Metasideronatrite: Crystal structure and its relation with sideronatrite

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ABSTRACT

Metasideronatrite was obtained as the first dehydration product of sideronatrite, \( Na_2 Fe(SO_4)_2(OH) \cdot 3H_2O \), 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 \( a = 7.3959(8) \), \( b = 16.0979(15) \), \( c = 7.1607(8) \), \( V = 852.5(2) \) \( \text{Å}^3 \), \( Z = 4 \). The crystal-chemical formula derived from this structural study is \( Na_3 Fe(SO_4)_2(OH) \cdot H_2O \). The backbone of the structure is the same as that in sideronatrite: infinite \( [Fe^{3+}(SO_4)_2(OH)]^- \) 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 \( (NaO_2H_2O) \) octahedra, which alternate to 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 \( (NaO_2H_2O) \) 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 metasideronatrite; (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 \( [Fe^{3+}(SO_4)_2(OH)]^- \) and \( Na^+ \) interstitial species. The weak hydrogen bonds and the particular arrangement of the face-sharing adjacent \( [NaO_2(H_2O)] \) octahedra are the main factors affecting the stability of metasideronatrite.

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

INTRODUCTION

Bandy (1938) described a new basic hydrated sulfate of sodium and ferrie iron, from Chuquicamata (Chile), as metasideronatrite to stress the lower water content relative to the related mineral sideronatrite, \( Na_2 Fe(SO_4)_2(OH) \cdot 3H_2O \). According to this author, metasideronatrite is orthorhombic dypiramidal, with an observed density of 2.46 g/cm\(^3\). Chemical analysis (Bandy 1938) led to the following chemical formula: \( Na_2Fe^{3+}(SO_4)_2(OH) \cdot 1.5H_2O \). For metasideronatrite, Césbron (1964) proposed a substantially identical chemical formula with less water content, \( Na_2Fe^{3+}(SO_4)_2(OH) \cdot H_2O \). Depending on humidity, metasideronatrite rehydrates quickly to sideronatrite. From this observation, Césbron (1964) inferred that the analysis quoted in Bandy (1938) was likely made on material in the course of rehydration/dehydration. Structural data for metasideronatrite are limited and low quality. Using Weissenberg, precession, and powder diffraction data, Finney (1973) confirmed metasideronatrite as orthorhombic, \( a = 7.357(3) \), \( b = 16.002(4) \), \( c = 7.102(8) \) \( \text{Å} \), space group \( Pbnm \) or \( Pn\bar{2}m \), with the formula proposed by Bandy (1938). On the basis of new DTA and TGA data combined with X-ray single-crystal Weissenberg photographs, Scordari and Milella (1982) concluded that Césbron's formula corresponds to a mixture of two metasideronatrite-like compounds of different water contents. Powder-diffraction data (Scordari et al. 1982) of differently hydrated metasideronatrite-like compounds support this hypothesis.

The exact structure and correct chemical formula of metasideronatrite is still unsolved. We report here for the first time: (1) the determination and refinement of the crystal structure of metasideronatrite; (2) the correct water content deduced from the structure; (3) the factors that influence the stability of the compound; and (4) the structural relation with sideronatrite.

EXPERIMENTAL AND STRUCTURE DETERMINATION

The crystals investigated here were obtained by spontaneous dehydration on a dry and hot day from sideronatrite from Sierra Gorda (Chile). A Bruker AXS X8 APEX II four-circle Kappa diffractometer equipped with a CCD area detector (Bruker 2003) was used for the structure data collection. A total of 1340 frames was recorded by a combination of several 0 and \( 0 \) rotation sets with 0.5° scan width. Data reduction, including intensity integration, correction for Lorentz, polarization, and background effects, and scale variation, was done using the package SAINT-IRIX (Bruker 2001). A semi-empirical absorption correction (Blessing 1995) was done using SADABS (Sheldrick 2004), and equivalent reflections were merged. Subsequent analysis of the intensity data, by XPREP (Sheldrick 2003), confirmed Finney’s results (1973) and indicated the centrosymmetric distribution of the normalized structure factors, allowing assignment of the unique space group \( Pbnm \). The final unit-cell parameters were obtained from the measured reflections after integration and are reported in Table 1, together with other crystallographic details. The crystal structure was solved by direct methods using SIR2004 (Burla et al. 2005), obtaining a satisfactory structural model for all independent non-H atoms. The structure was refined using the program CRYSTALS (Betteridge et al. 2003). Reflections with \( l > 3\sigma(l) \) were considered suitable for the structure refinement, in which scattering curves for neutral chemical species were used. Refined parameters were scale factor, atom positions, cation oc-

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