Defect Structures in the Brannerite-Type Vanadates. IV. The Crystal Structure of $Mn_{1-x}\emptyset_xV_{2-2x}Mo_{2x}O_6$; $x = 0.53$

ROMAN KOZŁOWSKI*

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland

AND KATARZYNA STADNICKA

Institute of Chemistry, Jagellonian University, Kraków, Poland

The crystal structure of $Mn_{1-x}\emptyset_xV_{2-2x}Mo_{2x}O_6$; $x = 0.53$ of the brannerite type has been refined to $R = 0.029$. The space group is $C2$. The bond length–bond strength calculations indicate a short-range ordering of Mo^{6+} and vacancies, resulting in the formation of $Mo–O–\emptyset–O–Mo$ clusters which are distributed at random in the host vanadate structure.

Introduction

In a recent paper it was shown that one may substitute Mo for V in the MnV_2O_6 structure to produce phases of the formula $Mn_{1-x}\emptyset_xV_{2-2x}Mo_{2x}O_6$ in which $\emptyset$ represents a vacancy at the Mn^{2+} site and Mo^{6+} replaces the V^{5+} ions. Both vacancies and Mo are distributed at random over Mn and V sites respectively (*1*).

In this paper we have undertaken a structural refinement of this compound, with x approximately equal to 0.5, in an attempt to discover how the introduction of defects into MnV_2O_6 affects its structure. Some structural rearrangement might well be expected in the vicinity of both vacancies and Mo cations, as well as local ordering of the Mo ions and vacancies in an effort to compensate for the excess positive charge introduced by $Mo^{6+}–V^{5+}$ replacement. Finally, the structure of the crystal surface will be discussed in anticipation of the results proving useful in the study of the relationship between structural and catalytic properties of the system.

Experimental

Single crystals were grown from a melt of 0.3 mole% of prereacted MnV_2O_6 and 1.4 mole% MoO_3, making use of the sublimation of MoO_3 at higher temperatures (see the phase diagram established for MnV_2O_6–MoO_3 system in (*1*)). The crystallization was performed in an open quartz tube by heating the mixture at 600°C for 20 hr. After cooling, a large number of dark brown, plate-shaped crystals were obtained. The Mn : V : Mo atomic ratio in the crystals, as determined by atomic absorption spectros-

* To whom correspondence should be addressed. Current address: Department of Physics, University of Warwick, Coventry CV4 7AL, England.

copy, was 0.42 : 0.96 : 1.00, giving an average x value of 0.53.

Attempts at grinding a crystal to a sphere for the X-ray experiment were unsuccessful, and a plate-shaped morphology was obtained throughout. The largest face corresponded to (201).

A crystal of dimensions 0.20 × 0.13 × 0.05 mm was used to collect intensity data up to $\Theta = 30°$ using an Enraf–Nonius CAD 4 diffractometer and graphite-monochromated $MoK\alpha$ radiation in the $\Theta/2\Theta$ scan mode and a scan range given by (0.80 + 0.42 tan Θ)°. Unit cell parameters (Table I) were obtained by least-squares refinement of the setting angles for 15 reflections used in the autoindexing procedure. It has been established from a least-square fit in (*1*) that Vegard's law is obeyed according to:

$$a = 9.310 + 0.1738x,$$

$$b = 3.537 + 0.1874x,$$

in the range from 0.00 to 0.40. This gives an average value of $x = 0.57$ for our single crystal.

The fluctuation of intensity for two standard reflections was less than 3% throughout. The intensities were corrected for geometrical factors but not for absorption. Of the 943 reflections measured 712 unique values were obtained by the sort–merge procedure used. One hundred sixty-six reflections with $|F_o| \leq 4\sigma(F_o)$ were treated as unobserved.

TABLE I

CRYSTAL DATA

$Mn_{1-x}\emptyset_xV_{2-2x}Mo_{2x}O_6$;	$x = 0.53(1)$
monoclinic	$D_x = 4.185$ Mg m^{-3}
$a = 9.412(5)$ Å	$Z = 2$
$b = 3.643(1)$ Å	$F(000) = 248$
$c = 6.767(3)$ Å	$\mu(MoK) = 6.179$ mm^{-1}
$\beta = 112.00(4)°$	Systematic absences hkl;
	$h + k = 2n + 1$
$U = 215.2$ Å^3	Space group $C2$ (C_2^3)

It was found that reflections with $h + k$ odd were absent suggesting that the crystal was C centered. No other systematic absences were observed. Three possible space groups were considered, $C2/m$, $C2$, and Cm. Refinement in $C2/m$ gave a large R factor (>8%) and it was observed that on Fourier maps the oxygen peaks appeared doubled. Since there was no evidence, either from powder diffraction or single-crystal analysis, for a superstructure, we could safely reject $C2/m$. Cm was rejected as no suitable structural model could be found in this space group, nor is this space group known in any similar compounds. We therefore refined the structure in $C2$. The metal atoms were initially assumed, by analogy with the similar brannerite-type vanadates, to be in the positions:

Mn	$2a$	0	0	0
V	$4c$	0.3	0.5	0.35
Mo	$4c$	0.3	0.5	0.35

TABLE II

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS (× 10^4)

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	$2a$	0	0	0	142(5)	191(6)	152(5)	0	41(4)	0
Mo, V	$4c$	3139.2(4)	5018(8)	3502(1)	95(1)	71(1)	114(1)	8(4)	58(1)	−2(3)
O(1)	$4c$	1705(3)	4444(9)	1170(5)	114(8)	210(11)	190(8)	−26(8)	38(7)	−27(8)
O(2)	$4c$	4749(3)	5237(11)	2950(4)	115(7)	115(9)	255(8)	−12(10)	101(6)	−11(10)
O(3)	$4c$	3084(3)	42(11)	4375(4)	187(7)	70(7)	243(8)	−34(11)	58(6)	45(11)

Note. Estimated standard deviations in parentheses; $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$.

A difference Fourier map gave corrected values for these coordinates and revealed, in addition, approximate positions for the oxygen atoms. Least-squares refinement was carried out by the SHELX-76 program (2). The coordinates of the V, Mo, and O atoms and the anisotropic temperature factors of Mn, V, Mo and O were refined, together with the site-occupancy factors of each atom, constrained to fit the chemical formula. The final values of the agreement factors, defined as $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_G = [\Sigma w(\Delta F)^2/\Sigma wF^2]^{1/2}$, were $R = 0.029$ and $R_G = 0.038$. The weighting scheme was $w = [\sigma(F_o)]^{-1}$. The final results are listed in Table II.[1] From the refined site-occupancy factors we found that $x = 0.53$, a value in good agreement with the results of atomic absorption measurements. The larger value of $x = 0.57$ found from Vegard's law is probably less accurate, since the linear expansion of the lattice is known only for x smaller than 0.40.

Discussion

The present compound was found to be isomorphous with other vanadates of the brannerite type. Some of them, such as MgV_2O_6 (3), CdV_2O_6 (4), and $NaVMoO_6$ (5) have been refined in space group $C2/m$; ZnV_2O_6 (4) on the other hand was refined in space group $C2$, as in our case.

The bond lengths and angles are listed in Table III. Figure 1 shows the projection of the structure onto (010) and a stereo view of part of the Mo/V–O chain along [010].

[1] See NAPS document No. 03838 for 3 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance in U.S. funds only for each NAPS Accession Number. Institutions may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

No evidence for ordering of Mo or vacancies is found in the refinement. The coordination of the oxygen atoms around M (M = Mo or V) is difficult to assign and it may be described as four-, five-, or sixfold, since two M–O bonds are much longer than the other four. If the coordination is regarded as sixfold the MO_6 octahedra exhibit a strong characteristic distortion. They contain two very short M–O bonds of 1.661 and 1.693 Å to terminal O(1) and quasiterminal

TABLE III

BOND LENGTHS (Å) AND ANGLES (°)

(a) Environment of M = Mo, V

M	–O(1)	1.661(3)	O(2) –M –O(1)	105.8(1)
M	–O(2)	1.693(3)	O(3) –M –O(1)	93.9(1)
M	–O(3)	1.913(5)	O(3)^{ii} –M –O(1)	107.8(2)
M	–O(3)^{ii}	1.930(5)	O(3) –M –O(2)	104.1(2)
M	–O(3)^{iii}	2.151(5)	O(3)^{ii} –M –O(2)	98.7(1)
			O(3)^{ii} –M –O(3)	142.9(2)
M	–O(2)^{i}	2.479(4)	O(1) –M –O(3)^{iii}	100.8(1)
			O(2) –M –O(3)^{iii}	153.4(2)
O(1)	–O(2)	2.675(4)	O(3) –M –O(3)^{iii}	73.4(1)
O(1)	–O(3)	2.618(4)	O(3)^{ii} –M –O(3)^{iii}	73.1(1)
O(1)	–O(3)^{ii}	2.905	O(1) –M –O(2)^{i}	162.8(2)
O(2)	–O(3)	2.754	O(2) –M –O(2)^{i}	75.7(1)
O(2)	–O(3)^{ii}	2.753	O(3) –M –O(2)^{i}	80.6(1)
O(3)	–O(3)^{ii}	3.643	O(3)^{ii} –M –O(2)^{i}	77.1(1)
O(1)	–O(3)^{iii}	2.954	O(3)^{iii}–M –O(2)^{i}	76.3(1)
O(2)	–O(3)^{iii}	3.742		
O(3)	–O(3)^{iii}	2.436(3)		
O(3)^{ii}–O(3)^{iii}		2.437(3)		
O(1)	–O(2)^{i}	4.095		
O(2)	–O(2)^{i}	2.634(6)		
O(3)	–O(2)^{i}	2.873		
O(3)^{ii}–O(2)^{i}		2.781		
O(3)^{iii}–O(2)^{i}		2.919		

(b) Environment of Mn

Mn	–O(1)	2.207(3)	O(1) –Mn–O(1)^{v}	100.7(2)
Mn	–O(2)^{iv}	2.098(3)	O(1) –Mn–O(2)^{vi}	89.2(1)
Mn	–O(1)^{v}	2.519(3)	O(1) –Mn–O(2)^{iv}	87.4(1)
			O(1)^{v} –Mn–O(2)^{iv}	91.1(2)
			O(1)^{v} –Mn–O(2)^{vi}	92.7(2)
			O(1) –Mn–O(1)^{vii}	85.6(1)
			O(1)^{v} –Mn–O(1)^{viii}	73.1(1)

Note. (i) $1 - x, y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (iv) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (v) $x, -1 + y, z$; (vi) $\frac{1}{2} - x, -\frac{1}{2} + y, -z$; (vii) $-x, +y, -z$; (viii) $-x, -1 + y, -z$.
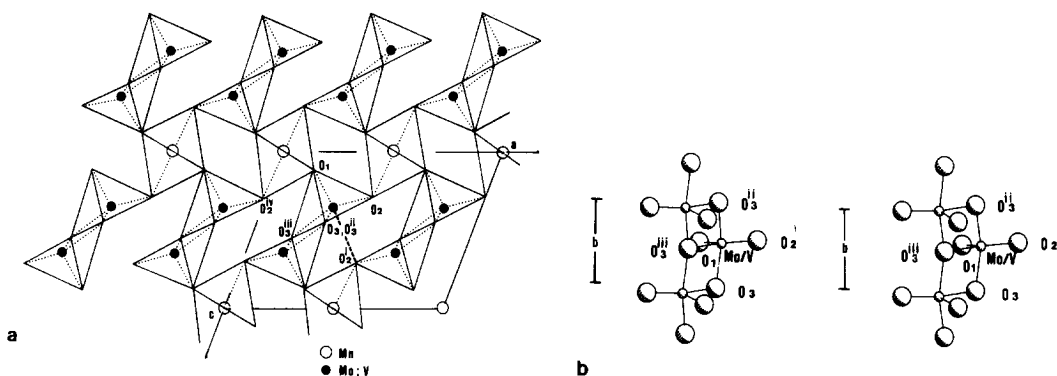
FIG. 1. (a) Projection of the $Mn_{1-x}\emptyset_xV_{2-2x}Mo_{2x}O_6$ structure onto the (010) plane. The dashed line from Mo/V to O(2)^i corresponds to 2.479 Å, and because it is so much longer than the other nearest-neighbor distances, it is not considered to be within the first coordination sphere. (b) Stereo view of part of Mo/V–O chain along [010].

O(2) atoms, two medium M–O bonds of 1.913 Å and 1.930 Å to the bridge-forming oxygens O(3) and O(3)^{ii} and two very long M–O distances of 2.151 and 2.479 Å. The last two bonds result from the small electron-donating character of the bridging O(3) and terminal O(2) atoms, respectively. O(2) forms, in this way, a very asymmetric M–O(2)–M bridge, whereas O(3) acquires coordination number 3.

Table IV shows the most important metal–oxygen interatomic distances in the structure, and the corresponding bond strength values, calculated from the equation:

$$s = (R/R_1)^{-N}, \qquad (1)$$

derived by Brown and Shannon (7), where s is the strength and R is the length of an appropriate bond. The functional relationships which relate bond strength to bond length have been derived by fitting the constants R_1 and N so that the sums of the bond strength around the cations equal as nearly as possible the valency in a large variety of oxide structures (43 for V, 50 for Mo). Brown and Shannon showed that the bond-strength sums around any atom normally lie within 5% of the valency value. The calculation of the bond-strength sums

provides thus a convenient method of testing the plausibility of a proposed crystal structure. In our case, the discrepancies are 6 and 5% for Mo and V respectively, and moreover they are opposite in sign. This might indicate that the refined M–O distances reflect the weighted mean between longer Mo–O and shorter V–O distances.

The bond lengths and bond strengths determined for the well-established brannerite-type structure of pure MgV_2O_6 (3) are given for comparison in Table IV. An inspection of this table shows a striking increase in bond strength of the two shortest M–O(1) and M–O(2) bonds when Mo^{6+} is substituted for V^{5+}. The bond strengths of the other four bonds remain practically unchanged. As to VO_6 octahedra, the bonding scheme of V^{5+} ions differs insignificantly from that in the pure vanadates (MgV_2O_6). The observed effects can be accounted for by assuming that there occurs a short-range ordering of Mo^{6+} and vacancies resulting in the formation of Mo–O–$\emptyset$–O–Mo clusters, which are distributed at random in the host vanadate structure. The effect may be illustrated by the bond-strength sums calculated around O(1) and O(2) (Table V). All the sums are about 2 if we assume that Mo^{6+} involves a va-

TABLE IV

BOND STRENGTH SUMS IN SOME BRANNERITE-TYPE AB_2O_6 COMPOUNDS[a]

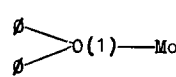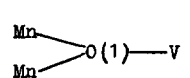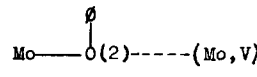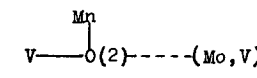| $Mn_{1-x}\varnothing_x V_{2-2x} Mo_{2x} O_6$; $x = 0.53$			MgV_2O_6 (Ref. (3))		$NaVMoO_6$ (Ref. (5))	
M–O [Å]	$s_{Mo^{6+}}$	$s_{V^{5+}}$	V–O [Å]	$s_{V^{5+}}$	M–O [Å]	$s_{Mo^{6+}}$
1.661	2.115	1.469	1.671	1.424	1.63	2.37
1.693	1.887	1.332	1.666	1.446	1.73	1.66
1.913	0.907	0.715	1.853	0.841	1.92	0.89
1.930	0.860	0.683	1.853	0.841	1.92	0.89
2.151	0.449	0.393	2.111	0.432	2.15	0.45
2.479	0.191	0.191	2.671	0.130	2.47	0.20
Σ_s	6.409	4.783		5.114		6.46
Mn–O [Å]	$s_{Mn^{+2}}$		Mg–O [Å]	$s_{Mg^{2+}}$	Na–O [Å]	s_{Na^+}
2.098(2×)	0.421		2.024(2×)	0.429	2.29(2×)	0.228
2.207(2×)	0.317		2.199(2×)	0.271	2.44(2×)	0.173
2.519(2×)	0.151		2.199(2×)	0.271	2.44(2×)	0.173
Σ_s	1.778			1.942		1.148

[a] Bond strength equations from (6); $s = (R/1.882)^{-6.0}$ for Mo^{6+}, $s = (R/1.791)^{-5.1}$ for V^{5+}, $s = (R/1.798)^{-5.6}$ for Mn^{+2}, $s = (R/1.622)^{-4.29}$ for Mg^{2+} and Na^+.

cancy whereas V^{5+} involves a Mn^{2+} cation in a neighboring M^{2+} site.

The lengthening of the M–O(3) and M–O(3)^{ii} distances in the symmetrical M–O–M bridges, compared with the MgV_2O_6 structure, is apparently due to changes in ionic size (the ionic radii of Mo^{6+} and V^{5+} are 0.60 and 0.54 Å respectively (8)). This

TABLE V

OXYGEN BOND-STRENGTH SUMS IN THE POSTULATED
MODEL OF $Mn_{1-x}\varnothing_x V_{2-2x} Mo_{2x} O_6$[a]

Postulated O(1) and O(2) environments	Σ_s
$\varnothing$, $\varnothing$ >O(1)—Mo	2.115
Mn, Mn >O(1)—V	2.098
Mo—O(2)-----(Mo,V), with $\varnothing$ above	2.084
V—O(2)-----(Mo,V), with Mn above	1.947

[a] Bond-strength equations as in Table IV

statement is confirmed by the increase of the unit cell parameter b parallel to the symmetric M–O(3)–M bridges, in accordance with Vegard's law, as found in the earlier work (1).

The M–O(2) bond in the solid solution acquires a more pronounced bridging character compared with that in pure vanadates. The two very short bonds to the terminal oxygens, which are of almost equal length in pure vanadates, become nonequivalent. The increase in the M–O(2) distance brings about a shortening of the M–O(2)^i distance to a value of 2.48 Å in order to maintain the bond strength around the M ions.

The distances found for the investigated compound fall fairly close to those determined for the isomorphous $NaVMoO_6$ structure (5) (see table IV); here Na^+ ions occupy the M^{2+} positions, whereas V^{5+} and Mo^{6+} are distributed at random over the M positions. The only difference is the shortening of the M–O(1) bond to a value of 1.63 Å, accompanied by the lengthening of the M–O(2) bond to 1.73 Å.

If we consider only five bonds involved in the closer coordination of M, with the exclusion of the very long M–O(2)^i bond, the dominating element in the structure is an infinite double chain of edge-linked distorted MO_5 tetragonal pyramids parallel to the b axis. The distortion of the fivefold coordination around the V and Mo atoms is due to their displacements in opposite directions, in order to minimize electrostatic repulsions, and the partly covalent character of Mo–O and V–O bonds. The double chains are linked to each other by Mn^{2+} atoms (Mn–O(2) bonds) forming sheets parallel to the (201) plane. The sheets are bound together by weak Mn–O(1) and M–O(2)^i bonds. The structure should show good cleavage on (201),[2] and this was confirmed in this work by the observed plate-like morphology of the investigated single crystals. The preferential cleavage on (201) exposes the M=O groups on the surface. The tendency of molybdenum to produce isolated Mo=O covalent bonds should bring with it the scope for increased concentration of Mo in the surface beyond the average concentration in the bulk of the structure.

Acknowledgment

References

1. R. Kozłowski, J. Ziółkowski, K. Mocała, and J. Haber, *J. Solid State Chem.* **35**, 1 (1980).
2. G. M. Sheldrick, "SHELX 76, Programme for Crystal Structure Determination," Cambridge University, England.
3. H. N. Ng and C. Calvo, *Canad. J. Chem.* **50**, 3619 (1972).
4. J. Angenault, *Rev. Chim. Miner.* **7**, 651 (1970).
5. B. Darriet and J. Galy, *Bull. Soc. Fr. Mineral. Cristallogr.* **91**, 325 (1968).
6. I. D. Brown and K. K. Wu, *Acta Crystallogr. Sect. B* **32**, 1957 (1976).
7. I. D. Brown and R. D. Shannon, *Acta Crystallogr. Sect. A* **29**, 266 (1973).
8. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25**, 925 (1969).

[2] The preferential cleavage on (201) was kindly pointed out to us by Dr. J. Ziółkowski on the basis of preferred orientation effects in X-ray powder diffractometer samples.