Synthesis and Crystal Structures of α- and β-CsTi₃P₅O₁₉

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Crystals of α-CsTi₃P₅O₁₉, the low temperature phase, and β-CsTi₃P₅O₁₉, the high temperature phase, have been obtained by flux growth methods and structurally characterized by single crystal X-ray diffraction techniques. Crystal data: α-CsTi₃P₅O₁₉, monoclinic, Cm, $a = 9.309(2)$ Å, $b = 14.081(3)$ Å, $c = 6.314(1)$ Å, $\beta = 105.82(3)°$, $V = 796.3$ Å³, $Z = 2$, $R = 0.027$ for 928 unique reflections; β-CsTi₃P₅O₁₉, monoclinic, $C2/c$, $a = 10.987(1)$ Å, $b = 16.588(1)$ Å, $c = 8.7618(8)$ Å, $\beta = 100.09(1)°$, $V = 1572.2$ Å³, $Z = 4$, $R = 0.038$ for 1678 unique reflections. The two polymorphs have different three-dimensional networks of vertex-sharing octahedra and tetrahedra. The framework of the α-phase consists of dimers of corner-sharing TiO_6 octahedra and discrete TiO_6 octahedra joined through PO_4 tetrahedra and P_2O_7 groups by corner-sharing. The β-phase is built up from discrete TiO_6 octahedra, PO_4 tetrahedra, and P_2O_7 groups. The structural formulas are $CsTi(Ti_2O)(PO_4)(P_2O_7)_2$ and $CsTi_3(PO_4)_3(P_2O_7)$ for the α- and β-phases, respectively. Both frameworks have tunnels where the cesium cations are located. The cesium cations in the β-phase are disordered. © 1995 Academic Press, Inc.

INTRODUCTION

Titanium phosphates of the stoichiometry $ATiOPO_4$ (A = alkali metals) exhibit several structure types. $LiTiOPO_4$ (1) is isostructural with β-$LiVOPO_4$ (2). α-$NaTiOPO_4$ (3) is structurally similar to the naturally occurring mineral $CaTiOSiO_4$ (4). β-$NaTiOPO_4$ (3) and $RbTiOPO_4$ (5) are isostructural with $KTiOPO_4$ (KTP) (6), which is a well-known second-harmonic-generation crystal for transforming infrared radiation from Nd:YAG laser ($\lambda = 1.06$ μm) into the green part of the optical spectrum ($\lambda = 532$ nm). The compound that remains in this family, $CsTiOPO_4$ (CsTP), has not been reported. Our preliminary synthetic work indicates that CsTP with the KTP structure does not exist. Airapetyan *et al.* reported the crystallization of $CsTiPO_5$ from melt-solutions (7), but the compound was not characterized and its X-ray powder pattern cannot be indexed based on the KTP structure.

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To our knowledge, $Cs_2TiOP_2O_7$ (8) is the only structurally characterized compound in the cesium–titanium–phosphate phase space. Therefore, we have undertaken an investigation of the phase space. This paper reports the results of our exploratory synthesis and single-crystal X-ray structural characterization of two cesium titanium phosphates, α- and β-CsTi₃P₅O₁₉.

EXPERIMENTAL SECTION

Synthesis. A mixture of CsH_2PO_4 (1.800 g), $NH_4H_2PO_4$ (0.485 g), and TiO_2 (0.160 g) (Cs:P mole ratio = 0.65) was placed in a 15-ml platinum crucible and thermally treated as follows: heat from RT to 1000°C over 8 hr; maintain at 1000°C for half an hour; cool to 800°C at 10°C/hr; maintain at 800°C overnight; quench to RT by removing the crucible from the furnace. The flux was dissolved with hot water and the solid product was obtained by suction filtration. The product contains colorless rod-like crystals of α-CsTi₃P₅O₁₉. The X-ray powder pattern of the bulk product taken with a Scintag powder diffractometer indicates that a single phase of α-Cs Ti₃P₅O₁₉ has been obtained. The α-phase was the only phase isolated after dissolving the flux. Other reaction products that were soluble in water were not characterized. An excess of Cs (e.g., Cs:P = 0.65) is necessary to help grow crystals with sizes adequate for single-crystal X-ray diffraction. The reaction using stoichiometric starting materials yielded polycrystalline α-CsTi₃P₅O₁₉ only.

For the crystal growth of β-CsTi₃P₅O₁₉, a mixture containing the same amount of starting materials was slowly heated to 1250°C, maintained at 1250°C for 1 hr, cooled to 1130°C at 60°C/hr, maintained at 1130°C for 20 hr, and then quenched to RT. The product contains colorless rod-like crystals of β-CsTi₃P₅O₁₉ and polycrystalline solid. Based on powder X-ray diffraction, the product is a mixture of the β-CsTi₃P₅O₁₉ and TiP_2O_7 (9).

Energy-dispersive X-ray fluorescence analysis on several crystals of both phases showed that the Cs:Ti:P mole ratio was 0.94:3:5.05 for the α-phase and 0.87:3:5.10 for the β-phase. The value of Cs for the β-phase is somewhat

lower than that obtained from single-crystal X-ray diffraction data.

Single-crystal X-ray diffraction. Two crystals of dimensions $0.08 \times 0.08 \times 0.35$ mm for α-CsTi₃P₅O₁₉ and $0.2 \times 0.3 \times 0.5$ mm for β-CsTi₃P₅O₁₉ were selected for indexing and intensity data collection on a Huber automated 4-circle diffractometer using graphite-monochromated MoKα radiation. Axial oscillation photographs were taken to check the symmetry properties and unit-cell parameters. Octants collected: $+h$, $+k$, $\pm l$ for both compounds. Both intensity data were corrected for Lp and absorption effects. Corrections for absorption were based on a ψ-scan of one suitable reflection with the χ value close to 90° using the program DIFABS (10). On the basis of systematic absences, statistical analysis of intensity distribution, and successful solution and refinement of the structures, the space groups were determined to be Cm (No. 8) and $C2/c$ (No. 15) for α- and β-CsTi₃P₅O₁₉, respectively. Both structures were solved by Patterson method and successive Fourier synthesis, and were refined by full-matrix least-squares refinement based on F values. The test for chirality was made for α-Cs Ti₃P₅O₁₉ by adding to the least-squares refinement one additional parameter, η. The low η value of 0.34 suggested that the crystal could be associated with enantiomorphic twinning. For β-CsTi₃P₅O₁₉, we earlier refined the structure with one Cs atom at a general position having the site occupancy of 0.5. The Cs atom exhibited a very large U_{33} value, indicative of positional disorder. A difference Fourier synthesis based on the atomic coordinates of Ti, P, and O atoms revealed two nonequivalent Cs atoms having the same site occupancy. Therefore, the structure was refined with two Cs atoms each having an occupancy factor of 0.25, subject to the constraint that the two Cs atoms have the same temperature factors. The multiplicities of the Cs atoms in both structures were allowed to vary. The results indicated that the Cs site in the α-phase is fully occupied, and the site occupancy in the β-phase is 0.238(1). The value is slightly lower than 0.25, which could be attributed to incomplete modeling of the disordered Cs atoms. The final cycle of refinement including atomic coordinates, anisotropic thermal parameters, and a secondary extinction coefficient converged at $R = 0.0270$ and $R = 0.0383$ for α- and β-CsTi₃P₅O₁₉, respectively. Secondary extinction corrections were performed because several strong reflections with low 2θ values have F_c values considerably greater than F_o. Calculations were performed by using SHELXTL programs (11). Neutral-atom scattering factors were used and corrections for anomalous dispersion were applied. The crystallographic data are listed in Table 1.

SHG Measurements. The second harmonic genera-

TABLE 1

Crystal Data for α-CsTi₃P₅O₁₉ (I) and β-CsTi₃P₅O₁₉ (II)

	I	II
Crystal system	Monoclinic	Monoclinic
Space group	Cm (No. 8)	$C2/c$ (No. 15)
a (Å)	9.309(2)	10.987(1)
b (Å)	14.081(3)	16.588(1)
c (Å)	6.314(1)	8.7618(8)
β (°)	105.82(3)	100.09(1)
V (Å³)	796.3	1572.2
Z	2	4
ρ_{calc} (g/cm³)	3.067	3.107
μ (cm⁻¹)	43.3	43.3
T (°C)	25	25
λ (Å)	0.71073	0.71073
Scan rate	6°/min	6°/min
Scan mode	$\theta - 2\theta$	$\theta - 2\theta$
Scan width	1.4° below $K\alpha_1$, 1.5° above $K\alpha_2$ (in 2θ)	1.4° below $K\alpha_1$, 1.5° above $K\alpha_2$ (in 2θ)
$2\theta_{max}$ (°)	55	55
Octants collected	$h, k, \pm l$	$h, k, \pm l$
No. of unique reflections	928 ($I > 3\sigma(I)$)	1678 ($I > 3\sigma(I)$)
Refined parameters	135	138
R^a	0.0270	0.0383
R_w^b	0.0314	0.0525
$(\Delta\rho)_{max,min}$	0.75, -1.09 $e/Å^3$	1.38, -1.70 $e/Å^3$
Secondary extinction coefficient	0.00141	0.00148

Note. $\eta = 0.3(1)$.

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. Weighting scheme of form $w^{-1} = \sigma^2(F)$.

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TABLE 2
Atomic Coordinates and Thermal Parameters for α-CsTi$_3$P$_5$O$_{19}$ (I) and β-CsTi$_3$P$_5$O$_{19}$ (II)

Atom	x	y	z	U_{eq} (Å²)[a]
		Compound I		
Cs	−0.09713	0	0.47621	0.0391(3)
Ti(1)	0.2353(2)	0	0.1564(3)	0.0109(5)
Ti(2)	0.1327(1)	0.37654(8)	−0.1813(2)	0.0112(3)
P(1)	0.3297(3)	0	0.6972(4)	0.0103(6)
P(2)	−0.4635(2)	0.1467(1)	0.2702(3)	0.0111(5)
P(3)	0.0000(2)	0.1845(1)	0.0000(3)	0.0107(4)
O(1)	0.2282(8)	0	0.460(1)	0.016(2)
O(2)	0.2256(8)	0	−0.152(1)	0.014(2)
O(3)	−0.3787(5)	0.1449(4)	0.5124(7)	0.016(1)
O(4)	0.4247(5)	0.0896(3)	0.7377(8)	0.013(1)
O(5)	0.3883(7)	0.0952(4)	0.2206(9)	0.024(2)
O(6)	−0.3622(6)	0.1124(3)	0.1351(8)	0.016(1)
O(7)	−0.5014(6)	0.2546(3)	0.2129(8)	0.019(2)
O(8)	−0.3149(8)	0	0.812(1)	0.017(2)
O(9)	0.0815(6)	0.0952(3)	0.0967(9)	0.018(1)
O(10)	0.0756(6)	0.2400(3)	−0.1422(8)	0.016(1)
O(11)	−0.1606(5)	0.1622(4)	−0.1137(9)	0.021(2)
		Compound II		
Cs(1)[b]	0.0113(4)	0.9261(2)	0.1989(9)	0.091(1)
Cs(2)[b]	−0.0049(4)	0.9348(2)	0.3393(8)	0.091(1)
Ti(1)	0.63994(6)	0.11029(4)	−0.01064(7)	0.0107(2)
Ti(2)	0.25	0.25	0	0.0116(3)
P(1)	0.87365(9)	0.20759(5)	0.1831(1)	0.0105(3)
P(2)	0.5	0.20327(8)	0.25	0.0113(4)
P(3)	0.65907(9)	−0.07232(5)	0.1281(1)	0.0109(3)
O(1)	0.5189(3)	−0.0744(2)	0.0917(3)	0.0158(8)
O(2)	0.8070(2)	0.1488(2)	0.0671(3)	0.0163(8)
O(3)	0.7176(3)	−0.1376(2)	0.0405(3)	0.0185(8)
O(4)	0.5814(3)	0.1486(2)	0.1669(3)	0.0163(8)
O(5)	0.9042(3)	0.2844(2)	0.1092(3)	0.0195(9)
O(6)	0.7037(3)	0.0817(2)	−0.1975(3)	0.0171(8)
O(7)	0.8126(3)	0.2193(2)	0.3233(3)	0.0205(9)
O(8)	0.7005(3)	0.0095(2)	0.0773(3)	0.0163(8)
O(9)	0	0.1619(2)	0.25	0.015(1)
O(10)	0.9160(2)	−0.2422(2)	0.1330(3)	0.0155(8)

^{a} U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.
^{b} The occupancy factors for Cs(1) and Cs(2) in β-CsTi$_3$P$_5$O$_{19}$ are fixed at 0.25. The refined occupancy factor is 0.2377(8).

tion (SHG) response of powder α-CsTi$_3$P$_5$O$_{19}$ was measured on an apparatus similar to that described by Dougherty and Kurtz in reflection mode (12). A Q-switched pulsed Nd:YAG laser operating at 1064 nm was used as the radiation source. The sample was loaded in a capillary of 1-mm inner diameter. The sample had a SHG signal about nine times that of quartz, confirming the absence of a center of symmetry in the structure.

RESULTS AND DISCUSSION

Atomic coordinates and thermal parameters are listed in Table 2. Selected bond lengths are given in Table 3.

It was surprising to find at the outset of this work that Cs$_2$TiOP$_2$O$_7$ was the only structurally characterized compound in the Cs–Ti–P–O phase space. The structure of Cs$_2$TiOP$_2$O$_7$, which is isotypic with that of Rb$_2$VOP$_2$O$_7$ (13), consists of sheets of corner-sharing TiO$_5$ square pyramids and P$_2$O$_7$ groups, with the Cs atoms located between the sheets. The two polymorphs of CsTi$_3$P$_5$O$_{19}$ were first reported by Ono in an attempt to synthesize Nasicon-type compounds (14). The composition was determined by electron-probe analysis. The X-ray powder pattern of the high temperature phase, β-CsTi$_3$P$_5$O$_{19}$, was indexed on the basis of a monoclinic unit cell with a = 10.966 Å, b = 16.572 Å, c = 8.754 Å, and β = 100.11°. A single crystal of the β-phase was indexed using a four-circle diffractometer, but its crystal structure was not determined. A single-crystal X-ray study of the low temperature polymorph, α-CsTi$_3$P$_5$O$_{19}$, was not performed because of the small crystal sizes. An unindexed X-ray powder pattern of the low temperature phase was re-

TABLE 3
Selected Bond Lengths (Å) for α-CsTi$_3$P$_5$O$_{19}$ (I) and β-CsTi$_3$P$_5$O$_{19}$ (II)

|		Compound I		
Cs–O(1)	3.058(8)		Cs–O(2)	3.268(6)
Cs–O(3)	3.378(5) (2×)		Cs–O(6)	3.215(5) (2×)
Cs–O(8)	3.310(8)		Cs–O(9)	3.532(6) (2×)
Cs–O(11)	3.620(6) (2×)			
Ti(1)–O(1)	1.935(8)		Ti(1)–O(2)	1.927(7)
Ti(1)–O(5)	1.917(6) (2×)		Ti(1)–O(9)	1.921(5) (2×)
Ti(2)–O(3)	1.931(5)		Ti(2)–O(4)	1.922(5)
Ti(2)–O(6)	1.991(6)		Ti(2)–O(8)	1.809(2)
Ti(2)–O(10)	2.027(5)		Ti(2)–O(11)	1.933(5)
P(1)–O(1)	1.538(7)		P(1)–O(2)	1.530(8)
P(1)–O(4)	1.522(5) (2×)			
P(2)–O(3)	1.517(5)		P(2)–O(5)	1.514(6)
P(2)–O(6)	1.513(6)		P(2)–O(7)	1.578(5)
P(3)–O(7)	1.598(6)		P(3)–O(9)	1.509(5)
P(3)–O(10)	1.502(6)		P(3)–O(11)	1.505(5)
		Compound II		
Cs(1)–O(2)	3.548(7)		Cs(1)–O(3)	3.448(5)
Cs(1)–O(3)	3.581(6)		Cs(1)–O(6)	3.136(6)
Cs(1)–O(6)	3.652(6)		Cs(1)–O(8)	3.665(5)
Cs(1)–O(8)	3.689(5)		Cs(1)–O(10)	3.002(5)
Cs(1)–O(10)	3.192(5)			
Cs(2)–O(2)	3.409(6)		Cs(2)–O(3)	3.370(5)
Cs(2)–O(6)	3.173(5)		Cs(2)–O(8)	3.522(5)
Cs(2)–O(10)	3.477(5)		Cs(2)–O(10)	3.090(4)
Ti(1)–O(1)	1.863(3)		Ti(1)–O(2)	1.951(3)
Ti(1)–O(4)	1.894(3)		Ti(1)–O(5)	1.971(3)
Ti(1)–O(6)	1.949(3)		Ti(1)–O(8)	1.911(3)
Ti(2)–O(3)	1.942(3) (2×)		Ti(2)–O(7)	1.872(3) (2×)
Ti(2)–O(10)	1.989(3) (2×)			
P(1)–O(2)	1.503(3)		P(1)–O(5)	1.494(3)
P(1)–O(7)	1.512(3)		P(1)–O(9)	1.600(2)
P(2)–O(4)	1.543(3) (2×)		P(2)–O(10)	1.546(3) (2×)
P(3)–O(1)	1.517(3)		P(3)–O(3)	1.533(3)
P(3)–O(6)	1.528(3)		P(3)–O(8)	1.523(3)
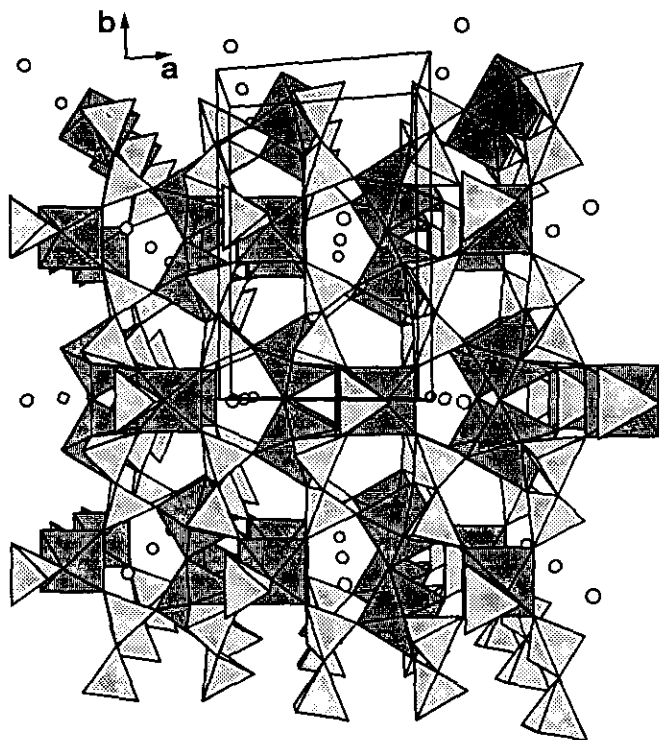
FIG. 1. Polyhedral view of the α-CsTi₃P₅O₁₉ structure along the [001] direction. In this representation the corners of octahedra and tetrahedra are O atoms and the Ti and P atoms are at the center of each octahedron and tetrahedron, respectively. Open circles are Cs atoms.

consists of two different tunnels along the c-axis. The Cs⁺ cations are located in the tunnel with pentagonal window which is formed by the edges of three octahedra and two tetrahedra. The other type of tunnel is empty. The coordination number of Cs⁺ is determined on the basis of the maximum gap in the Cs⁺–O distances ranked in increasing order. The agreement with the valence sum rule and the maximum cation–anion distance, L_{max}, suggested by Donnay and Allmann (15) was also checked. The cesium cation is coordinated by 11 oxygen atoms and the 12th oxygen atom is at 4.04 Å. The bond valence sum (16) for the cesium cation is 0.92. The P(1)O₄ tetrahedron is quite regular. The PO₄ tetrahedra of P₂O₇ group are in a semieclipsed configuration. The P atoms are displaced away from the bridging oxygen, O(7), so that one longer and three shorter P–O bonds are formed. The P–O–P bond angle is 131.1°. The Ti(1)O₆ octahedron is essentially regular. In contrast, each Ti atom in the dimeric Ti₂O₁₁ unit is in a distorted octahedral coordination of one bridging oxide ion and five phosphate oxygens. The titanium-to-bridging oxide distance is considerably shorter than the other Ti–O distances. The titanyl bridge is symmetric, the two TiO₆ octahedra are in eclipsed configuration, and the Ti–O–Ti bond angle is 147.9°. The Ti–O distortion in the dimeric unit is greatly reduced compared to that found in KTiOPO₄-type materials.

β-CsTi₃P₅O₁₉.   This structure is built up from TiO₆ octahedra, PO₄ tetrahedra, and P₂O₇ groups, but does not

ported. The X-ray powder patterns of α- and β-CsTi₃P₅O₁₉ prepared in the present study agree well with those of the low and high temperature forms, respectively. In the following section, single-crystal X-ray structures of the two polymorphs are reported.

α-CsTi₃P₅O₁₉.   As shown in Figs. 1 and 2, the framework of this polymorph consists of Ti(2)₂O₁₁ units formed by two corner-sharing Ti(2)O₆ octahedra, discrete Ti(1)O₆ octahedra, P(1)O₄ tetrahedra, and P(2)P(3)O₇ groups. Atoms Ti(1), P(1), and the bridging oxygen, O(8), in Ti₂O₁₁ sit on mirror planes. Each dimeric Ti₂O₁₁ unit shares corners with six different P₂O₇ groups and one PO₄ tetrahedron. Two of the six P₂O₇ groups are coordinated to the Ti atoms as bidentate ligands. The PO₄ tetrahedron bridges over the two Ti atoms in a dimeric unit. Each Ti(1)O₆ octahedron shares corners with four different P₂O₇ groups and two PO₄ tetrahedra. The building block of the framework consists of one TiO₆ octahedron, one dimeric Ti₂O₁₁ unit, two PO₄ tetrahedra, and eight P₂O₇ groups, [Ti(Ti₂O)(PO₄)₂(P₂O₇)₈]. Each PO₄ tetrahedron is coordinated to two TiO₆ octahedra belonging to two building blocks and each P₂O₇ group is bonded to four blocks such that a three-dimensional framework with the stoichiometry ³/∞[Ti(Ti₂O)(PO₄)₂/₂(P₂O₇)₈/₄] is formed. The framework

FIG. 2.   The coordination of phoshate ligands around dimeric Ti₂O₁₁ unit and monomeric TiO₆ octahedron in α-CsTi₃P₅O₁₉. Thermal ellipsoids are shown at the 60% probability level.
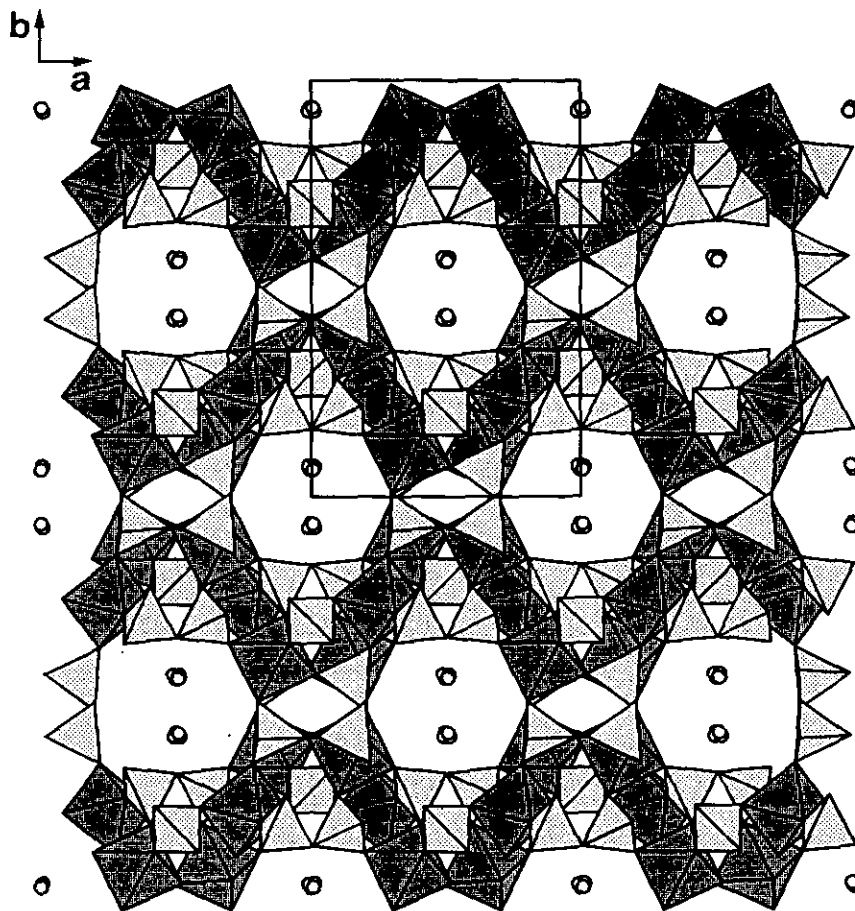
FIG. 3. Polyhedral view of the β-CsTi$_3$P$_5$O$_{19}$ structure along [001]. Open circles are Cs atoms.

contain a dimeric Ti$_2$O$_{11}$ unit as was observed in the α-phase. Atom P(2) and the bridging oxygen, O(9), in P$_2$O$_7$ sit on twofold axes, and atom Ti(2) lies on a site of $\bar{1}$ symmetry. Each Ti(1)O$_6$ octahedron shares six corners with two P(1)$_2$O$_7$ groups, one P(2)O$_4$, and three P(3)O$_4$ tetrahedra. Each Ti(2)O$_6$ octahedron shares corners with two P(1)$_2$O$_7$, two P(2)O$_4$, and two P(3)O$_4$. The building block of the framework consists of two Ti(1)O$_6$, one Ti(2)O$_6$, four P(1)$_2$O$_7$, two P(2)O$_4$, and eight P(3)O$_4$.

[$Ti(1)_2Ti(2)(P(1)_2O_7)_4(P(2)O_4)_2(P(3)O_4)_8$]. Each P(1)$_2O_7$ is coordinated to four Ti(1) and two Ti(2) belonging to four blocks, each P(2)O$_4$ is bonded to two blocks, and each P(3)O$_4$ links four blocks such that a three-dimensional framework with the stoichiometry $^3_\infty$[Ti$_2$Ti(P$_2$O$_7$)$_{4/4}$(PO$_4$)$_{2/2}$(PO$_4$)$_{8/4}$] is formed. As shown in Fig. 3, the framework consists of large straight tunnels along the c-axis, where the Cs$^+$ cations are located. The window of the tunnel is formed by the edges of four octahedra and five tetrahedra (Fig. 4). The diameter of the window is approximately 7 Å. Two adjacent windows along [001] are related by an inversion center. The Cs atoms are disordered in four closely spaced sites. The four sites form two groups which
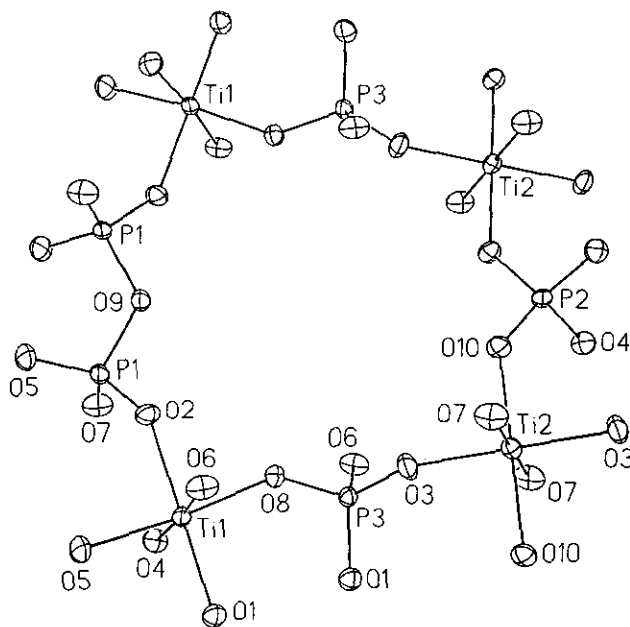

FIG. 4. A nine-sided window constituting the one-dimensional tunnel in β-CsTi$_3$P$_5$O$_{19}$. The view is along [001]. Thermal ellipsoids are shown at the 60% probability level.

are related by the symmetry element $-x$, y, $0.5 - z$. The Cs $\cdots$ Cs distances are very short (0.36–1.59 Å), precluding simultaneous Cs occupancy of these sites. A model of two Cs atoms at general positions each with a site occupancy of 0.25 was used in the structure refinement. The very anisotropic thermal parameters of the Cs atoms ($U_{33} \approx 6.5 U_{11} \approx 4.8 U_{22}$) indicate some further disorder in the tunnel direction. The bond valence sums for Cs(1) and Cs(2) are 0.72 and 0.54, respectively, indicating that they are loosely bound. Both P(2)O$_4$ and P(3)O$_4$ tetrahedra are quite regular with the PO$_4$ tetrahedra of the P$_2$O$_7$ group in a staggered configuration. The P–O–P bond angle involving the bridging oxygen, O(9), is 123.5°. The octahedral distortion can be estimated by using the equation $\Delta = (1/6)\Sigma[(R_i - \overline{R})/\overline{R}]^2$, where R_i is the individual bond length and $\overline{R}$ is the average bond length (17). The calculation results show that both TiO$_6$ octahedra in the β-phase are considerably more distorted than Ti(1)O$_6$ in the α-phase ($10^4 \times \Delta = 3.8$ and 6.2 vs 0.1).

We have presented the flux crystal growth and crystal structures of high and low temperature phases of a cesium titanyl phosphate. The two polymorphs have considerably different three-dimensional networks of vertex-sharing octahedra and tetrahedra. Both frameworks have tunnels where the cesium cations are located. There does not appear an obvious structural relationship between the two polymorphs. Compared to the low temperature phase, the structure of β-CsTi$_3$P$_5$O$_{19}$ is more disordered with a higher symmetry, and has a more open channel in which the Cs atoms have lower coordination numbers. However, α-CsTi$_3$P$_5$O$_{19}$ has a lower density, which may be attributed to the presence of empty tunnels.

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