Chapter 6

RESULTS AND DISCUSSION

The final structure data for $W_3V_5O_{20}$ are as follows : monoclinic system; space group C2/m; a=24.412 (2), b=7.4479 (8), c=3.9506 (3) Å, β=91.028 (7)°, Z=2. The atomic coordinates and the thermal parameters are listed in Table 5.9. The model built by using the atomic coordinates in Table 5.9 is shown in Fig 6.1

Bond Distances and Bond Angles

The bond distances and bond angles within 4 Å limit, were calculated by DISTAN program. The bond distances in $W_3V_5O_{20}$ structure are shown and compared with bond distances of $W_3V_5O_{20}$ by Kihlborg et al. in Table 6.1

Table 6.1 Interatomic distances in Å units (standard deviations in the last digits are given within parentheses) compared with bond lengths obtained by Kihlborg. Distances shorter than 4 Å are listed.

bond	Distance	
	This work	Kihlborg
$M_1 - M_3$	3.168 (8)	3.103 (8)
$- M_2$	3.236 (5)	3.235 (5)
$- M_1$ [100]	3.68 (1)	3.658 (9)
$- M_1$ [010]	3.72	3.714 (12)
$- M_1$ [010]	3.728	3.731 (12)

Table 6.1 (continued)

bond	Distance	
	This work	Kihlborg
- M_1 [001]	2 x 3.951 (1)	2 x 3.950 (1)
M_2 - M_1	3.236 (5)	2 x 3.235 (5)
- M_3 [100]	3.583 (9)	3.696 (9)
- M_3 [010]	2 x 3.725	3.727 (1)
- M_2 [001]	2 x 3.951	3.950 (1)
M_3 - M_1	2 x 3.168 (8)	2 x 3.103 (8)
- M_2 [100]	3.583 (9)	3.696 (9)
- M_2 [010]	2 x 3.725	2 x 3.3727 (1)
- M_3 [001]	2 x 3.951	2 x 3.950 (1)
M_1 - O_6	1.661 (24)	1.782 (35)
- O_1	1.842 (5)	1.831 (5)
- O_4	1.932 (13)	1.910 (9)
- O_2	1.911 (12)	1.914 (10)
- O_3	2.089 (29)	2.089 (31)
- O_6	2.293 (24)	2.177 (35)
M_2 - O_7	1.806 (44)	1.651 (34)
- O_5	1.749 (33)	1.739 (30)
- O_3	2 x 1.961	2 x 1.931 (33)
- O_4	2.152 (43)	2.248 (35)
- O_7	2.146 (44)	2.299 (34)
M_3 - O_8	1.611 (43)	1.451 (39)
- O_5	1.848 (34)	1.957 (31)
- O_3	2 x 1.944 (7)	2 x 1.981 (34)
- O_2	2.190 (39)	2.040 (35)

Table 6.1 (continued)

bond	Distance	
	This work	Kihlborg
- O_8	2.351 (43)	2.536 (39)
O_1 - O_2	2.854 (28)	-
- O_6	2 x 2.732 (22)	-
- O_4	2 x 2.911 (33)	-
- O_3	3.882 (28)	-
O_2 - O_3	2 x 2.557 (32)	-
O_2 - O_4	2 x 3.727 (2)	-
- O_8	3.009 (65)	-
O_3 - O_4	2 x 2.466 (34)	-
- O_7	2 x 2.611 (34)	-
- O_5	2 x 2.925 (33)	-
- O_8	2 x 2.757 (34)	-
O_4 - O_7	2 x 2.675 (55)	-
- O_6	2 x 2.69 (46)	-
- O_3	2 x 2.466 (34)	-
O_5 - O_3	2.626 (53)	-
- O_7	2.730 (53)	-
- O_8	2 x 2.538 (51)	-
- O_4	3.869 (54)	-
O_6 - O_7	3.059 (37)	-
- O_8	3.143 (36)	-

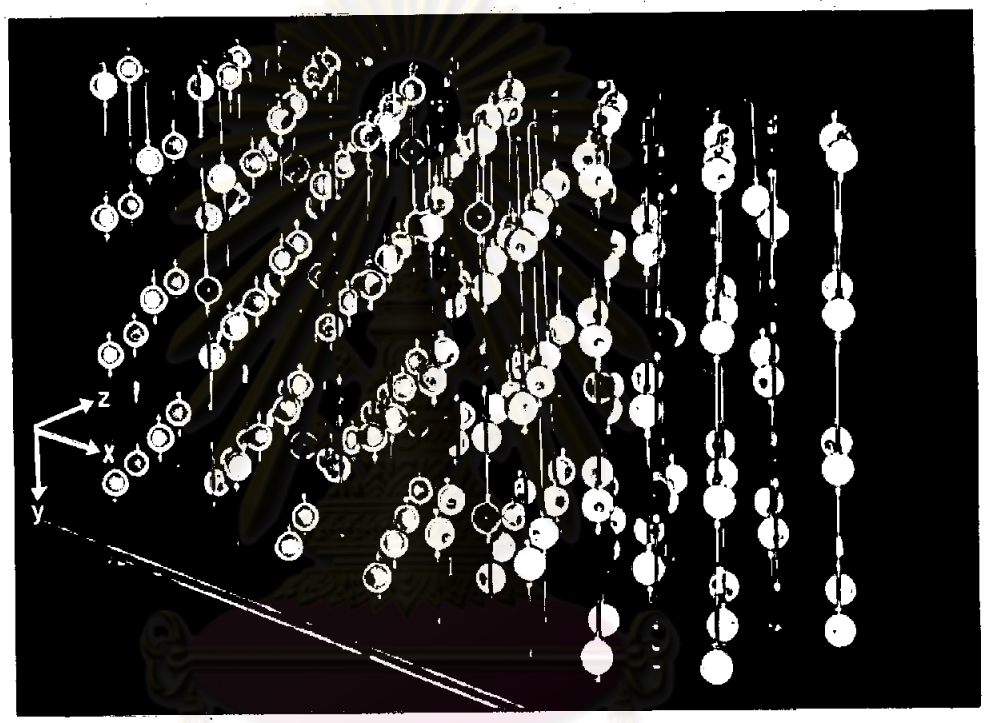

Fig. 6.1 The model of $W_3V_5O_{20}$

black = $M_1(W_{1/4}V_{3/4})$

pink = $M_2(W)$

green = $M_3(V)$

Discussion

From the values of coordinates of all atoms of $W_3V_5O_{20}$ earlier listed in Table 5.9, the structure projected along "b" and "c" axes are shown in Fig. 6.2. This structure is of the same type as R-Nb_2O_5 and $(Mo_{0.3}V_{0.7})_2O_5$ and composed of octahedra sharing edges and corners. These octahedra have M(1) ($W_{1/4}V_{3/4}$) or M(2) (W_2) or M(3) (V_2) atoms at center and six oxygen atoms at corners.

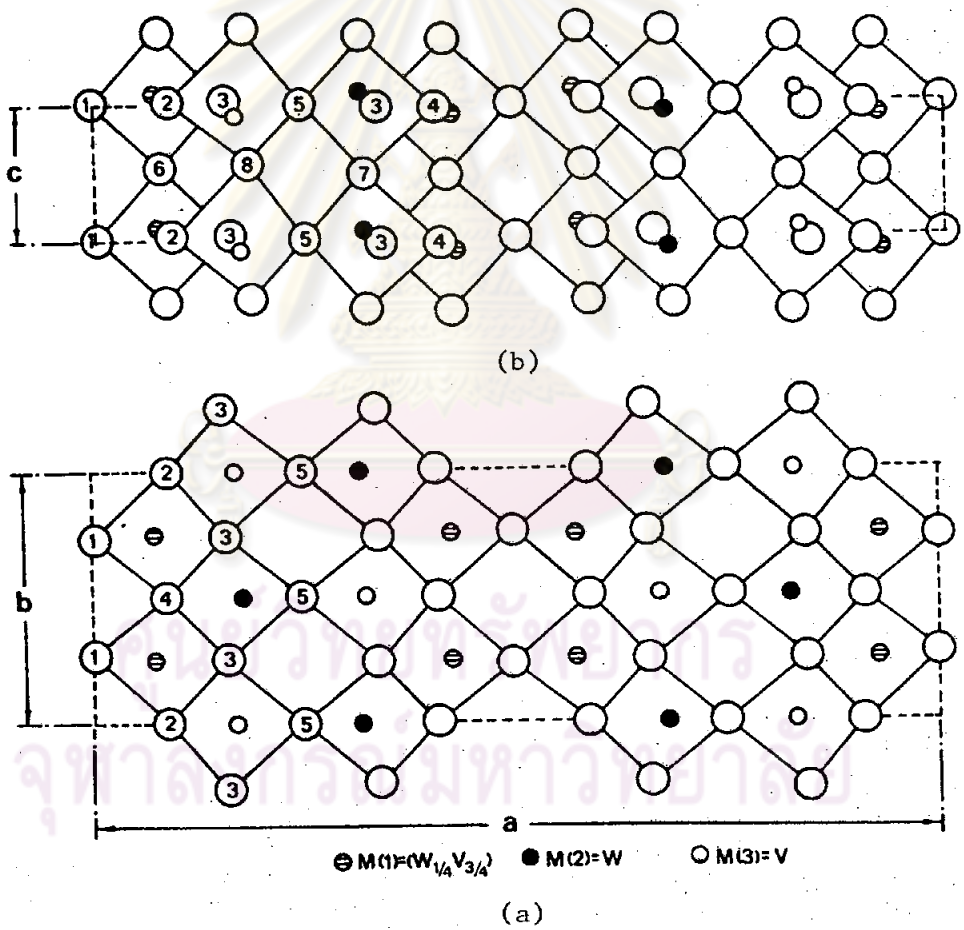

Fig. 6.2 The structure of $W_3V_5O_{20}$ in two projections.

(a) Viewed along the c axis

(b) Viewed along the b axis

Each of M_1, M_2 and M_3 atoms are surrounded by six oxygen atoms (Fig. 6.3a, 6.3b, 6.3c) the coordinates of these atoms are listed in Table 6.2a, 6.2b, 6.2c respectively. Interatomic distances of atoms are given in Table 6.3(a), 6.3(b), 6.3(c), respectively. Interatomic angles are given in Table 6.4(a), 6.4(b), 6.4(c) respectively

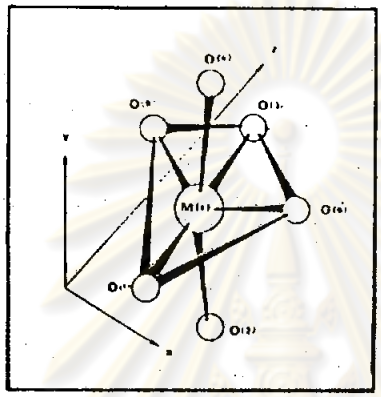

Fig. 6.3(a) The M(1) O_6 octahedron in $W_3V_5O_{20}$

Table 6.2(a) The coordinates of atoms in Fig. 6.3(a)

Atom	X	Y	Z
M (1)	0.0744	0.250	0.0867
O (1)	0.	0.255	0.
O (6)	0.0776	0.25	0.5070
O (6')	0.0776	0.25	0.4930
O (3)	0.159	0.25	0.019
O (4)	0.0929	0.5	0.0263
O (2)	0.0873	0.	0.0145

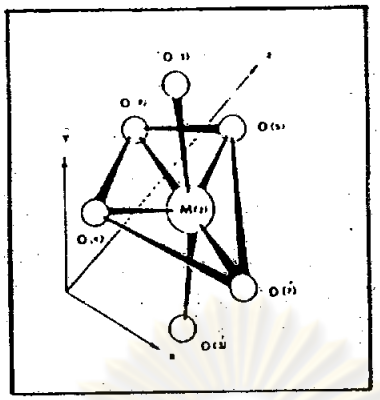

Fig. 6.3(b) The $M(2)O_6$ octahedron in $W_3V_5O_{20}$

Table 6.2(b) The coordinates of atoms in Fig. 6.3(b)

Atom	X	Y	Z
M (2)	0.179	0.5	0.928
O (3)	0.159	0.75	0.019
O (5)	0.251	0.5	-0.038
O (4)	0.093	0.5	0.026
O (7)	0.177	0.5	0.471
O (7')	0.177	0.5	-0.529

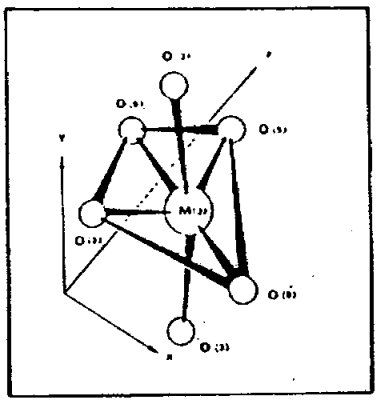

Fig. 6.3(c) The $M(3)O_6$ octahedron in $W_3V_5O_{20}$

Table 6.2(c) The coordinates of atom in Fig. 6.3(c)

Atom	X	Y	Z
M (3)	0.175	0.00	0.923
O (2)	0.087	0.00	0.015
O (8)	0.181	0.00	0.517
O (3)	0.159	0.25	0.019
O (5)	0.249	0.00	0.038
O (3)	0.159	-0.25	0.019
O (8')	0.181	0.00	-0.483

Table 6.3 shows that M-O bond lengths in the three different octahedra; $M(1)O_6$, $M(2)O_6$, $M(3)O_6$; are not the same. Of $M(1)O_6$, M(1)-O(6) is the shortest (1.661Å) , while M(1)-O(6´) is the longest (2.293Å). Of $M(2)O_6$, M(2)O(5) is the shortest (1.749Å) , whereas M(2)-O(6) is the longest. Of $M(3)-O_6$, M(3)-O(8) is the shortest but M(3)-O(8´)is the longest. It is also seen from Table 6.1 that the difference in six M-O bond lengths of M(2) octahedra is the smallest but of M(3) octahedra is the largest. Therefore, of the three octahedra , the smallest metal displacement is found in M(2) whereas the largest metal displacement is

in M(3). The distortion is due mainly to form off-centre displacements of the metal atoms in "c" axis.

Table 6.3(a) Interatomic distances of $M(1)O_6$ octahedron shorter than 4 Å in Fig. 6.3a

Bond	distance (Å)	Bond	distance (Å)
M (1) - O (1)	1.842 (5)	O (6) - O (3)	2.7944 (33)
- O (6)	1.661 (24)	O (6) - O (1)	2.732 (22)
- O (6')	2.293 (24)	O (6) - O (6')	3.951 (0)
M (1) - O (3)	2.089 (29)	O (2) - O (1)	2.854 (28)
- O (4)	1.932 (13)	O (2) - O (6')	2.743 (50)
- O (2)	1.911 (12)	O (6') - O (3)	2.811 (33)
O (6')- O (1)	2.741 (22)	O (3) - O (4)	2.466 (34)
O (2) - O (3)	2.557 (32)	O (6) - O (4)	2.690 (46)
O (2) - O (6)	2.706 (50)	O (4) - O (6')	2.790 (47)
O (4) - O (1)	2.911 (33)	O (1) - O (3)	3.882 (28)

Table 6.3(b) Interatomic distances of $M(2)O_6$ octahedron shorter than 4 Å in Fig. 6.3(b)

Bond	distance (Å)	Bond	distance (Å)
M (2) - O (7)	1.806 (44)	O (4) - O (7)	2.675 (66)
- O (7')	2.146 (44)	- O (5)	3.869 (54)
- O (3)	2 x 1.961 (8)	O (5) - O (7')	2.730 (53)
- O (4)	2.152 (43)	O (7) - O (5)	2.626 (53)
- O (5)	1.749 (33)	- O (3)	2 x 2.611 (36)
O (3) - O (7')	2 x 2.893 (37)	- O (7)	3.951 (0)
- O (5)	2 x 2.925 (33)	O (7') - O (4)	3.027 (68)
- O (4)	2 x 2.466 (34)		
- O (3)	3.724 (0)		

Table 6.3(c) Interatomic distances of $M(3)O_6$, shorter than 4 Å in Fig. 6.3(c)

Bond	distance (Å)	Bond	distance (Å)
M (3) - O (2)	2.190 (39)	O (5) - O (8)	2.538 (51)
- O (8)	1.611 (43)	- O (8')	2.619 (51)
- O (8')	2.351 (43)	- O (3)	2 x 2.925 (33)
- O (5)	1.848 (34)	O (2) - O (8')	3.048 (65)
- O (3)	2 x 1.944 (7)	- O (8)	3.009 (65)
O (8) - O (3)	2.757 (34)	- O (3)	2 x 2.557 (32)
- O (3')	2 x 7.80 (34)	- O (5)	3.952 (50)
- O (8')	3.951 (0)	O (3) - O (3')	3.724 (0)

Table 6.4(a) Interatomic angles of $M(1)O_6$ octahedron in Fig. 6.3(a)

Bond	Bond angle (degree)	Bond	Bond angle (degree)
O(4) -M(1)-O(3)	76 (1)	O(6')-O(3) -O(6)	90 (1)
-O(6')	32 (2)	-O(2)	61 (1)
-O(1)	101 (1)	O(6) -O(3) -O(2)	61 (1)
-O(6)	97 (2)		
-O(2)	152 (2)		
O(3) -M(1)-O(6')	80 (8)		
-O(1)	161.9 (7)		
-O(6)	96 (9)		
-O(2)	79 (1)		
O(6')-M(1)-O(1)	82 (6)		

Table 6.4 (a) (continued)

Bond	Bond angle (degree)	Bond	Bond angle (degree)
-O(6)	175 (1)		
-O(2)	81 (2)		
O(1) -M(1)-O(6)	102 (8)		
-O(2)	99 (1)		
O(6) -M(1)-O(2)	98 (2)		
O(3) -O(4)-O(6')	64 (1)		
-O(1)	92.1 (6)		
-O(6)	65.5 (9)		
O(6')-O(4)-O(1)	57.4 (8)		
-O(6)	92.2 (3)		
O(1) -O(4)-O(6)	58.2 (8)		
O(4) -O(3)-O(6')	63. (1)	O(3) -O(2) -O(6')	64 (1)
-O(6)	61. (1)	-O(1)	91.5 (5)
-O(2)	96. (1)	-O(6)	64.1 (9)
O(6')-O(2)-O(1)	59.6 (8)	O(1) -O(2) -O(6)	58.8 (8)
-O(6)	92.9 (2)		

Table 6.4(b) Interatomic angles of $M(2)O_6$ octahedron in Fig. 6.3(b)

Bond	Bond angle (degree)	Bond	Bond angle (degree)
O(4) -M(2)-O(3)	73.5 (8)		
-O(5)	165 (2)		
-O(7)	77 (2)		
-O(7')	99 (2)		
-O(3)	74 (8)		

Table 6.4 (b) (continued)

Bond	Bond angle (degree)	Bond	Bond angle (degree)
O(3) -M(2)-O(5)	103.9 (8)		
-O(7)	100 (7)	O(3) -O(4) -O(7')	61 (1)
-O(7')	78.8 (6)	-O(7)	63 (1)
-O(3)	143 (1)	-O(3)	98 (2)
O(5) -M(2)-O(7)	95 (2)	O(7')-O(4) -O(7)	87 (2)
-O(7')	88 (1)	-O(3)	63 (1)
-O(3)	103.9 (8)	O(7) -O(4) -O(3)	61 (1)
O(7) -M(2)-O(7')	176 (2)	O(3) -O(7) -O(5)	
-O(3)	100.3 (7)	-O(4)	
O(7')-M(2)-O(3)	78.8 (6)	-O(3)	
$O_5(1)-O_3(4)-O_7(1)$	59 (9)	O(5) -O(7) -O(4)	
-O(4)	91.3 (8)	-O(3)	
-O(7)	54 (1)	O(4) -O(7) -O(3)	
O(7) -O(3) -O(4)	64 (1)	O(5) -O(3) -O(7')	54 (1)
-O(7')	91.6 (4)	-O(4)	91.3 (9)
O(4) -O(3) -O(7')	68 (1)	-O(7)	59 (1)
O(3) -O(5) -O(7')	63 (1)	O(7')-O(3) -O(4)	68 (1)
-O(3)	79 (1)	-O(7)	91.6 (4)
-O(7)	54.9 (9)	O(4) -O(3) -O(7)	64 (1)
O(7')-O(5) -O(7)	95 (2)	O(7) -O(5) -O(3)	120 (1)
-O(3)	122 (1)		

Table 6.4(c) Interatomic angles of $M(3)O_6$ octahedron in Fig. 6.3 (c)

Bond	Bond angle (degree)	Bond	Bond angle (degree)
O(2) -M(3)-O(3)	76.2 (9)		
-O(3')	76.2 (9)		
-O(5)	128 (2)		
-O(8)	106 (2)		
-O(8')	83 (2)		
O(3) -M(3)-O(3')	147 (1)		
-O(5)	106 (7)		
-O(8)	102.5 (7)		
-O(8')	79.3 (7)		
O(3) -M(3)-O(5)	105.7 (7)	O(3) -O(2) -O(8')	59 (1)
-O(8)	102.5 (7)	-O(8)	59 (1)
-O(8')	79.3 (7)	-O(3')	93 (2)
O(5) -M(3)-O(8)	22 (1)	O(8')-O(2) -O(8)	81 (1)
-O(8')	150 (1)	-O(3')	59 (1)
O(8) -M(3)-O(8')	171 (2)	O(8) -O(2) -O(3')	59 (1)
O(5) -O(3)-O(8')	110 (1)	O(3) -O(8) -O(5)	
-O(2)	93.0 (8)	-O(2)	
-O(8)	102 (1)	-O(3')	
O(8')-O(3)-O(2)	70 (1)	O(5) -O(8) -O(2)	
-O(8)	91.1 (4)	-O(3')	
O(2) -O(3)-O(8)	69 (1)	O(2) -O(8) -O(3')	
		O(5) -O(3')-O(8')	
		-O(2)	
		-O(8)	
		O(8')-O(3')-O(2)	
		-O(8)	
		O(2) -O(3')-O(8)	

From Fig. 6.2 (a) there is a mirror plane normal to "a" axis at a/2 and a mirror plane normal to "b" axis at b/2.

From Fig. 6.2 (b) there is a mirror plane normal to "c" axis at c/2 and a two fold axis parallel to "b" axis at a/2.

From Fig. 6.2 it is also seen that octahedra sharing edges and corner zig-zag strings in"b" direction and connected to strings of corner sharing octaherdra in the c direction. Such a connection of these strings gives rise to layers consisting of octahedra at two levels. The octahedra at one level are filled alternatively with tungsten and vanadium in ordered way whereas those at the other level contain $W_{1/4}V_{3/4}$ in random distribution.

In the "bc" plane, the structure can be explained as a shear structure composed of octahedra forming ReO_3 type slabs, two octahedra thick, which are joined together by edge sharing.

The structure described above is confirmed structure proposed by Kihlborg (1970). However the R value ($R = \Sigma|F_{obs}-F_{cal}|/\Sigma|F_{obs}|$) of 0.113 is higher than the value 0.073 reported by Kihlborg. The reason for this is that the intensity data for even k layers were used to determine the structure but those used by Kihlborg were taken for every k values including the weak and diffuse reflections in odd k-layers.

On the Weissenberg photograph of the crystal mounted along "c" (Fig. 4.17) and the precession photograph of the crystal mounted along "b" and "c" as a precession axis (Fig. 4.24) The reflections hkl with k=2n were all sharp while those with k=2n+1 were throughout weak and diffuse, being marked by elongated along the bows corresponding

to the direction of a*. On the other Weissenberg photographs and precession photographs Fig.4.16 and Fig.4.22, diffuse spots did not appear. These indicated that the structural details exhibit no periodicity in the direction of "a" axis, a kind of one dimensional disorder. There is no evidence for mistakes in the periodicity along "b" and "c" since reflections are sharp in the directions perpendicular to a*. The sharp reflections would be index on the basis of the subcell with a'=½a and b'=½b. The superstructure indicated by the diffuse reflection is thus associated with stacking faults.[5]

The arrangement of atoms in $CoWO_4$ is order but in V_2MoO_8 is one-dimensional disorder. This might indicate that the one-dimensional disorder is probably due to vanadium atoms.

In conclusion the structure of $W_3V_5O_{20}$ obtained does confirm the structure reported by Kihiborg et al.[5].