Synthesis and Crystal Structure of CsTiP$_2$O$_7$

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CsTiP$_2$O$_7$의 합성과 결정구조

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Abstract

The compound cesium titanium(III) pyrophosphate, CsTiP$_2$O$_7$ has been obtained and the crystal structure of the compound has been determined by the X-ray diffraction techniques. It crystallizes in the space group, $P2_1/a$ of the monoclinic system with a=8.369(2) Å, b=10.208(2) Å, c=7.752(1) Å, β=104.77(2)°, V = 640.4(2) Å^3, and Z=4. The structure consists of the framework possessing corner-sharing TiO$_6$ octahedra and P$_2$O$_7$ pyrophosphate groups. As a result, a tunnel structure has been constructed and the Cs$^+$ cations reside inside the tunnel. CsTiP$_2$O$_7$ is isostructural with other trivalent metal pyrophosphate such as ATiP$_2$O$_7$(A=K, Rb), KAlP$_2$O$_7$ and AMoP$_2$O$_7$(A=K, Rb, Cs). The classical charge balance of the compound can be described as [Cs$^+$][Ti^{3+}][P$_2$O$_7^{4-}$].

요 약

Cesium titanium(III) pyrophosphate 화합물인 CsTiP$_2$O$_7$을 합성하고 X선 회절법을 이용하여 그 결정구조를 해석하였다. 이 물질은 단사정계의 $P2_1/a$ 공간군으로 결정화 되었고 a=8.369(2) Å, b=10.208(2) Å, c=7.752(1) Å, β=104.77(2)°, V=640.4(2) Å^3, Z=4이다. 이 물질의 구조는 모서리를 공유하고 있는 TiO$_6$ 팔면체와 P$_2$O$_7$ pyrophosphate group들로 구성된 framework로 구성되어 있으며 그 결과로 형성된 tunnel 안에는 Cs$^+$이온이 존재한다. CsTiP$_2$O$_7$은 ATiP$_2$O$_7$(A=K, Rb)와 KAlP$_2$O$_7$ 그리고 AMoP$_2$O$_7$(A=K, Rb, Cs)등 다른 +3금속 pyrophosphate들로 유사한 구조를 가지고 있다. 이 물질은[Cs$^+$][Ti^{3+}][P$_2$O$_7^{4-}$]의 식으로 표시할 수 있다.

1. Introduction

During the course of the search for new transition metal chalcogenides with the use of alkali metal halide fluxes, we have discovered many side products which had not been expected. Some of them provide interesting aspects as far as synthetic routes or structures are concerned. Titanium phosphates form a number of structurally interesting compounds that consist of mixed frameworks of AO$_{10}$ polyhedra(A=K, Rb, Cs, Ba), TiO$_6$ octahedra, and PO$_4$ tetrahedra.[1,2] The combination of complex and interactions of metal-oxide polyhedra have resulted in new compounds that possess framework structures with sizable tunnels. The phosphates have four main types of polyphosphates; general polyphosphates [P$_n$O$_{3n+1}$]$^{(n+2)-}$(n=1 to 16), infinite chain metaphosphates [(PO$_3$)$_n$]$^{n-}$, cyclic metaphosphates [(PO$_3$)$_n$]$^{n-}$ (n=3 to 10, or more), and ultraphosphates which contain branching units.[3] Diphosphate anion, P$_2$O$_7^{4-}$ (also known as pyrophosphate) is the simplest polyphosphate anion which is found in many solid materials.[1,2,5-9] This phosphate does not have notable chemical and physical properties due to the phosphate group itself. However, phosphate anions do not absorb UV/Vis and thus solid phosphates

could be used as optical materials such as glasses, phosphors, nonlinear optical materials and laser materials.[4] Here we report on the synthesis and crystal structure of $CsTiP_2O_7$ which contains $P_2O_7^{4-}$ pyrophosphate.

2. Experimental

Synthesis. Synthesis was carried out by reaction of Ti, P, Se with ratio of 1:1:2 in the halide flux of CsCl. The tube was evacuated (10^{-2} torr), sealed, and heated gradually to 850°C, where it was kept for 2 days. The tube was cooled at a rate of 6°C/hr to 200°C and the furnace was quenched. The excess halide flux was removed with distilled water. Dark blue colored rectangular crystals up to 0.4 mm in length were found. This compound is stable in air and does not decompose significantly in water. Analysis of these compounds with the microprobe of an EDAX equipped AMRAY 1200C scanning electron microscope indicated the presence of Cs, Ti and P. The source of the oxygen is believed to be water molecules present in the hygroscopic alkali metal halide flux.

Crystallographic Studies. The crystal structure of $CsTiP_2O_7$ was determined by single crystal X-ray diffraction methods. Preliminary examination and data collection were performed with MoKα radiation (λ=0.7107 Å) on an MXC3 diffractometer (Mac Science). The monoclinic cell parameters and calculated volume are: a=8.369(2) Å, b=10.208(2) Å, c=7.752(1) Å, β=104.77(2)°, V=640.4(2) Å³. The observed Laue symmetry and the systematic extinctions (h0l : h=2n+1; 0k0 : k=2n+1) are indication of the centrosymmetric $P2_1/a$ 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 23 reflections in the range $20° < 2\theta(MoK\alpha) < 28°$. Intensity data were collected with the ω-2θ scan technique. The intensities of two standard reflections, measured every one hundred reflections, showed no significant deviations during the data collection. The scan rate was 4.0°/min in ω axis. Additional crystallographic details are described in Table 1.

The initial positions for all atoms were obtained

by using direct methods of the SHELXS-86 program.[9] The structure was refined by full matrix least squares techniques with the use of the SHELXL-93 program.[10] The final cycle of refinement performed on F_o^2 with 1121 unique reflections afforded residuals wR2=0.0763 and conventional R index based on the reflections having $F_o^2 > 2\sigma$ (F_o^2) is 0.0283. With the composition established the data for $CsTiP_2O_7$ were corrected for absorption with the use of the analytical method of Tompa and de Meulenaer.[11] Examination of the search for potential additional symmetry with the use of the MISSYM and NEWSYM algorithm in the PLATON program

Table 1. Details of X-ray Data Collection and Refinement for $CsTiP_2O_7$

Formula mass, amu	354.75
Space group	C_{2h}^5 - $P2_1/a$
a, Å	8.369(2)
b, Å	10.208(2)
c, Å	7.752(1)
β^a, deg	104.77(2)
V, Å³	640.4(2)
Z	4
T, K	293(2)
Radiation	graphite monochromated MoKα (λ(MoKα)=0.7107 Å)
Linear absorption coefficient, mm^{-1}	7.43
Density, calc g/cm³	3.680
Transmission factors[b]	0.225-0.341
Crystal size, mm³	0.2×0.2×0.4
Scan type	ω-2θ
Scan speed, deg, min^{-1}	4.0 in ω
Scan range, deg,	0.95 + 0.35 tanθ
2θ limits, deg	$3° \leq 2\theta(MoK\alpha) \leq 50°$
Data collected	$-9 \leq h \leq 9, 0 \leq k \leq 12, 0 \leq l \leq 9$
No. of unique data with $F_o^2 > 0$	1121
No. of unique data with $F_o^2 > 2\sigma(F_o^2)$	1079
wR2 ($F_o^2 > 0$)	0.0763
R (on F_o for $F_o^2 > 2\sigma$ (F_o^2))	0.0283
Goodness-of-fit on F^2	1.135
Min. and Max. residual e⁻ density(e/Å³)	-1.035 and 1.075

[a] α and γ were constrained to be 90° in the refinement of cell constraints
[b] The analytical method as employed in the Northwestern absorption program, AGNOST, was used for the absorption correction.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $CsTiP_2O_7$

Atom	Wyckoff Letter	x	y	z	U_{eq}^a
Cs	4e	-4574(1)	7021(1)	1986(1)	19(1)
Ti	4e	2585(1)	3983(1)	2396(1)	7(1)
P(1)	4e	-1688(2)	4054(1)	1314(2)	8(1)
P(2)	4e	6819(2)	3721(1)	4256(2)	8(1)
O(1)	4e	7307(5)	2287(4)	4360(5)	13(1)
O(2)	4e	5058(5)	3969(4)	3221(5)	16(1)
O(3)	4e	-2651(5)	4982(4)	-87(5)	12(1)
O(4)	4e	150(5)	4162(4)	1578(5)	15(1)
O(5)	4e	2692(5)	2341(4)	920(5)	12(1)
O(6)	4e	2735(5)	5679(4)	3910(5)	13(1)
O(7)	4e	-2050(5)	4493(4)	3176(5)	13(1)

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

Table 3. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $CsTiP_2O_7$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	19(1)	18(1)	19(1)	2(1)	-2(1)	-6(1)
Ti	7(1)	2(1)	10(1)	0(1)	-1(1)	0(1)
P(1)	8(1)	3(1)	11(1)	1(1)	0(1)	1(1)
P(2)	9(1)	2(1)	12(1)	-1(1)	1(1)	1(1)
O(1)	16(2)	6(2)	14(2)	-1(2)	4(2)	2(2)
O(2)	10(2)	17(2)	18(2)	-2(2)	0(2)	1(2)
O(3)	9(2)	6(2)	19(3)	5(2)	1(2)	1(2)
O(4)	11(2)	13(2)	20(2)	5(2)	4(2)	1(2)
O(5)	13(2)	4(2)	16(2)	0(2)	0(2)	1(2)
O(6)	18(2)	7(2)	10(2)	-2(2)	0(2)	2(2)
O(7)	18(2)	6(2)	18(2)	-2(2)	7(2)	0(2)

Note. The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}]$.

could not find the other symmetry in this structure.[12] Final values of the atomic parameters and equivalent isotropic displacement parameters are given in Table 2. Anisotropic thermal parameters are given in Table 3.

3. Description of the Structure and Discussion

Selected bond distances and angles for $CsTiP_2O_7$ are listed in Table 4. $CsTiP_2O_7$ is isostructural with

Table 4. Bond Lengths [Å] and Angles [deg] for $CsTiP_2O_7$

Distance

Cs-O(1)#1	2.992(4)	Cs-O(5)#2	2.999(4)
Cs-O(2)#6	3.297(4)	Cs-O(5)#3	3.128(4)
Cs-O(3)	3.289(4)	Cs-O(6)#4	3.162(4)
Cs-O(3)#5	3.162(4)	Cs-O(6)#6	3.300(4)
Cs-O(4)#2	3.459(4)	Cs-O(7)	3.313(4)
Ti-O(1)#7	2.058(4)	Ti-O(4)	1.981(4)
Ti-O(2)	2.004(4)	Ti-O(5)	2.044(4)
Ti-O(3)#8	2.091(4)	Ti-O(6)	2.077(4)
P(1)-O(3)	1.510(4)	P(2)-O(1)	1.516(4)
P(1)-O(4)	1.503(4)	P(2)-O(2)	1.509(4)
P(1)-O(5)#7	1.520(4)	P(2)-O(6)#9	1.506(4)
P(1)-O(7)	1.613(4)	P(2)-O(7)#10	1.619(4)

Angle

O(1)#7-Ti-O(2)	93.5(2)	O(3)-P(1)-O(4)	113.1(2)
O(1)#7-Ti-O(3)#8	169.8(2)	O(3)-P(1)-O(5)#7	110.6(2)
O(1)#7-Ti-O(4)	89.6(2)	O(3)-P(1)-O(7)	106.4(2)
O(1)#7-Ti-O(5)	85.8(2)	O(4)-P(1)-O(5)#7	112.4(2)
O(1)#7-Ti-O(6)	96.3(2)	O(4)-P(1)-O(7)	106.1(2)
O(2)-Ti-O(3)#8	91.5(2)	O(5)#7-P(1)-O(7)	107.9(2)
O(2)-Ti-O(4)	175.1(2)		
O(2)-Ti-O(5)	89.1(2)	O(1)-P(2)-O(2)	113.8(2)
O(2)-Ti-O(6)	85.2(2)	O(1)-P(2)-O(6)#9	110.1(2)
O(3)#8-Ti-O(4)	85.9(2)	O(1)-P(2)-O(7)#10	108.2(2)
O(3)#8-Ti-O(5)	85.4(2)	O(2)-P(2)-O(6)#9	114.0(2)
O(3)#8-Ti-O(6)	93.0(2)	O(2)-P(2)-O(7)#10	105.3(2)
O(4)-Ti-O(5)	94.9(2)	O(6)#9-P(2)-O(7)#10	104.7(2)
O(4)-Ti-O(6)	90.7(2)		
O(5)-Ti-O(6)	174.0(2)	P(1)-O(7)-P(2)#6	126.6(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1 #2 -x-1/2,y+1/2,-z #3 -x,-y+1,-z
#4 x-1/2,-y+3/2,z #5 -x-1,-y+1,-z #6 x-1,y,z
#7 x-1/2,-y+1/2,z #8 -x,-y+1,-z #9 -x+1,-y+1,-z+1
#10 x+1,y,z.

$ATiP_2O_7$ (A=K, Rb),[1] $KAlP_2O_7$[7] and other quaternary pyrophosphate compounds.[5,6,8] The framework possesses corner-sharing TiO_6 octahedra and P_2O_7 pyrophosphate groups. These TiO_6 octahedra are interconnected by the P_2O_7 groups forming a three-dimensional $_\infty^3[TiP_2O_7]$ structure. Each TiO_6 octahedron shares its six corners with five pyrophosphate groups and, therefore, each pyrophosphate group shares its six corners with five TiO_6 octahedra. One
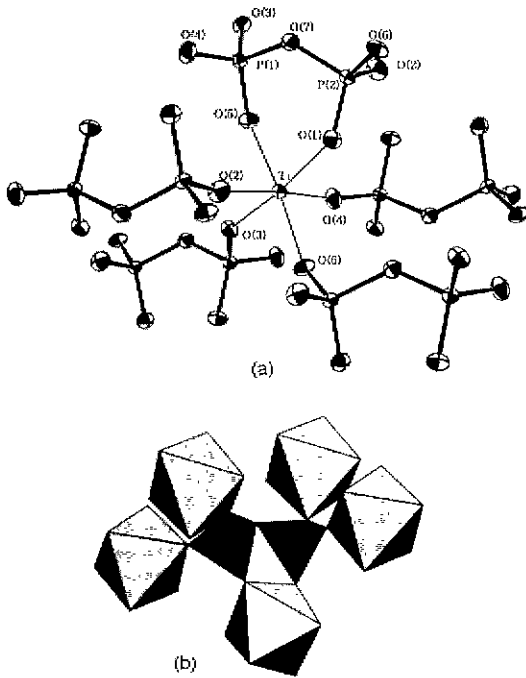
(a)

(b)

Fig. 1. a) ORTEP view of the TiO_6 and P_2O_7 pyrophosphate groups with the anisotropic thermal vibration ellipsoids. b) The polyhedron representation of the connectivities of the TiO_6 octahedra and P_2O_7 pyrophosphate groups in $CsTiP_2O_7$.

Fig. 2. Displaying the framework of $CsTiP_2O_7$ and the tunnels occupied by Cs^+ ions. The a-axis is approximately perpendicular to the this plane. In the polyhedral representation of the structure, the corner of the octahedra and tetrahedra are O^{2-} ions, the Ti and P ions are at the center of octahedron and tetrahedron respectively and the circles represent the Cs^+ ions.

of the five P_2O_7 linked to TiO_6 octahedra is coordination to the Ti atom as a bidentate ligand(see Fig. 1). The coordinations about Ti and P atoms are slightly distorted from ideal Oh and Td geometries, respectively. Ti-O and P-O distances are in good agreement with those calculated from crystal radii typical for these atoms in titanium phosphate structures.[1] Disorder of pyrophosphate can be evidenced by anomalous P-O(bridging oxygen) distance and O-P-O(between bridging oxygen and terminal oxygen) angles, and large amplitude of thermal vibration for the bridging oxygen. The linear P-O-P angles have centrosymmetric pyrophosphate groups and this is indicative of bridging oxygen disorder. The regular P-O(bridging oxygen) distances are 1.58-1.64 Å, and P-O-P angle ranges are 120°-160°.[4] In this compound, the pyrophosphate group is composed of the staggered configuration of the PO_4 tetrahedra. The bridging P-O bond(ave. P-O 1.616(4) Å) is slightly longer than the average ter-
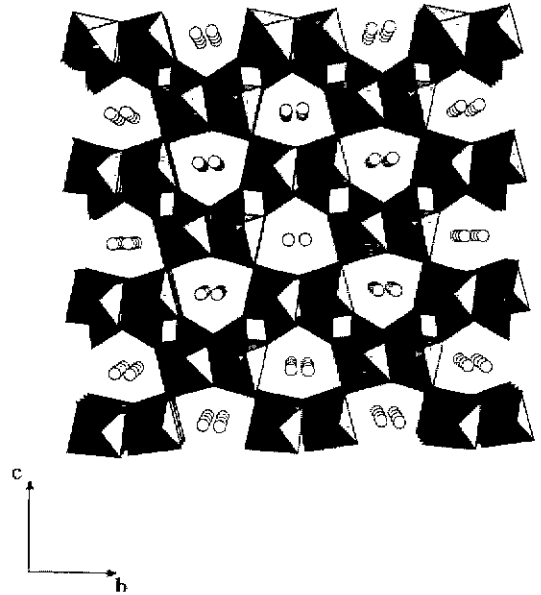
minal P-O bonds(ave. 1.511(4) Å) and the bridging angle P(1)-O(7)-P(2)(126.6(2)°) coincides with the ordered P-O-P angle ranges. This is consistent with other pyrophosphates.[1,2,5-8] Thus, bridging oxygen in P_2O_7 pyrophosphate is well ordered in this compound. The TiO_6 octahedra are nearly regular, with cis O-Ti-O angles between 85.2(2)° and 96.3(3)° and trans O-Ti-O angles ranging from 169.8(2)° and 175.1(2)° (see Table 4). This infinited three-dimensional $_\infty^3[TiP_2O_7^-]$ framework has channels along the [100] direction and the electropositive Cs^+ atoms reside inside this tunnel. The extended structure projected along the a axis is shown in Fig. 2. The unit cell consists of four cesium atoms, each of which is surrounded by an irregular polyhedron of 10 oxygen atoms, at distance ranging from 2.992 Å to 3.456 Å. This wide distribution in bond length is attributed to the complex electrostatic interaction and to the steric effect of the P_2O_7 pyrophosphate group. Four edges of the pyrophosphate group are

shared with that of CsO_{10} polyhedron. The size of the monovalent cations determines the geometry of the tunnels which are formed by the AO_{10} polyhedron(A=K, Rb, Cs). The results of bond-valence parameters calculation are +3.049 for Ti atom, +4.782 for P(1) atom, and +4.773 for P(2) atom.[13] The classical charge balance of $CsTiP_2O_7$ can be described as $[Cs^+][Ti^{3+}][P_2O_7^+]$.

Acknowledgment

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