Synthesis and Characterization of New Fluoride-Containing Manganese Vanadates $A_2Mn_2V_2O_7F_2$ ($A = Rb, Cs$) and Mn_2VO_4F

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Abstract

Large single crystals of $A_2Mn_2V_2O_7F_2$ ($A = Rb, Cs$) and Mn_2VO_4F were grown using a high-temperature ($\sim 600^\circ\text{C}$) hydrothermal technique. Single crystal X-ray diffraction and powder X-ray diffraction were utilized to characterize the structures, which both possess MnO_4F_2 building blocks. The $A_2Mn_2V_2O_7F_2$ series crystallizes as a new structure type in space group $Pbcn$ (no. 60), $Z = 4$ ($Rb_2Mn_2V_2O_7F_2$: $a = 7.4389(17) \text{ \AA}$, $b = 11.574(3) \text{ \AA}$, $c = 10.914(2) \text{ \AA}$; $Cs_2Mn_2V_2O_7F_2$: $a = 7.5615(15) \text{ \AA}$, $b = 11.745(2) \text{ \AA}$, $c = 11.127(2) \text{ \AA}$). The structure is composed of zigzag chains of edge-sharing MnO_4F_2 units running along the a -axis, and interconnected through V_2O_7 pyrovanadate groups. Temperature dependent magnetic susceptibility measurements on this interesting one-dimensional structural feature based on Mn^{2+} indicated that $Cs_2Mn_2V_2O_7F_2$ is antiferromagnetic with a Neél temperature, $T_N = \sim 3 \text{ K}$ a Weiss constant, θ , of $-11.7(1) \text{ K}$. Raman and infrared spectra were also analyzed to identify the fundamental V–O vibrational modes in $Cs_2Mn_2V_2O_7F_2$. $Mn_2(VO_4)F$ crystallizes in the monoclinic space group of $C2/c$ (no. 15), $Z = 8$ with unit cell parameters of $a = 13.559(2) \text{ \AA}$, $b = 6.8036(7) \text{ \AA}$, $c = 10.1408(13) \text{ \AA}$ and $\beta = 116.16(3)^\circ$. The structure is associated with those of triplite and wagnerite. Dynamic fluorine disorder gives rise to complex alternating chains of five- and six-coordinate Mn^{2+} . These interpenetrating chains are additionally connected through isolated VO_4 tetrahedra to form the condensed structure.

Keywords: hydrothermal, vanadate, manganese(II), antiferromagnetism

1. Introduction

The high temperature hydrothermal method ($T = 500\text{--}700^\circ\text{C}$, $P = 1\text{--}3\text{ kbar}$) is an excellent route to new solid-state compounds with promising physical properties including interesting optical, ferroic and magnetic behavior.[1-4] Recently we have been investigating tetrahedral vanadate, $[\text{VO}_4]^{3-}$, as an oxyanion building block in hydrothermal conditions, and found that it displays an extremely rich coordination chemistry as a structural unit for both rare earths [5] as well as d-block metal ions. [6-8] Vanadates are intriguing building blocks in that they are isostructural to the phosphates, which of course display an exceptionally rich and diverse coordination chemistry. However, the exploratory structural chemistry of the vanadates is not yet as fully developed as the corresponding phosphates. The vanadates differ somewhat in that they are measurably larger and most importantly, they introduce d-orbitals into the bridging ligand. [9-15] This has the potential to change the coupling behavior between the open shell metal ions and reverse the Goodenough-Kanamori-Anderson superexchange rules.[16,17] Thus the fuller development of the metal vanadates is clearly warranted.

One synthetic variable that can be manipulated to explore new synthetic chemistry using the hydrothermal method is the concentration and identity of the mineralizer. Typically the mineralizer is either hydronium or a small nucleophile such as OH^- , carbonate, or halide ions. Our previous work with the vanadates focused primarily on OH^- or carbonate as mineralizer species. In this work we describe our initial foray into the use of fluoride as a mineralizer in the vanadate system. It has a number of properties that make it an intriguing mineralizer. Previously we determined that fluoride displays excellent solubilizing and crystallization behavior in several other hydrothermal systems. [18,19] Fluoride has a similar charge and size as hydroxide and thus can act as a direct substitute for hydroxide in a lattice, which is attractive for several reasons.

Replacement of OH^- with F^- in a lattice should lead to significant increase in thermal stability since fluoride does not decompose as easily as hydroxide in solid state structures. Also, the use of fluoride as mineralizer also raises the possibility of introducing two different anion building blocks, which opens up an enormous range of possibilities for new structural types. The presence of a tetrahedral oxyanion as one building block and a single anion F^- as another building block in the lattice creates the possibility of a huge array of new structural variations.

It should be noted that combinations of vanadate oxyanions with fluoride are not especially common. There is a considerable range of structures reported by Poeppelmeier and co-workers using fluorovanadates (VO_xF_y)^{z-} as individual structural units. [20,21] These are not mixed anionic building blocks however. There are a number of solids containing transition metal fluoride phosphate building blocks generating a complex series of structures which suggests that an enormous range of new compounds awaits.[22-25] Most of these are prepared by hydrothermal reactions of fluoride sources and metal oxides in the presence of bases at moderate temperatures (150-230°C). Such materials can act as models and surrogates for vanadate fluorides but the vanadates are often capable of displaying considerably different chemistry than the more common phosphates. In addition to the aforementioned magnetic coupling differences, the vanadates have a somewhat greater tendency to form polyvanadates (V_xO_y)^{z-} relative to phosphates, creating an even larger library of structural types. For example, a recent report described a new series of metal vanadate fluorides where the chemical, structural and oxidation state versatility of vanadate and fluoride are on full display. [26] These were also prepared using a low temperature hydrothermal method. Other examples of this limited class of vanadate fluorides in the solid state structural literature appear confined to the vanadate fluorapatites [27-29] and the mineral mounanite. [30]

We were interested in determining if the use of fluoride mineralizer under high temperature/high pressure conditions is appropriate for the growth of new transition metal solids with anionic tetrahedral building blocks. In this manuscript we report our first synthetic efforts in the use of high temperature hydrothermal fluids to prepare compounds with first row transition metal vanadate building units along with fluoride. We found that the high temperature hydrothermal conditions are a suitable synthetic medium and that by replacing hydroxide mineralizer with fluoride we can isolate large single crystals of novel solids with both fluoride and vanadate building blocks. Both vanadate and pyrovanadate building blocks were isolated in this study and the magnetic properties are also reported for the low dimensional solid $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

2. Experimental Section

2.1. Hydrothermal Crystal Growth of $\text{A}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ ($\text{A} = \text{Rb}, \text{Cs}$) and $\text{Mn}_2\text{VO}_4\text{F}$.

All hydrothermal synthesis reactions were carried out at 580 °C for 6-7 days using 2.5 in. long silver ampoules with outer diameters of ¼ in. In these ampoules 60% of the total were filled with 0.2 g of reactants and the appropriate mineralizer. After that, the loaded silver ampoules were welded using a tungsten inert gas welder and placed in a Tuttle-seal autoclave filled with deionized water to achieve desirable counter pressure before heating the autoclave to 580 °C using ceramic band heaters. After the reaction period, autoclaves were cooled to room temperature and crystals were retrieved from the silver ampoules by washing with deionized water using the suction filtration method. All chemicals in this study were used as obtained: Cs_2CO_3 (Alfa Aesar, 99%), CsF (Alfa Aesar, 99%), Rb_2CO_3 (Alfa Aesar, 99%), RbF (Alfa

Aesar, 99%), MnO (Strem Chemicals, 99%), Mn₂O₃ (Alfa Aesar, 98%), and V₂O₅ (Alfa Aesar, 99.6%).

The A₂Mn₂V₂O₇F₂ (A = Rb, Cs) and Mn₂VO₄F series of compounds were synthesized using CsF and RbF as the mineralizers. Cs₂Mn₂V₂O₇F₂ single-crystals were isolated by reacting Cs₂CO₃ (0.0979 g), Mn₂O₃ (0.0474 g) and V₂O₅ (0.0547 g) in a molar ratio of 1:1:1 with 0.4 mL of 5 M CsF. After the completion of the reaction period, orange columnar crystals (1-2 mm, Figure 1) were recovered as the only product. Similarly, Rb₂Mn₂V₂O₇F₂ (orange columns, ~0.4 mm) can be also synthesized using a mixture of Rb₂CO₃ (0.0809g), Mn₂O₃ (0.0553g) and V₂O₅ (0.0637g) with a molar ratio of 1:1:1 using 5 M RbF as the mineralizer. However, a lower yield and small crystal size was observed for Rb₂Mn₂V₂O₇F₂, which was co-crystallized with an unidentified black powder. Crystals of Mn₂VO₄F resulted from a study of investigating mineralizer concentration, and were produced using identical reaction conditions as for Cs₂Mn₂V₂O₇F₂ but with 1 M CsF as the mineralizer, see the discussion below.

Figure 1. Hydrothermally grown crystals of Cs₂Mn₂V₂O₇F₂ (a) and Mn₂VO₄F (b).

2.2. X-ray Diffraction.

The structures of $A_2Mn_2V_2O_7F_2$ ($A = Rb, Cs$) and Mn_2VO_4F single crystals were investigated using a Rigaku AFC8S diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107\text{\AA}$) and a Mercury CCD detector. Data collection and processing, including corrections for absorption and Lorentz and polarization effects were performed using the CrystalClear software package. [31] Space group determinations were made based on the systematic absences. The structures were solved by direct methods using SHELXS-2014 and refined on F^2 by least-squares, Fourier difference techniques using SHELXL-2014.[32] All atoms were refined anisotropically. The structure of Mn_2VO_4F was initially refined as an ordered model with one fully-occupied fluorine atom. Larger anisotropic displacement parameters (ADPs) for this atom coupled with significant residual electron density in a good bonding arrangement with Mn atoms in the structure suggested a disordered model should be tested. Refinement according to this disordered model with two half-occupied fluorine atoms maintained the necessary charge balance, and resulted in ADPs comparable to the oxygen atoms in the structure. This accounted for all significant electron density, and resulted in improved refinement statistics. Thus the disordered model was preferred. Crystallographic data of the title compounds are summarized in Table 1, and selected interatomic distances and angles are given in Table 2. Further details of the structures may be obtained from Fachinformationszentrum Karlsruhe on quoting CSD deposition numbers 431166-431168. As further verification of the structural models, energy dispersive X-ray analysis (EDX) methods were utilized to determine the relative chemical concentration of the elements in each compound, and these results are reported in the Supplementary Information (Table S1).

Table 1: Crystallographic data for $A_2Mn_2V_2O_7F_2$, $A = Rb, Cs$ and $Mn_2(VO_4)F$.

empirical formula	$Rb_2Mn_2V_2O_7F_2$	$Cs_2Mn_2V_2O_7F_2$	Mn_2VO_4F
FW	532.70	627.58	243.82
crystal system	orthorhombic	orthorhombic	monoclinic
crystal dimension, mm	0.22 x 0.04 x 0.04	0.24 x 0.04 x 0.04	0.25 x 0.20 x 0.18
space group, Z	$Pbcn$ (no. 60), 4	$Pbcn$ (no. 60), 4	$C2/c$ (no. 15), 8
T , K	293	293	293
a , Å	7.4389(17)	7.5615(15)	13.559(2)
b , Å	11.574(3)	11.745(2)	6.8036(7)
c , Å	10.914(2)	11.127(2)	10.1408(13)
β , °	--	--	116.16(3)
V , Å ³	939.6(4)	988.2(3)	839.6(3)
d_{calc} , g cm ⁻³	3.766	4.218	3.858
μ (Mo $K\alpha$), mm ⁻¹	14.887	11.629	8.024
Tmin	0.5177	0.4122	0.8144
Tmax	1.0000	1.0000	1.0000
2 θ range	3.26-25.24	3.20-25.24	3.35-25.14
Reflections collected	7407	7560	3411
Unique reflections	848	891	750
Observed reflections ($I > 2\sigma(I)$)	776	859	701
No. of Restraints	0	0	0
No. of Parameters	72	72	83
final R [$I > 2\sigma(I)$] R1, wR2	0.0379/0.0971	0.0322/0.0802	0.0275/0.0681
final R (all data) R1, wR2	0.0405/0.0996	0.0330/0.0812	0.0295/0.0699
GoF	1.127	1.157	1.092
largest diff. peak/hole, e/ Å ³	1.114/-1.148	1.964/-1.531	0.512/-0.617

Table 2: Selected interatomic distances (Å) and angles (°) in $A_2Mn_2V_2O_7F_2$ ($A = Rb, Cs$) and Mn_2VO_4F .

	Rb₂Mn₂V₂O₇F₂	Cs₂Mn₂V₂O₇F₂	
Mn(1)			
Mn(1)–O(1) x 2	2.247(3)	2.307(3)	
Mn(1)–O(3) x 2	2.202(3)	2.240(3)	
Mn(1)–F(1) x 2	2.081(3)	2.058(3)	
Mn(2)			
Mn(2)–O(1) x 2	2.153(3)	2.188(3)	
Mn(2)–O(2) x 2	2.181(4)	2.195(3)	
Mn(2)–F(1) x 2	2.091(3)	2.073(3)	
V(1)			
V(1)–O(1)	1.694(3)	1.704(3)	
V(1)–O(2)	1.677(4)	1.678(3)	
V(1)–O(3)	1.680(3)	1.676(3)	
V(1)–O(4)	1.807(3)	1.809(2)	
Mn⋯Mn	3.255(1)	3.285(1)	
Mn(1)–O(2)–Mn(2)	95.42(2)	93.5(2)	
Mn(1)–F(1)–Mn(2)	102.57(2)	104.9(2)	
Mn₂VO₄F			
Mn(1)		Mn(2)	
Mn(1)–O(1)	2.114(3)	Mn(2)–O(1)	2.141(2)
Mn(1)–O(2)	2.148(3)	Mn(2)–O(3)	2.182(3)
Mn(1)–O(2)	2.187(3)	Mn(2)–O(4)	2.168(3)
Mn(1)–O(3)	2.135(3)	Mn(2)–O(4)	2.207(3)
Mn(1)–F(1)	1.940(5)	Mn(2)–F(1)	2.277(5)
Mn(1)–F(1)	2.262(5)	Mn(2)–F(2)	1.910(5)
Mn(1)–F(2)	2.339(5)	Mn(2)–F(2)	2.376(5)
V(1)			
V(1)–O(1)	1.718(2)		
V(1)–O(2)	1.706(3)		
V(1)–O(3)	1.712(2)		
V(1)–O(4)	1.706(3)		

All powder X-ray diffraction (PXRD) measurements were performed using a Rigaku Ultima IV diffractometer equipped with Cu K α radiation of $\lambda = 1.5406 \text{ \AA}$ [33]. Powder diffraction patterns were collected in 0.02 degree increments over the 2θ range of 5° – 65° at a rate of $0.1^\circ \text{ min}^{-1}$. Figure 2 shows the observed PXRD patterns for ground single crystals of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ versus the calculated pattern of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

Figure 2. Calculated (a) and experimental (b) PXRD patterns of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

2.3 Property Characterization.

Temperature and field dependent magnetic measurements were performed using a Quantum Design Magnetic Property Measurement System (MPMS) at Oak Ridge National Laboratory. The data were collected on a ground sample of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ single crystals weighing 5.6 mg. The magnetic susceptibility, χ , measurements were performed on cooling over a temperature range of 300–2 K under an applied magnetic field of 1.0 kOe. Field dependent magnetization measurements were performed at 2 K in applied magnetic fields up to 50 kOe. Infrared (IR) and Raman spectra were collected using ground single crystal samples of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$. In order to obtain the IR spectrum, the sample was mixed with KBr and ground

thoroughly before pressing into a pellet. Finally, the IR spectrum was collected using a Nicolet Magna IR Spectrometer 550 in the frequency range from 400 to 4000 cm^{-1} with a 4 cm^{-1} resolution. Raman spectroscopy was performed using an Ar laser with the wavelength of 514.5 nm (Innova 200, Coherent). Raman scattering was collected using a camera lens of f/1.2 in a 180° backscattering geometry and data were analyzed by a triple spectrometer (Triplemate 1877, Spex) equipped with a charge-coupled device (CCD) detector (iDUS 420 series, Andor) cooled to 60 °C. The instrument was calibrated using the Raman spectrum of Indene and the Raman spectrum of a 5:2 mixture of chloroform/bromoform. The typical spectrum acquisition time was 10 s.

3. Results and discussion

3.1. Synthesis and Phase Stability of $A_2Mn_2V_2O_7F_2$ ($A = Rb, Cs$) and Mn_2VO_4F .

Recently, we initiated investigations into new transition metal vanadate structures in order to understand the role of the vanadate group as a building block in extended structures. Through our investigation we found that high temperature hydrothermal crystal growth proved to be highly efficient not only to obtain new structures, but also to grow larger crystals for detailed investigation of magnetic and optical properties. It should be noted that in our previous work we employed hydroxides almost exclusively as mineralizers (typically 1–5 M NaOH or KOH). In a number of cases a hydroxide group incorporated into the structure. However, having the hydroxide group in the structure is not favorable for any potential neutron scattering studies due to the large scattering effect of hydrogen, which creates a large continuous background during the measurements. In addition, the presence of hydroxide in the lattice decreases the thermal stability of the material since it can dehydrate at several hundred degrees Celsius. Thus we were

motivated to employ fluoride mineralizers (1–5 M CsF or RbF) in the hopes of replacing the hydroxide group in the structure with a fluoride anion, thereby providing crystals more favorable for neutron diffraction studies, as well as providing a different chemical environment that might lead to new product formation. We did find that use of high concentration of fluoride enabled the formation of novel transition metal vanadate structures with fluoride incorporation. In our initial synthetic effort, $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ was synthesized using a mixture of Cs_2CO_3 , Mn_2O_3 and V_2O_5 in the presence of 5 M CsF at 580 °C. After the initial discovery of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$, further work was continued using RbF mineralizer with Rb_2CO_3 in order to replace Cs^+ ion with Rb^+ ion in $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$. This reaction produced $\text{Rb}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ (orange crystals, ~0.4 mm), which is isostructural with $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

The effect of mineralizer concentration was also investigated. Therefore, reactions were conducted using 1 and 3 M CsF as the mineralizer in order to compare the results to those using 5M CsF. When 5M CsF was used as the mineralizer only $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ crystals were produced. When 1 M CsF was used as the mineralizer, however, no $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ crystals were observed and the resultant product was a mixture of an unidentified black powder with a minor yield of $\text{Mn}_2\text{VO}_4\text{F}$, which is also a novel phase (see below). When 3 M CsF was used as the mineralizer, both $\text{Mn}_2\text{VO}_4\text{F}$ and $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ crystals were present, again along with a majority of the unidentified black powder. The use of mixed 5M (RbF/CsF) mineralizer led to the mixed Rb/Cs isostructural derivative of $\text{RbCsMn}_2\text{V}_2\text{O}_7\text{F}_2$. The structural data for $\text{RbCsMn}_2\text{V}_2\text{O}_7\text{F}_2$ are given in Supplementary Information, Table S2. It should also be noted that even though the metal ion is formally Mn^{2+} in the products reported here, when MnO is used as the manganese source, it displayed similar reactivity but lower crystal quality compared to using Mn_2O_3 as the manganese source. Attempts to use other divalent metal oxides as starting materials are also not satisfactory,

as those oxides had a tendency to simply recrystallize and not participate in a reaction with the vanadate and alkali fluoride reactants. We are not yet clear on the nature of the reduction of manganese, nor why the trivalent oxides are a better starting material.

3.2. Crystal Structure of $A_2Mn_2V_2O_7F_2$ ($A = Rb, Cs$).

The $A_2Mn_2V_2O_7F_2$ ($A = Rb, Cs$) compounds in the present study crystallize in the orthorhombic space group $Pbcn$ (no. 60). The two compounds are isostructural, with the Rb analog exhibiting slightly contracted lattice parameters compared to Cs. $Cs_2Mn_2V_2O_7F_2$ will be discussed in detail as the prototypical structure. The structure is based on six-coordinate MnO_4F_2 units and V_2O_7 pyrovanadate building blocks. There are two crystallographically distinct Mn^{2+} atoms in the structure, and both MnO_4F_2 units have the fluorine atoms in a *trans* arrangement. These MnO_4F_2 units connect to one another via shared oxygen-fluorine edges to form zigzag chains that propagate along the c-axis (Figure 3). These chains are then connected to one another through the V_2O_7 groups (Figure 4). Each V_2O_7 group shares oxygen atoms with five MnO_4F_2 units, bridging three of the parallel chains. This provides additional coupling along the length of two of the manganese oxyfluoride chains through oxygen edges of the vanadates, while an oxygen edge of one MnO_4F_2 unit in the third chain bridges across two remaining vertices of the pyrovanadate (Figure 5). The alkali cations occupy gaps in the resulting framework.

Figure 3. Structure of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ along $[100]$. Edge-sharing MnO_4F_2 units form zigzag chains propagating along the c -axis, and are connected through V_2O_7 units (shown as polyhedra). Cesium atoms omitted for clarity.

Figure 4: Structure of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ along $[001]$. Cesium atoms fit within gaps in the manganese oxyfluoride vanadate framework.

Figure 5: Connectivity of three chains through a common pyrovanadate building block in $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

The MnO_4F_2 units of the manganese oxyfluoride chains provide an interesting structural building block. The first manganese site, Mn(1), is in a distorted octahedral environment with coordination to two *trans*-fluoride atoms at distances of 2.058(3) Å, and four oxygen atoms, with two having bond lengths of 2.240(3) Å and two having somewhat longer bond lengths of 2.306(3) Å. The *cis*- bond angles range from 78.81(11)° to 101.15(11)°. The Mn(2) site is slightly less distorted, with Mn–F bond lengths of 2.072(3) Å, and Mn–O bond lengths of 2.188(3) and 2.195(3) Å. The *cis*- bond angles about Mn(2) range from 81.30(11)° to 98.70(11)°. The Mn(1) and Mn(2) centers share F(1) and O(1) edges along the length of the chains, with Mn(1)–O(1)–Mn(2) and Mn(1)–F(1)–Mn(2) bridging bond angles of 93.57(11)° and 104.97(12)°, respectively. The observed interatomic distances about the MnO_4F_2 units here correspond well to the ranges in other examples of $\text{Mn}^{\text{II}}\text{O}_4\text{F}_2$ in the literature (for example, Mn–F = 2.078(6) Å and Mn–O = 2.192(5) Å in $\text{NaMnMoO}_3\text{F}_3 \cdot \text{H}_2\text{O}$ [34]). Lastly, the V_2O_7 group is formed by one unique V^{5+} site at a general position bridged to a symmetry equivalent V^{5+} site through O(4) (which has 2-fold symmetry). The V–O bond distances vary from 1.694(3) to 1.807(3) Å. Elongation of the bridging bonds within the pyrovanadate group is common and

well-known. In the present structure this bridging occurs at an angle of $135.0(3)^\circ$ for V(1)–O(4)–V(1).

3.3 Crystal Structure of $Mn_2(VO_4)F$.

The structure of Mn_2VO_4F is fairly complex despite its deceptively simple formula. The structure bears similarity to the triplite-zwieselite phosphate mineral series $((Mn,Fe)_2PO_4F)$. [35-37] That structure type is adopted by several phosphate and arsenate compounds based on divalent metal cations. [38, 39] The crystal chemistry of this structure type is sufficiently broad-based to support substitution of sulfate as the tetrahedral component with concomitant substitution of a monovalent cation for a divalent cation (as in $NaMnSO_4F$), [40] or alternatively, tetravalent silicon, germanium, or vanadium at the tetrahedral site coupled with rare earth cations and oxide substitution for fluoride. [41-44] Specifically, the vanadate fluoride Mn_2VO_4F in the present study most closely resembles the average structure of the mineral wagnerite, Mg_2PO_4F , [45] in that the fluorine atoms half occupy two positions in a disordered arrangement, rather than having a single fluorine atom site at full occupancy. As a result of this dynamic disorder, the Mn(II) centers, Mn(1) and Mn(2), both alternate between five-coordinate MnO_4F and six-coordinate MnO_4F_2 units.

The structure is a condensed framework that can be described in terms of two types of interpenetrating chains comprised of either the five- or six-coordinate Mn building blocks. These are further linked to one another by VO_4 tetrahedra based on pentavalent vanadium cations. Manganese-oxygen bond lengths range from 2.114(2) to 2.207(3) Å. When Mn is in the five-coordinate geometry, the lengths of Mn–F bonds are shorter than those for Mn–O bonds, at 1.910(5) and 1.940(5) Å. In contrast, when Mn is in the six-coordinate geometry, the Mn–F

bond lengths are longer than the Mn–O bond lengths, ranging from 2.262(5) to 2.376(5) Å. The wide range of Mn–F distances observed here is common for metal-fluoride distances in the isotypic compounds. For example, the ordered model of $\text{Mn}_2\text{PO}_4\text{F}$ has Mn–F bonds ranging from 2.113(2) to 2.534(2) Å [36], while the disordered $\text{Mg}_2\text{PO}_4\text{F}$ exhibits Mg–F bonds ranging from 1.9416(10) to 2.1992(8) Å. [45] The respective chains are both formed by alternating Mn(1) and Mn(2) atoms. The chains propagate by oxygen corner sharing in the MnO_4F chains and oxygen-fluorine edge-sharing in the MnO_4F_2 chains (Figure 6). Interpenetration of the chains through shared oxygen and fluorine atoms creates the framework with small gaps that accommodate the vanadium atoms (Figure 7). There is one unique V^{5+} cation in the structure, forming a fairly regular tetrahedron with oxygen, having an average V–O bond length of 1.711(3) Å.

Figure 6: Manganese oxyfluoride building blocks in disordered $\text{Mn}_2\text{VO}_4\text{F}$: a) chains formed by six-coordinate MnO_4F_2 units; b) chains formed by five-coordinate MnO_4F units.

Figure 7: Structure of $\text{Mn}_2\text{VO}_4\text{F}$ in the ac plane: a) the manganese oxyfluoride network in $\text{Mn}_2\text{VO}_4\text{F}$ comprised of both five-coordinate and six-coordinate Mn(II) centers (vanadates omitted for clarity); b) isolated VO_4 tetrahedra fill gaps in the manganese oxyfluoride framework.

3.4. Magnetic properties $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

Temperature-dependent magnetization measurements of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ were investigated to identify any low-dimensional magnetic properties that can be associated with the pseudo-one-dimensional (1-D) nature in the zigzag chain. Figure 8a displays the molar magnetic susceptibility, χ_M , versus temperature, T , for $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ at applied magnetic field, H , of 1 KOe. According the magnetic susceptibility data, the molar susceptibility reaches a maximum of $0.2577 \text{ cm}^3 \text{ mol}^{-1}$ of Mn^{2+} at $\sim 3 \text{ K}$ which is the Néel temperature (T_N) of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$. Figure 8b shows the inverse susceptibility, which is seen to be very nearly linear from room temperature down to about 150 K, consistent with the Curie-Weiss law ($1/\chi = T/C - \theta/C$, where C is the Curie constant and θ is the Weiss temperature). This fit gives an effective moment of $5.4 \mu_B$ per Mn

and a Weiss temperature of 12 K. Deviation from this linear behavior is seen at lower temperatures. Fitting over a wider temperature range, down to 50 K, and including a temperature independent contribution to the susceptibility to account for the deviation from linearity of $1/\chi$ gives an effective moment of 6.1 μB per Mn^{2+} ion and a Weiss temperature of -12 K. For comparison, the expected spin only value for the Mn^{2+} ion is 5.91 μB . The sensitivity of the sign of the Weiss temperature, which indicates whether the interactions are ferromagnetic (positive) or antiferromagnetic (negative), to the details of the fitting may indicate that multiple types of magnetic interactions are important in this compound. One can speculate that ferromagnetic intrachain interactions may dominate at high temperature, and antiferromagnetic interchain interactions then result in long range order at lower temperatures. Neutron diffraction data would be desirable to confirm or refute this scenario. Finally, Figure 8c shows the field dependence of the measured magnetic moment per Mn atom at 300 and 2 K. The data are consistent with paramagnetism at 300 K and antiferromagnetism at 2 K.

Similar behavior has been observed in AMnVO_4 ($A = \text{Na, K, Rb and Ag}$).^[12,13,46] Particularly, NaMnVO_4 and RbMnVO_4 possess a similar structure to $\text{CsMn}_2\text{V}_2\text{O}_7\text{F}_2$ with pseudo 1-D Mn–Mn chains made from edge sharing MnO_6 -octahedra which are interconnected by VO_4 -tetrahedra. Furthermore, the Na and Ag compounds show broad maxima in their magnetic susceptibilities near 24 K, and a sharp feature at 11.8 and 12 K, respectively, indicating the onset of long range antiferromagnetic order. The broad maxima are attributed to low dimensional magnetic correlations developing along the Mn chains upon cooling, preceding the onset of 3-dimensional long range order. RbMnVO_4 behaves differently, showing only a sharp cusp in χ at 8 K, indicating long range antiferromagnetic order. Isothermal magnetization measurements below this temperature show a ferromagnetic-like component attributed to canting of the ordered

moments. $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ most closely resembles RbMnVO_4 , based on the absence of a broad maximum in χ (Figure 8a). This suggests neither compound has strong 1-D correlations above T_N . Note the deviation from the high temperature Curie-Weiss behavior seen below about 100K (Figure 8b) may be due to weak short ranged or low dimensional ordering. Unlike RbMnVO_4 , no evidence of canting is observed in the ordered state of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ (Figure 8c), so the underlying magnetic structures are likely different.

Figure 8: (a) Temperature dependence of the molar magnetic susceptibility, χ_M , of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$. The inset shows a detail of χ_M near the ordering temperature. (b) Temperature dependence of the inverse susceptibility with a linear (Curie-Weiss) fit from 150 to 300 K. The fit is extrapolated to lower temperatures for comparison with the low temperature data. (c) Isothermal magnetization data collected at 2 and 300 K.

3.5. Infrared and Raman Spectra of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

Infrared and Raman spectra of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ are displayed in Figure 9. It should be noted that the IR spectrum does not contain a band at $\sim 3600\text{ cm}^{-1}$ for OH^- (Figure 9a). This further confirms that the use of 5 M CsF mineralizer avoids the incorporation of OH^- into the structure. Furthermore, it seems reasonable to assign the IR bands in the range of $1000\text{-}700\text{ cm}^{-1}$ to the symmetric and asymmetric stretching vibrations of terminal V–O bonds in the $[\text{V}_2\text{O}_7]$ group. [47]

The Raman spectrum of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ from $100\text{ to }1000\text{ cm}^{-1}$ is reported in Figure 9b, and is in good agreement with that previously reported for a volborthite-type structure, $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ containing a coordinated pyrovanadate [48]. Previous work demonstrated a significant dependence of vanadate vibrational frequencies on the nature of the transition metal ion as well as the alkaline earth ions. [49] These factors plus the additional complexity of the pyrovanadate groups can introduce some ambiguity in the vibrational band assignments. The bands in the range of $800\text{-}900\text{ cm}^{-1}$ can be assigned to the vibrations of terminal V–O bonds in the $[\text{V}_2\text{O}_7]$ group. The Raman bands at 912 and 870 cm^{-1} can be attributed to the symmetric stretching vibrations, ν_1 , of the terminal V–O bonds. The asymmetric stretching vibrations, ν_2 , of terminal V–O bonds are present at 855 , 830 and 810 cm^{-1} . It is noteworthy to mention that the Raman band at 870 cm^{-1} has the highest intensity, so it is reasonable to assign this peak to a

symmetric stretching mode of the terminal V–O bonds. Consequently, the band at 855 cm^{-1} can be assigned to the asymmetric stretching of the terminal V–O bonds. The Raman band at 537 cm^{-1} is attributed to the symmetric stretching vibration in ν_3 , bridging V–O–V bond in the $[\text{V}_2\text{O}_7]$ group. The bending vibrations ν_2 , are given at 329 , 358 and 409 cm^{-1} for terminal V–O bonds in the $[\text{V}_2\text{O}_7]^{4-}$ group. Furthermore, the V–O–V bending vibrations can be observed at 241 cm^{-1} . Finally, Raman bands from 100 to 200 cm^{-1} are due to the lattice vibrations.

Figure 9: Infrared (a) and Raman (b) spectra of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$.

4. Summary and Conclusions

In an attempt to extend the rich high temperature hydrothermal chemistry of transition metal vanadates, fluoride mineralizers were explored instead of hydroxide mineralizers. The purpose of this change was two-fold. First, it was hoped that the change in mineralizer could lead to a variation in the descriptive chemistry and allow for the isolation of new phases. Second, it was postulated that the use of fluoride would preclude the introduction of coordinated hydroxide in the lattice. Fluoride has several potential advantages over hydroxide as a building block in a lattice. Since there is no obvious dehydration pathway the fluoride containing material should be more thermally stable than a corresponding hydroxide. Further, the elimination of protons in the lattice can also improve sensitivity to neutron scattering experiments as well as any high power optical applications such as laser hosts or non-linear optics.

In this paper we describe two new phases that resulted from hydrothermal solutions containing fluoride mineralizers as opposed to hydroxides. Both structure types can be prepared as relatively large, high quality single crystals from high temperature hydrothermal fluids using manganese oxides and vanadium oxide as starting materials and do indeed contain fluoride building blocks. The $A_2Mn_2V_2O_7F_2$ ($A = \text{Rb, Cs}$) phase can be isolated from relatively higher concentrations of fluoride ($\geq 3-5\text{M F}^-$), and consists of trans MnO_4F_2 octahedral building blocks forming edge-bridging zigzag chains that are further linked to each other by $[V_2O_7]$ pyrovanadate units. Reducing the concentration of fluoride (1-3M) leads to formation of another phase, $Mn_2(VO_4)F$, which despite its relatively straightforward formula, has a fairly complex structure. It contains two distorted Mn(II) environments, six-coordinate MnO_4F_2 and five-coordinate MnO_4F depending on the occupancy pattern of disordered fluorine atoms. These form a series of disordered chains that are also linked by the vanadate groups to form a condensed

framework. In addition to single crystal structures of the new phases, the vibrational and magnetic properties of $\text{Cs}_2\text{Mn}_2\text{V}_2\text{O}_7\text{F}_2$ were investigated due to their interesting one-dimensional arrangement of edge-shared MnO_4F_2 units. Antiferromagnetic ordering was observed from the temperature dependent magnetic susceptibility.

The work described herein establishes several important points. The first is that fluoride is a satisfactory mineralizer for the chemistry and crystal growth of transition metal vanadates. This provides another tool in the continuing development of the extensive and interesting chemistry of new metal vanadates. Also the use of fluoride as a mineralizer has, at least in these cases, eliminated the appearance of hydroxide as a structural unit, a fact that has several advantages in terms of stability and physical properties. Finally, the use of fluoride as a mineralizer/building block also leads to the formation of new phases, which serves to extend the already rich chemistry of this exciting and interesting class of materials.

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