ordering, electron diffraction, XPS