



Hydrothermal synthesis of single crystals of transition metal vanadates in the glaserite phase



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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 2–3 mm/edge. This method can be generalized for large crystal growth to enable magnetic and neutron diffraction studies that require relatively large single crystals.

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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, Bridgman–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” (0.1–0.3 mm) 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

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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], rutenates [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 1/4 in. Reactants (~0.2 g 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%), $Ba(OH)_2$ (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 $A_2AEM(VO_4)_2$ via stoichiometric reactions

As a typical example, $Na_2BaMn(VO_4)_2$ 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 M 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 analogs such as $Na_2BaFe(VO_4)_2$ (thick black hexagonal plates) and $Na_2BaCo(VO_4)_2$ (thick purple hexagonal plates) were synthesized in similar fashion as phase-pure products. Additionally, $Li_2BaMn(VO_4)_2$ (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 5 M LiOH, and $K_2BaMn(VO_4)_2$ (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 $NaBa_2M(VO_4)_2$ analogs, both $LiBa_2Mn(VO_4)_2$ and $KBa_2Mn(VO_4)_2$ reactions also produced unidentified black powders in addition to the target phase. Crystals of $Na_2SrMn(VO_4)_2$ (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 $Na_2SrCo(VO_4)_2$ (purple hexagonal plates) were prepared similarly, using Co_3O_4 (0.0342 g). Fig. 1 shows the

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