Ba$_3$Mn$_2$O$_8$ determined from neutron powder diffraction

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Abstract

The structure of tribarium dimanganese octaoxide, Ba$_3$Mn$_2$O$_8$, has been refined from neutron powder diffraction data, establishing that the phase is hexagonal in space group $R\bar{3}m$, with unit-cell dimensions $a = 5.71$ and $c = 21.44$ Å. Two distinct Ba sites are observed, and the Mn is present in a slightly distorted tetrahedral environment.

Comment

Materials of the stoichiometry $A_3M_2O_8$, where A = Sr, Ba or Ca, and M = V, Cr or Nb (Baran & Aymonino, 1968; Kemmler-Sack & Treiber, 1981) have been structurally characterized and the Raman spectra investigated. In this structure, there are two A sites, one of which has a tenfold coordination environment, whilst the other can be regarded as either six- or 12-fold coordinated, depending on the A—O bond lengths included in the calculation. The M site cations are typically in a slightly distorted tetrahedral environment, *i.e.* as MO_4^{3-} anions. The change in structure of Ba$_3$V$_2$O$_8$ and Sr$_3$V$_2$O$_8$ with increasing pressure has been investigated by Raman spectroscopy (Grzechnik & McMillan, 1997), which indicated that the hexagonal layered structure present under ambient conditions undergoes a pressure-induced transition involving condensation of the tetrahedral VO$_4^{3-}$ groups into octahedra. These materials have proved interesting as possible luminophors and it has been reported that A_3V$_2$O$_8$:Mn^{5+} (A = Sr or Ba) displays near-IR laser action (Merkle *et al.*, 1992, Buijesse *et al.*, 1995).

Other trivalent tetrahedral anions include hypermanganate, MnO$_4^{3-}$, which is found in the series of compounds Ba$_5$(PO$_4$)$_{3-x}$(MnO$_4$)$_x$Cl (Reinen *et al.*, 1986). However, to date there has been no structural investigation by X-ray or neutron diffraction of Ba$_3$Mn$_2$O$_8$. This material is of interest because of its intense colour, and also because it is relatively rare to find a stable Mn^V oxide. This work describes the preparation of Ba$_3$Mn$_2$O$_8$ and its characterization by powder X-ray and neutron diffraction data, leading to a complete structural model for this material.

The X-ray powder diffraction pattern indicated that a hexagonal phase had been produced, with a unit cell of approximately $a = 5.71$ and $c = 21.44$ Å. This material appeared to be structurally similar to materials of the type $A_3M_2O_8$, where A = Sr or Ba, and M = V or Nb (Kemmler-Sack & Treiber, 1981; Liu & Greedan, 1994), and also to recently produced oxynitrides of stoichiometry Ba$_3M_2$(ON)$_8$, where M = W or Mo (Weller & Skinner, 1999; Subramanya Herle *et al.*, 1997). The IR spectrum, with bands at 822 and 758 cm^{-1}, was in good agreement with that reported previously (Baran & Aymonino, 1968), indicating the presence of the MnO$_4^{3-}$ species and confirming the Mn oxidation state as +5.

The lattice parameters determined from the X-ray powder diffraction pattern were found to be similar to those reported for Ba$_3M_2$O$_8$, where M = V or Nb (Kemmler-Sack & Treiber, 1981; Liu & Greedan, 1994). This was later used for the initial model in the refinement of the neutron powder diffraction data recorded from Ba$_3$Mn$_2$O$_8$. In this model, Ba and Mn were assigned to the 3a and 6c sites in the $R\bar{3}m$ space group and a Rietveld refinement of this model using *GSAS* (Larson & von Dreele, 1994) provided a good fit to the neutron powder diffraction data (Fig. 1). The refined structural model is shown in Table 1.
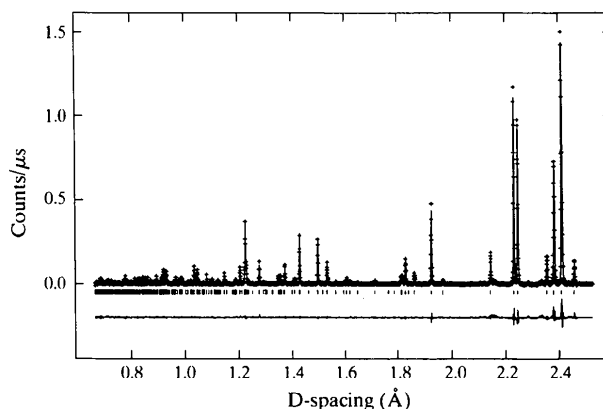

Fig. 1. Showing the fit achieved to the neutron powder diffraction profile from the title compound (++++ experimental data, — the calculated profile). The difference profile is shown underneath. Tick marks indicate the reflection positions.

The structure of Ba$_3$Mn$_2$O$_8$ contains two distinct Ba–O polyhedra and is similar to that described previously (Grzechnik & McMillan, 1997) for Sr$_3$(VO$_4$)$_2$ and analogous compounds. The first of these polyhedra, Ba2, is ten-coordinate and of a type described by Dussarrat *et al.* (1994), in which the central Ba is surrounded by an equidistant hexagon of O atoms at 2.9062 (3) Å, in the same plane. This is capped by a single O atom at a shorter distance [2.621 (2) Å] above the plane, while a further three O atoms lie in a trian-

gular configuration below the plane, at 2.8302 (10) Å. A second polyhedron, with an unusually low coordination number of six, is also observed [6 × Ba1—O1 at 2.7562 (10) Å (Fig. 2a)], in a trigonal antiprismatic arrangement. This site could also be described as having a 12-coordinate icosahedral geometry if a further 6 × Ba—O at 3.29813 (5) Å are included in the coordination polyhedron (Fig. 2b). The ten-coordinate polyhedra face-share with the six-coordinate polyhedra. The Mn atoms are in a distorted tetrahedral environment, with one Mn—O bond [1.671 (3) Å] slightly shorter than the other three [1.7057 (13) Å].
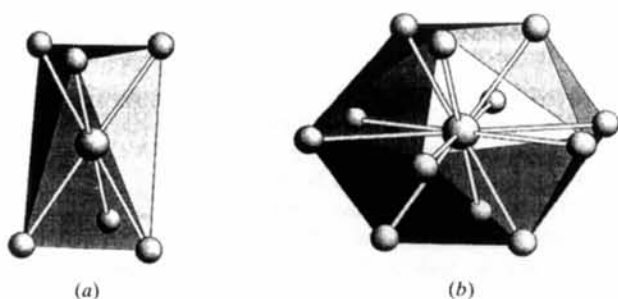

Fig. 2. Showing a comparison of (a) the sixfold Ba1–O1 coordination polyhedron and (b) the 12-fold Ba1–O coordination polyhedron.
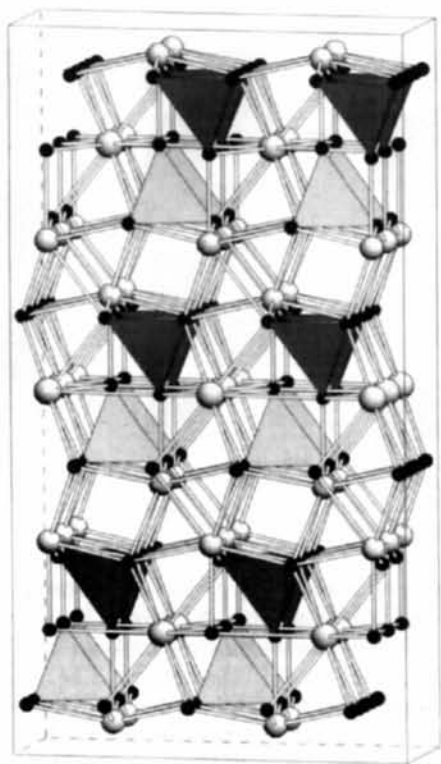

Fig. 3. The structure of $Ba_3Mn_2O_8$ viewed obliquely down (010). MnO_4 polyhedra are shown.

Experimental

Barium carbonate, $BaCO_3$, and manganese(III) oxide, Mn_2O_3, were combined in stoichiometric quantities and intimately mixed by grinding under acetone. This mixture was placed in an alumina crucible and heated in air at 1173 K for 24 h. After cooling, a bright green material was obtained. X-ray powder diffraction data were recorded on a Siemens D5000 diffractometer using Cu $K\alpha_1$ radiation, to enable phase purity to be established. Neutron powder diffraction data were collected for 6 h at the 1 m position on the High Resolution Powder Diffractometer (HRPD) at ISIS, CLRC Rutherford Appleton Laboratory, Oxfordshire, England. The data were normalized and corrected as usual.

Crystal data

$Ba_3Mn_2O_8$	Neutron radiation
$M_r = 649.891$	Cell parameters from
Trigonal	whole diffractogram
$R\bar{3}m$	$T = 295$ K
$a = 5.710728\,(16)$ Å	Powder
$c = 21.44383\,(10)$ Å	Dark green
$V = 605.64$ Å^3	
$Z = 3$	

Data collection

High Resolution Powder Diffractometer (HRPD) at ISIS	Specimen mounting: vanadium can
	$T = 295$ K
Measurement method: neutron scattering, time-of-flight scans	347 measured reflections
	4378 observations

Refinement

$R = 0.064$	26 parameters
$wR = 0.070$	$(\Delta/\sigma)_{max} = 0.001$
$R_{exp} = 0.0412$	Scattering factors from
$S = 1.70$	Koester *et al.* (1994)
Profile function: exponential pseudo-Voigt convolution	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)*

	x	y	z	U_{iso}
Ba1	0	0	0	0.0149 (5)
Mn1	0	0	0.40708 (10)	0.0094 (5)
Ba2	0	0	0.20692 (6)	0.0082 (4)
O1	0.16175 (12)	0.3235 (2)	0.56538 (4)	0.0134 (2)
O2	0	0	0.32914 (7)	0.0257 (4)

Table 2. *Selected bond lengths (Å)*

Mn1—O1	×3	1.7055 (13)	Ba2—O2		2.621 (2)
Mn1—O2		1.671 (3)	Ba2—O1	×6	2.9062 (3)
Ba1—O1	×6	2.7563 (10)	Ba2—O1	×3	2.8304 (16)
Ba1—O2	×6	3.29831 (5)			

Program(s) used to refine structure: *GSAS* (Larson & von Dreele, 1994).

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NH$_4$VO(NH$_3$)PO$_4$

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Abstract

Ammonium ammine oxovanadium phosphate, NH$_4$VO-(NH$_3$)PO$_4$, crystallizes in the monoclinic system in space group $P2_1$. The structure contains VO$_4$(NH$_3$) square pyramids and PO$_4$ tetrahedra which are connected *via* common O atoms forming double chains running along [010]. The bond distances are in the usual

ranges and similar to those of other vanadium phosphate compounds.

Comment

In connection with investigations of the catalytic process of ammoxidation of substituted methyl aromatics and methyl heteroaromatics to their corresponding nitriles, ammonium oxovanadium(IV) phosphates and oxovanadium(IV) phosphates are of great interest. Ammonium oxovanadium(IV) phosphates can act in these catalytic processes either as a catalyst or as an intermediate. Our investigation studied the NH$_3$/V^{IV}/P$_2$O$_5$ system and led to the new title compound NH$_4$VO(NH$_3$)PO$_4$.

The crystal structure of the title ammonium oxovanadium(IV) phosphate consists of distorted VO$_4$(NH$_3$) square pyramids and PO$_4$ tetrahedra. These polyhedra are alternately connected *via* common O atoms, forming double chains running along [010]. Each VO$_4$(NH$_3$) square pyramid is connected by three common O atoms (O1, O2 and O3) to three PO$_4$ tetrahedra. Two O atoms link VO$_4$(NH$_3$) and PO$_4$ polyhedra in the [010] chain direction and a third O atom is shared with a PO$_4$ tetrahedron of a neighbouring parallel chain (Fig. 1). Four hydrogen bonds starting at NH$_4$ connect the double chains along [001]. An ammonia H atom (N1—H1$\cdots$O5) links the chains along [100] through a second hydrogen bond to O3 within the double chain.
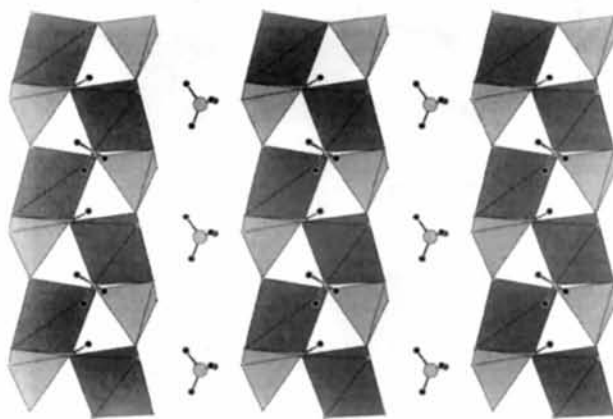

Fig. 1. View along [100] showing the alternately linked chains of VO$_4$(NH$_3$) square pyramids. The *b* direction is vertical and the *c* direction is horizontal.

The base of the square pyramid is formed by three O atoms and the ammonia N1 atom. The three equatorial V—O bond distances vary between 1.972 (2) and 1.988 (2) Å; the V—N1 distance is 2.147 (3) Å. The apical O atom (O4) has a V—O distance of 1.600 (2) Å. This is a typical bond distance for an oxovanadium(IV) cation, as found in other VO^{2+} compounds (Leonowicz *et al.*, 1985; Worzala *et al.*, 1998; Fratzky *et al.*, 1998). The P—O bond lengths vary between 1.512 (2) and