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Structural Investigation of the Potassium Vanadomolybdate Crystal

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Potassium vanadomolybdate $KVMoO_6$ crystallizes in the orthorhombic system (space group *Pnma*, $a = 10.3478(1)$ Å, $b = 3.6967(1)$ Å, $c = 13.3769(2)$ Å, $Z = 4$). With an X-ray powder diffraction technique, its structure was solved and refined by direct and Rietveld methods, respectively ($R_F = 3.33$, $R_I = 4.70$, $R_{wp} = 12.44$). The crystals are isostructural with PbV_2O_6. Octahedra of two types build chains parallel to the *b* direction; there is disorder in the octahedra described by different occupation numbers of V and Mo atoms: 0.721(4) and 0.279(4), respectively. Potassium atoms occupy the space between the octahedra chains. They play a decisive role, due to the large ionic radius, in generating both $KVMoO_6$ and pseudobrannerite, $K_xV_xMo_{2-x}O_6$ ($0.76 \le x \le 0.82$) structures, contrary to other alkali-metal vanadomolybdates of the brannerite structure type. The melting point of $KVMoO_6$ was detected at 480°C using the DTA method. © 1999 Academic Press

***Key Words*: structure; structure determination; X-ray powder diffraction; vanadomolybdates.**

INTRODUCTION

Investigations of crystal phases of vanadomolybdates and metavanadates have shown that most are isostructural with brannerite (1). This kind of structure is typical of monovalent metal vanadomolybdates $LVMoO_6$ (L = Li, Na, Ag) (2–4) and metavanadates MeV_2O_6 (Me = Mg, Mn, Co, Zn, Cd) (5). The structure of brannerite is layered and contains distorted VO_6 and MoO_6 octahedra sharing edges. Li, Na, and Ag cations are located in the interlayer positions.

Some metavanadates (MeV_2O_6, Me = Mg, Mn, Cd) (5–7) and potassium vanadomolybdate $K_{0.8}V_{0.8}Mo_{1.2}O_6$ (2, 8) can also exhibit structures similar to that of brannerite but differing in the rotation of VO_6 or MoO_6 zigzag chains around the *b* direction. This results in an increase in distance between one of the oxygen atoms and the central atom, V or Mo (so the coordination of the central atom becomes 5), and also in the decrease in the β angle to 102° from about 111°. This type of structure is most often called pseudobrannerite.

Metavanadates of such metals as Pb, Hg, Sr, and Ba (9) create crystals with orthorhombic symmetry. Among them only the structure of PbV_2O_6 has been established (10). It is composed of two types of VO_6 octahedra which built pillars parallel to the shortest period direction. The octahedra are very strongly deformed so the coordination of the central atom becomes 5 and V–O distances range from 1.611 to 2.732 Å.

Potassium vanadomolybdate was first obtained by a solid-state reaction (11) and was known as γ-$KVMoO_6$. Recently, during investigation of the MnV_2O_6–$KVMoO_6$–MoO_3 triangle solid solution system (8) the pure phase of γ-$KVMoO_6$ was obtained using the citrate method (12).

A preliminary study of $KVMoO_6$ allowed us to index the XRD pattern in the orthorhombic system (8). In the current work the crystal structure investigation based on the Rietveld refinement and a DTA study are presented.

EXPERIMENTAL

Potassium vanadomolybdate ($KVMoO_6$) was synthesized by the amorphous citrate method (12). All of the reactants [NH_4VO_3 (Fluka Chemika), $K_2CO_3 \cdot 3H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$, 0.1 M HNO_3, and citric acid (Polskie Odczynniki Chemiczne)] were of p.a. grade. After mixing all of the components at stoichiometric rates, water was slowly evaporated and the viscous mixture obtained was dried at 120°C. It was then preheated at 360°C in a stream of oxygen for 36 h to burn out the organic components. Finally, it was heated at 400, 450, 475, and 500°C for 24–72 h at each temperature, and every stage of the reaction was monitored by XRD. $KVMoO_6$ formation was observed to begin at 360°C and was completed at 475°C.

The X-ray diffraction pattern was obtained using a Siemens D5005 diffractometer with a graphite monochromator and a scintillation detector in the range from 9° to 75° (Cu$K\alpha$ radiation). The pattern was indexed to determine the unit-cell parameters (8) and, from the systematic extinctions, a possible space group, which was eventually assumed to *Pnma* (noncentrosymmetric space group $Pn2_1a$ was also possible; nevertheless, the refinement did not converge).

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Then the structure was solved by the direct method using an integrated EXPO package (13, 14).

The structure was refined by the Rietveld method using the DBWS-9411 program (15) with the following assumptions:

1. The profile shape was described by the Pearson VII function.
2. The March–Dollase model was used for the [010] preferred orientation direction.
3. Only two positions of Mo and V atoms were assumed, temperature factors for both atoms being equal in each position.
4. Temperature factors for all oxygen atoms were constrained to be equal.

In Table 1 the most important parameters of the structure refinement are presented. In Fig. 1 the observed, calculated and residual patterns are shown.

Interatomic distances and angles were calculated by the PARST package (16) and plots of structures were drawn using the ORTEP program (17).

DTA and TGA measurements were performed in the range 20 to 500°C using a Paulik, Paulik and Erdey DTA-TGA thermal analysis system (10°/min, Pt crucibles, sample of 0.45715 g).

RESULTS

The final parameters of the $KVMoO_6$ structure and selected interatomic distances and angles are presented in Tables 2 and 3. All the atoms lie on mirror planes. The structure of the $KVMoO_6$ crystal is composed of pillars perpendicular to the (010) planes (Figs. 2, 3). Every pillar consists of four octahedra MO_6, two of which are related by 2_1 axis to the two other ones. As the independent octahedra exhibit slightly different geometry, they have been distinguished as two types. The central fragment of the pillar is constructed of type I octahedra. They share the edge between two O2 atoms (O2A and O2B in Table 3) and also remain in contact with type II octahedra by the edge O2–O1 (if central atoms of octahedra lie in different planes) or O2–O3 atoms (in the other case). The pillar-like structure seems to be a satisfactory explanation for the texture of the powder sample, observed in the direction perpendicular to the (010) plane.

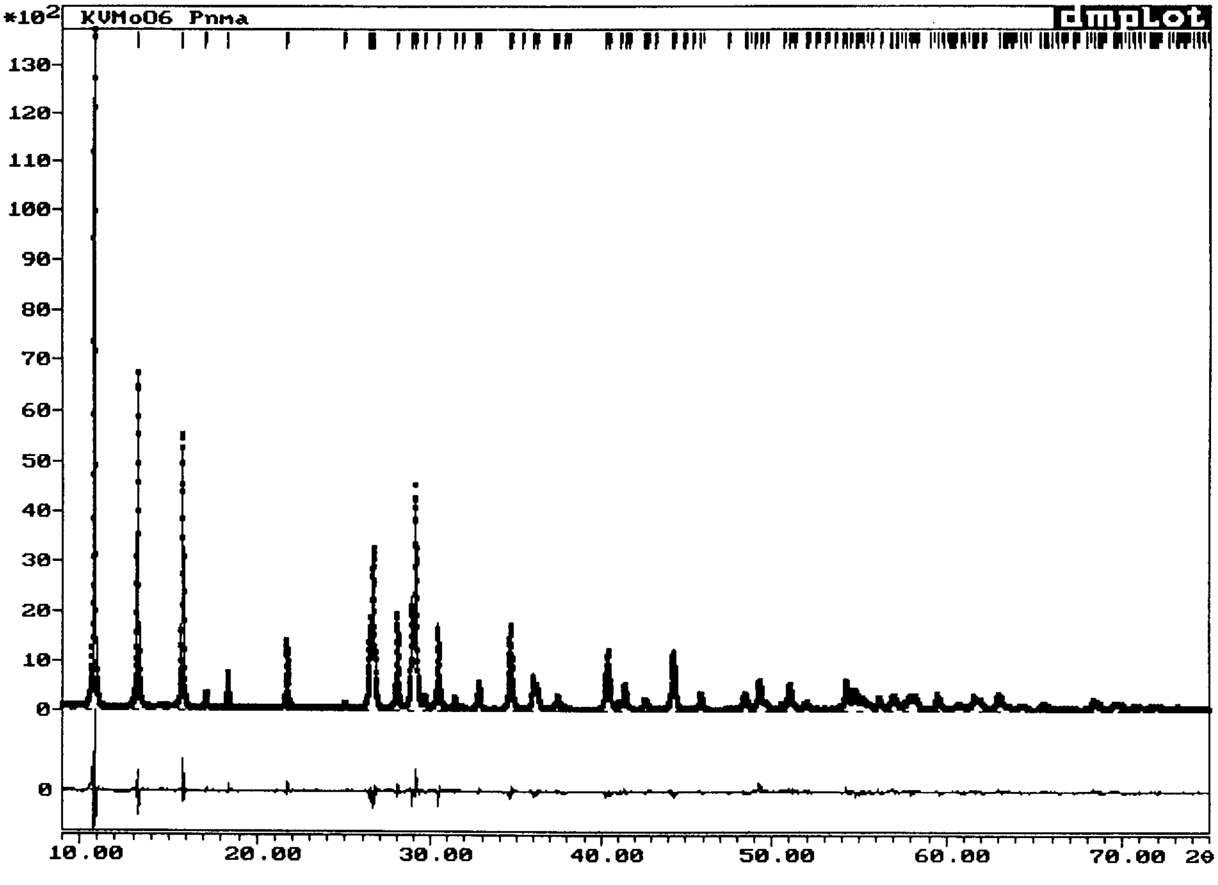


FIG. 1. X-ray powder patterns: observed (■), calculated (solid line), and difference pattern for potassium vanadomolybdate.

TABLE 1
Details of X-ray Data Collection and Structure Refinement

Chemical formula	$KVMoO_6$
Formula weight	281.925 amu
Color	Yellow-brown
Diffractometer	Siemens D5005 (graphite monochromator, scintillation detector)
Wavelength (Å)—$K\alpha_1/K\alpha_2$/ratio	1.5406/1.5444/0.5
Scan range	9°–75° 2θ
Step size	0.01° 2θ
Temperature (K)	295
Experimental/calculated density	3.6(1)/3.658 g/cm^3
Space group	*Pnma*
Z	4
Cell parameters	
a	10.3478(1) Å
b	3.6967(1) Å
c	13.3769(2) Å
Number of reflections	328
Zero point	0.0080(2)° 2θ
Number of parameters	36
Termination criteria	EPS $\leq$ 0.01
R_F	3.33%
R_I	4.70%
R_{wp}	12.44%
$R_{expected}$	7.26%

TABLE 2
Atomic Fractional Coordinates (all atoms in 4*c* position), Isotropic Thermal Parameters, and Occupancies[a]

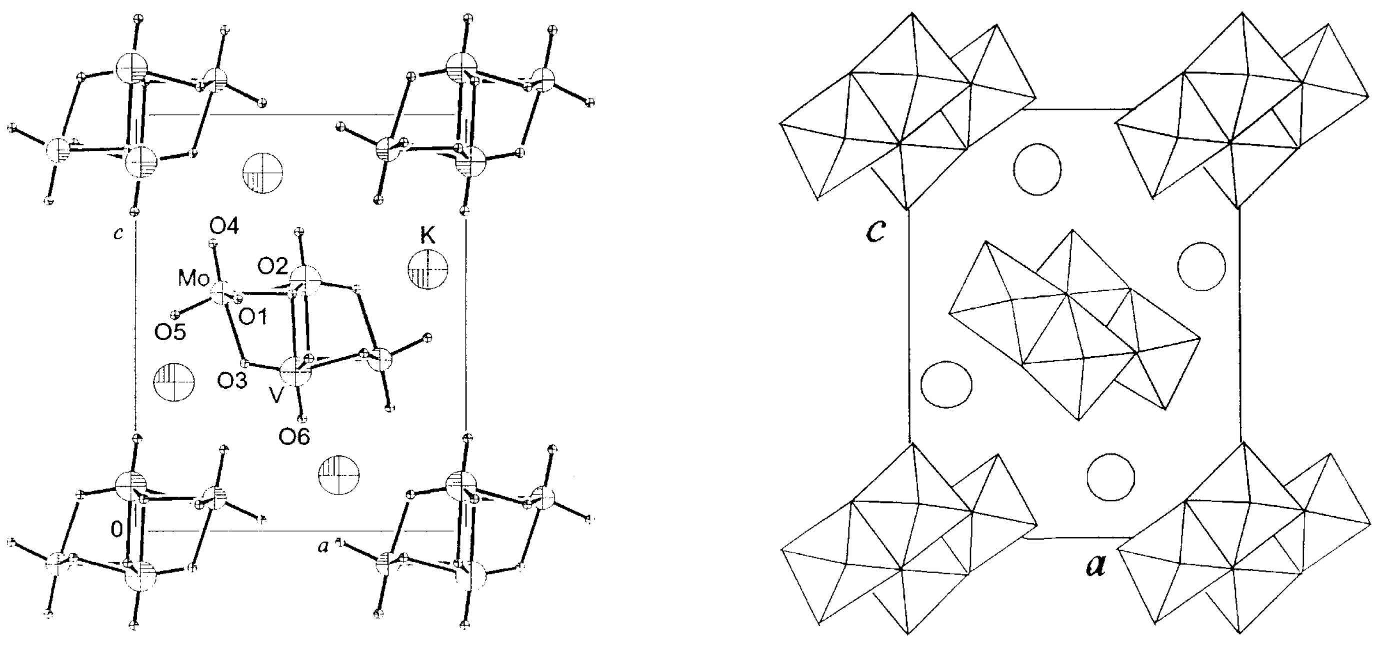
Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso}	*N*
V(I)	0.4854(2)	0.2500	0.3903(2)	1.6(1)	0.721(4)
Mo(I)	0.4854(2)	0.2500	0.3903(2)	1.6(1)	0.279(4)
Mo(II)	0.2616(2)	0.2500	0.5804(1)	0.97(6)	0.721(4)
V(II)	0.2616(2)	0.2500	0.5804(1)	0.97(6)	0.279(4)
K	0.8848(3)	0.2500	0.6356(3)	2.8(1)	1
O1	0.3095(7)	− 0.2500	0.5643(6)	0.2(1)	1
O2	0.4752(8)	0.2500	0.5775(6)	0.2(1)	1
O3	0.3314(7)	0.2500	0.4112(5)	0.2(1)	1
O4	0.2326(9)	0.2500	0.6988(6)	0.2(1)	1
O5	0.1175(8)	0.2500	0.5273(6)	0.2(1)	1
O6	0.5048(8)	0.2500	0.2741(7)	0.2(1)	1

[a] Numbers in parentheses designate type of octahedra in which Mo and V atoms are located.

As shown in Fig. 2, O1 and O2, atoms are placed between octahedra so they belong to three (O1) or four (O2) octahedra. Due to a competition effect, interactions between *M* cations and shared O1 and O2 oxygen atoms are weaker than other *M*–O interactions and result in long *M*–O1 and *M*–O2 distances (1.925–2.506 Å).

Four remaining oxygen atoms (O3–O6) are located in the external part of the pillar. Each is connected by a short bond (1.56–1.652 Å) with one central atom.

The occupancies of metal atoms have been refined to 27.9(4)% of Mo in type I octahedra and 72.1(4)% in type II (analogous values of the occupancies of V atoms fulfill to 1).



(a) (b)

FIG. 2. (a) Projection of the $KVMoO_6$ structure on the (010) plane. Only Mo and V atoms in positions with higher occupancy (V in type I octahedron and Mo in type II octahedron) are indicated. (b) Projection of the $KVMoO_6$ octahedra on the (010) plane.

TABLE 3
Selected Interatomic Distances (Å) and Bond Angles (°)

Type I octahedra		Type II octahedra	
M-O1	2.208(8)	M-O1(×2)	1.925(2)
M-O2A (×2)	1.941(3)	M-O2A	2.210(9)
M-O2B	2.506(9)	M-O3	2.376(7)
M-O3	1.618(8)	M-O4	1.612(8)
M-O6	1.56(1)	M-O5	1.652(9)
O1-M-O2A	74.75(1)	O1-M-O2A	74.97(1)
O1-M-O2B	76.4(3)	O1-M-O3	79.35(1)
O1-M-O3	154.0(3)	O1-M-O4	99.08(1)
O1-M-O6	98.6(4)	O1-M-O5	100.62(1)
O2A-M-O2B	77.71(1)	O2-M-O3	71.3(3)
O2A-M-O3	77.6(3)	O2-M-O4	101.7(4)
O2A-M-O6	175.1(4)	O2-M-O5	153.5(4)
O2B-M-O3	99.70(1)	O-M-O4	173.0(3)
O2B-M-O6	101.14(1)	O3-M-O5	82.2(3)
O3-M-O6	107.3(4)	O-M-O5	104.7(4)
K-O3 (×2)	2.968(6)		
K-O4	2.718(9)		
K-O5 (×2)	2.857(7)		
K-O6 (×2)	2.855(8)		

[a] Atom O2A lies in the plane below or above M atom, O2B lies in the same plane as M atom.

The larger occupancy factor for vanadium in the central octahedra can explain the very short distance M–O6 equal to 1.56 Å.

Potassium atoms are situated in the interpillar positions. They are located in free space between neighboring pillars and each is surrounded by 7 oxygen atoms: three coplanar with potassium and the remaining four related in pairs by the mirror plane. Distances between potassium and oxygen atoms are equal or slightly exceed the sum of K and O ionic radii.

The DTA curve (Fig. 4) shows the melting temperature of $KVMoO_6$ at 480°C is preceded by two weak endothermic effects at 377 and 410°C. There is no weight loss detected at these points. A similar non-identified endothermic effect was observed in $Pb_2V_2O_6$ about 55°C below its melting point.

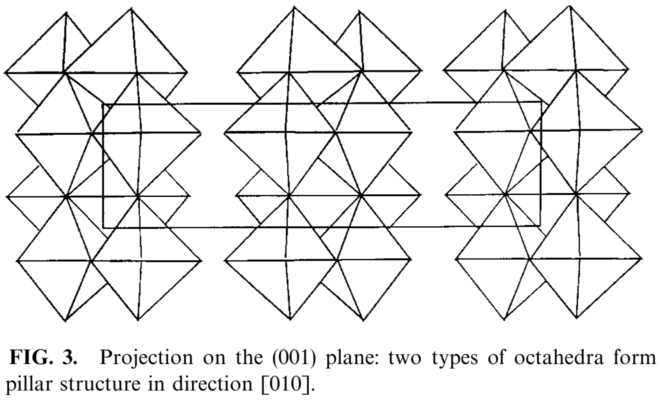


FIG. 3. Projection on the (001) plane: two types of octahedra form a pillar structure in direction [010].

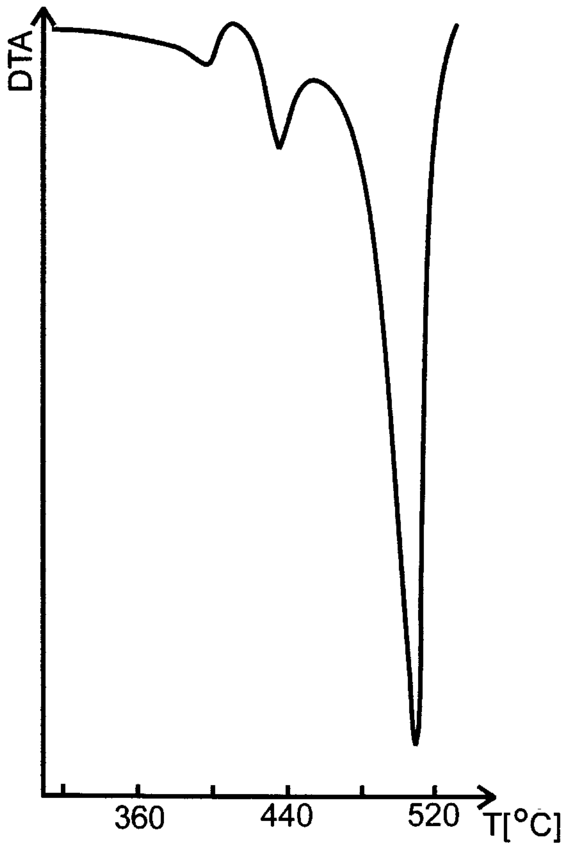


FIG. 4. DTA curve of $KVMoO_6$.

DISCUSSION

The pillar-like structure of $KVMoO_6$ is completely different from the layered structure of brannerites (L = Li, Na, Ag). This is due to the fact that the ionic radius of potassium is significantly larger those of the other elements [$Li^+ = 0.59$ Å, $Na^+ = 1.02$ Å, $Ag^+ = 1.15$ Å and $K^+ = 1.38$ Å (18)], forcing the increase in interpillar or interplanar separation. In the case of pseudobrannerites, e.g., $K_xV_xMo_{2-x}O_6$ ($0.76 \leq x \leq 0.82$), it results in decreasing β angle from about 111°, typical of brannerites, to 101°40′. In the structure investigated, where $x = 1$, further decrease in β angle takes place leading to the orthorhombic unit cell. Moreover, instead of the vanadomolybdate layers the separated pillars are created. It is worthwhile mentioning that both types of octahedra in $KVMoO_6$ are strongly compressed, which results in very short bonds between the metal and the external oxygen atoms.

The octahedra forming the pillar-like structure of $KVMoO_6$ are strongly deformed. Oxygen atoms O1 and

O2 are located in larger distances from the central atoms (up to more than 2.50 Å), significantly exceeding values calculated as the sum of ionic radii for the appropriate atoms (O^{2-} and Mo^{6+} or V^{5+}). This causes a decrease in the coordination number in these octahedra to 5, which is also observed in the pseudobrannerite structure. The deformation is especially displayed in the central octahedra (type I) in which exist both very short bonds of 1.56 Å (M–O6) and a very long distance, 2.506 Å (M–O2B).

A situation similar to that in $L\mathrm{VMoO_6}$ occurs in $Me\mathrm{V_2O_6}$ which can crystallize either as a brannerite (Me = Mg, Co, Mn, Zn, Cd) and pseudobrannerite (Me = Mg, Mn, Cd, Ca) (5) or in the orthorhombic unit cell (Me = Pb, Hg, Sr, Ba). PbV_2O_6 is isostructural with $KVMoO_6$. As the ionic radii of both ions, K^+ (1.38 Å) and Pb^{2+} (1.32 Å), are similar, cation size seems to be the main reason for building the orthorhombic structure.

Nevertheless, there are three main structural differences between $KVMoO_6$ and PbV_2O_6 crystals. Comparison of central atom–oxygen bond lengths shows that in PbV_2O_6 octahedra are deformed more strongly (M–O in the range 1.647–2.732 in type I and 1.611–2.569 Å in type II octahedra) than in the reported structure (1.56–2.506 and 1.612–2.376 Å for the appropriate octahedra). Each potassium atom is connected to seven oxygen atoms and Pb to nine oxygen atoms. The K–O distances are also a little larger in $KVMoO_6$ (2.718–2.968 Å) than Pb–O in PbV_2O_6 (2.643–2.694 Å).

The melting temperature of $KVMoO_6$ at 480°C is much lower than those of the other brannerite-type monovalent vanadomolybdates (651°C for $LiVMoO_6$, 623°C for $NaVMoO_6$, 610°C for $AgVMoO_6$) (5), suggesting that $KVMoO_6$ is less stable than the other $Me\mathrm{VMoO_6}$. It can be caused by the weaker bonding of MoO_6 and VO_6 octahedra by potassium ions. The stability of PbV_2O_6 is greater than that of $KVMoO_6$ as lead ions connect the octahedra by shorter bonds and are present in greater number. Thus, its melting point of 600°C does not differ significantly from those of the other metavanadates.

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