Hydrothermal Synthesis of Single Crystals of Transition Metal Vanadates in the Glaserite Phase

Liurukara D. Sanjeewa, Colin D. McMillen, Daniel Willett, George Chumanov, Joseph W. Kolis*

Department of Chemistry and Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, South Carolina 29634-0973, USA

Abstract

A series of transition metal vanadate crystals were prepared using a high temperature (580 °C) hydrothermal method. The compounds all had the general formula $A_2AEM(VO_4)_2$ ($A = K, Na, Li$; $AE = Ba, Sr$; $M = Co, Fe, Mn$). They are all variations of the glaserite structural type and range in symmetry from $P-3m1$ to $P-3$ to $P2_1/c$. Most of the derivatives contain a planar three-fold rotation operation, making them possible spin frustration candidates. Single crystal structural analyses were performed on many of the derivatives to obtain a detailed understanding of the distortions of the tetrahedral building blocks that accommodate the symmetry distortions. A hydrothermal growth method was developed to grow high quality single crystals of sizes up to 2-3mm/edge. This method can be generalized for large crystal growth to enable magnetic and neutron diffraction studies that require relatively large single crystals.

Keywords: hydrothermal, crystal growth, glaserite, vanadate, transition metal

1. Introduction

When discussing the concept of “crystal growth” it is important to ask what the growth process will ultimately accomplish. This will aid in the selection of growth method and experimental design. It must be borne in mind that each order of magnitude increase in size of the crystal is a major investment in time, effort and money. Thus there is a considerable difference in experimental design if one wants to determine structure using single crystal X-ray diffraction, for example, which only requires single crystals of 0.1-0.3 mm, or measure bulk optical, thermal or magnetic properties, which may require single crystals of several millimeters, or even a centimeter in size. [1,2] Although it seems like a relatively small increment of crystal growth, such a size differential is actually very significant, over one or two orders of magnitude, and in fact the divide is rarely bridged. Consider the enormous number of single crystal structures that are reported each year. Contrast that with the much smaller number of single crystals that are grown to multi-centimeter dimensions of sufficient quality for accurate optical, magnetic or electronic measurements.

Most of the classical methods used to grow centimeter sized single crystals involve some aspect of melting the target compound. This list includes Czochralski growth, Bridgeman-Stockbarger growth, zone melting, skull melting or optical furnace growth. [3,4] These methods are extremely successful when employed judiciously to solve properly selected problems. They all suffer from one obvious, inherent limitation however, which is that the target compound must be thermodynamically stable at the melt temperature of the material (congruent melting). Since the target materials are often metal oxides or covalent species, these melting points are often extremely high and impose considerable experimental difficulties. Thus, significant effort is employed to examine other growth methods that can be performed at lower temperatures.

Methods employing fluxes, such as flux growth or top seeded solution growth (crystal pulling from fluxes) do lead to growth from “solution” (molten salts) at lower temperatures. [5] Other methods such as vapor transport (chemical vapor transport or physical vapor transport) can lead to growth of high quality single crystals when applied to appropriate systems.

One method that can be suitable both for initial exploratory synthesis of new materials, as well as the all-important transition from “small” (0.1-0.3mm) to “large” (1-10 mm) single crystals is the hydrothermal method. [6-11] The technique is suitable for rapid, descriptive exploration of new phase space. Furthermore, once attractive candidate materials are identified, the growth methodology can be modified slightly to lead to larger single crystals suitable for physical property measurements. At this point it is worthwhile to distinguish between the terms low temperature hydrothermal growth and high temperature hydrothermal growth. In the most generic sense, hydrothermal chemistry involves any reactions performed above the boiling point of water. Thus the initial experimental challenge is to contain the aqueous phase in some pressurized apparatus and prevent boil off of the solvent.

The most common technique for hydrothermal chemistry involves reactions performed in autoclaves lined with a perfluorinated inert polymer (generically, but often imprecisely, called Teflon). This provides a convenient, commercially available experimental platform well-suited for exploratory reactions. An important advantage for this method is the exceptional chemical stability of the fluoropolymer liner, enabling reaction conditions ranging from strong acid to base and oxidizing conditions. Unfortunately the fluoropolymers all begin to creep and decompose above about 240-250 °C, strictly limiting reaction temperatures to around 225°C and below. Therefore we arbitrarily label this well-developed temperature regime the low temperature hydrothermal regime. The temperature regime still enables a broad range of new chemistry and

often leads to single crystal growth suitable for single crystal x-ray diffraction. Unfortunately it does present considerable practical limitation for more refractory and less soluble systems and does not lend itself to designed large (mm-cm) single crystal growth. To circumvent these temperature limitations it is common to employ inert or noble metal liners, such as silver, gold or platinum. Under appropriate conditions these liners, coupled with suitable high-pressure autoclaves, provide access to much higher thermal regimes (300-700°C), which we again arbitrarily label the high temperature hydrothermal regime. [12]

Since the thermodynamic critical point of water is 374°C any reactions performed above this critical point are said to be done in a supercritical fluid. It should be noted however that the designated critical point is an ideal value only for pure water. Since any chemical reactions inherently involve complex solutions, the concept of the critical point is only a very general one and has only broad bearing on actual experimental design or performance. It is important to realize that high temperature hydrothermal fluids have very low viscosity and are exceptionally mobile. Thus they must be treated as high pressure gases in terms of their containment so all noble metal containers must be *completely* sealed, either through in-situ pressure welding or actual electro-arc welding beforehand. [13] It is this factor that makes the process considerably more experimentally demanding than low temperature hydrothermal reactions.

Previously we identified a new series of rare earth vanadate phases prepared hydrothermally, with the intriguing glaserite structure. [14-16] The glaserite phase is actually a fairly broad family of compounds containing a several unique metal sites and a tetrahedral linking group. The parent glaserite is actually the deceptively simple sodium impurity phase of potassium sulfate with the ideal formula $K_3Na(SO_4)_2$. [17] Appropriately it is named after Christopher Glaser, perhaps the first practicing descriptive inorganic chemist. [18] It has an

enormous range of derivatives, [19] whereby the potassium site can range from alkali to alkaline earth ions, [20] the sodium site can be occupied by metals ranging from transition metals [21] to rare earths in a variety of oxidation states, [22] and the tetrahedral building block can be virtually any known tetrahedron including phosphates, vanadates, [14, 23,24] chromates, [17] ruthenates [25] and silicates. [26] As such the phase behaves as a highly adaptive solid-state structure. [27] The materials can adopt multiple structural variations, but can often contain sites with a planar threefold rotation axis. Thus if such sites are occupied by magnetic centers, particularly d block ions, then the materials have the possibility of containing spin frustration and other unusual and important magnetic effects. [28,29].

It is important to both obtain single crystal X-ray structures of these compounds to fully understand their subtle structural features (vide infra), and also grow larger single crystals for subsequent single crystal neutron and magnetic structures. Therefore we feel that this class of compounds presents an ideal demonstration system to develop both aspects of hydrothermal crystal growth. The large number of experimental variables make the system very rich for exploratory development while the possibility of important magnetic effects drive the growth of larger single crystal of sufficient size for single crystal neutron diffraction and single crystal magnetic measurements. In this manuscript we describe the synthesis of a series of new first row transition metal glaserites, $A_2AEM(VO_4)_2$ ($A = K, Na, Li$; $AE = Ba, Sr$; $M = Co, Fe, Mn$), along with detailed single crystal studies. Since many of these new compounds contain the metals on threefold rotation sites, which may lead to magnetic spin frustration, we also performed growth of larger single crystals for future detailed physical property studies.

2. Experimental Section

2.1. General Procedure for Hydrothermal Crystal Growth.

All hydrothermal reactions were conducted in 2.5-in. long silver ampoules with an outer diameter of ¼ in. Reactants (~0.2 grams total) were loaded with 0.4 mL of the desired aqueous hydroxide mineralizer solution. The silver ampoules were welded shut and placed in a Tuttle-seal autoclave filled with water to provide suitable counter pressure. The autoclaves were heated to the desired temperature for 6-7 days. After the reaction period, crystals were retrieved from the silver ampoules by washing the entire product with deionized water. Analytical grade reagents were used as received in all reactions. The chemicals used in this study: Li_2CO_3 (Aldrich, 99+%), Na_2CO_3 (Aldrich, 99%), K_2CO_3 (Alfa Aesar, 99.997%), BaO (Alfa Aesar, 99.5%), SrO (Alfa Aesar, 99.5%), $\text{Ba}(\text{OH})_2$ (Alfa Aesar, 98%) Mn_2O_3 (Alfa Aesar, 98%), Fe_2O_3 (Alfa Aesar, 99.99%), Co_3O_4 (Alfa Aesar, 99.7%), MnO (Alfa Aesar, 99%), FeO (Alfa Aesar, 99.5%), CoO (Alfa Aesar, 99.5%), and V_2O_5 (Alfa Aesar, 99.6%).

2.2. Hydrothermal Synthesis of $\text{A}_2\text{AEM}(\text{VO}_4)_2$ via Stoichiometric Reactions.

As a typical example, $\text{Na}_2\text{BaMn}(\text{VO}_4)_2$ was synthesized using Na_2CO_3 (0.0408 g), BaO (0.0590 g), Mn_2O_3 (0.0304 g), V_2O_5 (0.0699 g). This corresponds to a 2:1:1:2 molar ratio of the constituent metal ions. The component oxides were added to the silver ampoule along with 5 M NaOH and the ampoule was sealed and heated at 580 °C and for 6 days, generating 1.2 kbar of pressure. Thick, yellow hexagonal plate-like single crystals were isolated as the only product. The other analogues such as $\text{Na}_2\text{BaFe}(\text{VO}_4)_2$ (thick black hexagonal plates) and $\text{Na}_2\text{BaCo}(\text{VO}_4)_2$ (thick purple hexagonal plates) were synthesized in similar fashion as phase-pure products. Additionally, $\text{Li}_2\text{BaMn}(\text{VO}_4)_2$ (thin yellow hexagonal plates) was synthesized using Li_2CO_3 (0.0303 g), BaO (0.0628 g), Mn_2O_3 (0.0323 g), V_2O_5 (0.0745 g) with 5M LiOH , and

$\text{K}_2\text{BaMn}(\text{VO}_4)_2$ (thick yellow-green hexagonal plates) synthesized using K_2CO_3 (0.0502 g), BaO (0.0554 g), Mn_2O_3 (0.0285 g), V_2O_5 (0.0658 g) with 5 M KOH . Unlike the $\text{NaBa}_2\text{M}(\text{VO}_4)_2$ analogs, both $\text{LiBa}_2\text{Mn}(\text{VO}_4)_2$ and $\text{KBa}_2\text{Mn}(\text{VO}_4)_2$ reactions also produced unidentified black powders in addition to the target phase. Crystals of $\text{Na}_2\text{SrMn}(\text{VO}_4)_2$ (orange hexagonal plates) were isolated by the hydrothermal reaction of Na_2CO_3 (0.0451 g), SrO (0.0441 g), Mn_2O_3 (0.0336 g) and V_2O_5 (0.0773 g) as components using a 5 M NaOH mineralizer. Crystals of $\text{Na}_2\text{SrCo}(\text{VO}_4)_2$ (purple hexagonal plates) were prepared similarly, using Co_3O_4 (0.0342 g). Figure 1 shows the PXRD patterns of representative examples of the trigonal and monoclinic glaserites prepared in this study (other analogs are shown in the Supplementary Information, Figure S1).

Figure 1. Calculated (a) and experimental (b) PXRD patterns of $\text{Na}_2\text{SrMn}(\text{VO}_4)_2$ (monoclinic, $P2_1/c$), and calculated (c) and experimental (d) PXRD patterns of $\text{Na}_2\text{BaMn}(\text{VO}_4)_2$ (trigonal, $P-3m1$).

2.3 Hydrothermal Growth of Larger $\text{A}_2\text{AEM}(\text{VO}_4)_2$ Single Crystals Using Feedstock Obtained via Solid State Synthesis.

The growth of larger crystals than those obtained from the stoichiometric hydrothermal reactions above involved a two-step process. First, phase pure powders of the target glaserite compounds were prepared using high temperature solid state reactions. For example, preparation of $\text{Na}_2\text{BaMn}(\text{VO}_4)_2$ powder was achieved using an appropriate mixture of Na_2CO_3 , BaO , MnO and V_2O_5 in a 1:1:1:1 molar ratio. Approximately 1 g of total reactants were mixed and loaded into a platinum crucible, then heated to 800 °C in a nitrogen atmosphere for 48 hours. The product was reground and reheated as necessary until the phase pure glaserite powder was obtained. Powders of the other derivatives were prepared in similar fashion by varying the alkali carbonate, alkaline earth oxide and transition metal oxide as desired. These powders were then used for hydrothermal recrystallization to grow larger crystals. The hydrothermal reactions utilized identical conditions to those above, but used 0.2 g of the target glaserite powders as the feedstock, along with 0.4 mL of an appropriate mineralizer (5M NaOH, 5 M KOH, 5 M LiOH). In this way, larger single crystals were obtained after 7 days, and described in more detail below.

2.4. X-Ray Diffraction.

Single crystal X-ray diffraction was carried out on well-formed single crystals mounted on glass fibers for analysis. Data were collected at room temperature using a Mercury CCD detector. Diffraction images were obtained by ω -scans using a Rigaku AFC8-S diffractometer equipped Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator. Instrument control, data processing, and correction for absorption, Lorentz and polarization effects was performed using the CrystalClear software package. [31] The structures were determined by direct methods, with refinement on F^2 by full-matrix least squares techniques using the SHELX software suite. [32] All atoms were refined anisotropically. A weak ISOR restraint ($s = 0.02$) was applied to the

O1 anisotropic displacement parameters in the $\text{Na}_2\text{BaM}(\text{VO}_4)_2$ series to appropriately model the disorder and stacking faults present in those crystals. The structural contents of each compound were verified by energy dispersive X-ray analysis, and the resulting chemical analyses are reported in the supplementary information (Table S1).

Symmetry determinations were made based on the intensity data and systematic absences. The various glaserites display a wide range of subtle structural variations (*vide infra*), so the space group symmetry determination requires considerable care. In particular, the reflection data for $\text{Na}_2\text{SrMn}(\text{VO}_4)_2$ and $\text{Na}_2\text{SrCo}(\text{VO}_4)_2$ indicated monoclinic symmetry (space group $P2_1/c$), rather than the trigonal symmetry observed for the other crystals studied. Also, since the β angle of the monoclinic compounds is close to 90 degrees, particular attention was paid to the Laue symmetry of the reflections. In these cases the equivalent intensities were limited to (hkl), ($-\text{h}-\text{k}-\text{l}$), (h-kl), and ($-\text{hk}-\text{l}$), indicating 2/m Laue symmetry and confirming the choice of space group $P2_1/c$ over any higher symmetry options that would necessarily possess other equivalent reflections. Among the trigonal structures, $\text{Li}_2\text{BaMn}(\text{VO}_4)_2$ was best modeled in space group $P-3$, while all other glaserites in this study were found to crystallize in $P-3m1$. Several test refinements were performed in lower symmetry space groups (namely $P3$ and $P1$), and conversion to the appropriate higher symmetry space group was confirmed using the PLATON software suite. [33] Tables 1 and 2 report the data from the structure refinements for the trigonal and monoclinic glaserites, respectively. Selected interatomic distances are reported in Table 3.

Table 1: Structure refinement data for trigonal $A_2BaM(VO_4)_2$ glaserites.

Chemical Formula	$K_2BaMn(VO_4)_2$	$Na_2BaCo(VO_4)_2$	$Na_2BaFe(VO_4)_2$	$Na_2BaMn(VO_4)_2$	$Li_2BaMn(VO_4)_2$
F.W. (g/mol)	500.36	472.13	469.05	468.14	436.04
Temperature (K)	293	293	293	293	293
Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal
Space group	$P-3m1$ (no. 164)	$P-3m1$ (no. 164)	$P-3m1$ (no. 164)	$P-3m1$ (no. 164)	$P-3$ (no. 147)
Unit cell parameters					
a (Å)	5.7340(8)	5.5489(8)	5.5731(8)	5.5921(8)	5.2887(7)
c (Å)	7.3859(15)	7.0741(14)	7.1034(14)	7.1628(14)	7.3026(15)
Volume (Å ³)	210.30(6)	188.63(5)	191.07(5)	193.98(5)	176.89(5)
Z	1	1	1	1	1
D (calcd) (g/cm ³)	3.951	4.156	4.076	4.007	4.093
μ , mm ⁻¹	9.239	9.835	9.437	9.053	9.800
F(000)	229	215	214	213	197
Crystal size (mm ³)	0.26 x 0.24 x 0.15	0.23 x 0.20 x 0.14	0.25 x 0.24 x 0.12	0.21 x 0.21 x 0.10	0.19 x 0.18 x 0.12
2 θ range, °	2.76-26.03	2.88-26.34	2.87-26.07	2.84-25.91	4.45-25.97
Indices (min)	[-7, -7, -9]	[-6, -6, -8]	[-6, -6, -8]	[-5, -6, -8]	[-6, -6, -9]
(max)	[7, 7, 9]	[6, 6, 8]	[6, 6, 8]	[6, 6, 8]	[6, 6, 8]
Reflns. collected	1834	1707	1701	1714	1526
Indep. reflections	185, $R_{int} = 0.0696$	172, $R_{int} = 0.0472$	168, $R_{int} = 0.0420$	170, $R_{int} = 0.0617$	233, $R_{int} = 0.0484$
Obs. reflns. ($I > 2\sigma(I)$)	182	172	168	170	232
Parameters	22	21	21	33	23
Final R ($I > 2\sigma(I)$)					
R	0.0224	0.0265	0.0322	0.0258	0.0207
wR	0.0541	0.0631	0.0766	0.0766	0.0550
Final R (all data)					
R	0.0225	0.0265	0.0322	0.0258	0.0207
wR	0.0542	0.0631	0.0766	0.0766	0.0551
Goodness of fit (S)	1.124	1.125	1.194	1.184	1.190
Extinction coeff.	0.229(17)	0.39(3)	0.123(16)	0.16(2)	-

Table 2: Structure refinement data for monoclinic $A_2\text{Sr}M(\text{VO}_4)_2$ glaserites.

Chemical Formula	$\text{Na}_2\text{SrCo}(\text{VO}_4)_2$	$\text{Na}_2\text{SrMn}(\text{VO}_4)_2$
F.W. (g/mol)	422.41	418.42
Temperature (K)	293	293
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Unit cell parameters		
a (Å)	13.677(3)	13.823(3)
b (Å)	5.5025(11)	5.5671(11)
c (Å)	9.5767(19)	9.6686(19)
β (°)	90.01(3)	90.09(3)
Volume (Å ³)	720.7(2)	744.0(3)
Z	4	4
D (calcd) (g/cm ³)	3.893	3.735
μ , mm ⁻¹	12.267	11.350
F(000)	788	780
Crystal size (mm ³)	0.22 x 0.16 x 0.10	0.24 x 0.18 x 0.12
2 θ range, °	2.98-25.25	2.95-25.14
Indices (min)	[-16, -6, -11]	[-16, -6, -11]
(max)	[16, 6, 11]	[16, 6, 11]
Reflns. collected	5692	6133
Indep. reflections	1301, $R_{\text{int}} = 0.0562$	1336, $R_{\text{int}} = 0.0319$
Obs. reflns. ($I > 2\sigma(I)$)	1101	1251
Parameters	130	131
Final R ($I > 2\sigma(I)$)		
R	0.0509	0.0230
wR	0.1174	0.0555
Final R (all data)		
R	0.0609	0.0249
wR	0.1283	0.0572
Goodness of fit (S)	1.196	1.118
Extinction coeff.	-	0.0184(7)

Table 3: Selected Interatomic Distances (Å) in Vanadate Glaserite Structures.

K₂BaMn(VO₄)₂		Na₂BaCo(VO₄)₂		Na₂BaFe(VO₄)₂		Na₂BaMn(VO₄)₂	
Mn1–O1 (x6)	2.186(3)	Co1–O1 (x6)	2.067(6)	Fe1–O1 (x6)	2.091(8)	Mn1–O1 (x6)	2.14(2), 2.180(19)
V1–O2	1.654(9)	V1–O2	1.682(9)	V1–O2	1.673(11)	V1–O2	1.682(9)
V1–O1 (x3)	1.726(4)	V1–O1 (x3)	1.686(7)	V1–O1 (x3)	1.687(8)	V1–O1 (x3)	1.71(2), 1.73(2)
K1–O2	2.576(10)	Na1–O2	2.350(10)	Na1–O2	2.343(13)	Na1–O2	2.342(10)
K1–O1 (x6)	2.8749(5)	Na1–O1 (x6)	2.7765(5)	Na1–O1 (x6)	2.7887(6)	Na1–O1 (x6)	2.42(2), 2.46(2)
K1–O1 (x3)	3.030(4)	Na1–O1 (x3)	2.917(7)	Na1–O1 (x3)	2.955(8)	Na1–O1 (x3)	2.90(2), 3.14(2)
Ba1–O1 (x6)	2.860(3)	Ba1–O1 (x6)	2.782(6)	Ba1–O1 (x6)	2.783(8)	Ba1–O1 (x6)	2.69(2), 2.94(2)
Ba1–O2 (x6)	3.3110(5)	Ba1–O2 (x6)	3.2037(5)	Ba1–O2 (x6)	3.2177(5)	Ba1–O2 (x6)	3.2286(5)
Li₂BaMn(VO₄)₂		Na₂SrCo(VO₄)₂		Na₂SrMn(VO₄)₂			
Mn1–O1 (x6)	2.180(16)	Co1–O6 (x2)	2.017(6)	Mn1–O6 (x2)	2.099(2)		
V1–O2	1.690(4)	Co1–O1 (x2)	2.074(7)	Mn1–O1 (x2)	2.147(2)		
V1–O1 (x3)	1.7276(17)	Co1–O2 (x2)	2.181(6)	Mn1–O2 (x2)	2.231(2)		
Li1–O1 (x3)	1.967(3)	Co2–O4 (x2)	2.075(6)	Mn2–O4 (x2)	2.139(2)		
Li1–O2	2.081(15)	Co2–O3 (x2)	2.085(7)	Mn2–O3 (x2)	2.174(2)		
Ba1–O1 (x6)	2.8646(19)	Co2–O5 (x2)	2.125(6)	Mn2–O5 (x2)	2.171(3)		
Ba1–O2 (x6)	3.0554(4)	V1–O7	1.654(7)	V1–O7	1.667(3)		
		V1–O2	1.702(6)	V1–O2	1.716(2)		
		V1–O6	1.723(6)	V1–O6	1.713(2)		
		V1–O1	1.723(6)	V1–O1	1.722(2)		
		V2–O8	1.664(7)	V2–O8	1.677(2)		
		V2–O5	1.703(6)	V2–O5	1.717(3)		
		V2–O4	1.706(6)	V2–O4	1.716(2)		

	V2-03	1.727(6)	V2-03	1.725(2)	
	Sr1-01	2.525(7)	Sr1-01	2.536(3)	
	Sr1-03	2.535(6)	Sr1-03	2.529(2)	
	Sr1-08	2.690(6)	Sr1-08	2.696(3)	
	Sr1-04	2.751(6)	Sr1-04	2.757(2)	
	Sr1-07	2.768(7)	Sr1-07	2.728(3)	
	Sr1-06	2.776(7)	Sr1-06	2.761(3)	
	Sr1-02	2.796(6)	Sr1-02	2.840(2)	
	Sr1-05	2.821(7)	Sr1-05	2.874(3)	

Powder X-ray diffraction measurements were performed using a Rigaku Ultima IV diffractometer. Data were collected using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over the range of 5-65 degrees in two-theta, using a scan speed of 0.1 degrees per minute at a resolution of 0.02 degrees. These measurements were performed to identify the purity of the resulting products, as well as to compare the diffraction patterns to those calculated from the single crystal structure refinements.

2.5. Spectroscopic Characterization.

Raman and infrared spectra were collected using samples consisting of well-ground single crystals of $A_2AEM(VO_4)_2$. For the infrared analysis, the ground single crystals were mixed into a KBr matrix and pressed into a semi-transparent pellet for analysis. The infrared spectra of the pellets were measured using a Nicolet Magna IR Spectrometer 550 in the frequency range of 400 cm^{-1} to 4000 cm^{-1} with a 4 cm^{-1} resolution.

For the Raman analysis, a 514.5 nm wavelength Ar laser (Innova 200, Coherent, 90 mW) was used as the Raman scattering excitation source. Raman scattering was measured using a camera lens of f/1.2 in a 180° backscattering geometry and a triple spectrometer (Triplemate 1877, Spex) equipped with a CCD detector (iDUS 420 series, Andor). The typical spectrum acquisition time was 10 s. The Raman spectrum of Indine and a 5:2 mixture of chloroform:bromoform were used for spectral calibration. A glass capillary holder was fabricated for suspending the polycrystalline sample of the glaserite compounds analyzed, with the plane of the sample normal to the collection optics.

3. Results and Discussion

3.1. Synthesis, Phase Space and Crystal Growth of the $A_2BM(VO_4)_2$ Series.

In continuing our search for new transition metal-vanadates, [14-15] we isolated a large group of crystals having glaserite-type structures. This work was initiated with the discovery of $Na_2BaMn(VO_4)_2$ as a side product from our previously reported brackebuschite-type structures. [30] After the initial discovery, several targeted attempts were made to synthesize this compound, and other derivatives, in higher yield and as large, high quality crystals for further characterization. The phase pure $Na_2BaMn(VO_4)_2$ product was achieved by a stoichiometric hydrothermal reaction at 580 °C for seven days with 5 M NaOH as the mineralizer. As the next step, divalent Fe- and Co-containing derivatives were also synthesized as phase pure products using similar hydrothermal reactions. Further work was performed utilizing LiOH and KOH mineralizers with Li_2CO_3 and K_2CO_3 to replace the Na^+ ion in $Na_2BaMn(VO_4)_2$ with Li^+ and K^+ ions to see their effects on the size and structure of the crystals. Substitution of SrO for BaO in the stoichiometric hydrothermal reactions with NaOH also led to the synthesis of

$\text{Na}_2\text{SrMn}(\text{VO}_4)_2$ and $\text{Na}_2\text{SrCo}(\text{VO}_4)_2$. In most of these cases, the resulting high quality glaserite single crystals were about 0.5 to 1 mm in size, as shown in Figure 2.

Figure 2: $A_2AEM(\text{VO}_4)_2$ single crystals (0.5 to 1 mm) grown from stoichiometric hydrothermal reactions: (a) $\text{Na}_2\text{BaFe}(\text{VO}_4)_2$, (b) $\text{Na}_2\text{BaCo}(\text{VO}_4)_2$ and (c) $\text{Na}_2\text{SrMn}(\text{VO}_4)_2$.

The growth of larger crystals was achieved via a two-step process involving the solid-state preparation of glaserite powder feedstock followed by hydrothermal crystallization. Reactions that involve *synthesis* and *crystal growth* in the same process tend to be less efficient. In this case individual components of the stoichiometric hydrothermal reactions all have different solubilities in the hydrothermal fluid, which when coupled with the chemical complexity of the reaction can detract from the crystal growth process. Generally growth of large single crystals requires constant conditions and a “quiet” growth zone. Because synthesis inherently involves a dynamic process of consumption of starting material and formation of product in a complex kinetic mixture, it is not usually the optimum environment for growth of large single crystals. Thus to grow larger crystals we prepared a feedstock of premade homogeneous glaserite powder which would be expected to exhibit simpler solubility behavior. This improves the conditions for growth onto existing nucleation sites via transport mechanisms, as the fluid does not become enriched or depleted in certain components as it would in a reactive growth process. Indeed, we

found this approach to be preferable for the hydrothermal growth of larger glaserite crystals, and 2-3 mm size single crystals were obtained from these hydrothermal reactions (Figure 3). This bodes well for future crystal growth prospects by seeded transport growth, and for further properties characterization using oriented single crystals.

Figure 3: $A_2AEM(VO_4)_2$ single crystals grown from hydrothermal recrystallization of the glaserite feedstock (top: $Na_2BaFe(VO_4)_2$, bottom: $Na_2SrMn(VO_4)_2$).

3.2. Crystal Chemistry of Hydrothermally-grown $A_2BM(VO_4)_2$.

The glaserite structure type represents an interesting example of an adaptable structure, capable of flexible chemical substitution at several different crystallographic sites. In its highest symmetry form, space group $P-3m1$, the basic components of the structure are the tetrahedral

oxyanion (SiO_4 , PO_4 , VO_4 , with the cation at a $2d$ site) charge balanced by three unique metal cation sites ($1a$, $1b$ and $2d$ sites). Oxygen atoms of the oxyanion occupy $2d$ and $6i$ sites. Thus, a vast array of combinations of oxyanions and metal cations can be accommodated. Subtleties in the crystal chemistry of the glaserite structure type arise from these various combinations, and some lower symmetry modifications of the structure are established in the literature for vanadate glaserites. [23,24,28,29,34-36] One of the primary mechanisms for lowering the symmetry is distortion and rotation of the M-O-V layer. In the present study, we observe several occurrences of the ideal glaserite structure type as well as some lower symmetry modifications. Here we examine the effects of varying the size of the A and B site cations to induce the structural distortion and lower the symmetry. These structures are shown in Figure 4. It should be noted that even in the distorted structures the general triangular lattice is maintained, making all interesting candidates for further magnetic studies. [23,28,29]

Figure 4: Ideal and distorted glaserite structures in the present study. Vanadate tetrahedra are shown as yellow polyhedra, transition metal octahedral as blue polyhedra, alkali metals as purple spheres, and alkaline earth metals as gray spheres. Alkali and alkaline earth metals are omitted from a) to c) for clarity. Approximately equivalent orientations shown are: a) [001], b) [001], c) [100], d) [110], e) [110], f) [010]

Beginning with $\text{K}_2\text{BaMn}(\text{VO}_4)_2$, we observe the ideal structure type in space group $P\text{-}3m1$ (Figure 4a and 4d). This is identical to what we observed in the rare earth glaserites, $\text{K}_3\text{RE}(\text{VO}_4)_2$ (analogously written as $\text{K}_2\text{KRE}(\text{VO}_4)_2$) in a previous study. [14] In that case, the slightly larger size of K^+ compared to Ba^{2+} allows expansion of the lattice to accommodate rare earth ions without inducing a distortion (for example, $\text{Y-O} = 2.224(5) \text{ \AA}$). Likewise, slight contraction of the lattice due to Ba^{2+} at the B site provides a good fit for Mn^{2+} ($\text{Mn-O} = 2.186(3) \text{ \AA}$) in the current study.

The lattice is more greatly contracted by substitution of Na for K at the A site, as in $\text{Na}_2\text{BaMn}(\text{VO}_4)_2$, and the Fe and Co analogs. Here we observe the first clues of departure from ideal symmetry, though we still observe overall $P\text{-}3m1$ space group symmetry in our crystals. In the Na-containing structures, the $6i$ oxygen atom exhibits larger anisotropic displacement parameters (ADPs) than in $\text{K}_2\text{BaMn}(\text{VO}_4)_2$, or those in $\text{K}_3\text{RE}(\text{VO}_4)_2$ of the previous study. This has been attributed to stacking faults in the crystal, [29] which may be indicative of some structural strain. The stacking faults can be modeled by disorder of the $6i$ oxygen site into two $12j$ sites, corresponding to rotations of the M-O-V layers. In the case of the Mn^{2+} analog, modeling this disorder significantly improved the structure. For the slightly smaller Fe^{2+} and

Co^{2+} analogs, disordering the $6i$ site was not necessary to obtain a satisfactory refinement, though the ADPs were still large enough to suggest the presence of some of these stacking faults.

To validate the observed $P-3m1$ symmetry, $\text{Na}_2\text{BaCo}(\text{VO}_4)_2$ was subjected to several test refinements. An initial test refinement was performed in space group $P-3$ to see whether the data would better correspond to a structure having entirely rotated layers, where the mirror symmetry of $P-3m1$ is broken by the rotation [29] In this test case the oxygen atom was found at a $6g$ site (0.6630, 0.8302, 0.6812) corresponding to very little rotation of the layer, as oxygen edges between the vanadate and transition metal groups are oriented at 90.4 and 89.6 degrees to one another. There was no other significant electron density to suggest an alternative, rotated arrangement. The use of the PLATON software package to search for additional symmetry indicated that this test solution should indeed be converted to space group $P-3m1$ (where oxygen edges are oriented at 90 degrees to one another). A second test refinement was performed on our data (again, ultimately solved in $P-3m1$) in space group $P-3$ using the coordinates of Mueller-Buschbaum for $\text{Ag}_2\text{BaMn}(\text{VO}_4)_2$, [35] which clearly does exhibit rotation of the M-O-V layers (those oxygen edges are oriented at 105.6 and 74.4 degrees to one another). In this test case of our data, the $6g$ oxygen atom exhibits extremely unsatisfactory thermal parameters, and the R1 value (0.0715) was noticeably larger than what we had obtained in our refinement in $P-3m1$ (0.0239) and the first test refinement in $P-3$ (0.0252). A large peak of residual electron density was also present at (0.6633, 0.7836, 0.6801), closely corresponding to the refined position of the $6g$ oxygen atom (0.6620, 0.8302, 0.6812) in our initial test refinement in $P-3$ that could be converted to higher symmetry $P-3m1$. These details are significant in that both the metal site symmetry and the overall lattice symmetry of the crystals are essential for the interpretation of the complex magnetic behavior of these materials. [28]

Although stacking faults may be indicative of some strain introduced into lattice, crystals of $\text{Na}_2\text{BaM}(\text{VO}_4)_2$ grown using our synthetic approach appear to retain the mirror symmetry of $P\text{-}3m1$. The structure of $\text{K}_2\text{BaMn}(\text{VO}_4)_2$ suggests that a larger alkali metal can relieve these faults and stabilize the ordered, ideal glaserite structure in $P\text{-}3m1$. The analogous Li compound, $\text{Li}_2\text{BaMn}(\text{VO}_4)_2$, however, does exhibit the M-O-V rotation characteristic of $P\text{-}3$ symmetry (Figures 4b and 4e). Here, the oxygen edges between the vanadate and transition metal polyhedra are oriented at 113.9 and 66.1 degrees to one another (exhibiting more rotation than $\text{Ag}_2\text{BaMn}(\text{VO}_4)_2$ [35]). The $6g$ oxygen atom is clearly ordered at a single site in a similar position to that reported in $\text{Ag}_2\text{BaMn}(\text{VO}_4)_2$. Furthermore, the Li position in the structure is shifted along the c -axis toward the vanadate regions of the layers compared to Ag of $\text{Ag}_2\text{BaMn}(\text{VO}_4)_2$ and Na of $\text{Na}_2\text{BaM}(\text{VO}_4)_2$ (Figure 4e). This allows Li to maintain four contacts of appropriate distances (1.967(3) and 2.081(15) Å) with oxygen. It also accounts for the observed lattice expansion along the c -axis compared to $\text{Na}_2\text{BaMn}(\text{VO}_4)_2$, since the Li displacement pushes the transition metal vanadate layers farther apart. This is consistent with the behavior of Li in powders of $\text{Li}_2\text{BaMg}(\text{PO}_4)_2$, crystallizing in $P\text{-}3$. [37] Alternatively, the position of the Na atom appears somewhat influenced by longer oxygen contacts of (~ 3.025 Å) that pull it toward the M regions of the layers. The K atom of $\text{K}_2\text{BaMn}(\text{VO}_4)_2$ is similarly pulled toward the Mn regions of the transition metal vanadate layer, and c -axis expansion (compared to $\text{Na}_2\text{BaMn}(\text{VO}_4)_2$) in that case occurs because of lengthening of the bond between the alkali metal and the $2d$ oxygen atom.

The structure of $\text{Na}_2\text{SrMn}(\text{VO}_4)_2$ exhibits an even greater degree of distortion, resulting in a lowering of the symmetry to space group $P2_1/c$, sometimes referred to as the merwinite distortion of the glaserite structure (Figure 4c and 4f). [26] The distortion creates two unique

transition metal vanadate layers that are rotated relative to one another. Furthermore, there is some tilting of the vanadate tetrahedra along the a-axis of the monoclinic structure that breaks the three fold symmetry exhibited by the trigonal glaserites in *P-3* and *P-3m1*. This tilting likely occurs to position the oxygen atoms to better accommodate the shorter interactions with Sr instead of Ba. The size of the alkaline earth metal has previously been shown to have been the key influence in this structural transition observed in powders of silicate and phosphate glaserites, for example $\text{Sr}_3\text{Mg}(\text{SiO}_4)_2$ in space group *P2₁/a* versus $\text{BaSrCaMg}(\text{SiO}_4)_2$ in space group *P-3m1*, and $\text{Na}_2\text{SrMg}(\text{PO}_4)_2$ in *P2₁/c* versus $\text{Na}_2\text{BaMg}(\text{PO}_4)_2$ in *P-3*. [38,39] In many ways this behavior involving the tilted tetrahedra is reminiscent of that of the tilted octahedra in distorted perovskites. [40]

3.3. Infrared and Raman Spectroscopy.

Infrared and Raman spectroscopy were used to probe the vanadate group in the three structure types of glaserite series in this study. Figure 5a shows the infrared spectrum from 2000 – 500 cm^{-1} for examples of the three glaserite structure types encountered. The infrared spectra show no significant features from the lattice above 1400 cm^{-1} , confirming the absence of OH^- in these crystals. All of the infrared spectra exhibit a strong, broad band centered 1150 – 1050 cm^{-1} , and a weaker band around 850 cm^{-1} which can be assign to stretching vibrations, $\nu(\text{V-O})$ in the VO_4 group. [41,42] Figure 5b shows the Raman spectra for the glaserite series. These are in good agreement with previously reported rare-earth glaserite phases, and with other orthovanadate samples. [42,14] Symmetric and asymmetric stretching vibrations, ν_1 and ν_3 , of the VO_4^{3-} -orthovanadate group produces bands in the range of 750-950 cm^{-1} , with the strong band near 850 cm^{-1} as the Γ_1 band. Further, several symmetric and asymmetric bending modes of

VO_4^{3-} were observed in the region of 300 to 500 cm^{-1} . The sharp band at 337 cm^{-1} in $\text{K}_2\text{BaMn}(\text{VO}_4)_2$ spectrum is likely due to the symmetric bending mode while two other bands at 375 and 397 cm^{-1} can be assigned to asymmetric bending modes. The Raman spectra of $\text{Na}_2\text{BaM}(\text{VO}_4)_2$ crystals are similar to the other trigonal glaserites $\text{K}_2\text{BaMn}(\text{VO}_4)_2$ and $\text{Li}_2\text{BaMn}(\text{VO}_4)_2$, and are included in the SI (Figure S2). We note that the Raman spectrum of $\text{Na}_2\text{SrMn}(\text{VO}_4)_2$ in Figure 5b appears just slightly more complicated than those of the trigonal glaserites. This is likely due to the lower symmetry of the monoclinic Sr-based phase, in particular the presence of two unique vanadate tetrahedra in the structure. Furthermore, the tilted arrangement of the vanadate tetrahedra in those structures may possibly contribute to the observed shifts. Finally, the Raman bands below 300 cm^{-1} may be attributed to lattice vibrations.

Figure 5: Infrared (a) and Raman (b) spectra of $A_2\text{BaMn}(\text{VO}_4)_2$, $A = \text{K}$ and Li , and $\text{Na}_2\text{SrMn}(\text{VO}_4)_2$.

4. Conclusions

A series of transition metal vanadates have been crystallized in the glaserite structure. They were originally isolated as side products of other low dimensional metal vanadate syntheses in hydrothermal fluids. Since the transition metal glaserite derivatives have complex and non-obvious three-fold symmetry elements, and have been shown to display interesting spin frustration in their magnetic properties we thought this was an ideal system for further crystal growth development. Using hydrothermal *reaction* conditions we grew a series of high quality single crystals of sufficient size for detailed single crystal X-ray diffraction studies to determine a number of important but subtle structural issues. We were then able to use hydrothermal *growth* conditions to prepare much larger (2-3mm) single crystals for subsequent single crystal neutron and magnetic studies, which are presently underway. Three different glaserite-based structure types have so far been obtained for transition metal vanadates by varying the identities of the alkali and alkaline earth metals. Smaller sized cations can be accommodated by distortions of the transition metal vanadate layers which lower the symmetry. The ideal glaserite structure type in space group $P-3m1$ appears stable and this should lead to interesting magnetic properties. It also appears clear that the high temperature (500-650°C) hydrothermal method is an excellent tool for the synthesis and single crystal growth of low dimensional transition metal structures linked by tetrahedral building blocks.

Acknowledgements

The authors thank the National Science Foundation, Grant #DMR-1410727, for financial support.

References

1. *50 Years Progress in Crystal Growth* R.S. Feigelson Ed. Elsevier, Amsterdam 2004 and references therein.
2. *Crystal Growth Technology* H.J. Scheel, T. Fukuda Eds. Wiley, Chichester England 2003.
3. *The Growth of Single Crystals* R.A. Laudise Prentice-Hall Englewood Cliffs NJ 1970.
4. *Bulk Crystal Growth* P. Clapper Wiley, Chichester England 2005.
5. *Crystal Growth from High Temperature Solutions* D. Elwell, H.J. Scheel Academic Press London 1975.
6. *Handbook of Hydrothermal Technology* K. Byrappa, M. Yoshimura Noyes Publications Park Ridge NJ 2001.
7. R.A. Laudise, Prog. Inorg. Chem. 3 (1962) 1-56.
8. R.A. Laudise, J.W. Nielsen, Sol. St. Phys. 12 (1961) 149-222.
9. L.N. Demianets, A.N. Lobachev, Curr. Top. Mater. Sci. 7 (1981) 483-586.
10. A. Rabenau, Angew. Chem. 24 (1985) 1026-1040.
11. C.D. McMillen J.W. Kolis, Phil. Mag. 92 (2012) 2686-2711.
12. G.C. Ulmer and H.L. Barnes (eds.), Hydrothermal Experimental Techniques, Wiley Interscience, New York, 1987.
13. R.A. Laudise. P.M. Bridenbaugh, T. Iradi, J. Cryst. Growth 140 (1994) 51-56.
14. M. M. Kimani, L. Thompson, W. Snider, C. D. McMillen, J. W. Kolis, Inorg. Chem. 51 (2012) 13271-13280.
15. M.M. Kimani, McMillen, C.D. H. Chen, J. Anker, J.W. Kolis, J. Sol. State Chem. 226 (2015) 312-319.

16. M.M. Kimani, C.D. McMillen, J.W. Kolis, J. Sol. State Chem. 226 (2015) 320-325.
17. W. Eysel, Am. Mineral. 58 (1973) 736-747.
18. C. deMilt, J. Chem. Ed. (1942) 53-60.
19. P.B. Moore, Am. Mineral. 58 (1973) 32-42.
20. C. Calvo, R. Faggiani, Can. J. Chem. 53 (1975) 1849-1853.
21. V. A. Morozov,, B. I. Lazoryak, A. P. Malakho, K. V. Pokholok, S. N. Polyakov, T. P. Terekhina, J. Sol. State Chem. 160 (2001) 377-381
22. J.M. Farmer, L.A. Boatner, B.C. Chakoumakos, C.J. Rawn, D. Mandrus, R. Jin, J.C. Bryan, J. Alloys Comp. 2014, 588, 182-189.
23. N.E. Amuneke, D.E. Gheorghe, B. Lorenze, A. Möller, Inorg. Chem. 2011, 50, 2207-2214.
24. N.E. Amuneke, J. Tapp, C.R. de la Cruz, A. Möller, Chem. Mater. 2014, 26, 5930-5935.
25. K.M. Mogare, W. Klein, E-M. Peters, M. Jansen, Sol. State Sci. 8 (2006) 500-507.
26. P.B. Moore, T. Araki, Am. Mineral. 1972, 57 1355-1374.
27. J.P. Smit. P.C. Stair, K.R. Poeppelmeier, Chem. Eur. J. 12 (2006) 5944-5953.
28. A. Möller, N.E. Amuneke, P. Daniel B. Lorenz, C.R. de la Cruz, M. Gooch, P.C.W. Chu, Phys. Rev. B 85 (2012) 214422.
29. G. Nakayama, S. Hara, H. Sato, Y. Narumi, H. Nojiri, J. Phys. Condens. Matter 25 (2013) 116003.
30. L. D. Sanjeewa, M. McGuire, V. O. Garlea, L. Hu, G. Chumanov, C. D. McMillen, J. W. Kolis, Inorg. Chem. (2015) *accepted*.
31. Molecular Structure Corporation & Rigaku, CrystalClear, Rigaku Corporation, Tokyo, Japan, and MSC, The Woodlands, TX, USA, 2006.
32. G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.-122.
33. A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7-13.
34. M. von Postel, Hk. Müller-Buschbaum, Z. Anorg. Allgem. Chem. 618 (1992) 107-110.
35. R. Rettich, Hk. Müller-Buschbaum, Z. Naturforsch. B 53 (1998) 291-295.

36. R. Rettich, Hk. Müller-Buschbaum, Z. Naturforsch. B 53 (1998) 279-282.
37. Y. Yonesaki, C. Matsuda, Q. Dong, J. Sol. State Chem. 196 (2012) 404-408.
38. Y. Yonesaki, T. Takei, N. Kumada, N. Kinomura, J. Sol. State Chem. 182 (2009) 547-554.
39. Y. Yonesaki, C. Matsuda, J. Sol. State Chem. 184 (2011) 3247-3252.
40. P.M. Woodward, Acta Crystallogr. B53 (1997) 32-43.
41. C.Z. Bi, J.Y. Ma, J. Yan, X. Fang, D.Z. Yao, B.R. Zhao, X.G. Qiu, Eur. Phys. J. B 51 (2006) 167-171.
42. R.L. Frost, S.J. Palmer, J. Cejka, J. Sejkora, J. Plasil, S. Bahfenne, E.C. Keeffe, Raman Spectrosc. 42 (2011) 1701-1710.