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The first anhydrous metal fluorosulfate $Na_3Fe(SO_4)_2F_2$ with layered structure prepared via the interesting "tailor" role of fluorine ions based on $Na_3Fe(SO_4)_2$

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ABSTRACT

A ferric(III) fluorosulfate $Na_3Fe(SO_4)_2F_2$ has been synthesized under hydrothermal conditions and characterized by X-ray powder diffraction (*Pnca*, $a = 6.6419$ Å, $b = 8.8115$ Å, $c = 14.0023$ Å). Its crystal structure is constructed by corner-sharing FeO_4F_2 octahedra and SO_4 tetrahedra, which shows a layered character with numerous four- and eight-membered polyhedral rings. These rings further connect and intersect with each other to form the three-dimensional layers. Sodium ions are located at the interspace of these layers and keep the charge balance. This is the first time to note the participation of fluorine atoms in the formation of two-dimensional structure of anhydrous transition metal fluorosulfates. Meanwhile, an interesting "tailor" role of the fluorine ions has also been investigated by comparing the structures of $Na_3Fe(SO_4)_2F_2$ and $Na_3Fe(SO_4)_2$, indicating the feasibility of fabricating compounds from some known structures with the assistance of halogen ions.

1. Introduction

Transition metal sulfates in A–M–S–O quaternary systems (A = an electropositive cation, M = a transition metal cation) have drawn considerable attention due to their potential applications as catalysts, ion exchangers, molecular sieves and magnetism [1]. Of particular interest is the family of iron sulfates with worldwide abundance, low cost, environmental benignity and rich valence state [2–6]. Up to now, a remarkable range of iron sulfates with various dimensionalities and stoichiometries have been synthesized [7–10]. However, most of them are in aqueous phases, which have poor thermal and chemical stability, and thereby limits their industrial applications [11–14]. Meanwhile, works concerning about anhydrous transition fluorosulfates are still rare, and only four types of structure topology have been reported so far, which are $AMSO_4F$ (A = Li, Na; M = Mg, Mn, Fe, Co, Zn) with three-dimensional framework, $A_2M(SO_4)F_3$ (A = K, Rb, Cs; M = Al, Sb, Mn), $KSnSO_4F$ and $K_2ZrSO_4F_4$ with one-dimensional structure [15–19].

Generally, fluorine and chlorine ions can serve as structural linkers or "tailor" in the synthesis process [20–25]. For example, halogen ions can replace the OH^- groups as terminals in the structures, resulting in enhancement of the structural stability and the formation of low-dimensional frameworks. Recently, a novel anodic material $LiFeSO_4F$ for lithium ionic battery was successfully prepared by ion exchange of $FeSO_4{\cdot}H_2O$, suggesting the transformation of aqueous to anhydrous phase via F^- ions is a promising way to fabricate functional compounds [26]. Moreover, halogen ions can also act as a "tailor" to modify the structures by cutting off partial bonds, resulting in novel low-dimensional or porous structures [27–29]. Very recently, Huang's group reported that the switch from the two-dimensional layered structure to the one-dimensional band structure in the system of transition metal germanophosphates can be achieved by the addition of a small amount of $KF{\cdot}2H_2O$ [30]. In any case, the corresponding mechanism and rules is still unclear till now.

In dealing with the iron sulfate system, we created an F^- enriched reaction environment, in which the F^- may lead to the formation of novel compounds. Our efforts have resulted in the successful synthesis of a novel sodium ferrous fluorosulfate compound, $Na_3Fe(SO_4)_2F_2$. This is also the first time that anhydrous transition fluorosulfates with layered structure is reported. In this work, we present the synthesis, crystal structure and magnetic study of the $Na_3Fe(SO_4)_2F_2$ sample, and the "tailor" role of the fluorine ions is also discussed.

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2. Experimental

2.1. Synthesis

For a typical synthesis, 0.526 g of iron(III) citrate and 0.568 g of Na_2SO_4 were dissolved in a mixture with *n*-butanol (11.2 mL) and distilled water (3.60 mL), and stirred until a homogeneous solution formed. 0.360 mL of 49% HF and 0.325 mL of 85% H_2SO_4 were then added in the solution drop by drop. Afterwards, the solution was transferred into a PTFE-lined bomb and heated at 150 °C for 5 days before cooling to room temperature naturally. The resulting pale yellow plate crystals denoted as “**1**” were washed with ethanol and distilled water, collected by centrifugation and dried at 353 K. The yields were 45% based on Fe.

2.2. Structure determination

One single crystal was mounted on a thin glass fiber under an optical microscope, and the data sets were collected at 295 K on a Nonius Kappa CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Herein, the position of all atoms were resolved with single-crystal data, and the structures were solved by direct methods using the program SHELXS-97-2 [31]. Fourier calculations and subsequent full-matrix least-squares refinements were carried out using SHELXL-97-2. All calculations were performed with the WinGX crystallographic software package [32], and all the metal atoms and oxygen atoms were refined isotopically. The atomic structure of synthetic was refined by least-squares refinement. The corresponding crystal data and structure refinement information are given in Table 1. The atomic positional and displacement parameters are given in Table S1 and the selected distances are listed in Table S2.

2.3. Other characterizations

The crystal X-ray diffraction (XRD) patterns were determined by a diffractometer (Rigaku D, max 2550V) employing Cu Kα radiation ($\lambda = 0.15418$ nm). The patterns were entirely consistent with those calculated from the structure determined by single crystal X-ray diffraction. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed on an EPMA-8705QH2 electron microscope equipped with a LINKS ISIS. The presence of F element in compound **1** was confirmed by EDS, and element analysis gives a Fe/S ratio of 1.12:2 (calcd 1:2). Thermogravimetric analyses were performed on a STA-409PC/4/H LUXX DSC-TGA instrument at a heating rate of 10 K min^{-1} in a flow of N_2 to a maximum temperature of 1273 K. The result indicates that compound **1** has good thermal stability. As shown in Fig. S1, compound **1** can keep stable up to 500 °C, and then two steps of decomposition in the range of 500–900 °C can be identified. The weight loss between 500 and 720 °C is 11.2%, which is ascribed to the remove of fluorine atoms (calcd 10.7%). The weight loss between 720 and 930 °C is 34.4% and corresponds to the release of SO_2 (calcd 35.9%). All the above characterization is consistent with the crystal structure of compound **1** determined by X-ray diffraction.

Table 1
Crystal and structure refinement data for $Na_3Fe(SO_4)_2F_2$.

Empirical formula	$F_2FeNa_3O_8S_2$
Formula weight	354.94
λ (Å)	0.71073
T (K)	293
Crystal system	orthorhombic
Space group	*Pnca* (60)
a (Å)	6.642
b (Å)	8.812
c (Å)	14.002
V (Å^3)	819.53
Z	4
D_{calc} (cm^{-3})	2.877
Absorption coefficient (mm^{-1})	2.57
θ range (°)	2.73–28.33
$F(000)$	692
Goodness-of-fit (GOF) on F^2	1.272
Total data collected	1018
Independent reflection	945
R_{int}	0.0166
R indices[$I > 2\sigma(I)$], R_1, wR_2	0.0194, 0.0684
Final R indices, R_1[a], wR_2[a]	0.0212, 0.0694

[a] $w = 1/[\sigma^2(F_O)^2 + (0.0882P)^2]$ where $P = [F_O^2 + 2F_C^2]/3$.

3. Results and discussion

3.1. Crystal structure

The structure of the new compound was determined from single crystal X-ray diffraction, and the calculated XRD pattern is consistent with the measured one (Fig. S2). Compound **1** has a layered structure made up of FeO_4F_2 octahedra and SO_4 tetrahedra. As shown in Fig. 1, the asymmetric unit contains 9 non-hydrogen atoms. The independent ferrous atom shares four oxygen corners with four SO_4 tetrahedra (Fe–O = 2.253(3) and 2.353(3) Å), and the remaining corners are occupied by two terminal fluorine atoms (Fe–F = 2.476(1) Å), defining a fairly distorted octahedral geometry. Sulfur atom is tetrahedrally coordinated by four O atoms with S–O bond distances ranging from 1.480(1) Å to 1.482(1) Å, which only deviates slightly from the ideal geometry.

In the structure of compound **1**, each FeO_4F_2 octahedron shares all the oxygen corners with four neighboring SO_4 groups, and each SO_4 group bridges two adjacent FeO_4F_2 octahedra, resulting in a polyhedral two-dimensional network. The fluorine vertices of the ferrous octahedra are found on the outside of the layers, whose terminal nature can be considered as the reason for the formation of the low-dimensional structure (Fig. 2a). As shown in Fig. 2b, numerous eight-ring “windows” (i.e., a loop consisted of eight corner-shared alternating ocatahedra and tetrahedra) can be identified in the layer. The connection among these “windows” via FeO_4F_2 octahedra endows the layer an interesting honeycomb topology. Due to the zigzag-like stack of FeO_4F_2 octahedra along *b* axis in the layers, the layer motif exhibits a puckered character.

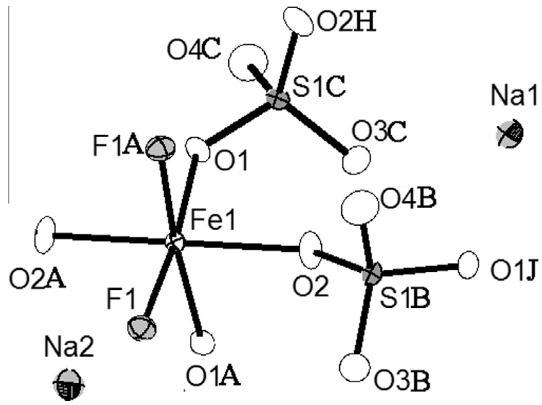

Fig. 1. Thermal ellipsoid plot (50% probability) and atomic labeling scheme of $Na_3Fe(SO_4)_2F_2$. Atom labels having “A”, “B”, “C”,”J” or “H” refer to symmetry-generated atoms.