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Metasideronatrite: Crystal structure and its relation with sideronatrite

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Abstract

Metasideronatrite was obtained as the first dehydration product of sideronatrite, $Na_2Fe(SO_4)_2(OH)\cdot 3H_2O$, from Sierra Gorda, Chile. The crystal structure of metasideronatrite was solved by direct methods and refined by full-matrix least-squares to $R = 0.039$, using 574 independent reflections with $I > 3.0\sigma(I)$. It is orthorhombic, space group *Pbnm*, with $a = 7.3959(8)$, $b = 16.0979(15)$, $c = 7.1607(8)$ Å, $V = 852.5(2)$ Å^3, $Z = 4$. The crystal-chemical formula derived from this structural study is $Na_2Fe(SO_4)_2(OH)\cdot H_2O$. The backbone of the structure is the same as that in sideronatrite: infinite $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ chains of interconnected octahedra and tetrahedra parallel to the *c* axis. These chains are linked primarily by Na atoms to build a 3-dimensional network of strong (Fe-O-S) and weak (Na-O) bonds. Another prominent feature of the structure is the arrangement of distorted (NaO_5H_2O) octahedra, which alternately share one edge and one face to form columns parallel to the $[Fe^{3+}(SO_4)_2(OH)]$ chains. Subsidiary intra-chain bonds are provided by H atoms belonging to OH^- groups shared by adjacent Fe octahedra, and to the unique water molecule shared between two adjacent (NaO_5H_2O) octahedra. At normal conditions of relative humidity (RH) and temperature (i.e., RH > 60% and $T < 40$ °C), metasideronatrite rehydrates rapidly to sideronatrite.

The structure solution has allowed us to: (1) investigate the strong relation between sideronatrite and metasideronitrite; (2) elucidate the mechanism involved in the transformation of metasideronatrite into the order/disorder (OD) structure of sideronatrite; and (3) get insight into the stability of this mineral from the valence-matching principle applied to the main structural unit $[Fe^{3+}(SO_4)_2(OH)]^2$ and Na^+ interstitial species. The weak hydrogen bonds and the particular arrangement of the face-sharing adjacent $[NaO_5(H_2O)]$ octahedra are the main factors affecting the stability of metasideronatrite.

Keywords: Metasideronatrite, structure, crystal chemistry, dehydration, sideronatrite