Expanded chemistry and mixed ionic-electronic conductivity in vanadium-substituted variants of γ-Ba₄Nb₂O₉

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Two new compositional series with the previously unique γ-Ba₄Nb₂O₉ type structure, γ-Ba₄VₓTa₂₋ₓO₉ and γ-Ba₄VₓNb₂₋ₓO₉ (x = 0-2/3), have been synthesised via solid-state methods. Undoped Ba₄Ta₂O₉ forms a 6H-perovskite type phase, but with sufficient V doping the γ-type phase is thermodynamically preferred and possibly more stable than γ-Ba₄Nb₂O₉, forming at a 200 °C lower synthesis temperature. This is explained by the fact that Nb⁵⁺ ions in γ-Ba₄Nb₂O₉ simultaneously occupy 4-, 5- and 6-coordinate sites in the oxide sublattice, which is less stable than allowing smaller V⁵⁺ to occupy the former and larger Ta⁵⁺ 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 H₂O per formula unit) under ambient conditions, like the parent γ-Ba₄Nb₂O₉ 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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