

The high-pressure form of cadmium vanadate, CdV_2O_6

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Received 13 March 2007

Accepted 9 April 2007

Online 14 June 2007

The crystal structure of a new high-pressure modification of cadmium divanadium hexaoxide, CdV_2O_6 , was refined from X-ray single-crystal data. It contains zigzag chains of edge-sharing VO_6 octahedra. Octahedra in adjacent chains share corners and form corrugated layers. Octahedrally coordinated Cd atoms, which lie on twofold axes, are situated between the layers. The columbite-like structure results in a strong distortion of the CdO_6 octahedra which may be stabilized only at high pressure.

Comment

Complex vanadium(V) oxides have received renewed interest as electrode materials and catalysts. A number of compounds with the general formula MV_2O_6 ($M = \text{Mg}, \text{Ca}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ and Cd) have been studied in the last decade (Rao & Palanna, 1996; Fuentes *et al.*, 1999; Wei *et al.*, 2005, 2006). Among these compounds, CuV_2O_6 (Cao *et al.*, 2006) and CdV_2O_6 (Chen *et al.*, 2004) have been shown to be promising cathode materials for rechargeable lithium batteries. Numerous MV_2O_6 oxides exist at ambient pressure (Rao & Palanna, 1996; Mocala & Ziolkowski, 1987; Tsuzuki *et al.*, 1989) and their crystal structures have been reported by different authors for $M = \text{Mg}$ (Ng & Calvo, 1972), Ca (Bouloux *et al.*, 1972), Mn (Mueller-Buschbaum & Kobel, 1991a), Co (Jasper-Toennies & Mueller-Buschbaum, 1984; Mueller-Buschbaum & Kobel, 1991a), Ni (LeBail & Lafontaine, 1990; Mueller-Buschbaum & Kobel, 1991b), Cu (Lavaud & Galy, 1972; Calvo & Manolescu, 1973), Zn (Angenault & Rimsky, 1968; Andreetti *et al.*, 1984) and Cd (Bouloux & Galy, 1969; Bouloux *et al.*, 1972). Although the symmetry of the MV_2O_6 structures at ambient pressure is changed from orthorhombic to triclinic, all of them belong to the brannerite or thorutite (ThTi_2O_6) structure type. Except for $M = \text{Mn}$, MV_2O_6 transforms at high pressure to the orthorhombic columbite (FeNb_2O_6) structure type (Gondrand *et al.*, 1974). The high-temperature polymorph of HgV_2O_6 also has a

columbite-like structure (Mormann & Jeitschko, 2000), which is the only columbite-like MV_2O_6 vanadate stable at ambient pressure.

High-pressure polymorphs are usually denser (6–10% for MV_2O_6 phases) than their ambient pressure counterparts, and often have layered or close-packed structures. Layered structures are quite promising for applications as cathode materials. Therefore, the investigation of the high-pressure MV_2O_6 polymorphs in addition to the ambient pressure modifications may also be useful for their possible applications. However, the crystal structures of the MV_2O_6 compounds at high pressure have not been investigated yet, although their X-ray patterns have been reported (Gondrand *et al.*, 1974). In this paper, we report the preparation of single crystals of a high-pressure modification of CdV_2O_6 and its crystal structure.

Two types of MO_6 octahedra are present in the title CdV_2O_6 structure. The VO_6 octahedra are connected *via* edge sharing and form zigzag chains running along the a direction (Fig. 1a). Octahedra in adjacent chains share corners and form corrugated layers separated by layers of Cd^{2+} cations; the Cd atoms lie on twofold axes. The VO_6 octahedron is strongly distorted (Fig. 2b) and the V atom is shifted towards atom O3 away from atoms O1 and O2, due to the formation of a vanadyl bond [1.6548 (10) Å]. As a result, the V–O2 bond opposite the vanadyl bond is elongated to 2.3505 (10) Å. The O2–V–O3 angle is 167.72 (4)°. Bond-valence-sum (BVS) calculations give values of 5.23 and 4.87 for six- and five-coordinated vanadium, respectively (Schindler *et al.*, 2000). This type of distortion of the coordination polyhedron is typical for pentavalent vanadium, and similar distances and angles for the VO_6 octahedron were found, for instance, in the columbite-like structure of HgV_2O_6 (Mormann & Jeitschko, 2000). The CdO_6 octahedra are linked by edge sharing into a zigzag chain running along the a direction. The chains are not connected to each other (Fig. 1b). The CdO_6 octahedra are also strongly distorted (Fig. 2a) and have three pairs of Cd–O distances, *viz.* 2.1961 (10), 2.3071 (10) and 2.4311 (10) Å. The largest O–Cd–O angle is 155.82 (4)°. BVS calculation (Brown & Altermatt, 1985; Brese & O’Keeffe, 1991) gives a value of 2.06, in spite of the strong distortion of the polyhedron. One may

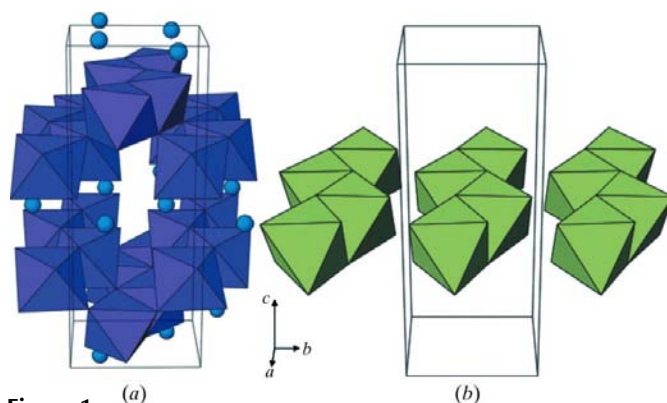


Figure 1 The crystal structure of CdV_2O_6 , showing (a) corrugated layers of VO_6 octahedra and (b) chains of CdO_6 octahedra.

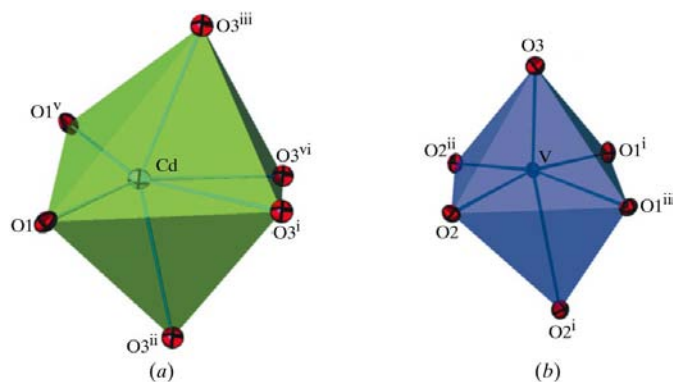


Figure 2
Coordination polyhedra for (a) the Cd atoms and (b) the V atoms. [Symmetry codes as in Table 1; plus (v) $-x + \frac{3}{2}, y, -z + 2$; (vi) $-x + \frac{3}{2}, y + 1, -z + 2$.]

speculate that this distortion is a consequence of the almost pyramidal coordination of the V atom.

One may suggest that the strong distortion of the coordination polyhedra in the high-pressure structure is a reason for the instability of this modification at ambient pressure. In the brannerite-like structure, the Cd atom has an almost regular octahedral coordination with a small difference between the equatorial and apical Cd–O distances (2.287 and 2.199 Å, respectively). The coordination polyhedron of the V atom should be considered as a trigonal bipyramid with two vanadyl bonds of 1.687 and 1.708 Å (Zavalij & Whittingham, 1999). In the high-pressure structure, the V atoms have six O-atom neighbours. However, the sixth V–O2 distance is 2.3505 (10) Å, and it is possible to use the τ parameter (Addison *et al.*, 1984) to distinguish between the VO₅ square-pyramidal and trigonal-bipyramidal geometries. The τ parameter is 0.12, indicating that, if the sixth O2 atom is ignored, the VO₅ polyhedron is a square pyramid. Thus, the coordination arrangement of the V atom in both CdV₂O₆ and HgV₂O₆ is a distorted octahedron. In HgV₂O₆, the VO₆ polyhedron ($\tau = 0.17$) is very similar to that in CdV₂O₆ but the sixth V–O bond is longer (2.442 Å). The main difference between the two structures arises from the coordination of the Hg atom, with two very short (2.040 Å) and four long (2.643 and 2.677 Å) Hg–O distances. Such a coordination stabilizes a columbite-like structure, in spite of the nearly square-pyramidal coordination of the V atom. One should note that in other known columbite-like compounds both cations have a nearly regular octahedral coordination. This is not the case for CdV₂O₆ and, although the cation–cation distances are very close in both modifications, the O-atom environments for these cations are significantly different. Thus, one may conclude that the MV₂O₆ columbite-like structure results in a strong distortion of the MO₆ octahedra which may be stabilized only at high pressure.

Experimental

A mixture of CdO (99.9%) and V₂O₅ (99.9%) in a 1:1 ratio was placed in a gold capsule and treated at 6 GPa and 1473 K in a belt-type high-pressure apparatus for 60 min (heating rate of

120 K min⁻¹). After heat treatment, the sample was quenched to room temperature and the pressure was released slowly. The product consisted of small black single crystals suitable for X-ray crystal structure analysis. Powder X-ray diffraction revealed the crystals to be CdV₂O₆.

Crystal data

CdV ₂ O ₆	$V = 399.39 (8) \text{ \AA}^3$
$M_r = 310.29$	$Z = 4$
Orthorhombic, <i>Pnab</i>	Mo $K\alpha$ radiation
$a = 4.9495 (6) \text{ \AA}$	$\mu = 9.79 \text{ mm}^{-1}$
$b = 5.6949 (7) \text{ \AA}$	$T = 293 \text{ K}$
$c = 14.1692 (17) \text{ \AA}$	$0.22 \times 0.11 \times 0.06 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	1727 independent reflections
Absorption correction: Gaussian (<i>JANA2000</i> ; Petříček & Dušek, 2000)	1349 reflections with $I > 3\sigma(I)$
$T_{\min} = 0.314$, $T_{\max} = 0.565$	$R_{\text{int}} = 0.020$
4388 measured reflections	2 standard reflections frequency: 120 min intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	43 parameters
$wR(F^2) = 0.028$	$\Delta\rho_{\max} = 0.58 \text{ e \AA}^{-3}$
$S = 1.19$	$\Delta\rho_{\min} = -0.49 \text{ e \AA}^{-3}$
1349 reflections	

Table 1

Selected bond lengths (Å).

Cd–O1	2.1961 (10)	V–O2	2.0225 (10)
Cd–O3 ⁱ	2.4311 (10)	V–O2 ^{iv}	1.7494 (10)
Cd–O3 ⁱⁱ	2.3071 (10)	V–O2 ⁱⁱⁱ	2.3505 (10)
V–O1	2.0472 (10)	V–O3	1.6548 (10)
V–O1 ⁱⁱⁱ	1.7853 (10)		

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $x + \frac{1}{2}, -y + 1, z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$.

The nonstandard setting of the *Pbcn* space group was used for better representation of the CdV₂O₆ structure, which is built of zigzag chains of VO₆ octahedra arranged in crimped layers. Thus, the entire structure may be considered as stacking of V₂O₆ and Cd layers along the *c* axis. This was the main reason for choosing the nonstandard setting of the space group. For example, Bi_{2+*x*}Sr_{2–*x*}CuO_{6+*d*} crystallizes in the *A2/a* space group, with cell parameters about $a = 5.4 \text{ \AA}$, $b = 5.4 \text{ \AA}$ and $c = 24.6 \text{ \AA}$, and $\alpha = \beta = \delta = 90^\circ$, which corresponds to the standard setting *C2/c*. Nevertheless, it is always refined in the *A2/a* space group for better presentation of layer stacking.

The structure was refined isotropically to $R = 0.032$ and anisotropically to $R = 0.016$. Difference Fourier syntheses revealed the highest residual peaks in the vicinity of the Cd and V sites. Anharmonic displacement parameters based on the Gram–Charlier expansion of the structure factor were refined up to the fourth order. Although the depths of the negative regions in the probability density function maps were about 3–6%, only a few parameters had a significance level above 3σ and the reduction of the *R* factor was about 0.001. Therefore, in the final refinement cycles, all atoms were refined anisotropically. At the final stage, the occupancies of all sites were refined in turn, with deviations from unity less than 3σ in all cases. Fixed full occupancies were then used for all atoms. The use of the $I > 2\sigma(I)$ cut-off instead of $I > 3\sigma(I)$ added only eight extra observed reflections and raised the *R* index only slightly (0.018).

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Manual*; data reduction: *JANA2000* (Petříček &

Dušek, 2000); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2000); program(s) used to refine structure: *JANA2000*; molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *JANA2000*.

The authors are grateful to RFBR (grant No. 07-03-00890) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3043). Services for accessing these data are described at the back of the journal.

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