Crystal structure of Na$_3$Fe(SO$_4$)$_3$: A high-temperature product ($\sim$400 °C) of sideronatrite [Na$_3$Fe(SO$_4$)$_3$OH·3H$_2$O]  

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ABSTRACT  

The iron sulfate Na$_3$Fe(SO$_4$)$_3$ studied here has been obtained as a high-temperature (HT) product ($\sim$400 °C) from the thermal decomposition of sideronatrite from Sierra Gorda (Chile) having composition Na$_3$Fe(SO$_4$)$_3$(OH)·3H$_2$O. The structure determination was carried out using synchrotron X-ray powder diffraction. Structural data refined by the Rietveld method, up to $R_p = 11.9\%$, are: space group $R3$, lattice parameters $a = b = 13.6231(1)$ Å and $c = 9.0698(1)$ Å, $V = 1457.76(2)$ Å$^3$; and $Z = 6$. The structure of Na$_3$Fe(SO$_4$)$_3$ can be described in terms of FeO$_6$ octahedra connected to sulfate tetrahedra by corner-sharing to form infinite chains [Fe(SO$_4$)$_3$]$_\infty$, running along c. These chains are joined together by Na atoms to build up a three-dimensional network of strong (Fe-O-S) and weak (Na-O) bonds. The topological relationships of Na$_3$Fe(SO$_4$)$_3$ to the structure of some analog minerals are also discussed.  

Keywords: Iron sulfate, synchrotron, structure solution, Rietveld refinement  

INTRODUCTION  

Synthetic Na$_3$Fe(SO$_4$)$_3$ plays an important role in several high-temperature solid-state reactions in the industrial processes related to pigment manufacturing, catalysts, and magnetic materials. Alkali iron sulfates, such as Na$_3$Fe(SO$_4$)$_3$, formed by the interaction of SO$_3$ in fuel gas with alkalis and iron oxide, are invariably found as highly corrosive deposits on superheater/reheater boiler tubes in power plants (Viswanathan et al. 2005).  

Following the results of a thermogravimetric analysis (Césbron 1964), the iron sulfate Na$_3$Fe(SO$_4$)$_3$ studied here, has been obtained as a high-temperature (HT) product ($\sim$400 °C) of the thermal decomposition of a hydrated sulfate of sodium and ferric iron, sideronatrite [Na$_3$Fe(SO$_4$)$_3$(OH)·3H$_2$O], coming from Sierra Gorda, Chile (Scordari and Ventruti 2009). Recently a new mineral having the same composition of the synthetic phase, Na$_3$Fe(SO$_4$)$_3$, was found among fumarolic encrustations at Eldfell volcano, Heimaey Island, Iceland (Balić-Žunić et al. 2009). The mineral is hygroscopic and is not stable in the open air. It is rarely found as highly corrosive deposits on superheater/reheater boiler tubes in power plants (Césbron 1964).  

Crystallographic data for Na$_3$Fe(SO$_4$)$_3$, are limited in the literature. In fact, an indexed powder pattern of a pure synthetic Na$_3$Fe(SO$_4$)$_3$ compound is reported in the PDF-2 database (ICDD PDF-2 entry 39-0243), but no structural model has been proposed to date.  

The development of X-ray powder diffraction profile-fitting methods combined with the use of high-resolution powder diffraction data from high-intensity synchrotron sources makes the ab initio structure determination of microcrystalline inorganic compounds possible. In this work, the crystal structure of Na$_3$Fe(SO$_4$)$_3$ has been solved and refined using synchrotron powder diffraction data. A description of the basic structural features and the relationship with some analog phases is also reported.  

EXPERIMENTAL METHODS  

The Na$_3$Fe(SO$_4$)$_3$ sample was obtained by heating a sample of sideronatrite, Na$_3$Fe(SO$_4$)$_3$(OH)·3H$_2$O, from Northern Chile (Scordari and Ventruti 2009). Intensities for the structure solution were collected at the Italian beamline MCX at ELETTRA (Trieste, Italy). Powder data were collected at the fixed wavelength of 0.82660 Å calibrated against the NBS-640b Si standard with $a = 5.43094(4)$ Å at 298 K. The sideronatrite sample was ground in an agate mortar to particle sizes below 400 mesh and loaded into 0.3 mm silica glass capillary. The capillary was mounted on a standard goniometer head and kept spinning during the collection to minimize the effects of preferred orientation. The temperature was raised to a fixed temperature $T = (-390 \, ^\circ C)$ using the hot air flow from a heating gun system and monitored with a thermocouple positioned about 0.5 mm below the capillary. In the first stage of the structure determination, the positions of 31 resolvable peaks of the Na$_3$Fe(SO$_4$)$_3$ phase in the range 6–30 °2θ were selected. The peaks were all successfully indexed, with the figures of merit $M(30) = 72$ and $F(30) = 176$ (0.002187, 78), using the program Treor linked to the Crysfire suite (Shirley 2002). The lattice parameters obtained were refined in the space group $R3$, to the values $a = 13.626(3)$ Å and $c = 9.070(2)$ Å; using the program CELREF (Laugier and Boschu 1999).  

A reasonable structural model was obtained through the Endeavour software (Putz et al. 1999), a direct space ab initio program, which combines the global optimization method, based on the simulated annealing algorithm, with the potential energy calculation of the system. This model was subsequently refined, through the GSAS (Larson and Von Dreele 2000) Rietveld program. The diffraction peaks were modeled using a pseudo-Voigt function with three Gaussian and two Lorentzian line-broadening coefficients. The background was fitted with a Chebyshev polynomial with 19 coefficients to account for the incoherent contribution of the silica glass capillary. The diffraction pattern shows a minor phase, α-Fe$_2$O$_3$ (Blake and Hessevick 1966), which was included in the refinement. Some extra peaks (not identified) at 5.92, 4.05, 3.50, 3.13, 3.04, 2.96, 2.87, and 2.61 Å, corresponding to small amounts of other impurity phases, were present in the pattern and were left out of the refinement. The zero shift correction, two scale factors, and the unit-cell