

BRIEF COMMUNICATION

On the Tetragonal Forms of KMo_4O_6

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A reexamination of the X-ray diffraction data for the tetragonal form of KMo_4O_6 prepared by fused salt electrolysis leads to the conclusion that the crystal structure is better described by using space group $P4/mbm$ and not $P\bar{4}$ as previously reported. However, refinement in the new space group does not result in any significant changes in the atomic arrangement. Possible reasons for the significant difference between the c lattice parameter of this form of KMo_4O_6 and that prepared at high pressures are also discussed. © 1995 Academic Press, Inc.

INTRODUCTION

KMo_4O_6 has been reported to exist in three different modifications: an orthorhombic form (I), space group $Pbam$, prepared by a solid-state reaction at normal pressure (1); a tetragonal form (II), space group $P4/mbm$, prepared at high pressure but studied at normal pressure (1); and a second tetragonal form (III), space group $P\bar{4}$, prepared by fused salt electrolysis (2). These compounds are of interest because they contain infinite chains formed by *trans*-edge-sharing of bonded molybdenum atoms in Mo_6O_{10} clusters to form infinite metal-bonded chains, resulting in quasi-low dimensional electronic behavior. The structure of (I) is based on the substructure found for $\text{Ba}_{0.6}\text{Mo}_4\text{O}_6$ (3) while (II) and (III) have the NaMo_4O_6 structure (4). However, (II) has an unusually long c (tetragonal) axis, 2.950(1) Å, compared to the 2.879(1) Å in (III) typical of other phases having this structure.

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The length of c represents the distance between those waist Mo's that lie along this direction and between apical Mo's of successive Mo_6 octahedra, as well as the distance between K^+ ions (which lie within distorted O_8 cubes). We therefore believed that the reported differences between the two tetragonal structures—the abnormal length of c in (II) and the lowering of symmetry in (III)—represented different ways of relieving electrostatic repulsions between K^+ ions. However, we have now reexamined the diffraction data for (III) and conclude that the space group is the same as that of (II), $P4/mbm$.

EXPERIMENTAL

Our reinvestigation of the structure of form (III) was based on the diffraction data reported previously (2). Averaging the intensities according to Laue symmetry $4/mmm$ resulted in an R_{merge} of 0.010 for 470 pairs of equivalent reflection, an excellent value that leads us to the conclusion that Laue symmetry $4/mmm$ is more appropriate than the $4/m$ assumed previously. Included in the list of intensities were 58 reflections of the type $0kl$ with k odd (or $h0l$ with h odd), which are extinguished in space group $P4/mbm$; all 58 were quite weak, many bordering on "unobservable," although a few had intensities 3–5% as large as the strongest reflections. To check further on the situation, we have reexamined Weissenberg photographs that we had prepared during the earlier study of (III) (2). Although reflections which appear to violate the extinction rules for $P4/mbm$ were clearly evident, a more careful look revealed that different reflections of the same form often had appreciably different intensities and

in most cases at least one of these reflections was absent. Since this type of behavior is typical of the double-reflection phenomenon (Renninger effect), we are now convinced that the photographs are compatible with space group $P4/mbm$.

Full-matrix least-squares refinement in $P4/mbm$ began with the $P\bar{4}$ coordinates, suitably transformed and averaged. Convergence was quickly reached at $R = 0.028$ for 557 reflections; for comparison, the earlier $P\bar{4}$ model led to an R of 0.036 for 1117 reflections. (The improvement in R probably results primarily from the averaging of data that was possible in the higher Laue symmetry.) Included in our final model was a population factor for the site of the K^+ ion; the final value was 0.95(1), suggesting a slight deficiency (see below).

DISCUSSION

Final coordinates are given in Table 1. They are statistically identical to those reported for the $P\bar{4}$ refinement with the exception of apical Mo(2), which is now modeled to lie on a mirror plane ($z = 0.5$) whereas it was displaced by about 0.02 Å earlier. In the revised $P4/mbm$ model, this atom shows a large displacement coefficient U_{33} (Table 2) which appears to be typical of this structure type; Mo(2) can be equally well represented as disordered between two half-occupied sites, displaced by about 0.09 Å (assuming isotropic coefficients U_{ij}) to either side of $z = 0.5$.

Comparisons of this revised structure of (III) with that of (II) are somewhat complicated. Atom coordinates are very similar, but there is a large difference in the length of the c axis: 2.950(1) Å in (II) and 2.879(1) Å in (III); the values of a (and b) are also somewhat different, 9.612(2) Å in (II) and 9.636(1) Å in (III). It seems unlikely, but barely possible, that differences so large could arise from systematic errors in measurement. In this respect we note that

TABLE 1
Coordinates for the Space Group $P4/mbm$ ($x, y, z \times 10^5$;
 $U_{eq} \times 10^4$)^a

om	x	y	z	U_{eq} or B
	0	0	50000	145(2)
Mo(1)	60101(3)	10101	0	42(1)
Mo(2)	14273(6)	64273	50000	70(1)
1)	20574(28)	29426	50000	75(4)
2)	24326(30)	4593(31)	0	79(4)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)](\mathbf{a}_i \cdot \mathbf{a}_j)$$

^b Site population, 0.95(1).

TABLE 2
Anisotropic Coefficients for the Space Group $P4/mbm$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	141(6)	141	152(8)	0	0	0
Mo(1)	40(1)	40	45(1)	-2(1)	0	0
Mo(2)	39(1)	39	133(2)	-3(1)	0	0
O(1)	86(9)	86	53(12)	39(11)	0	0
O(2)	71(10)	109(11)	57(8)	20(7)	0	0

Note. U_{ij} values have been multiplied by 10^4 . The form of the displacement factor is $\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$.

the data used for the determination of lattice constants for (II) were obtained from a Gandolfi camera, and presumably did not extend to high diffraction angles; while a Nelson-Riley extrapolation procedure was used, it is quite possible that absorption could have led to errors considerably larger than the reported esd's. But there is also a possibility that the differences are real, at least in part. We note that our refinement of form (III) suggests a slight deficiency of K^+ in this specimen. (We have carried out an electron microprobe analysis of the crystal used for the X-ray study of (III); the indicated amount of K^+ was an inconclusive 0.98(2) per formula unit.) It seems possible, then, that a small change in the amount of potassium in the sample might have a large effect on the length of c . However, we further note that a recent synthesis of KMo_4O_6 by solid-state reactions in a sealed molybdenum tube at 1430°C (5) led to crystals, again in space group $P4/mbm$, with $a = 9.613(2)$ Å, essentially identical to that reported for (III), and $c = 2.878(1)$ Å, essentially identical to that reported for (II); there was no indication of deficiency of K^+ (occupancy, 1.02(8)).

So, we remain baffled: are there real structural differences between various preparations of KMo_4O_6 , perhaps due to small changes in stoichiometry? Or are the differences only chimerical, caused by systematic errors in the experimental data? Further investigations seem warranted.

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