

## Expanded chemistry and mixed ionic-electronic conductivity in vanadium-substituted variants of $\gamma$ -Ba<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub>

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Two new compositional series with the previously unique  $\gamma$ -Ba<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> type structure,  $\gamma$ -Ba<sub>4</sub>V<sub>x</sub>Ta<sub>2-x</sub>O<sub>9</sub> and  $\gamma$ -Ba<sub>4</sub>V<sub>x</sub>Nb<sub>2-x</sub>O<sub>9</sub> ( $x = 0-2/3$ ), have been synthesised *via* solid-state methods. Undoped Ba<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> forms a 6H-perovskite type phase, but with sufficient V doping the  $\gamma$ -type phase is thermodynamically preferred and possibly more stable than  $\gamma$ -Ba<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub>, forming at a 200 °C lower synthesis temperature. This is explained by the fact that Nb<sup>5+</sup> ions in  $\gamma$ -Ba<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> simultaneously occupy 4-, 5- and 6-coordinate sites in the oxide sublattice, which is less stable than allowing smaller V<sup>5+</sup> to occupy the former and larger Ta<sup>5+</sup> to occupy the latter. We characterised the structures of the new phases using a combination of X-ray and neutron powder diffraction. All compositions hydrate rapidly and extensively (up to 1/3 H<sub>2</sub>O per formula unit) under ambient conditions, like the parent  $\gamma$ -Ba<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> phase, and show moderate but improved mixed-ionic electronic conduction. At lower temperatures the ionic conduction is predominately protonic, while at higher temperatures it is dominated by oxide and electron-hole conduction.

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