Stabilisation of an unusual "γ-phase": Selective site doping, crystal structures and hydration of the γ-$Ba_4V_xTa_{2-x}O_9$ and γ-$Ba_4V_xNb_{2-x}O_9$ (x = 0-2/3) solid solutions

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Mixed ionic-electronic conductors have a wide range of applications, including in solid oxide fuel cells, oxygen sensors and batteries. The compounds in the $Ba_4M_2O_9$ (M = Nb, Ta) system are known to substantially hydrate and show mixed ionic-electronic conduction (MIEC).[1-3] The high temperature phase γ-$Ba_4Nb_2O_9$ forms a unique structure type, consisting of Nb in tetrahedral, trigonal bi-pyramidal and octahedral coordination sites.[1] This phase forms by heating the low temperature polymorph α-$Ba_4Nb_2O_9$ above 1200 °C. The equivalent tantalum compound $Ba_4Ta_2O_9$ also forms the low temperature α polymorph but at high temperatures instead forms a 6H perovskite.[2] Studies focusing on the hydration and conduction mechanisms in these compounds show that fully hydrated γ-$Ba_4Nb_2O_9$ uptakes 1/3 H2O per f.u. via hydroxylation and shows reasonable proton conduction at low temperatures.[3]

In this presentation I will show that two new compositional series can form the γ-phase: γ-$Ba_4V_xTa_{2-x}O_9$ and γ-$Ba_4V_xNb_{2-x}O_9$ (x = 0-2/3). Synthesis of the γ-tantalum phases are significant as this is the first time it has been shown that this structure type can form in the absence of niobium. For the $Ba_4V_{2/3}Ta_{4/3}O_9$ composition the γ-phase appears to be the thermodynamically preferred structure, forming at 200 °C lower that the parent compound (γ-$Ba_4Nb_2O_9$). We hypothesise that the stabilisation of the γ-phase is driven by the ionic size and bonding variability of the period 5 elements, with the smaller V^{5+} cations preferentially occupying the tetrahedral and trigonal bipyramidal sites. Structural determination of these phases was undertaken using X-ray and neutron powder diffraction. X-ray absorption spectroscopy collected from the Australian Synchrotron support Ta in only the octahedral sites, implying that V must occupy the lower coordination sites. SEM imaging and energy dispersive spectroscopy (EDS) are used to compliment the diffraction analysis and thermogravimetric analysis (TGA) has been used as a preliminary tool to study the changes during dehydration across the series.

References:

1. Ling C.D. *et al., Chem. Mater.* 2009, 21, 16, 3853–3864
2. Ling C.D. *et al., Chem. Mater.* 2010, 22, 2, 532–540
3. Wind J. *et al., Chem. Mater.* 2018, 30, 15, 4949–4958