Synthesis, Crystal Structure, and Magnetic Properties of the Oxometallates KBaMnO_4 and KBaAsO_4

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Abstract Single crystals of KBaMnO_4 and KBaAsO_4 were grown using the hydroflux method and characterized by single crystal X-ray diffraction. Both compounds crystallize in the orthorhombic space group $Pnma$ with $a = 7.7795(4) \text{ \AA}$, $b = 5.8263(3) \text{ \AA}$, and $c = 10.2851(5) \text{ \AA}$ for the manganate and $a = 7.7773(10) \text{ \AA}$, $b = 5.8891(8) \text{ \AA}$, and $c = 10.3104(13) \text{ \AA}$ for the arsenate. The materials exhibit a three-dimensional crystal structure consisting of isolated MnO_4^{3-} or AsO_4^{3-} tetrahedra, with the charge balance maintained by K^+ and Ba^{2+} . Each tetrahedron is surrounded by six K^+ and five Ba^{2+} , and shares its corner/edge with KO_{10} polyhedra and corner/edge/face with BaO_9 polyhedra, respectively. The crystal growth, crystal structure and magnetic properties are discussed.

Keywords Crystal growth · Crystal Structure · Magnetism · Hydroflux · KBaMnO_4 · KBaAsO_4

Introduction

The ability to crystallize and characterize new materials often depends on the availability of an appropriate synthetic method for the compositions of interest. Hence, developing new methods for growing single crystals are of general interest, especially if they permit the exploration of chemical systems that previously have proven difficult to obtain. Arsenates and manganates (Mn^{5+}) are examples of classes of materials that have proven difficult to prepare using typical crystal growth approaches.

Pentavalent manganese is rare in extended structures. Mn^{5+} was first prepared in a complex oxide by Lux from strong alkali solutions[1]. Most Mn^{5+} compounds previously synthesized were prepared by the solid state method under O_2 flow near 1000 °C[2-4]. More recent investigations have prepared manganates via low temperature routes such as hydrothermal synthesis or flux growth. Much of the literature has focused on the intense colors exhibited by Mn^{5+} compounds[5], while other investigations have focused on the near infrared emission of manganates and their potential use in laser materials[6]. More recent studies of the magnetic properties of $\text{Ba}_3\text{Mn}_2\text{O}_8$ have brought renewed interest in the magnetic properties of solids containing Mn^{5+} [7-10].

Arsenates have recently raised environmental concerns when they are found in ground water and significant research has focused on methods to remove arsenic from water[11]. In solid-state chemistry, arsenates have been identified as useful building blocks for inorganic framework materials, such as MOFs and zeolites, where the AsO_4^{3-} unit can sometimes be used in place of phosphate, PO_4^{3-} [12].

Hydroflux synthesis offers a reaction media that bridges the gap between wet hydroxide fluxes and aqueous hydroxide reactions and represents a simple approach for exploratory crystal growth. The typical operating temperature for a hydroflux ranges from 200-240°C, significantly less than temperatures used for typical hydroxide flux crystal growth (500-850°C), and comparable to the temperatures used for mild hydrothermal crystal growth. An added advantage of the hydroflux is the absence of high pressure, simplifying the experimental set up. Previously, we have demonstrated the utility of hydrofluxes for the crystal growth of both hydroxides and oxides[13-15]. We sought to determine if the hydroflux approach to crystal growth could be extended to main group elements and become a route to growing arsenate single crystals. Using this

approach, we were able to prepare both manganates and arsenates, KBaMnO_4 and KBaAsO_4 , single crystals out of a potassium hydroxide hydroflux. Herein, we report on the synthesis and crystal structure of the new arsenate KBaAsO_4 and the crystal structure, optical and magnetic properties of KBaMnO_4 .

2. Experimental Details

2.1 Crystal Growth

Single crystals of KBaAsO_4 were grown out of a hydroflux of potassium hydroxide containing approximately 33% water by weight. The reaction was carried out in a 23 mL polytetrafluoroethylene (PTFE) lined stainless steel autoclave. A mixture of 0.75 mmol of As_2O_3 (0.1320 g) (Alfa Aesar, 99.95%), 1 mmol of $\text{Ba}(\text{NO}_3)_2$ (0.2614 g) (Alfa Aesar, 99.95%), 8 g of KOH (VWR, 85%), and 4 ml of deionized water were added to the autoclave, which was sealed. The autoclave was heated to 230° at 5°C/minute, held for 24 hours, and then cooled slowly to 33°C at a rate of 0.3°/minute, at which point the oven was shut off. After cooling, the liquid in the autoclave was poured out, and the crystals inside were dislodged from the sides and rinsed out of the autoclave with methanol.

Single crystals of KBaMnO_4 were grown from a mixed NaOH/KOH hydroflux. Crystal growth was carried out in a custom fabricated, virgin PTFE vessel with ~23 mL total volume. No secondary containment was necessary for pressure. 1.5 mmols of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Alfa Aesar, 99+%) and 1 mmol of KMnO_4 (Fisher Scientific, ACS Grade) were added to a hydroflux made from 5.6 g of KOH (Fisher Scientific, ACS grade pellets) 4.3 g of NaOH (Fisher Scientific, ACS grade pellets) and 4 g of water. The reaction mixtures were heated to 230 °C at 5°C per minute and held for 12 hours before being cooled at a rate of 0.3 °C per minute to 80 C.

2.2 Single Crystal X-Ray Diffraction

X-ray intensity data from single crystals of KBaMnO_4 and KBaAsO_4 were collected at 298(2) K using a Bruker SMART APEX diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$)[16]. The raw area detector data frames were reduced with SAINT+[16]. Data were corrected for absorption effects using the multi-scan technique implemented in

SADABS[16]. The reported unit cell parameters were determined by least-squares refinement of large sets of strong reflections taken from each data set. Full-matrix least-squares refinement against F^2 of the structural models and difference Fourier calculations were performed with SHELXTL[17]. Detailed crystallographic data and selected interatomic distances are reported in Tables 1, 2, and 3.

2.3 Energy-Dispersive Spectroscopy (EDS)

Elemental analysis was performed on the crystals using a Tescan Vega 3 scanning electron microscope (SEM) with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 30 kV accelerating voltage and an accumulation time of 15 s. As a qualitative measure, the EDS confirmed the presence of each element and corroborated the approximate elemental ratios.

2.5 Magnetic Susceptibility Measurements

The DC magnetic susceptibility of KBaMnO_4 was measured as a function of temperature using a Quantum Design MPMS SQUID VSM. For a typical temperature sweep experiment, the sample was first cooled to 2 K under zero-field cooled (zfc) conditions and data were collected upon warming to 300 K in an applied field of 1000 Oe. Data were then collected under field cooled cooling (fcc) from 300 K to 2 K in an applied field of 1000 Oe. Radial offset and sample shape corrections were applied to the magnetization data using a fitting routine involving data collected at 30 K under both DC and VSM modes[18].

3. Results and Discussion

Synthesis. Single crystals of KBaAsO_4 were grown out of a hydroflux of potassium hydroxide containing approximately 33% water by weight at 230°C for 24 hours. The colorless, well faceted polyhedral crystals were obtained in essentially quantitative yield as a phase pure product. (Figure 1) The crystals were isolated by decanting the liquid hydroflux and by washing the crystals quickly with methanol. Phase pure samples of KBaMnO_4 crystals were obtained from hydroflux synthesis with a yield of 72% (Figures 2 and 3) using the experimental conditions detailed herein. Initially,

crystals were grown from an open atmosphere reaction in a PTFE cup on a hot plate with the same hydroflux composition. Crystal quality was greatly increased by switching to sealed vessels and slow cooling in an oven. After cooling to room temperature, the solid hydroflux was still green after the reaction, indicating the incomplete reaction of MnO_4^{3-} . Crystals were isolated by sonication in methanol. Small amounts of BaCO_3 were also formed and removed with a sieve. The single crystal structures were determined and both compounds were found to be isostructural with KBaVO_4 and are members of the Arcanite family, named after the mineral K_2SO_4 .

Crystal Structure. The $\beta\text{-K}_2\text{SO}_4$ structure type (A_2MO_4), including structural variants, is often observed for oxometallates and simple salts such as Tl_2SO_4 , Ba_2TiO_4 [19], Ba_2CoO_4 [20], Ba_2CrO_4 [21], K_2CrO_4 [22], and Tl_2CrO_4 [23]. More complex compositions, namely those containing two cations ($\text{AA}'\text{MO}_4$) ($\text{A} = \text{Na}, \text{K}; \text{A}' = \text{Sr}, \text{Ba}$) are found among the phosphates and vanadates, such as KBaPO_4 [24], KBaVO_4 [25], and some structurally related phases are found among the aluminates and gallates, including BaLaAlO_4 [26] and BaLaGaO_4 [27].

KBaMnO_4 and KBaAsO_4 crystallize in the orthorhombic space group $Pnma$. The structure, shown in Figure 4, consists of isolated MnO_4^{3-} or AsO_4^{3-} tetrahedra with the charge balance maintained by K^+ and Ba^{2+} cations. Each tetrahedron is surrounded by six K^+ and five Ba^{2+} cations, and shares its corner/edge with KO_{10} polyhedra and corner/edge/face with BaO_9 polyhedra, respectively. The KO_{10} polyhedra are connected to each other via face-sharing along the b -axis and corner/edge-sharing in the ac -plane. One interesting structural feature is the presence of hexagonal channels, created by the arrangement of the KO_{10} polyhedra, along the a -axis, which contain Ba^{2+} cations. (Figure 5) The BaO_9 polyhedra share their face, corner, and edge along the a -, b -, and c -axes, respectively, forming a 3D structure. The Mn-O bond distances in the MnO_4 tetrahedra range from 1.680(5) Å to 1.692(4) Å, and the As-O bond distances in the AsO_4 tetrahedron range from 1.680(5) Å to 1.692(4) Å, both of which fall into the normal bond length ranges observed in the literature. Both K^+ and Ba^{2+} cations are observed in irregular polyhedra with distances to oxygen atoms of 2.774(5) – 3.205(4) and 2.688(4) – 3.133(2) for KO_{10} and BaO_9 polyhedra in the manganese analog and 2.713(5) – 3.273(4) and 2.680(3) – 3.205(2) for KO_{10} and BaO_9 polyhedra in the arsenic analog, respectively.

Bond Valence Analysis. Bond valence sum calculations were performed for both compounds on an Excel spreadsheet using bond valence parameters by Brown[28]. For KBaAsO_4 , bond valence sums of 2.11, 0.82, and 5.02 for barium, potassium, and arsenic, respectively, are in good agreement with the expected values for Ba^{2+} , K^+ and As^{5+} . For KBaMnO_4 , bond valence sum calculations yielded values of 2.20 and 0.87 for barium and potassium, respectively. These values are in good agreement with the expected oxidation states for Ba^{2+} and K^+ . There is no bond valence parameter listed for Mn^{5+} . However, using the parameter for Mn^{6+} (1.79) yields a bond valence sum for manganese of 5.20, consistent with what is expected based on the phase composition.

Magnetism. The temperature dependence of the magnetic susceptibility (χ) for KBaMnO_4 was measured under zfc and fcc conditions. A sample consisting of ground crystals, phase pure by powder X-ray diffraction, was used for the magnetic measurements. The temperature dependence of the inverse susceptibility data were fit to the Curie-Weiss law where $\chi = C/(T-\theta)$, where C is the Curie constant, and θ is the Weiss temperature. KBaMnO_4 exhibits an effective magnetic moment of $2.74 \mu_B$, in good agreement with the moment expected for Mn^{5+} ($\mu_{\text{eff}} = 2.83 \mu_B, S = 1$). (Figures 6 and 7) The data indicate antiferromagnetic interactions at low temperature and a maximum in the magnetic susceptibility is observed at 4.16 K, consistent with an observed Weiss constant of -4.86 K. A Néel temperature, defined as the peak in the $d\chi T/dT$ plot [29], of 3.64 K can be extracted from the magnetic susceptibility data, which is reasonably low considering that the shortest manganese-manganese distance in KBaMnO_4 is $4.97 \text{ \AA}$.

4. Conclusion

Crystals of KBaMnO_4 and KBaAsO_4 have been grown for the first time using a low temperature hydroflux method. These compounds take on the Arcanite or $\beta\text{-K}_2\text{SO}_4$ structure type. The KBaAsO_4 crystals are clear and colorless, while the KBaMnO_4 crystals have a deep green color due to the presence of Mn^{5+} . The optical properties of KBaMnO_4 are reported. The magnetic properties of KBaMnO_4 ($\text{Mn}^{5+}; d^2$) have been investigated and KBaMnO_4 was found to order antiferromagnetically with a Néel temperature of 3.64 K.

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Table 1 Crystallographic data for KBaMO_4 ($M = \text{Mn, As}$).

formula	KBaMnO_4	KBaAsO_4
formula weight	295.38	315.36
temperature (K)	298(2)	298(2)
color and habit	blue/green, polyhedral	colorless, polyhedral
crystal system	Orthorhombic	Orthorhombic
space group	$P n m a$	$P n m a$
a (Å)	7.7795(4)	7.7773(10)
b (Å)	5.8263(3)	5.8891(8)
c (Å)	10.2851(5)	10.3104(13)
V (Å ³)	466.18(4)	472.23(11)
Z	4	4
ρ_c (g cm ⁻³)	4.209	4.436
μ (mm ⁻¹)	11.884	16.136
$F(000)$	528	560
crystal size (mm ³)	$0.15 \times 0.08 \times 0.03$	$0.09 \times 0.06 \times 0.06$
2 theta range (°)	6.56 to 56.54	6.56 to 56.60
completeness (%)	100	100
reflections collected	5970	5146
independent reflections	632	643
R (int)	0.0302	0.0199
GOF (F^2)	1.172	1.213
$R(F)^a$	0.0245	0.0223
$R_w(F_o^2)^b$	0.0684	0.0607
Largest diff. peak and hole (e Å ⁻³)	1.691 and -0.672	0.750 and -1.413
$R(F)^a = \Sigma F_o - F_c /\Sigma F_o $. $R_w(F_o^2)^b = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$		

Table 2 Atomic coordinates and equivalent isotropic displacement parameters U_{eq} for KBaMO_4 ($M = \text{Mn, As}$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
KBaMnO ₄				
Ba(1)	0.5093(1)	0.25	0.3070(1)	0.015(1)
K(1)	0.8416(2)	0.25	0.5833(2)	0.015(1)
Mn(1)	0.2677(1)	0.25	0.5819(1)	0.011(1)
O(1)	0.1941(7)	0.25	0.4265(5)	0.017(1)
O(2)	0.1973(5)	0.0105(6)	0.6582(4)	0.022(1)
O(3)	0.4851(6)	0.25	0.5809(6)	0.023(1)
KBaAsO ₄				
Ba(1)	0.5052(1)	0.25	0.3007(1)	0.014(1)
K(1)	0.8352(2)	0.25	0.5816(1)	0.019(1)
As(1)	0.2707(1)	0.25	0.5819(1)	0.011(1)
O(1)	0.1916(6)	0.25	0.4290(4)	0.019(1)
O(2)	0.2026(4)	0.0156(5)	0.6593(3)	0.021(1)
O(3)	0.4865(6)	0.25	0.5768(5)	0.025(1)

Table 3Selected interatomic distances (Å) for KBaMO_4 ($M = \text{Mn, As}$).

	KBaMnO_4	KBaAsO_4
Ba(1)-O(2)	2.680(3)	2.688(4)
Ba(1)-O(2)	2.680(3)	2.688(4)
Ba(1)-O(1)	2.774(4)	2.742(5)
Ba(1)-O(1)	2.777(4)	2.764(4)
Ba(1)-O(2)	2.790(3)	2.764(4)
Ba(1)-O(2)	2.790(3)	2.799(5)
Ba(1)-O(3)	2.850(5)	2.823(6)
Ba(1)-O(3)	3.205(2)	3.133(2)
Ba(1)-O(3)	3.205(2)	3.133(2)
K(1)-O(3)	2.713(5)	2.774(5)
K(1)-O(2)	2.950(3)	2.927(4)
K(1)-O(2)	2.950(3)	2.927(4)
K(1)-O(1)	2.954(1)	2.929(1)
K(1)-O(1)	2.954(1)	2.929(1)
K(1)-O(2)	3.179(3)	3.182(5)
K(1)-O(2)	3.179(3)	3.194(4)
K(1)-O(1)	3.187(4)	3.194(4)
K(1)-O(2)	3.273(4)	3.205(4)
K(1)-O(2)	3.273(4)	3.205(4)
M(1)-O(3)	1.680(5)	1.691(5)
M(1)-O(2)	1.680(3)	1.692(4)
M(1)-O(2)	1.680(3)	1.692(4)
M(1)-O(1)	1.692(4)	1.698(5)

Figure 1. Optical image of a set of KBaAsO₄ crystals.

Figure 2. Optical image of a set of KBaMnO₄ crystals.

Figure 3. Scanning electron micrograph image of a KBaMnO_4 crystal.

Figure 4. Unit cell of KBaMO_4 ($M = \text{Mn, As}$), with oxygen atoms in red, manganese in green, barium atoms in grey, and potassium atoms in blue. All atoms are drawn as thermal ellipsoids at 50% probability.

Figure 5. Extended view of the crystal structure of KBaMO_4 ($M = \text{Mn, As}$), with oxygen atoms in red, MO_4 tetrahedra in green, barium atoms in grey, and potassium coordination polyhedra shown down the a axis.

Figure 6. Temperature dependence of the molar magnetic susceptibility, χ_m , and inverse molar magnetic susceptibility, $1/\chi_m$, for KBaMnO_4 .

Figure 7. Low temperature region of the molar magnetic susceptibility, χ_m , and inverse molar magnetic susceptibility, $1/\chi_m$, for KBaMnO_4 .