



The homometallic warwickite V_2OBO_3

Elizabeth M. Carnicom^{a,*}, Karolina Górnicka^b, Tomasz Klimczuk^b, Robert J. Cava^{a,*}

^a Department of Chemistry, Princeton University, Princeton, NJ 08544, United States

^b Department of Physics, Gdansk University of Technology, Gdansk 80-233, Poland



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ABSTRACT

The synthesis, structure and elementary magnetic characterization of the homometallic warwickite V_2OBO_3 are reported. The material adopts the orthorhombic warwickite structure type at room temperature, space group $Pnma$ (No. 62) with lattice parameters $a = 9.2317(1)$ Å, $b = 3.1172(1)$ Å, and $c = 9.5313(1)$ Å. Temperature-dependent magnetic susceptibility, electrical resistivity, and specific heat measurements show anomalies near 35 K, between 135 K and 150 K, and near 260 K, with the transition at ~ 35 K likely to a ferrimagnetic state. High resolution synchrotron powder X-ray diffraction data at temperatures between 295 K and 90 K display significant peak splitting upon cooling, indicating that at least one crystallographic symmetry change occurs at low temperatures.

1. Introduction

Warwickites [1,2] are a group of metal-containing oxyborates, and have been the focus of many studies in the past due to their structural, magnetic, and electronic properties [3–11]. The general formula for this structure-type is $M^{2+}M^{3+}OBO_3$, where the divalent (M^{2+}) and trivalent (M^{3+}) atoms can be lanthanide, alkaline earth, or transition metals. The structure is orthorhombic, in space group $Pnma$ and contains trigonal BO_3 groups that share their corners with ribbons of edge-sharing distorted MO_6 octahedra. The ribbons are four octahedra wide in a $M2-M1-M1-M2$ arrangement, where $M1$ and $M2$ are crystallographically inequivalent sites, occupied by the metal cations in the center of the ribbon (site $M1$) or on the edge of the ribbon (site $M2$). The trivalent and divalent metal cations are frequently randomly distributed across the two inequivalent sites, leading to disorder in the warwickite structure [11]. In addition, the linear ribbons can behave as independent units resulting in the low-dimensional electronic and magnetic properties often seen in these materials [9,11]. It is this low dimensionality that allows for warwickites to be considered as candidates for use in various electronic devices [12] or in quantum computing due to quantum entanglement [13,14].

Many heterometallic warwickites, where $M^{2+} \neq M^{3+}$, such as $CaScOBO_3$ [3], $CaInOBO_3$ [15], $CoFeOBO_3$ [14], $MgScOBO_3$ [5,16], and $MgTiOBO_3$ [3,10], have been synthesized. Heterometallic warwickites are often found to be spin glasses due to the disordered metal cations, which result in only short range magnetic interactions [9,10,17,18].

Homometallic warwickites are more rare, and are at the same time more complex because they are mixed-valent. Such materials, exemplified by Mn_2OBO_3 [6,19–22] and Fe_2OBO_3 [7,8,12,23,24], can display structural or magnetic transitions under different conditions. In the homometallic Mn and Fe warwickites, charge ordering [25] is reported that is accompanied by a lowering of the symmetry of the crystal structure. Below 317 K, for example, Fe_2OBO_3 has the monoclinic space group $P2_1/c$ [7,8,23], with mixed site occupancy, while in Mn_2OBO_3 , the Mn^{2+} atoms occupy site $M2$ and the Mn^{3+} atoms occupy site $M1$ [21] in the monoclinic space group $P112_1/n$ [19]. In addition to the monoclinic structural distortions, Mn_2OBO_3 has been shown to display long range antiferromagnetic ordering below 26 K [19] and Fe_2OBO_3 possesses a small ferrimagnetic moment below 155 K due to the inexact cancellation of the magnetic moments of the Fe^{2+}/Fe^{3+} atoms on sites $M1$ and $M2$ [7,19].

Here we describe the synthesis and characterization of the previously unreported homometallic warwickite V_2OBO_3 prepared as a polycrystalline material. We characterized the crystal structure and physical properties of V_2OBO_3 through high resolution synchrotron powder X-ray diffraction, temperature-dependent magnetic susceptibility, field-dependent magnetization, temperature-dependent electrical resistivity, and specific heat measurements. We show that V_2OBO_3 adopts the orthorhombic space group $Pnma$ (No. 62) at room temperature and undergoes one or more structural phase transitions as the material is cooled. Further, temperature-dependent magnetic susceptibility data indicate that V_2OBO_3 undergoes a transition to a likely ferrimagnetic state, below ~ 35 K.

* Corresponding authors.

E-mail addresses: carnicom@princeton.edu (E.M. Carnicom), rcava@exchange.princeton.edu (R.J. Cava).

2. Materials and methods

The starting materials for the synthesis of V_2OBO_3 were V_2O_5 (99.6%, 10 mesh, Alfa) and elemental boron (submicron particles, Callery Chem.). Powders of the starting materials V_2O_5 and B were weighed out in a 1:2 ratio, ground using a mortar and pestle to create an intimate mixture and pressed into a pellet using a hydraulic press. The pellet was then placed in an alumina crucible, sealed in an evacuated silica tube, and heated to 1100 °C for 12 h with heating and cooling rates of 180 °C/h (no melting was observed). The samples were ground, pressed into a pellet, and then reheated at 1100 °C two additional times to ensure homogeneity. Samples of V_2OBO_3 are stable in air and do not decompose after an extended time.

The purity of the V_2OBO_3 samples was checked using a Bruker D8 Advance Eco powder diffractometer, Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$), with a LynxEye-XE detector, at room temperature. The room temperature structure was determined by using high resolution synchrotron powder X-ray diffraction data that was collected at beamline 11-BM of the Advanced Photon source (APS) using a wavelength of $\lambda = 0.412731 \text{ \AA}$. Data was also collected at 280 K, 240 K, 160 K, 120 K, and 90 K to track the phase transitions. The FullProf Program Suite was used to perform a Rietveld refinement of the resulting powder diffraction pattern taken at 295 K using Thompson-Cox-Hastings pseudo-Voigt peak shapes and the structure of an isostructural warwickite [1] as a starting model. Individual peaks in the temperature dependent data were fitted by a pseudo-Voigt function in the program Origin. In those fits, the peak shapes and widths determined unambiguously at 295 K were maintained at all temperatures (FWHM = 0.01534; profile shape factor = 0.7635). The crystal structure images were produced using the program VESTA [26].

A Quantum Design Physical Property Measurement System (PPMS) Dynacool equipped with a vibrating sample magnetometer was used to measure the temperature-dependent magnetic susceptibility and field-dependent magnetization of V_2OBO_3 . The temperature-dependent magnetic susceptibility (defined as M/H where M is the sample magnetization and H is the applied field) was measured both on cooling and heating in the temperature range 300–1.7 K with an applied magnetic field of 500 Oe. The field-dependent magnetization was measured at 1.7, 30, 65, 100, 200, and 300 K with a field sweep from $\mu_0 H = 0\text{--}9 \text{ T}$. The resistivity option of the PPMS was used to measure the temperature-dependent electrical resistivity using a standard four-probe method in the temperature region from 300 K to 140 K under constant power mode and zero applied magnetic field. The specific heat for V_2OBO_3 was measured with a Quantum Design PPMS Evercool II using the 2τ relaxation method on a flat polished sample. Data were collected under zero applied magnetic field using Apiezon L grease for the high temperature measurements and Apiezon N for the low temperature measurements [27].

3. Results and discussion

The previously unreported homometallic warwickite V_2OBO_3 , prepared by solid-state synthesis, was structurally analyzed using high resolution synchrotron powder X-ray diffraction. The ambient temperature Rietveld refinement of V_2OBO_3 (Fig. 1) shows that this material adopts the orthorhombic warwickite structure ($Pnma$, No. 62) with lattice parameters $a = 9.2317(1) \text{ \AA}$, $b = 3.1172(1) \text{ \AA}$, and $c = 9.5313(1) \text{ \AA}$, similar to other warwickite-type materials. Table 1 shows the results from the Rietveld refinement of V_2OBO_3 at room temperature. The fit of the model to the data is excellent. The crystal structure is shown in Fig. 2 (left), looking down on the ribbons of edge-sharing VO_6 octahedra. The triangular BO_3 groups are between ribbons.

The electronic and magnetic properties are determined by the vanadium-oxygen array. Fig. 2 (top right) shows the vanadium-oxygen array in a single ribbon. The ribbons, consisting of an arrangement of

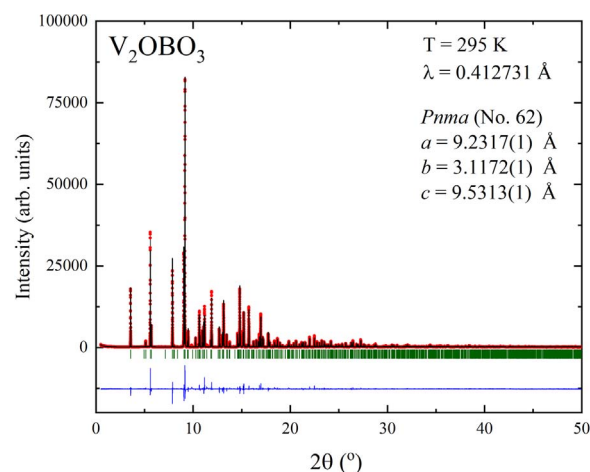


Fig. 1. Rietveld refinement of V_2OBO_3 using high resolution synchrotron powder X-ray diffraction data from 11-BM at 295 K. Experimentally observed data is shown with red circles, the calculated fit to the diffraction pattern is shown with a black line, the green vertical lines show expected Bragg reflections for space group $Pnma$ (No. 62), and the difference between the calculated and the observed data is shown with the blue line. Rietveld refinement results: $\chi^2 = 9.17$; $wR_p = 20.2\%$; $R_p = 18.9\%$; $R(F^2) = 18.5\%$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Ambient temperature crystal structure of V_2OBO_3 . Space group $Pnma$ (No. 62) $a = 9.2317(1) \text{ \AA}$, $b = 3.1172(1) \text{ \AA}$, $c = 9.5313(1) \text{ \AA}$, $V = 274.281(1) \text{ \AA}^3$, $Z = 4$. $\chi^2 = 9.17$; $wR_p = 20.2\%$; $R_p = 18.9\%$; $R(F^2) = 18.5\%$.

Atom	Wyckoff Position	Occupancy	x	y	z	$B_{iso} (\text{Å}^2)$
V1	4c	1	0.38415(6)	1/4	0.56113(5)	0.525(4) ^a
V2	4c	1	0.38873(5)	1/4	0.19414(5)	0.525(4) ^a
B1	4c	1	0.3392(3)	1/4	0.8763(5)	0.66(5)
O1	4c	1	0.4836(2)	1/4	0.8715(3)	0.44(1) ^b
O2	4c	1	0.2588(2)	1/4	0.7499(2)	0.44(1) ^b
O3	4c	1	0.2658(2)	1/4	0.0035(2)	0.44(1) ^b
O4	4c	1	0.4917(2)	1/4	0.3775(3)	0.44(1) ^b

^a Values were constrained so that V1 and V2 had the same thermal parameters.

^b Values were constrained so that O1, O2, O3, and O4 had the same thermal parameters.

edge-shared VO_6 octahedra, 4 octahedra wide, and only one octahedron thick, infinitely extend along the b -direction. Each of the rows along the length of a ribbon consists of the same crystallographic site, having the sequence V2-V1-V1-V2 across the 4-octahedron width of the ribbon. The bottom right part of Fig. 2 shows one extracted 4-octahedron-wide section of VO_6 octahedra comprising the width of the ribbon. The ribbons of edge-sharing octahedra are joined half-way along their lengths and at their ends through corner-sharing.

Table 2 shows selected distances between the V2 and V1 atoms, and also between the central vanadium atoms V1 and V2 and the surrounding oxygen atoms in the octahedra. The average bond lengths of the V2 and V1 atoms to their surrounding oxygen atoms are the same within 0.01 Å ($\sim 2.07 \text{ \AA}$), suggesting that the V^{2+} and V^{3+} cations are randomly distributed among the crystallographically distinct V2 and V1 sites, in other words that there is no structural indication of static charge ordering at ambient temperature. In addition, the distributions of long and short bond distances for V1-O and V2-O are not very different, suggesting that orbital ordering [28] is not likely to be present at ambient temperature. The V1-V1 separation is somewhat less than that of V2-V1, but for systems like this, superexchange often plays a major role in determining the magnetic properties and thus the V-O-V array is of particular interest. Table 3 shows the V2-O-V1 bond angles across the width of the ribbon and also the V2-O-V2 and V1-O-V1 angles along the length of the ribbon (Fig. 2, top right).

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