Unexpected Structural Properties in 4*d* and 5*d* Metal Oxides

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Carbon-neutral energy-generation is being developed in Australia in order to combat climate change. One such technology is the development of next-generation ion conductors for solid-oxide fuel cells. However, a bottleneck to the large-scale uptake of solid-oxide fuel cells is the poor performance of the proton-conducting electrolytes that separate the anode from the cathode. Various lanthanoid Fergusonite structures ($LnBO_4$) have recently been proposed as potential solid electrolytes in solid-oxide fuel cells, with high-temperature proton conductivity being measured in chemically doped lanthanum orthoniobates ($LaNbO_4$) [1].

In order to understand the effects of chemical doping on the structure and electrochemical properties of these Fergusonite structures, substitutions into the $LnBO_4$ Fergusonites have been investigated [2-3]. Of interest is the substitution of Nb for Ta on the *B*-site, which has shown a decrease in the unit cell volume of the structure [4]. This is particularly remarkable, given the two metal cations have the same ionic radius and Ta has an extra 5*d* valence shell compared to the 4*d* shell of Nb.

Two solid-solution series – $Sm(Nb_{1-x}Ta_x)O_4$ and $Ho(Nb_{1-x}Ta_x)O_4$ – have been synthesised using conventional solid-state methods. Both synchrotron X-ray diffraction and neutron powder diffraction have been used to investigate their structures in order to determine the role of the *B*–O bonds on both the unit cell volume and the observed first-order phase transitions. The experimental data has been further reinforced by ground state energy calculations performed using density functional theory.

These results will be presented, along with a judgement as to whether inducing chemical doping into the $LnBO_4$ Fergusonite structures may lead to them being viable candidates for solid electrolytes in solid-oxide fuel cells.

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