

(H₂O)[V^{III}₂F₆] and Pyr-VF₃ : Hydrothermal Synthesis, Structure Determination, and Magnetic Characterization of New Fluorides with the Pyrochlore Type

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

Small green triangular crystals of a new tridimensional hydrated vanadium(III) fluoride have been hydrothermally prepared in a simple way by heating a mixture of V : HF : H₂O in the molar ratio 1 : 1 : 50 at 200°C for 3 days. Its structure was solved by X-ray diffraction in the cubic space group *Fd $\bar{3}m$* (No. 227) with $a = 10.4636(2)$ Å. (H₂O)[V^{III}₂F₆] presents the structure of the well-known pyrochlore type. The cavities contain water molecules which are lost by heating ($T < 250^\circ\text{C}$) without any structural change. The thermal stability of this new form of VF₃ (Pyr-VF₃) with the pyrochlore structure is compared to that of the already known Pyr-FeF₃ (1). The magnetic behavior of Pyr-VF₃ is described. © 2001 Elsevier Science

vanadium metal (200 mesh/99.5 + %, Chempur), fluorhydric acid (48%, Prolabo), and deionized water in a molar ratio 1:1:50. The optimal synthesis requires heating of the mixture at 200°C for 5 days in a Teflon-lined stainless-steel autoclave and cooling to room temperature for 1 day. The pH of the solution varies from 1 to 2–3 throughout the synthesis. After filtration, a homogenous green polycrystalline powder is obtained with a yield of 50% based on vanadium. It is then washed and dried at room temperature. Examination of the pure sample under polarized light shows the presence of small green triangular single crystals.

INTRODUCTION

In the 1970s and the 1980s, a lot of work was devoted to the pyrochlore structure (2) which was a good model for chemical exchanges and physical properties [see for instance Ref. (3) and references therein]. The inorganic framework contained either two types of cations with different charges, the anions being either F, O, or S, or one type of cation with two different anions with different charges (mainly O and F). Only two examples, Pyr-FeF₃ (4) and, further, Pyr-WO₃ (5), obtained by “chimie douce” reactions, contained one cation and one anion. Further attempts to obtain new pyrochlores of this type failed.

We present here the hydrothermal synthesis, the structure, and the magnetic properties of two new examples of this kind: (H₂O)[V^{III}₂F₆] and its isotopic anhydrous form, Pyr-VF₃.

EXPERIMENTAL

Synthesis

The title compound is obtained as a pure phase by hydrothermal synthesis under autogenous pressure by mixing

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Chemical Analysis

The thermogravimetric analysis of the product was performed under oxygen flow on a TA Instrument TGA2050 apparatus with a heating rate of 5°C/min from 20°C to 600°C. Two weight losses are observed. The first one (9.1%), occurring between 50 and 250°C, is in good agreement with the departure of the water molecules located in the cavities of the structure (th. = 7.7%). The second (16.4% between 250 and 400°C, th. = 14.5%) corresponds to the oxidation of VF₃ into V₂O₅ as shown by the diffractogram of the residue.

The measured density (2.78(2)), obtained under helium with a Micromeritics multipycnometer, compares well with the theoretical value (2.714).

Structure Determination

One of the small triangular crystals was glued on a glass fiber and analyzed by single-crystal X-ray diffraction on a Siemens three-circle diffractometer equipped with a CCD detector and working with the MoK α monochromatized wavelength ($\lambda = 0.71073$ Å). The SAINT program was used to reduce the collected data and to correct them for Lorentz-polarization effects. The SADABS program allowed a semi-empirical absorption correction to be applied.

TABLE 1
Crystallographic and Chemical Data

Chemical formula	(H ₂ O)[V ₂ ^{III} F ₆]
Formula weight (g · mol ⁻¹)	234
Crystal size	0.05 × 0.02 × 0.02 mm
Lattice parameters	<i>a</i> = 10.4636(2) Å
System	Cubic
Space group	<i>Fd</i> $\bar{3}$ <i>m</i> (No. 227)
Volume/ <i>Z</i>	1145.63(4) Å ³ , 8
<i>d</i> _{calculated} (g · cm ⁻³)	2.714
<i>d</i> _{measured} (g · cm ⁻³)	2.78(2)
Collected int.	1849
Ref (<i>I</i> ≥ 2σ(<i>I</i>))	102
<i>R</i> _{int}	0.1641
<i>R</i> ₁ , <i>wR</i> ₂ (<i>F</i> _o ²)	0.056, 0.171
Residual electronic density	1.397, -0.883 e.Å ⁻³

The structure was solved and refined using SHELX-TL in the cubic space group *Fd* $\bar{3}$ *m* (No. 227). The vanadium was first located from direct methods. Further Fourier difference syntheses provided the positions of fluorine and oxygen atoms. An anisotropic thermal factor was applied to all nonhydrogen atoms. After the final refinement using (32*e*) sites for the water molecules, the reliability factors *R*₁(*F*_o) and *wR*₂(*F*_o²) converged to 0.056 and 0.171 respectively for 1849 reflections (*I* ≥ 2σ(*I*)). These relatively high values for the reliability factors could be explained by the very small size of the crystal (0.05 × 0.02 × 0.02 mm) and consequently by the rather poor quality of the data.

All data collection conditions are reported in Table 1. Table 2 provides the atomic coordinates. Anisotropic thermal factors can be obtained by request from the authors.

Thermodiffractometry experiments were carried out under vacuum between 50 and 800°C (1°C/min) on a Siemens D5000 diffractometer using a Pt strip heating element and an HTK 16 Anton Parr furnace. Diagrams were recorded every 30°C up to 250°C, and then, every 10°C.

Magnetism

The magnetization (*M*) of the sample was measured on anhydrous Pyr-VF₃ as a function of the temperature in the range 2–500 K with a Quantum Design Squid device. The resulting magnetic susceptibility was then deduced. More-

TABLE 2
Atomic Coordinates (× 10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for (H₂O)[V₂^{III}F₆]

Atoms	Wyckoff	<i>x</i>	<i>y</i>	<i>z</i>	<i>T</i> _{X_{occup}}	<i>U</i> (eq)
V	16 <i>d</i>	0	5000	0	1	8(1)
F	48 <i>f</i>	1250	6250	-659(4)	1	20(2)
Ow	32 <i>e</i>	1491(18)	1491(18)	1491(18)	0.25	29(11)

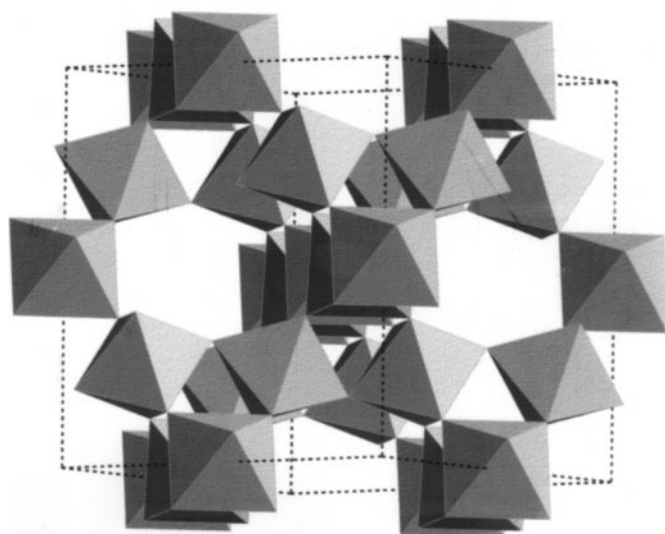
over, field-cooled and zero-field-cooled experiments were performed to get accurate information on the magnetic ordering temperature.

DISCUSSION

(H₂O)[V₂^{III}F₆] exhibits the well-known tridimensional pyrochlore type structure which exhibits cages delimited by six-membered-ring windows and containing the water molecules.

The structure is built up from the connection of infinite tilted chains of octahedra of vanadium oriented in two perpendicular directions (Fig. 1). These octahedra are very regular with six equivalent distances V–F of 1.974(2) Å and F–V–F angles of 88.6(2)°, 91.4(2)°, and 180.0°. Each octahedron is linked via its two trans fluorine apices to two octahedra of the same chain. The four remaining atoms ensure the connection between three chains, one perpendicular to the two others with V–F–V angles values of 139.1(2)°. The inorganic framework generates the presence, in the [111] direction, of intersecting tunnels. The free aperture of the hexagonal windows is approximately 2.6 Å. The trivalent oxidation state of the vanadium (calculated, 2.88) is confirmed by the valence bond calculation using the data of Brese and O'Keeffe (6).

The originality of this work resides principally in the simplicity of the synthesis compared to that of isostructural compound FeF₃, which needed more steps. Unfortunately, the attempts to synthesize iron(III) fluoride in the same way failed: instead of FeF₃, FeF₂ · 4H₂O is obtained. Moreover, although FeF₃, (H₂O)[V₂^{III}F₆], and Pyr-VF₃ have the same structural type, their thermal behaviors are quite different.

**FIG. 1.** Perspective view of the (H₂O)[V₂^{III}F₆] pyrochlore structure (water molecules are omitted for clarity).

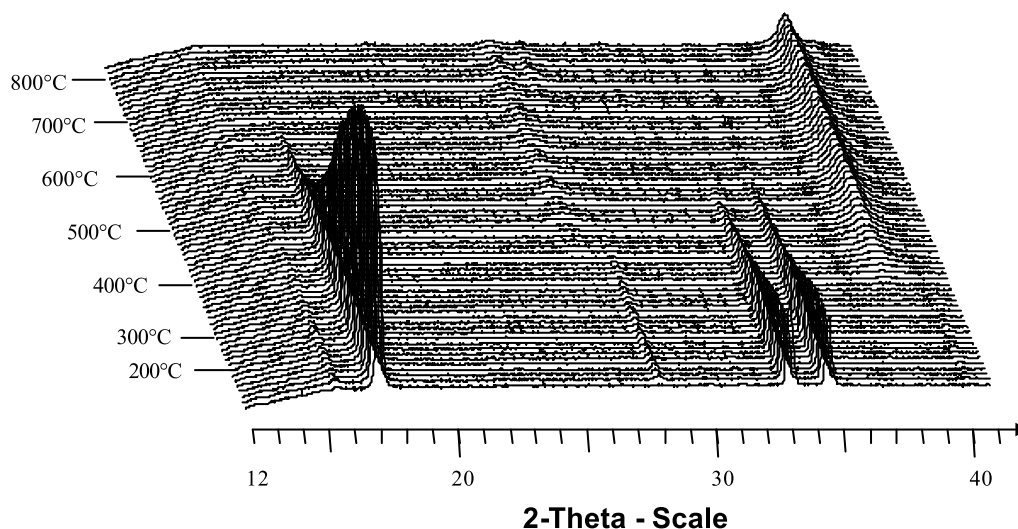


FIG. 2. Thermodiffractograms performed under vacuum, of $(\text{H}_2\text{O})[\text{V}_2^{\text{III}}\text{F}_6]$ from 25 to 800°C.

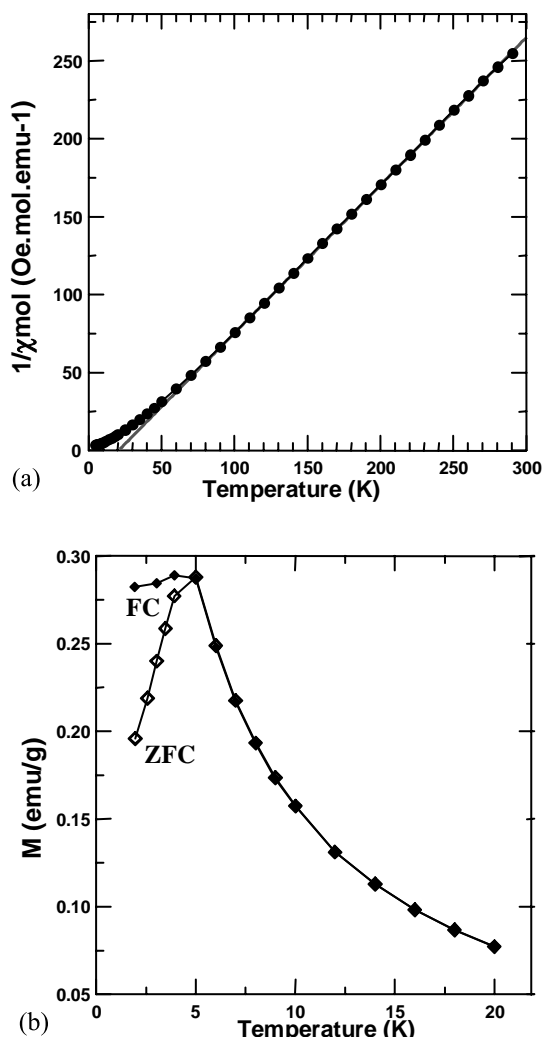


FIG. 3. (a) $\chi^{-1} = f(T)$ curve for Pyr- VF_3 . (b) Zero-field-cooled and field-cooled ($H = 100$ G) curves for Pyr- VF_3 .

Whereas Pyr- FeF_3 transformed successively into HTB (hexagonal tungsten bronze) at ca. 300°C and into ReO_3 -type FeF_3 (1) at ca. 380°C, the stability of the homologous vanadium solid is much lower. Indeed, the thermodiffractogram performed under vacuum (Fig. 2) shows that the dehydration of $(\text{H}_2\text{O})[\text{V}_2^{\text{III}}\text{F}_6]$, beginning at 50°C, is structurally characterized by an increase of the (111) reflection, without any change in the diffraction pattern. That means that the dehydrated Pyr- VF_3 form keeps the pyrochlore structure. Moreover, the decrease of I_{111} above 250°C indicates that Pyr- VF_3 begins to decompose at this temperature, before any transformation into $\alpha\text{-VF}_3$, with the simultaneous appearance of the peaks corresponding to V_2O_3 . This oxide probably comes from the hydrolysis of Pyr- VF_3 by the water molecules remaining in the chamber.

Pyr- VF_3 is antiferromagnetic below 5.0(1) K as proved both by the $\chi^{-1}(T)$ (Fig. 3a) and FC/ZFC curves (Fig. 3b). The former exhibits an unusual positive asymptotic Curie temperature ($\theta_p = 20$ K) indicating ferromagnetic couplings, which can be explained by the d^2 electronic structure of V^{3+} (7) involved in a 180° superexchange interaction. The difference between FC and ZFC curves below T_N is consistent with a nonaligned magnetic structure. It may be assumed that, as Pyr- FeF_3 (8), the frustrated magnetic structure is formed by four magnetic subnetworks with spins at 109° one from each other. This could also explain the low T_N value of Pyr- VF_3 , which is in the same range as that of Pyr- FeF_3 (19 K).

Finally, the cages which appear in the pyrochlore structure after removal of the water could be filled by alkaline ions via exchange reactions for providing new mixed-valence $\text{V}^{\text{II}}\text{-V}^{\text{III}}$ fluorides. The study is currently in progress and will be published elsewhere.

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