

KTiP₂O₇의 결정구조

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Crystal Structure of KTiP₂O₇

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요 약

Titanium (III) pyrophosphate 화합물인 KTiP₂O₇을 합성하고 X-선 회절법으로 그 결정구조를 해석하였다. 이 물질은 단사정계의 P₂₁/a 공간군으로 결정화되었고 a=8.210(3), b=10.292(2), c=7.434(1)Å, β=106.71(2)°인 단위 세포 상수를 갖는 세포에 4개의 분자식을 포함하고 있다. 이 물질의 구조는 모서리를 공유하고 있는 TiO₆ 팔면체와 pyrophosphate group(P₂O₇⁴⁻)으로 형성된 framework로 구성되었으며 이 결과 형성된 tunnel 안에 K⁺ 양이온이 존재한다. KTiP₂O₇은 KAlP₂O₇ 및 RbTiP₂O₇ 등 다른 금속 pyrophosphate 화합물들과 유사한 구조를 갖고 있으나 alkali metal들의 크기에 따라 구조의 변화가 초래된다. 이 물질은 [K⁺][Ti³⁺][P₂O₇⁴⁻]의 식으로 표시 할 수 있다.

ABSTRACT

The compound titanium (III) pyrophosphate, KTiP₂O₇ has been prepared and the crystal structure of the compound has been determined by the X-ray diffraction techniques. It crystallizes in the space group P₂₁/a of the monoclinic system with four formula units in a cell of dimensions a=8.210(3), b=10.292(2), c=7.434(1)Å and β=106.71(2)°. The structure consists of the framework possessing corner-sharing octahedral TiO₆ and pyrophosphate groups. As a result, a tunnel structure has been constructed and the K⁺ cations reside inside the tunnel. KTiP₂O₇ is isostructural with other trivalent metal pyrophosphates such as KAlP₂O₇ and RbTiP₂O₇ but the size difference of the alkali metals causes the variation in the structure. The classical charge balance of the compound can be described as [K⁺][Ti³⁺][P₂O₇⁴⁻].

INTRODUCTION

During the search for new transition metal chalcogenides with the use of alkali metal halide fluxes, we have discovered many side products which have not been expected. However, some of them provide interesting aspects as far as synthetic routes or structures are concerned. Among these compounds were KTiP_2O_7 , a titanium(III) pyrophosphate, whose preparation from the alkali metal carbonates has been reported and the crystal structure has been assumed to be isostructural with RbTiP_2O_7 from the X-ray powder diffraction pattern.¹⁾ Rubidium trivalent titanium pyrophosphate (RbTiP_2O_7)¹⁾ has been known and structurally characterized with single crystal X-ray diffraction techniques. Here we report the synthesis of KTiP_2O_7 with the use of alkali metal halide fluxes and its crystal structure.

EXPERIMENTAL

Synthesis. The compound KTiP_2O_7 was prepared as an impurity phase by the reactions of elements Ti powder (CERAC 99.5%), P powder (CERAC 99.5%), and S powder (Aldrich 99.999%) with an elemental ratio of 1:1:3 in the reactive halide flux of KCl/LiCl. The starting materials were mixed thoroughly and loaded into a silica tube. The mass ratio of reactants and flux was 1.0:3.0. The tube was evacuated ($\sim 10^{-2}$ Torr), sealed, and heated gradually to 650°C, where they were kept for 4 days. The tube was cooled to

200°C at 5°C/hr and then quenched to room temperature. The excess halide flux was removed with distilled water and blue colored needle-shaped crystals up to 0.3mm in length were found. The compound was air-stable during the X-ray diffraction data collection. Analysis of these compounds with the microprobe of an EDAX-equipped AMRAY 1200C scanning electron microscope indicated the presence of K, Ti, P. The source of the oxygen is believed to be the water molecule present in the hygroscopic alkali metal halide fluxes.

Crystallographic Studies. The crystal structure of KTiP_2O_7 was determined by single crystal X-ray diffraction methods. Preliminary examination and data collection were performed with $\text{MoK}\alpha_1$ radiation ($\lambda=0.7093\text{\AA}$) on an MXC³ diffractometer (Mac Science). The monoclinic cell parameters and calculated volume are: $a=8.210(3)\text{\AA}$, $b=10.292(2)\text{\AA}$, $c=7.434(1)\text{\AA}$, $\beta=106.71(2)^\circ$, $V=601.6(2)\text{\AA}^3$. The observed Laue symmetry and the systematic extinctions ($h0l:h=2n+1;0k0:k=2n+1$) are indicative of the centrosymmetric $\text{P2}_1/a$ space group. The unit cell parameters and the orientation matrix for data collection were obtained from the least-squares refinement, using the setting angles of 24 reflections in the range $20^\circ < 2\theta(\text{MoK}\alpha) < 28^\circ$. Additional crystallographic details are described in Table 1. Intensity data were collected with the $\omega-2\theta$ scan technique. The intensities of two standard reflections, measured every hundred reflections, showed no significant deviations during the data collection. The scan rate was 4.0°/min (in ω axis). With

KTiP₂O₇의 결정구조

Table 1. Details of X-ray Data Collection and Refinement for KTiP₂O₇

Formula mass,amu	277.97
Space group	C _{2h} ⁵ - P2 ₁ /a
a, Å	8.210(3)
b, Å	10.292(2)
c, Å	7.434(1)
β ^a , deg.	106.71(2)
V, Å ³	601.6(2)
Z	4
T, K	293(2)
Radiation	graphite monochromated Mo Kα1 (λ(Kα1)=0.7093Å)
Linear absorption coefficient, cm ⁻¹	24.23
Density, calc. g/cm ³	3.069
Transmission factors ^b	0.877-0.949
Crystal size, mm ³	0.44 x 0.05 x 0.02
Scan type	ω-2θ
Scan speed, deg/min	4.0 in ω
Scan range, deg.	0.95+0.35tanθ
2θ limits, deg.	3° ≤ 2θ(Mo Kα1) ≤ 50°
Data collected	+h, +k, ±l
No. of unique data with Fo ² > 0	977
No. of unique data with Fo ² > 2(Fo ²)	824
wR2 (Fo ² > 0)	0.0940
R (on Fo for Fo ² > 2(Fo ²))	0.0406
Goodness-of-fit on F ²	1.071

^a α and γ were constrained to be 90° in the refinement of cell constraints.

^bThe analytical method as employed in the Northwestern absorption program, AGNOST, was used for the absorption correction²⁾.

the composition established the data for KTiP₂O₇ were corrected for absorption with the use of the analytical method of Tompa and de Meulenaer²⁾.

The initial positions for all atoms were obtained by using direct methods of the SHELXS-86 program³⁾. The structure was refined by full matrix least squares techniques with the use of the SHELXL-93 program⁴⁾. The final cycle of refinement performed on Fo² with 977 unique reflec-

tions afforded residuals wR2=0.0940 and conventional R index based on the reflections having Fo²>2σ(Fo²) is 0.0406. A difference Fourier synthesis calculated with phase based on the final parameters shows no peaks of heights greater than 5.02% that of an O atom. Final values of the atomic parameters and equivalent isotropic displacement parameters are given in Table 2. Anisotropic thermal parameters are given in Table 3.

Table 2. Atomic Coordinates ($\times 10^3$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for KTiP_2O_7

atom	x	y	z	U _{eq} ^a
K	-4430(2)	6777(1)	1799(2)	26(1)
Ti	2602(1)	3993(1)	2345(1)	9(1)
P(1)	-1723(2)	4025(1)	1332(2)	10(1)
P(2)	6904(2)	3616(1)	4446(2)	10(1)
O(1)	7378(5)	2171(4)	4570(5)	16(1)
O(2)	5114(5)	3899(4)	3223(6)	19(1)
O(3)	-2781(5)	5042(4)	47(5)	12(1)
O(4)	120(5)	4090(4)	1447(6)	20(1)
O(5)	2546(5)	2318(4)	804(5)	12(1)
O(6)	2710(5)	5807(4)	3625(5)	19(1)
O(7)	-1833(5)	4364(4)	3437(5)	17(1)

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

Table 3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for KTiP_2O_7

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
K	20(1)	30(1)	25(1)	0(1)	3(1)	-3(1)
Ti	6(1)	8(1)	11(1)	-1(1)	1(1)	0(1)
P(1)	7(1)	9(1)	12(1)	1(1)	1(1)	2(1)
P(2)	7(1)	11(1)	11(1)	0(1)	1(1)	0(1)
O(1)	17(2)	10(2)	20(2)	5(2)	1(2)	-5(2)
O(2)	6(2)	26(2)	22(2)	-1(2)	-2(2)	0(2)
O(3)	11(2)	9(2)	16(2)	3(2)	5(2)	3(2)
O(4)	10(2)	23(2)	25(2)	2(2)	5(2)	11(2)
O(5)	16(2)	9(2)	10(2)	-2(2)	0(2)	1(2)
O(6)	21(2)	17(2)	18(2)	1(2)	4(2)	-2(2)
O(7)	23(2)	16(2)	19(2)	2(2)	16(2)	1(2)

^aThe anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^*2U_{11}+k^2b^*2U_{22}+l^2c^*2U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}]$$

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Selected bond distances and angles for KTiP_2O_7 are listed in Table 4. The structure of the compound can be described as

a cage-like structure. The framework made of $\text{[TiP}_2\text{O}_7]^{4-}$ is built up from corner-sharing TiO_6 octahedra and the pyrophosphate $\text{P}_2\text{O}_7^{4-}$ groups (see Fig. 1). The coordinations about Ti and P atoms are slightly distorted from ideal Oh and Td geometries (see Table 4). Ti-O and P-O distances are in good agreement with those calculated from crystal radii typical for these atoms in titanium phosphate structures. The P_2O_7 group is composed of two PO_4 tetrahedra sharing distance, The bridging P-O bond (ave. P-O distance, 1.634 Å) is slightly longer than the average terminal P-O bonds (1.511 Å). This is consistent with other pyrophosphates^{1,5,7}. The TiO_6 octahedra are nearly regular, with cis O-Ti-O angles between 85.4(2)° and 91.8(2)° (see Table 4) and trans O-Ti-O angles ranging from 173.0(2)° and 179.4(2)°. This $\text{[TiP}_2\text{O}_7]^{4-}$ framework has channels along the [100] direction and the electropositive K^+ atoms reside inside this tunnel. KTiP_2O_7 is isostructural with RbTiP_2O_7 . However, some structural deviations have been caused by the size difference between K^+ and Rb^+ cations. The bridging angle P(1)-O(7)-P(2) in KTiP_2O_7 has been reduced to 123.8(3)° from 127.0(5)° in RbTiP_2O_7 . This is probably due to the fact that the K^+ ion is smaller than Rb^+ ions. The classical charge balance of KTiP_2O_7 can be described as $[\text{K}^+][\text{Ti}^{3+}][\text{P}_2\text{O}_7^{4-}]$. The electrostatic valence calculation according to Brese et al.⁸) leads for titanium valence of 3.069, which is in excellent agreement with the estimated oxidation state(III) from the classical charge balance.

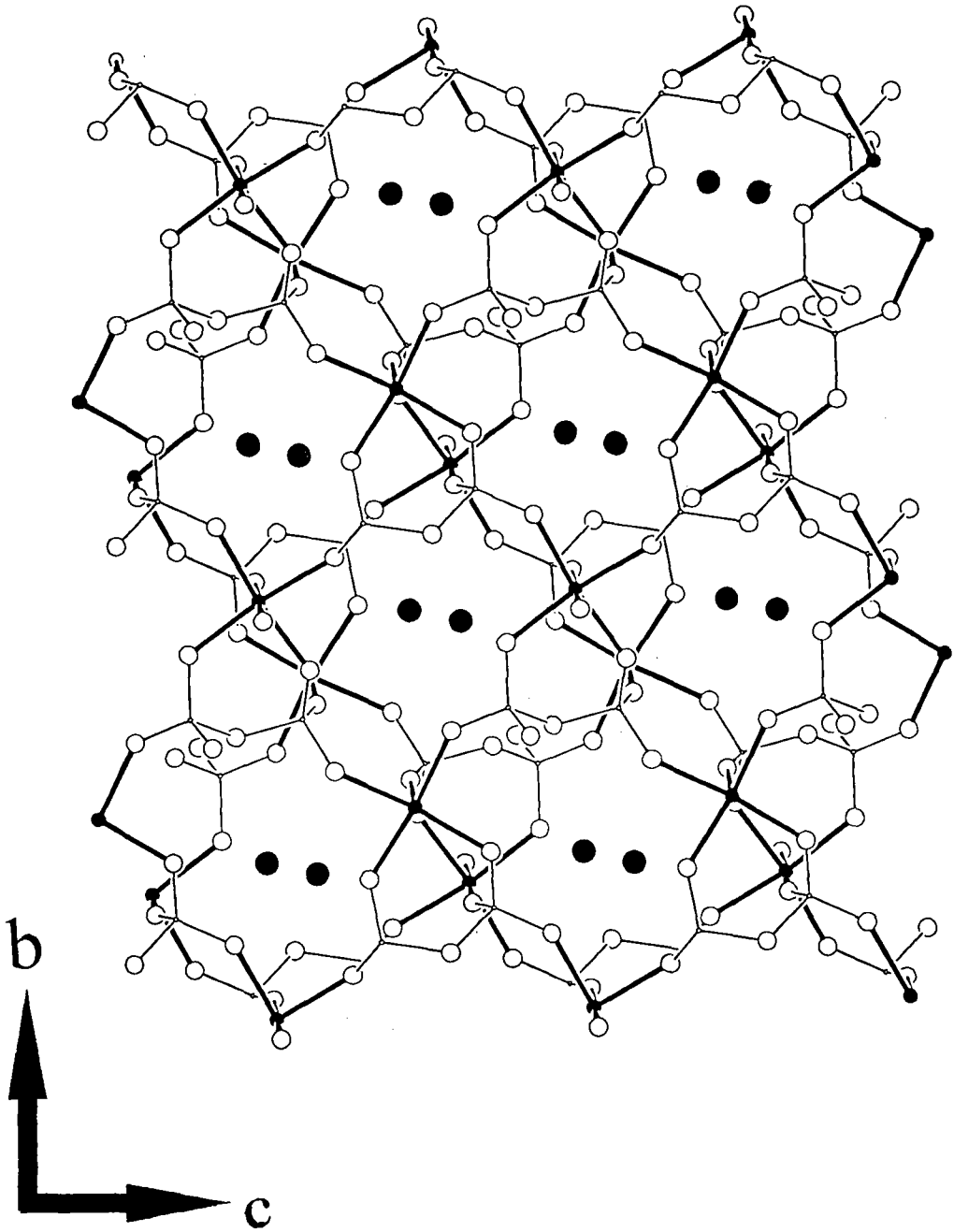


Fig. 1. A labeled view down the a-axis of the KTiP_2O_7 structure, Ti atoms are small filled circles; K atoms are large filled circles; P atoms are small open circle; O atoms are large open circles. The bonds between Ti and O atoms are thickened.

KTiP₂O₇의 결정구조

Table 4. Bond Lengths [Å] and Angles [deg] for KTiP₂O₇

Distances			
Ti-O(4)	1.956(4)	Ti-O(2)	1.978(4)
Ti-O(5)	2.062(4)	Ti-O(3) #1	2.078(4)
Ti-O(6)	2.086(4)	Ti-O(1) #2	2.093(4)
P(1)-O(4)	1.492(4)	P(1)-O(3)	1.511(4)
P(1)-O(5) #2	1.514(4)	P(1)-O(7)	1.631(4)
P(2)-O(6) #4	1.500(4)	P(2)-O(2)	1.518(4)
P(2)-O(1)	1.533(4)	P(2)-O(7) #3	1.637(4)
Angles			
O(4)-Ti-O(2)	179.4(2)	O(4)-Ti-O(5)	89.9(2)
O(2)-Ti-O(5)	89.8(2)	O(4)-Ti-O(3) #1	90.4(2)
O(2)-Ti-O(3) #1	89.0(2)	O(5)-Ti-O(3) #1	85.4(2)
O(4)-Ti-O(6)	90.8(2)	O(2)-Ti-O(6)	89.4(2)
O(5)-Ti-O(6)	173.0(2)	O(3) #1-Ti-O(6)	87.6(2)
O(4)-Ti-O(1) #2	88.8(2)	O(2)-Ti-O(1) #2	91.8(2)
O(5)-Ti-O(1) #2	88.1(2)	O(3) #1-Ti-O(1) #2	173.5(2)
O(6)-Ti-O(1) #2	98.8(2)		
O(4)-P(1)-O(3)	113.2(2)	O(4)-P(1)-O(5) #2	112.1(2)
O(3)-P(1)-O(5) #2	110.9(2)	O(4)-P(1)-O(7)	105.7(2)
O(3)-P(1)-O(7)	106.2(2)	O(5) #2-P(1)-O(7)	108.4(2)
O(6) #6-P(2)-O(2)	113.5(2)	O(6) #6-P(2)-O(1)	110.3(2)
O(2)-P(2)-O(1)	114.1(2)	O(6) #6-P(2)-O(7) #3	105.4(2)
O(2)-P(2)-O(7) #3	105.5(2)	O(1)-P(2)-O(7) #3	107.5(2)
P(1)-O(7)-P(2) #5	123.8(3)		
Symmetry transformations used to generate equivalent atoms:			
#1 -x, -y+1, -z	#2 x-1/2, -y+1/2, z	#3 x+1, y, z	
#4 -x+1, -y+1, -z+1	#5 x-1, y, z	#6 -x+1, -y+1, -z+1	

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KTiP₂O₇의 결정구조

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