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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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Large single crystals of $A_2Mn_2V_2O_7F_2$ (A=Rb, Cs) and Mn_2VO_4F were grown using a high-temperature (~600 °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), $Z=4$ ($Rb_2Mn_2V_2O_7F_2$: $a=7.4389(17)$ Å, $b=11.574(3)$ Å, $c=10.914(2)$ Å; $Cs_2Mn_2V_2O_7F_2$: $a=7.5615(15)$ Å, $b=11.745(2)$ Å, $c=11.127(2)$ Å). 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, $T_N=\sim3$ K and a Weiss constant, θ, of $-11.7(1)$ K. Raman and infrared spectra were also analyzed to identify the fundamental V–O vibrational modes in $Cs_2Mn_2V_2O_7F_2$. $Mn_2(VO_4)F$ crystalizes in the monoclinic space group of $C2/c$ (no. 15), $Z=8$ with unit cell parameters of $a=13.559(2)$ Å, $b=6.8036(7)$ Å, $c=10.1408(13)$ Å and $\beta=116.16(3)°$. 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.

1. Introduction

The high temperature hydrothermal method (T=500–700°C, P=1–3kbar) 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, $[VO_4]^{3-}$, 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

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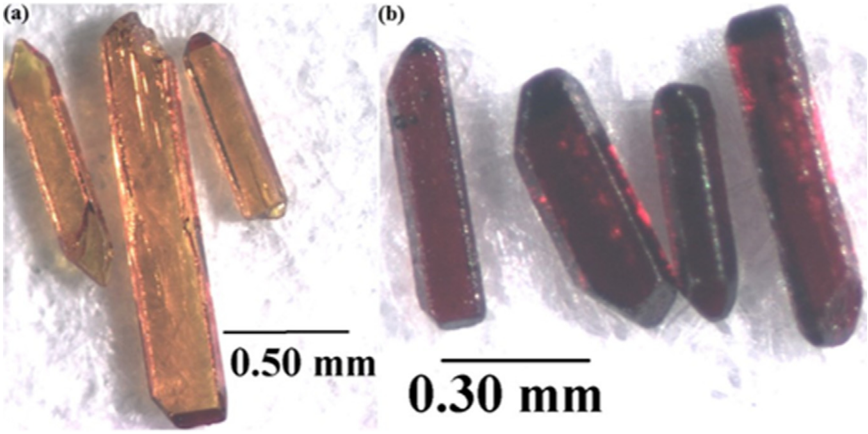

Fig. 1. Hydrothermally grown crystals of $Cs_2Mn_2V_2O_7F_2$ (a) and Mn_2VO_4F (b).

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 bock 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 $(VO_xF_y)^{z-}$ is 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 $Cs_2Mn_2V_2O_7F_2$.

2. Experimental section

2.1. Hydrothermal crystal growth of $A_2Mn_2V_2O_7F_2$ (A=Rb, Cs) and Mn_2VO_4F

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%), Mn_2O_3 (Alfa Aesar, 98%), and V_2O_5 (Alfa Aesar, 99.6%).

The $A_2Mn_2V_2O_7F_2$ (A=Rb, Cs) and Mn_2VO_4F series of compounds were synthesized using CsF and RbF as the mineralizers. $Cs_2Mn_2V_2O_7F_2$ single-crystals were isolated by reacting Cs_2CO_3 (0.0979 g), Mn_2O_3 (0.0474 g) and V_2O_5 (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, Fig. 1) were recovered as the only product. Similarly, $Rb_2Mn_2V_2O_7F_2$ (orange columns, ~0.4 mm) can be also synthesized using a mixture of Rb_2CO_3 (0.0809 g), Mn_2O_3 (0.0553 g) and V_2O_5 (0.0637 g) 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 $Rb_2Mn_2V_2O_7F_2$, which was co-crystallized with an unidentified black powder. Crystals of Mn_2VO_4F resulted from a study of investigating mineralizer concentration, and were produced using identical reaction conditions as for $Cs_2Mn_2V_2O_7F_2$ but with 1 M CsF as the mineralizer, see the discussion below.

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 Kα radiation (λ=0.71073 Å) and a Mercury CCD detector. Data collection and processing, including corrections for absorption and Lorentz and