

β -K₂V₃P₄O₁₇: A Vanadium(IV) Pyrophosphate with a Layer Structure

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The high-temperature β -polymorph of the compound of formula K₂V₃P₄O₁₇ has been synthesized and its structure established by single-crystal X-ray diffraction method. Blue-green plate crystal of β -K₂V₃P₄O₁₇ crystallizes in the monoclinic space group $P2_1/c$ (14) with $a = 9.298(3)$, $b = 4.879(2)$, $c = 17.998(9)$ Å, $\beta = 114.98(3)^\circ$, $V = 740.1$ Å³, $Z = 2$, $R = 0.055$, and $R_w = 0.050$ for 586 unique reflections. The title compound consists of layers of vanadium(IV) phosphorus oxide with the potassium atoms between the layers. Each layer is built up from corner-sharing VO₅ square pyramids and P₂O₇ groups. Both differential thermal analysis and powder X-ray diffraction indicate that the phase transition from the low temperature α -polymorph to the high temperature β -polymorph occurs at ca. 915°C, and that the β -polymorph melts with decomposition at ca. 950°C. The phase transition is reconstructive and involves considerable bond scission and reformation between the two phases. © 1990 Academic Press, Inc.

Introduction

We and others have recently reported the crystal structures of A₂V₃P₄O₁₇ (A = Cs, Rb, K) which contain tunnels where the alkali metal cations are located (1–3). The framework of these isostructural compounds can be described as consisting of V₂O₁₀ units formed from one VO₅ square pyramid and one VO₆ octahedron sharing a corner, and infinite chains of VO₆ octahedra sharing opposite corners, which are linked in three dimensions through the pyrophosphate groups. Bond strength sums using the formula by Brown and Altermatt (4) were calculated on the A–O bonds of two crystallographically different A ions in each of these pyrophosphates, and the results were Cs

+ 1.03, + 1.09; Rb + 0.68, + 0.83; K + 0.50, + 0.77. The bond strength sums for the Rb and K compounds are much lower than the expected value + 1, suggesting that the tunnels appear too big for Rb and K cations which is also indicated by their high thermal parameters. Single-phase product of either the Cs or the Rb compound could be readily obtained, but reactions to prepare single-phase K₂V₃P₄O₁₇ revealed the presence of an unknown phase above about 850°C. It was speculated that K₂V₃P₄O₁₇ was polymorphic, and that at high temperature a phase transition occurred in order to stabilize the small K cation. Therefore, reactions were performed to obtain a single crystal of the unknown phase for crystal structure determination. The present work deals with

the synthesis, differential thermal analysis, and crystal structure of the high-temperature β -polymorph of $K_2V_3P_4O_{17}$. The structure reported by Leclaire *et al.* (3) is referred to as the low-temperature α -polymorph.

Experimental

Synthesis

$K_4V_2O_7$ (99.9%), VO_2 (99.5%), V_2O_3 (99.9%), V_2O_5 (99.9%), and P_2O_5 (99.9%), obtained from Cerac Inc., were used as received. $K_4P_2O_7$, obtained from Johnson Matthey Inc., was dried under vacuum at 300°C overnight. Loading of the reactants was carried out in a glovebox which was flushed with nitrogen. Blue-green plate crystals were obtained by heating a mixture of $K_4V_2O_7$, VO_2 , V_2O_3 , and P_2O_5 (mole ratio 1:2:1:4) in a sealed silica tube at 900°C for 2 days followed by slow cooling. The solution of the X-ray intensity data showed that the blue-green plate crystal and α - $K_2V_3P_4O_{17}$ had the same composition (*vide infra*), but had quite distinct crystal structures. For identification purposes, powder X-ray diffraction patterns were obtained by using a Rigaku powder diffractometer with filtered copper radiation. It was found that β - $K_2V_3P_4O_{17}$ could be prepared as a major product by reacting the same starting materials at 850°C but not by reaction below ~825°C. The reaction below ~825°C yielded the α -polymorph as a major product. By taking the β -polymorph prepared at 850°C and subsequently heating it at 750°C for 2 days, it was then found to convert into a mixture of approximately equal amounts of the two polymorphs. These results indicated that the α -polymorph transformed into the β -polymorph at ~850°C, and the transformation was reversible. Because both phases were always contaminated with a small amount of KVP_2O_7 (5), different starting materials were used in order to obtain single-phase products. The low-temperature α -polymorph was obtained as a single-phase

material by heating a reaction mixture of $K_4P_2O_7$, VO_2 , and P_2O_5 in a 1:6:3 molar ratio in a sealed silica tube at 750°C for 2 days and then furnace-cooled to room temperature. The powder X-ray pattern compared well with that calculated from the single-crystal X-ray data. Reactions at 850°C for 2 days yielded the β -polymorph as the major product with a small amount of the α -polymorph. The high-temperature β -polymorph could be prepared by heating the reactants at 910°C for 2 days, furnace-cooled to 850°C, and then rapidly cooled to room temperature (rt) by opening the door of a box furnace. The β -polymorph melted with decomposition at ~950°C. X-ray powder patterns of three samples of the α -polymorph that have been heated at 950°C for 4 hr, cooled at 300°C/hr to 800 (sample 1), 690 (sample 2), and 600°C (sample 3), respectively, and then quenched to rt revealed the presence of KVP_2O_7 as the major product in each sample with increasing amount of the β -polymorph from samples 1 to 3. The X-ray powder patterns did not show any other products except that the pattern for sample 1 had a relatively high background between $2\theta = 10$ and 40°.

Thermal Analysis

Differential thermal analysis (DTA) was performed on both the α - and the β -polymorphs, using a DuPont DTA system. The experiments were performed in a N_2 atmosphere with both the heating and cooling rates at 8°C/min. Alumina was used as the reference.

Single-Crystal X-Ray Diffraction Study

Peak profile analysis (ω -scan) on the blue-green plate crystals using a Nicolet R3/V diffractometer with $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) indicated that most of them were not suitable for indexing and intensity data collection. Many had to be selected from the reaction products before a satisfac-

tory crystal was obtained. Finally a piece with the dimensions $0.3 \times 0.1 \times 0.02$ mm was chosen. Some of its reflections also showed broad peak profiles but the diffracted X-rays from the crystal diverged by such a small angle that the intensity data were considered to contain enough information to make an elucidation of the structure possible. The unit cell parameters, $a = 9.298(3)$, $b = 4.879(2)$, $c = 17.998(9)$ Å, $\beta = 114.98(3)^\circ$, $V = 740.1$ Å³ were determined by a least-squares fit of 17 peak maxima with 2θ ranging from 16 to 30°. The intensity data were collected up to $2\theta = 55^\circ$ with ω - 2θ scan. A periodic check of three standard reflections did not reveal any significant variation in intensity. A total of 586 unique reflections with $I > 3\sigma(I)$ were corrected for absorption, Lorentz, and polarization effects. Corrections for absorption were based on ψ scans of a few suitable reflections with χ values close to 90° (T_{\max} , $T_{\min} = 0.950, 0.865$; $\mu = 28.8$ cm⁻¹) (6). All calculations were performed on a DEC MicroVAX II computer system using the SHELXTL-Plus programs (7). Based on the systematic absences, $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $h0l$ reflections, the space group $P2_1/c$ (14) was chosen. Classical methods for structure determination were used: direct method and successive Fourier syntheses. The refinement of atomic coordinates and isotropic thermal parameters showed that atoms V(2) and O(8), which were located at inversion centers, exhibited very large thermal parameters ($U_{\text{eq}} \sim 0.06$ Å² for V(2), ~ 0.08 Å² for O(8)). At this point an electron density map using the phases derived from K, V(1), P, and O atoms revealed two peak maxima for V(2). The two sites were inversion center related and were too closely spaced to be simultaneously occupied. Presumably, atom O(8) was disordered in a similar way because it was bonded only to V(2) and K. Therefore, a displacement of V(2) and O(8) from the special positions was allowed with their occupancy fac-

tors fixed at 0.5. A few cycles of least-squares refinement converged at lower agreement factors with reasonable thermal parameters for V(2) and O(8). Due to the limited amount of data, the K, V, and P atoms were refined anisotropically and the O atoms were refined isotropically. The large U_{11} and U_{22} values for the K atom ($U_{11}, U_{22}; 0.11, 0.11$; $U_{33}; 0.03$ Å²) suggested positional disorder and could be rationalized by the channels between the layers in the (001) plane in the structure. The very anisotropic thermal parameters for atom V(1) ($U_{11}, U_{22}, U_{33}; 0.017, 0.003, 0.025$ Å²) and atom V(2) ($U_{11}, U_{22}, U_{33}; 0.009, 0.033, 0.016$ Å²) could be attributed to incomplete absorption correction, disordering of V(2), or even poor crystal quality. The multiplicities of the K and V atoms were allowed to refine but did not deviate significantly from full occupancy. Therefore, all atom sites were considered fully occupied in the final cycles of least-squares refinement. The refinement based on F values of 83 parameters with the weighting scheme $1/w = \sigma^2(F_0) + 0.000184 F_0^2$ converged at $R = 0.055$, $R_w = 0.050$, goodness of fit = 1.898. In the final difference Fourier map the deepest hole was -0.65 e/Å³, and the highest peak 0.92 e/Å³.

Results and Discussion

Structure

Final atomic coordinates and thermal parameters are given in Table I. Selected bond distances are listed in Table II. As shown in Fig. 1, the title compound adopts a markedly different structure from the α -polymorph, and consists of layers of vanadyl pyrophosphate with the K⁺ ions between the layers. The transformation between the two phases involves major reorganization of the crystal structure, and their structural relationship is not obvious. The layer is built up from corner-sharing VO₅ square pyramids and P₂O₇ groups (see Fig. 2). Each V(1)O₅ square pyramid shares its four oxygen

TABLE I
 ATOMIC COORDINATES AND THERMAL FACTORS^a FOR β -K₂V₃P₄O₁₇

Atom	x	y	z	$U_{eq}(\text{\AA} \times 100)^b$
K	0.3214(6)	-0.018(3)	0.8278(2)	8.8(2)
V(1)	0.1348(2)	0.022(1)	0.1484(1)	1.53(9)
V(2)	0.499(2)	0.5902(8)	0.0002(9)	1.9(2)
P(1)	-0.1251(3)	0.507(2)	0.0711(2)	1.8(1)
P(2)	0.3038(3)	0.505(2)	0.1043(2)	1.7(1)
O(1)	0.281(1)	0.206(2)	0.1189(6)	2.9(2)
O(2)	0.175(1)	-0.081(2)	0.2405(6)	3.4(3)
O(3)	0.293(1)	-0.310(2)	0.1676(6)	2.3(2)
O(4)	0.2846(8)	-0.953(2)	0.4254(4)	1.8(2)
O(5)	0.4577(8)	-0.041(2)	0.5939(4)	1.9(2)
O(6)	0.164(1)	-0.100(2)	0.5202(5)	2.1(2)
O(7)	-0.042(1)	0.223(2)	0.0817(7)	3.5(3)
O(8)	0.512(6)	-0.426(3)	0.506(3)	4.2(7)
O(9)	0.027(1)	-0.789(2)	0.3718(6)	2.8(2)

^a The oxygen atoms were refined with isotropic thermal parameters. The occupancy factors for V(2) and O(8) are 0.5.

^b U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

atoms with four different P₂O₇ groups with the fifth vertex, O(2), being unshared and pointing into the interlayer space. In the α -polymorph, two VO₅ square pyramids have a similar orientation, and the apical vanadyl oxygen of a square pyramid is weakly coordinated to the other V atom, thus forming a

V₂O₁₀ unit. Atom V(2) of the title compound is disordered in two sites mainly along the *b*-axis. Each V(2)O₅ shares its four basal oxygen atoms with two different P₂O₇ groups with the apical oxygen atom, O(8), pointing to the open square face of a neighboring V(2)O₅, thus forming [VO(P₂O₇)₂]_∞ along the *b*-axis. In the α -polymorph, each P₂O₇ group forms a bridge over two adjacent vanadium atoms within a V=O·V=O·V=O infinite chain. The P₂O₇ group of the title compound is bonded to a V(2)O₅ square pyramid through bidentate bonding, and to four V(1)O₅ polyhedra through monodentate bonding. Each P₂O₇ group of the α -polymorph is also bonded to five different VO₅ square pyramids, but in a different manner. The maximum bond distance for K-O can be determined by using the procedure by Donnay and Allmann (8) with the revised radii of Shannon (9) leading to 3.35 Å. Accordingly, each K ion of the title compound is coordinated by eight oxygen atoms ranging from 2.518(16) to 3.326(17) Å. Bond valence sum of the eight

TABLE II
 SELECTED BOND DISTANCES (Å) FOR β -K₂V₃P₄O₁₇

K-O(2)	3.326(17)	K-O(2)	2.518(16)
K-O(3)	2.907(12)	K-O(4)	2.997(17)
K-O(4)	3.222(17)	K-O(5)	3.030(17)
K-O(5)	3.205(17)	K-O(8)	2.77(5)
K-O(8)'	2.95(5)	V(1)-O(1)	1.883(13)
V(1)-O(2)	1.618(11)	V(1)-O(3)	2.117(12)
V(1)-O(7)	1.852(11)	V(1)-O(9)	2.059(12)
V(2)-O(4)	1.896(15)	V(2)-O(4)	1.996(14)
V(2)-O(5)	2.002(20)	V(2)-O(5)	1.898(20)
V(2)-O(8)	1.642(18)	V(2)-O(8)	2.521(18)
V(2)-V(2)'	0.881(8)	O(8)-O(8)'	0.758(36)
P(1)-O(4)	1.523(9)	P(1)-O(6)	1.614(10)
P(1)-O(7)	1.563(15)	P(1)-O(9)	1.442(12)
P(2)-O(1)	1.513(15)	P(2)-O(3)	1.490(13)
P(2)-O(5)	1.529(9)	P(2)-O(6)	1.591(8)

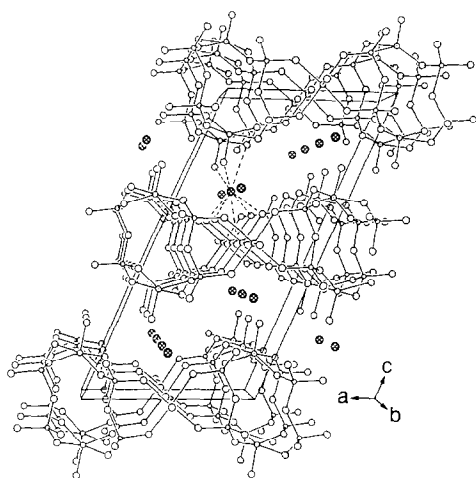


FIG. 1. A view of the structure of β - $K_2V_3P_4O_{17}$ along the b -axis. The K, V, P, and O atoms are represented by cross-hatched, dotted, small open, and large open circles, respectively. The K-O bonds are represented by dashed lines.

K-O bonds using the formula by Brown and Altermatt (4) is +0.95, which is in a good agreement with the expected value +1. Since O(8) is disordered in two sites, an average K-O(8) distance was used for the

bond-valence calculation. On the basis of bond valence sums, the K ions in the α -polymorph are loosely bonded compared to those in the β -polymorph.

The coordination environment of V(1) is distorted square pyramidal. The geometry is "distorted" in the sense that the vanadium atom lies above the plane of the four basal oxide ligands. The V(1) ion is displaced 0.49 Å from the least-squares plane toward the apical oxygen atom. The axial V(1)-O bond is about 0.3 Å shorter than the four equatorial V(1)-O bonds. Vanadium ions at V(2) sites have a common environment which is a gross distortion of octahedron: one short V-O bond length of 1.642(18) Å which is about 0.3 Å shorter than the four equatorial V-O bonds, but the sixth bond is much longer (2.521(18) Å), and the coordination is better regarded as distorted square pyramidal. The V(2) ion is displaced 0.43 Å from the least-squares plane toward the apical oxygen. The geometry of square pyramid often occurs with complexes containing oxovanadium(IV) ion or oxovanadium(V) ion. The blue-green color of the compound indicates that vanadium(IV) is present. Using the

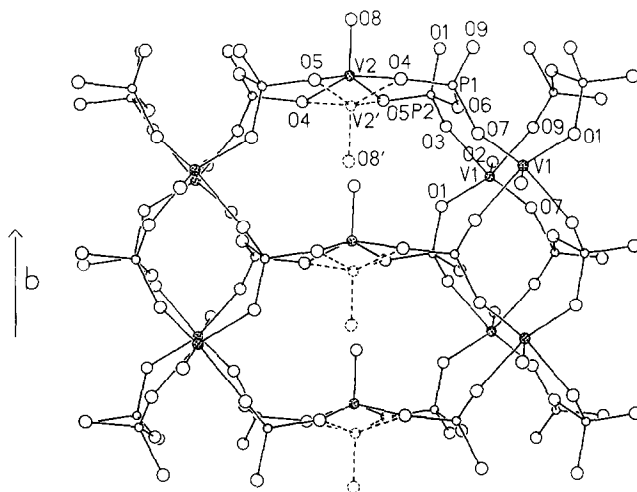


FIG. 2. A view of a layer in β - $K_2V_3P_4O_{17}$. Atoms V(2) and O(8) are disordered in two sites. One site is represented by a dotted circle.

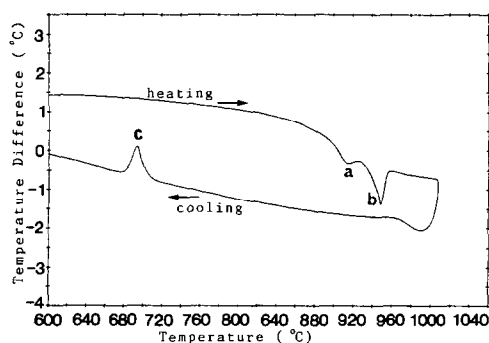


FIG. 3. DTA curve of α - $K_2V_3P_4O_{17}$ measured at a rate of $8^\circ/\text{min}$ in N_2 atmosphere.

Brown–Altermatt form for the bond length–bond valence relation for $V^{4+}-O$, we obtain +4.05 and +4.06 for V(1) and V(2), respectively, which is consistent with the value +4 based on the stoichiometry. The PO_4 tetrahedra forming the pyrophosphate group exhibit a semieclipsed configuration. The P atoms are displaced away from the bridging atom, O(6), giving three shorter and one longer P–O bonds. The P(1)–O(6)–P(2) bond angle is $128.0(7)^\circ$. Bond valence sums for P(1) and P(2) are +5.06 and +5.08, respectively, which are close to the expected value +5.

Thermal Analysis

Figure 3 shows the DTA curve of α - $K_2V_3P_4O_{17}$ in the temperature range from 600 to 1000°C . The sample gave endothermic peaks at $\sim 915^\circ\text{C}$ (a) and $\sim 950^\circ\text{C}$ (b) on heating, and an exothermic peak at $\sim 695^\circ\text{C}$ (c) on cooling. Below 600°C , the sample did not show either exothermic or endothermic peaks. On heating a sample of the β -polymorph only a peak at $\sim 950^\circ\text{C}$ was observed, and on cooling a peak at $\sim 695^\circ\text{C}$ was observed.

The transition from the α -polymorph to the β -polymorph occurs at $\sim 915^\circ\text{C}$. Peak a is preceded by a premonitory drift in the baseline and the onset temperature for the phase transition is $\sim 850^\circ\text{C}$. The transformation is reversible but quite sluggish. At higher temperature the β -polymorph melts with decomposition to yield KVP_2O_7 as the major product, giving a second endotherm (peak b). Other decomposition products should include vanadium(V) compounds in order to balance the charge. Since the phase transition is reconstructive and involves considerable bond scission and reformation between the two phases, on cooling no signal due to $\beta \rightarrow \alpha$ phase transition is observed on the DTA curve. The exothermic peak c is close to the melting point of V_2O_5 (690°C) but the X-ray data did not reveal the presence of it. Further research is in progress in order to interpret the exothermic peak.

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