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Prototype Sandia Octahedral Molecular Sieve (SOMS) $Na_2Nb_2O_6 \cdot H_2O$: Synthesis, Structure and Thermodynamic Stability

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A new microporous phase $Na_2Nb_2O_6 \cdot H_2O$, which transforms to $NaNbO_3$ perovskite on heating, has been synthesized by the hydrothermal method. Rietveld analysis of powder synchrotron X-ray diffraction data reveals that the structure comprises a framework of $[NbO_6]$ and $[NaO_6]$ octahedra with other Na^+ being located in the channels (space group $C2/c$; $a =$ 17.0511(9) Å; $b = 5.0293(2)$ Å; $c = 16.4921(9)$ Å; $\beta = 113.942(2)°$). This phase belongs to the recently synthesized Sandia octahedral molecular sieves (SOMS) family, $Na_2Nb_{2-x}M_xO_{6-x}(OH)_x \cdot H_2O$ (M = Ti, Zr) and is the archetype for the substituted structures. Using drop-solution calorimetry into molten $3Na_2O \cdot 4MoO_3$ at 974 K, the enthalpies of formation of $Na_2Nb_2O_6 \cdot H_2O$ from the constituent oxides and from the elements have been determined to be -295.4 ± 4.8 and -2895.5 ± 6.4 kJ/mol, respectively. From the drop-solution calorimetric data for $Na_2Nb_2O_6 \cdot H_2O$ and its dehydrated perovskite phase, the enthalpy of the dehydration reaction, $Na_2Nb_2O_6 \cdot H_2O \rightarrow 2NaNbO_3 + H_2O$, has been derived, and its implications for phase stability are discussed.