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Structure of Metastable Lead Metavanadates: the Monoclinic PbV_2O_6(II) Modification

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Abstract. $M_r = 405{\cdot}07$, monoclinic, $C2/m$, $a = 15{\cdot}525\,(2)$, $b = 3{\cdot}6960\,(6)$, $c = 9{\cdot}436\,(4)$ Å, $\beta = 110{\cdot}44\,(1)^\circ$, $V = 507{\cdot}3\,(2)$ Å^3, $Z = 4$, $D_x = 5{\cdot}30$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 36{\cdot}75$ mm^{-1}, $F(000) = 704$, $T = 293$ K; final $R = 0{\cdot}046$ for 313 observed reflections. All the atoms lie on mirror planes. The structure of PbV_2O_6(II) differs from that of other MX_2O_6 systems and consists of columns of double chains of edge-sharing VO_5 square pyramids which extend infinitely along the b axis; Pb atoms are interspersed.

Introduction. Recent studies on the equimolar $PbO.V_2O_5$ system (Calestani, Montenero, Pigoli & Bettinelli, 1984) show the existence of two new lead metavanadate phases, which crystallize from the melt when the cooling rate is extremely high; they are imbedded in a vitreous matrix. These phases, indicated as PbV_2O_6(II) and (III), are metastable at room temperature and present structures which differ from that of all other MX_2O_6 systems. Both transform on heating to the well known stable phase PbV_2O_6(I) (Jordan & Calvo, 1974) and must be considered as an intermediate lattice arrangement between the stable form and the glass.

The crystal-structure analysis of these compounds is therefore quite interesting for the comprehension of the structural evolution leading to the vitreous state. We present here the structural study of PbV_2O_6(II), *i.e.* of the first step of this transition between the ordered and disordered state.

Experimental. PbV_2O_6(II) can be obtained imbedded in a vitreous matrix by quenching near equimolar $PbO.V_2O_5$ melts on a steel vessel. Because of the tendency of the glass, at this cooling rate, to enrich itself in V_2O_5, the separation of crystalline PbV_2O_6(II) from the glass is followed by the formation of PbV_2O_7 (chervetite) for a V_2O_5/PbO molar ratio less than 1·2.

The separation of PbV_2O_6(II) single crystals from the quenched mass was quite difficult, since polycrystalline agglomerates appear, because of the high growth rate, as a compact mass in which the single components are practically indistinguishable. In spite of this, some small dark-brown crystals could be isolated by repeatedly breaking the samples.

Intensity data collected from a twin member of a small needle crystal ($0{\cdot}03 \times 0{\cdot}03 \times 0{\cdot}2$ mm), automated Philips PW 1100 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 2–30° θ range, max. range h,k,l: 20,5,12, θ–2θ scan, 1·4° scan width, $0{\cdot}1^\circ$ s^{-1} scan rate; backgrounds estimated from 5 s counts at each end of scan. Lattice parameters determined by least-squares refinement of setting angles of 16 reflections in range $9 < \theta < 18^\circ$. One standard reflection (020), max. intensity variation 2·2%. 882 reflections measured of which 353 with $I > 3\sigma(I)$ considered observed and after correction for Lorentz and polarization effects resulted in 313 unique reflections, $R_{\text{int}} = 0{\cdot}042$. The strong high-$\chi$ ($\sim 90^\circ$) 002 and 004 reflections were not included in the list because of overlap with reflections from other twins. The absorption correction performed by the ψ-scan method (North, Phillips & Mathews, 1968) was affected by the same phenomenon and therefore was not utilized in the structure analysis. All calculations performed on a Gould SEL 32/77 computer using a local version of *SHELX76* (Sheldrick, 1976). Structure solved by

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Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B
Pb	0·1262 (1)	0	0·2224 (2)	0·94 (5)
V(1)	0·1640 (4)	0	0·6349 (7)	0·6 (2)
V(2)	0·3967 (1)	0	0·1563 (8)	0·8 (2)
O(1)	0·93 (2)	0	0·458 (3)	1·3 (5)*
O(2)	0·490 (2)	0	0·821 (3)	1·7 (5)*
O(3)	0·272 (2)	0	0·636 (3)	1·0 (5)*
O(4)	0·338 (2)	0	0·978 (3)	1·7 (5)*
O(5)	0·110 (2)	0	0·792 (3)	1·0 (5)*
O(6)	0·332 (2)	0	0·303 (3)	0·7 (5)*

* Refined isotropically.

standard heavy-atom techniques. Final model with anisotropic thermal parameters for Pb and V and an isotropic thermal parameter for O refined by least-squares ($\sum w\Delta F^2$ minimized) using scattering factors for neutral Pb, V and O including the anomalous-scattering factor (*International Tables for X-ray Crystallography*, 1974) to give $R = 0{\cdot}046$, $R_w = 0{\cdot}045$; $w = 1{\cdot}5018/[\sigma^2(F) + 0{\cdot}00027F^2]$. $(\Delta/\sigma)_{max} = 0{\cdot}016$. Max. and min. height in final difference Fourier map 3·09 (at 1·1 Å from Pb) and 2·2 e Å^{-3}.

Discussion. All the atoms lie on mirror planes. Atomic coordinates and isotropic thermal parameters are shown in Table 1, selected bond distances and angles in Table 2.* Fig. 1 shows the structure of PbV_2O_6(II) projected onto the *ac* plane. There are two types of V atom in the structure each bonded to five O atoms in the form of a distorted square pyramid, V—O bond distances ranging from 1·61 (3) to 1·98 (3) Å.

Translationally equivalent pyramids share corner O atoms and extend infinitely along the *b* axis. $V(1)O_5$ and $V(2)O_5$ groups form pairs by sharing an edge; these pairs of pyramids share edges connecting O atoms on adjacent mirror planes so the structure consists of columns of double chains parallel to the *b* axis related by centers of symmetry (Fig. 2).

The Pb^{2+} ions are interspersed and share eight O atoms with four of these double chains. Five of the O atoms lie at a distance ~2·5 Å, while the remaining three are significantly farther away [2·83 (2)–3·01 (2) Å]. The O atoms form a bicapped trigonal prism with symmetry *m* around the Pb^{2+} ion; two O atoms lie on the mirror plane which relates the remaining six in pairs.

Table 2. *Bond distances* (Å) *and selected bond angles* (°)

Pb—O(1)	2·45 (3)	V(1)—O(1)	1·65 (2)
Pb—O(2)	2·51 (2) ×2	V(1)—O(3)	1·67 (3)
Pb—O(3)	2·50 (1) ×2	V(1)—O(5)	1·95 (3)
Pb—O(4)	2·83 (2) ×2	V(1)—O(6)	1·93 (1)×2
Pb—O(6)	3·01 (2)		
		V(2)—O(4)	1·61 (3)
		V(2)—O(2)	1·70 (3)
		V(2)—O(6)	1·98 (3)
		V(2)—O(5)	1·92 (1) ×2
O(6)—V(1)—O(6)′	145·8 (7)	O(5)—V(2)—O(5)′	148·2 (8)
O(5)—V(1)—O(6)	75·34 (3)	O(6)—V(2)—O(5)	74·96 (3)
O(5)—V(1)—O(6)′	75·34 (3)	O(6)—V(2)—O(5)′	74·96 (3)
O(3)—V(1)—O(6)	93·9 (1)	O(2)—V(2)—O(5)	96·31 (9)
O(3)—V(1)—O(6)′	93·9 (1)	O(2)—V(2)—O(5)′	96·31 (9)
O(3)—V(1)—O(5)	134·0 (12)	O(2)—V(2)—O(6)	132·2 (12)
O(1)—V(1)—O(6)	104·42 (4)	O(4)—V(2)—O(5)	101·76 (5)
O(1)—V(1)—O(6)′	104·42 (4)	O(4)—V(2)—O(5)′	101·76 (5)
O(1)—V(1)—O(5)	117·3 (13)	O(4)—V(2)—O(6)	119·4 (13)
O(1)—V(1)—O(3)	108·6 (13)	O(4)—V(2)—O(2)	108·3 (14)
V(1)—O(5)—V(2)	105·42 (4)	V(1)—O(6)—V(2)	103·89 (4)

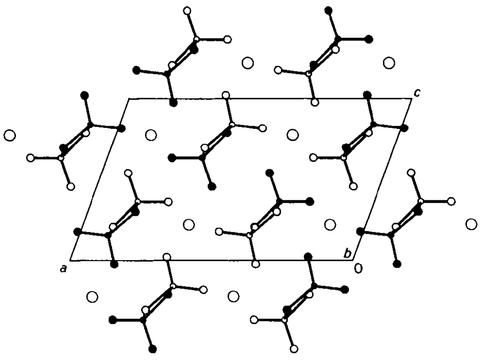

Fig. 1. Projection of the PbV_2O_6(II) structure onto the *ac* plane. The largest circles are Pb atoms and the smallest ones are V atoms. Open and shaded atoms lie in the mirror planes at $b = 0$ and $\frac{1}{2}$ respectively.

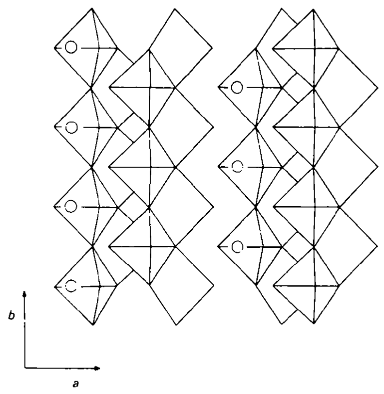

Fig. 2. An idealized view of the edge-shared VO_5 chains in PbV_2O_6(II).

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* Lists of observed and calculated structure factors and of anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39819 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of PbV_2O_6(II) differs from that of other MX_2O_6 systems. Most of the previously investigated metavanadates as for example β-CdV_2O_6 (Bouloux & Galy, 1969), MgV_2O_6 (Ng & Calvo, 1972), CoV_2O_6 (Sauerbrei, 1972), ZnV_2O_6 (Angenault & Rimsky, 1968; Andreetti, Calestani, Montenero & Bettinelli, 1984), and CuV_2O_6 (Calvo & Manolescu, 1973) have structures based upon, or derived from, the brannerite structure (Ruh & Wadsley, 1966) which can be considered a distortion of a hexagonal pseudo close-packed array of O atoms with both M and V atoms octahedrally coordinated. The distorted octahedral coordination around V atoms, characterized by five strong and one weak (~2·6 Å) V—O interactions, is present in other structures of metavanadates as for example in β-HgV_2O_6 (Angenault, 1970) and PbV_2O_6(I) (Jordan & Calvo, 1974).

The loss of the sixth weak interaction characteristic of the PbV_2O_6(II) structure was found in CaV_2O_6 and α-CdV_2O_6 (Bouloux, Perez & Galy, 1972). The structure of these compounds consists, as in PbV_2O_6(II), of columns of double chains parallel to the b axis, but the arrangement of the chains and consequently of the interspersed Pb atoms is different.

As concerns the transition between PbV_2O_6(I) and PbV_2O_6(II), four phenomena may be noted:

(*a*) the significant decrease of the density from 5·89 (I) to 5·30 Mg m^{-3} (II), which agrees with thermodynamic data;

(*b*) the decrease of the coordination number of lead from 9 to 8;

(*c*) the decrease of the vanadium coordination from 6 to 5 by loss of the weak V—O interaction present in PbV_2O_6(I);

(*d*) the formation in PbV_2O_6(II) of void channels parallel to the b axis between the double chains centered in the xz plane at $(0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2})$.

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Structures of Metastable Lead Metavanadates: the Orthorhombic PbV_2O_6(III) Modification

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Abstract. $M_r = 405·7$, orthorhombic, $C222$, $a = 8·273$ (2), $b = 12·422$ (2), $c = 7·685$ (1) Å, $V = 789·8$ (3) Å^3, $Z = 6$, $D_x = 5·11$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 35·42$ mm^{-1}, $F(000) = 1056$, $T = 293$ K; final $R = 0·042$ for 522 observed reflections. The structure of PbV_2O_6(III) differs from that of other MX_2O_6 systems and consists of zigzag chains of corner-sharing VO_4 tetrahedra, which cross on adjacent

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