Investigating the modulated structures in the La(Nb,W)O_{4+d} family of oxide ion conductors

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Oxide ion conductors, used in separation membranes, electrolysers and fuel cells, are typically three dimensional isotropic materials, providing fast ion diffusion pathways. These are typically oxides that have been aliovalently substituted to enhance the concentration of mobile defects, most notably oxygen vacancies. One alternative strategy is to consider materials with anisotropic conduction pathways, and with *excess* oxygen, accomodated as interstitials. Based on this strategy we have recently investigated a series of oxides, including $CeTaO_{4.17}$, $CeNbO_{4+d}$ (d = 0, 0.08, 0.25) and developed from this our interest in the structurally related La(Nb,W)O_{4+d} compositions.

Each of these oxidised Ce based phases are known to adopt either a commensurate of incommensurate modulated structure, depending on the level of excess oxygen accommodated [1,2], but from a device perspective performed poorly as the Ce^{3+}/Ce^{4+} ratio introduced undesriable electronic conductivity. In an effort to maintain the modulated structure(s), suppress electronic charge transport and enhance oxygen transport, we have targeted the $LaNb_{1-x}W_xO_{4+d}$ sereis of materials. Our studies have developed the solid solution series phase chemistry and from application of X-ray, neutron and electron diffraction techniques, identified a sequence of modulated monoclinic and tetragonal phases. We have probed the ion transport of a select number of these phases, proving their capability as oxide ion conductors. We highlight the local structrure and variation in the coordination environments that facilitate the fast ion transport, offering routes to optimise and develop new functional oxides.

Keywords: La(Nb, W)O_{4+d}, Phase Diagram, Modulation, Oxygen Transport