

The atomic structure of deuterated boyleite $\text{ZnSO}_4 \cdot 4\text{D}_2\text{O}$, ilesite $\text{MnSO}_4 \cdot 4\text{D}_2\text{O}$, and bianchite $\text{ZnSO}_4 \cdot 6\text{D}_2\text{O}$

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ABSTRACT

Deuterated boyleite $\text{ZnSO}_4 \cdot 4\text{D}_2\text{O}$, was synthesized and the atomic structure, including D positions, was successfully refined in a combined histogram neutron diffraction refinement. The cell dimensions for boyleite are $a = 5.9144(2)$, $b = 13.5665(4)$, $c = 7.8924(2)$ Å, and $\beta = 90.668(2)^\circ$ with space group $P2_1/n$ and $Z = 4$. The atomic structure including D positions of the isostructural mineral ilesite, $\text{MnSO}_4 \cdot 4\text{D}_2\text{O}$, was refined and the cell dimensions are $a = 5.9753(1)$, $b = 13.8186(3)$, $c = 8.0461(1)$ Å, and $\beta = 90.826(2)^\circ$. Deuterated bianchite $\text{ZnSO}_4 \cdot 6\text{D}_2\text{O}$ was synthesized and the atomic structure, including D positions, was successfully refined with a unit cell of $a = 9.969(1)$, $b = 7.2441(7)$, $c = 24.249(3)$ Å, and $\beta = 98.488(5)^\circ$ in space group $C2/c$ and $Z = 8$. A comparison of the hydrogen bonding in $\text{M}^{2+}\text{SO}_4 \cdot 4\text{D}_2\text{O}$ with that in $\text{M}^{2+}\text{SO}_4 \cdot 6\text{D}_2\text{O}$ shows that bifurcated hydrogen bonds are common in the tetrahydrate sulfates but nonexistent in the hexahydrate structures. This is a result of the packing constraints of the rings of the sulfate and metal-containing octahedra in the tetrahydrates. In the hexahydrate sulfates there is no direct linkage between the sulfate and metal-containing octahedra and hydrogen bonds are optimized without packing constraints, and no bifurcated hydrogen bonds are observed.

Keywords: Bianchite, boyleite, ilesite, hexahydrate, moorhouseite, Ni-hexahydrate, rozenite, crystal-structure refinement, neutron diffraction, hydrogen bonding