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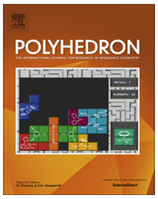

NH_4MSO_4F (M = Mn, Fe, Co, Ni): A series of thermally stable transition metal fluorosulfates with KTP-type structure

Gen-wu Ge [a,*], Wen Luo [a], Xin-lei Zhang [a], Xiao-di Du [a], Li-li Liang [b,*]

[a] Henan Key Laboratory of Rare Earth Functional Materials, The Key Laboratory of Rare Earth Functional Materials and Applications, Zhoukou Normal University, Zhoukou 466001, PR China

[b] Department of Chemistry, Bengbu Medical College, Bengbu 233030, PR China

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ABSTRACT

Four new transition metal fluorosulfates NH_4MSO_4F (M = Mn, **1**; Fe, **2**; Co, **3**; Ni, **4**) were solvothermally synthesized in the solvent of N,N-dimethylacetamide (DMA) with HF as the mineralization agent. The X-ray single crystal diffraction analyses revealed that **1**–**4** are isomorphous, and possess a three-dimensional framework with the same structural topology as the known nonlinear optical material $KTiOPO_4$ (KTP). The four compounds were constructed from MO_4F_2 octahedra and SO_4 tetrahedra to form two kinds of intersecting 6-membered ring channels along the *a* and *c* axes, respectively. Within the channels locate the NH_4^+ cations from the decomposition of DMA molecules. All the compounds are thermally stable up to 330 °C. The magnetic studies of **1**–**4** revealed the antiferromagnetic interaction behaviors in the range of 1.8–300 K.

1. Introduction

Porous solid materials based on TO_4 (T = Si, Al, P, etc.) tetrahedra have been extensively studied due to their potential applications in the fields of catalysis, separation and ion-exchange [1]. The similarities of coordination chemistry and geometry between SO_4 and PO_4 tetrahedra suggest the possibility to prepare a large family of open-framework metal sulfates with diverse structures. Compared to the abundance and diversity of metal phosphates reported in the literature [2], however, the metal sulfates constructed from SO_4 tetrahedra have not been paid much attention until a few transition metal sulfates and rare earth sulfates with interesting framework structures and properties were reported in the past decades [3]. Recently, alkali ion containing metal fluorosulfates $LiMSO_4F$ (M = Mn, Fe, Co, Ni, Zn, etc.) with olivine, tavorite and sillimanite structures have been of particular interests because these materials exhibit excellent electrochemical properties with promising applications in lithium-ion based batteries [4]. By using the methods of preparation of zeolites and aluminophosphates, i.e., hydrothermal synthesis with the presence of structure-directing agents and/or mineralizer F^- ion, a number of metal sulfates have been reported [5], which exhibit rich structural chemistry. The incorporation of fluoride into the transition metal sulfate frameworks results in linkage of MO_4F_2 or MO_2F_4 units through vertex, edge, or face sharing to form additional M–F–M linkages, this allows the control of the structural dimensionality and linking fashion of the polyhedra [6], while most known 3D framework sulfates are formed by strict alternation of MO_6 or MO_4 and SO_4 units without any direct connection between two MO_6 octahedra or MO_4 tetrahedra.

On the other hand, it is known that $KTiOPO_4$ (KTP) is an outstanding nonlinear optical material for second harmonic generation (SHG) due to its high power conversion efficiencies [7]. The Ti and P atoms in the KTP framework can be replaced by other transition or main-group metals, and other group V elements, respectively, while the K^+ ions can also be substituted with other alkali, ammonium ions, and organic amines etc. [8]. There have been a number of metal phosphates [9] and arsenates [10] with KTP-type structure reported in the literature. However, the metal sulfates with KTP-type structure have not been reported so far. We herein report the synthesis and characterization of four new transition metal fluorosulfates NH_4MSO_4F (M = Mn, **1**; Fe, **2**; Co, **3**; Ni, **4**) possessing KTP-type structure.

2. Experimental

2.1. Synthesis

All reagents were of analytical grade and used as received without any further purification. The four compounds were

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* Corresponding authors.
E-mail addresses: gegenwu@163.com (G.-w. Ge), liangjyt@163.com (L.-l. Liang).

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solvothermally prepared by using nearly identical methods from a mixture of metal nitrate, concentrated H_2SO_4 and aqueous HF. A typical procedure is as follows: 0.5 mmol of metal nitrates (0.375 g of 50% $Mn(NO_3)_2$ solution for **1**, 0.202 g of $Fe(NO_3)_3{\cdot}9H_2O$ for **2**, 0.146 g of $Co(NO_3)_2{\cdot}6H_2O$ for **3** and 0.375 g of 33% $Ni(NO_3)_2$ solution for **4**) were first dissolved in 6 ml of N,N-dimethylacetamide (DMA), followed by dropwise addition of 2 mmol of concentrated H_2SO_4 (98%, 0.11 ml) under stirring. To the above solution was added 2 mmol of 40% HF solution (be cautious!) with a syringe. The clear solution after stirring for 30 min was transferred into a 15 ml Teflon-lined stainless steel autoclave, and heated at 180 °C for 5 days. After cooling to room temperature naturally, colourless diamond crystals (**1** and **2**), red (**3**) or light green (**4**) bipyramid crystals were obtained by filtration, and washed with ethanol and acetone, then dried in air.

2.2. Characterization

Powder X-ray diffraction (PXRD) data were obtained using Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.54056 Å), with a step speed of 0.2° per second. FT-IR spectra were recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 cm^{-1} using the KBr pellet method. Thermogravimetric analyses (TGA) were conducted on a Perkin-Elmer Pyris I thermogravimetric analyzer with a heating rate of 20 °C min^{-1} in an N_2 atmosphere. The temperature-dependent magnetic susceptibility measurements of compounds **1**–**4** were performed on the powdered samples in the temperature range of 1.8–300 K at a 2000 Oe external field with a Quantum Design MPMS-XL7 SQUID magnetometer.

2.3. Crystal structure determinations

Suitable single crystals of **1**–**4** were selected for single-crystal X-ray diffraction analyses. The measurements were carried out on a Bruker SMART APEX CCD diffractometer operating at room temperature. Intensities were collected with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. Data reductions and absorption corrections were performed using the SAINT and SADABS programs [11], respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on F^2 using the SHELXL-97 program [12]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Details of the crystal parameters, data collection and refinement results are summarized in the Table 1. Selected interatomic bond lengths and angles with their estimated standard deviations and further details can also be obtained from the Supplementary information.

3. Results and discussion

3.1. Synthesis

The four title compounds were solvothermally synthesized from the DMA solution of metal nitrates, concentrated H_2SO_4 and aqueous HF. Even though the DMA molecules were not incorporated into the final products, part of the DMA molecules may decompose to NH_4^+ ion in the acidic solution under high temperature and press. It is noted that although Fe(III) nitrate was used during the synthesis, the valence of iron in the final product turned to be divalent while ammonia decomposed from the solvent of DMA may act as the reducing agent in the reduction procedure

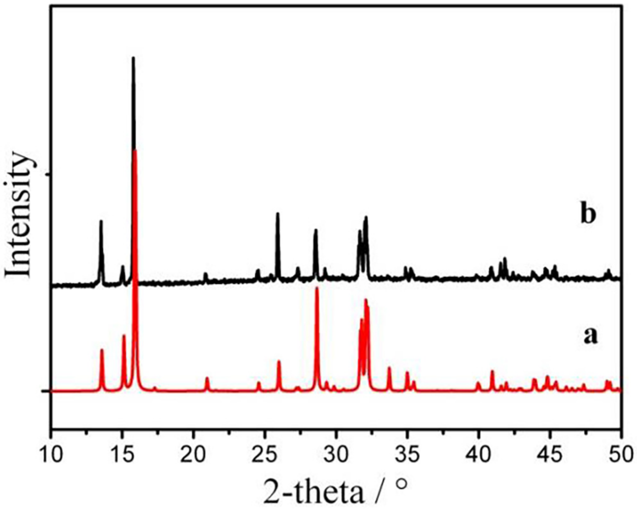

Fig. 1. PXRD patterns of **1**: (a) calculated, (b) as-synthesized.

Table 1
Crystallographic and structural data for **1**–**4**.

Compound reference	1	2	3	4
CCDC No.	843552	843553	843554	843555
Chemical formula	NH_4MnSO_4F	NH_4FeSO_4F	NH_4CoSO_4F	NH_4NiSO_4F
Formula mass	188.04	188.95	192.03	191.81
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Unit cell dimensions				
a (Å)	13.4004(12)	13.2721(9)	13.1861(7)	13.0229(16)
b (Å)	11.0933(10)	10.8809(7)	10.6969(5)	10.6215(13)
c (Å)	6.7101(6)	6.6449(4)	6.6201(3)	6.5487(8)
V ($Å^3$)	997.49(15)	959.61(11)	933.77(8)	905.83(19)
T (K)	291(2)	291(2)	291(2)	291(2)
Space group	*Pnna*	*Pnna*	*Pnna*	*Pnna*
Number of formula units per unit cell, *Z*	8	8	8	8
Number of reflections measured	4918	4766	4561	4529
Number of independent reflections	986	947	921	893
R_{int}	0.0689	0.0606	0.0607	0.0602
Final R_1 values ($I > 2\sigma(I)$)[a]	0.0542	0.0567	0.0505	0.0515
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[a]	0.0974	0.1249	0.1079	0.0927
Final R_1 values (all data)[a]	0.0809	0.0724	0.0700	0.0763
Final wR (F^2) values (all data)[a]	0.1032	0.1291	0.1131	0.0969
Goodness of fit (GOF) on F^2	1.014	1.066	1.089	1.022

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.