

Stoichiometric molecular hydration of interstitial sites in a close-packed ionic lattice

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The hexagonal perovskite-type oxide $6\text{H-Ba}_4\text{Ta}_2\text{O}_9$ undergoes an unconventional symmetry lowering lattice distortion when cooled below 1100 K in the presence of atmospheric water. This temperature corresponds to the onset of hydration, which reaches a stoichiometric value $6\text{H-Ba}_4\text{Ta}_2\text{O}_9 \cdot \frac{1}{2}\text{H}_2\text{O}$ by ~ 500 K. In the study to be presented here, we used a combination of diffraction, *ab initio* calculations and spectroscopy to show that both processes are due to the incorporation of intact water molecules into the close-packed ionic lattice. The presence of very large Ba^{2+} cations in octahedral interstitial sites (perovskite *B* sites) forces adjacent vacant octahedral interstitial sites to also expand, making room for occupation by water molecules, while also destabilizing the structure in a way that cannot be adequately addressed by conventional symmetry-lowering pathways on cooling. This gives rise to a synergistic hydration-distortion mechanism, which, to the best of our knowledge, is unique among close-packed ionic compounds. We will discuss the implications of our model for protonic and oxide ionic conductivity in hexagonal perovskites as fuel-cell membrane materials, and for earth sciences given the possibility that more examples could exist under high-temperature and pressure conditions.

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