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Crystal structure refinements of borate dimorphs inderite and kurnakovite using ^{11}B and ^{25}Mg nuclear magnetic resonance and DFT calculations

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Abstract

Borate minerals composed of [Bϕ_3] triangles and/or [Bϕ_4] tetrahedra (ϕ = O or OH) commonly exhibit complex polymerizations to form diverse polyanion groups. High-resolution solid-state magic angle spinning (MAS) ^{11}B and ^{25}Mg NMR spectroscopy at moderate to ultrahigh magnetic fields (9.4, 14.1, and 21.1 T) allows for very accurate NMR parameters to be obtained for the borate dimorphs, inderite, and kurnakovite, [$MgB_3O_3(OH)_5 \cdot 5H_2O$]. Improved agreement between experimental results and ab initio density functional theory (DFT) calculations using Full Potential Linear Augmented Plane Wave (FP LAPW) with WIEN2k validates the geometry optimization procedures for these minerals and permits refinements of the hydrogen positions relative to previous X-ray diffraction crystal structures. In particular, the optimized structures lead to significant improvements in the positions of the H atoms, suggesting that H atoms have significant effects on the ^{11}B and ^{25}Mg NMR parameters in inderite and kurnakovite. This study shows that combined high-resolution NMR spectroscopy and ab initio theoretical modeling provides an alternative method for the refinement of crystal structures, especially H positions.

Keywords: Borate dimorphs, saline lakes in Tibet, ^{11}B NMR, ^{25}Mg NMR, solid-state NMR, ultrahigh field NMR, ab initio calculations, FC LAPW, NMR crystallography