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The order-disorder character of $FeOHSO_4$ obtained from the thermal decomposition of metahohmannite, $Fe^{3+}_2(H_2O)_4[O(SO_4)_2]$

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ABSTRACT

The iron sulfate $FeOHSO_4$ studied was obtained as a dehydration product of metahohmannite $Fe_2(H_2O)_4[O(SO_4)_2]$ during a synchrotron real-time powder diffraction experiment. As quoted in the literature, $FeOHSO_4$ has iron atoms octahedrally coordinated with two hydroxyl groups and four sulfate O atoms, while each hydroxyl group is bonded to two iron atoms. This compound is commonly described in the orthorhombic system with space group *Pnma*, lattice parameters $a_J = 7.33$, $b_J = 6.42$, and $c_J = 7.14$ Å (a_J, b_J, and c_J are the Johansson lattice parameters), and $Z = 4$. However a preliminary Rietveld refinement of the pattern at about 220 °C using the structural model from the literature yielded a poor fit of the observed data and a final R_p value of about 23%. A careful analysis of the calculated powder diffraction pattern showed unexpected peaks, not observed in the experimental trace, for $h = 2n + 1$, while sharp reflections for $h = 2n$ seemed to point to different lattice constants and space group. The recognition of the order-disorder character of the $FeOHSO_4$ compound was the key to successfully interpreting the unexpected features of the experimental powder pattern and the misfit with respect to the calculated pattern. In fact, $FeOHSO_4$ belongs to a family of OD structures formed by equivalent layers of symmetry *Pbmm*. Only two MDO (Maximum Degree of Order) polytypes are possible. MDO1 results from a regular alternation of stacking operators $2_{1/2}$ and $2_{-1/2}$, and yields an orthorhombic structure with space group *Pnma* and lattice parameters $a_J = 7.33$, $b_J = 6.42$, and $c_J = 7.14$ Å. MDO2 results from the $2_{1/2}|2_{1/2}|2_{1/2}$... sequence of symmetry operators and yields a monoclinic structure with space group $P2_1/c$, $a_M = 7.33$, $b_M = 7.14$, $c_M = 7.39$ Å, and $\beta = 119.7°$.

The analysis of one-dimensional stacking disorder was performed by fitting the observed XRPD pattern with a calculated intensity curve generated by DIFFaX. The disorder model was investigated by taking into account a probability matrix for the occurrence of OD layer sequences. The best fit ($R_p = 0.009$) to the observed powder pattern was obtained with a 61:39 ratio of monoclinic and orthorhombic polytypes for a fully disordered OD layers sequence.