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Journal of Solid State Chemistry 179 (2006) 3681–3687

JOURNAL OF SOLID STATE CHEMISTRY

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A crystal structure of mixed-metal dianionic phosphate $Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$

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Received 7 June 2006; received in revised form 13 July 2006; accepted 3 August 2006
Available online 17 August 2006

Abstract

The single crystals of caesium magnesium titanium (IV) tri-oxo-tetrakis-diphosphate bis-monophosphate, $Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$, crystallize in sp. gr. *P*-1 (No. 2) with cell parameters $a = 6.3245(4)$, $b = 9.5470(4)$, $c = 15.1892(9)$ Å, $\alpha = 72.760(4)$, $\beta = 85.689(5)$, $\gamma = 73.717(4)$, $z = 1$. The titled compound possesses a three-dimensional tunnel structure built by the corner-sharing of distorted $[TiO_6]$ octahedra, $[Ti_2O_{11}]$ bioctahedra, $[PO_4]$ monophosphate and $[P_2O_7]$ pyrophosphate groups. The Cs^+ cations are located in the tunnels. The partial substitution of Ti positions with Mg atoms is observed. The negative charge of the framework is balanced by Cs cations and Mg atoms leading to pronounced concurrency and orientation disorder in the $[P_2O_7]$ groups, which coordinate both.

Keywords: Phosphates; Crystal structure; Single-crystal X-ray diffraction; Disorder; Dianionic; Tunnel structure

1. Introduction

A wide variety of complex transition metals phosphates of caesium are known nowadays among them containing titan, molybdenum, tantalum, etc. These compounds frequently form low symmetry crystals: triclinic $Cs_4Mo_{10}P_{18}O_{66}$ [1], $CsTa_2P_5O_{18}$ [2], etc., and also monoclinic $Cs_2Mo_4P_6O_{26}$ [3], $Cs_3Mo_8O_{11}(PO_4)_8$ [4], $CsPr(PO_3)_4$ [5]. A large size of caesium cation and its high coordination numbers enables to form condensed phosphate anions (such as diphosphate, triphosphate and polyphosphates) in order to stabilize phosphates frameworks. Caesium phosphates with cyclo-polyphosphate anions are well known compounds. These were synthesized cyclo-triphosphate $CsCdP_3O_9$ [6], cyclo-tetraphosphates $CsLnP_4O_{12}$ ($Ln =$ La–Lu) [7], cyclo-hexaphosphates $CsUO_2(PO_3)_3$ [8], $CsZnV(P_6O_{18})$ [9], $Cs_3Mn_4(P_6O_{18})_2$ [10], $CsMn_2(P_6O_{18})$ [10], $Cs_3M^{II}_3M^{III}(P_6O_{18})_2$ (M^{II}—Mg, Zn, Cd; M^{III}—V, Mn, In) [11], cyclo-dodecaphosphate $Cs_3V_3(P_{12}O_{36})$ [12], etc. Another family of caesium phosphates is represented by the compounds containing catena-polyphosphate anions: diphosphates $Cs_2SrP_2O_7$ [13], $Cs_2VOP_2O_7$ [14], $Cs_2UO_2P_2O_7$ [15], $CsM^{III}P_2O_7$ (M^{III}—Cr, Mo, V, Fe, Yb, Y) [16–21], triphosphates $Cs_2M^{III}P_3O_{10}$ (M^{III}—Ga, Al, Cr) [22], pentaphosphates $CsM^{III}_2P_5O_{16}$ (M^{III}—V, Fe) [23] and varies polyphosphates $CsLnP_4O_{12}$ ($Ln =$ La–Lu) [7], $Cs_2M^{II}P_4O_{12}$ (M^{II}—Co, Mn) [24,25]. Some complex phosphate with the same general formula can have different structure. For example, compounds with general composition of $CsLnP_4O_{12}$ ($Ln =$ La–Lu) [7] crystallize forming 3d-structure which are build up from the infinite polyphosphate chains or from the cyclo-tetraphosphate anions interlinked with metal polyhedra. Usually such phosphates can be obtained in different polymorphs depending on their preparation technique.

There are many mixed anionic caesium containing phosphates. Usually they are formed combining cyclo- and catena-anions which contain different quantities of phosphorus atoms. $CsTa_2(PO_4)_2P_3O_{10}$ [2] contains orthophosphate and

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doi:10.1016/j.jssc.2006.08.013

triphosphate anions, $Cs_3Pb_2(P_4O_{12})(PO_3)_3$ [26] contains cyclotetraphosphate and polyphosphate anions.

A large number of new frameworks have been discovered during the investigation of various titanium (IV) phosphates. Nevertheless, only a few Ti(IV) phosphates containing caesium are actually known: $CsTiPO_5$ [27], $Cs_2TiP_2O_8$ [28], α-, β-$CsTi_3P_5O_{19}$ [29] and $Cs_3Ti_5P_7O_{29}$ [30]. Starting from the earlier observations [31,32], the application of multicomponent fluxes, which contain simultaneously alkaline and alkaline-earth metals enables to crystallize novel phosphates unique with respect to building units in their frameworks or the frameworks topology.

Assessing the potentialities of the complex fluxes, we have examined the Cs–Mg–Ti–P–O system, having supposed that the caesium–magnesium pair is capable to stabilize original phosphates frameworks. We report here the crystal structure of caesium magnesium titanium (IV) tri-oxo-tetrakis-diphosphate bis-monophosphate $Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$ and denoted hereafter as (I) obtained for the first time.

2. Experimental

2.1. Synthesis

Compound (I) was easily obtained in two steps combining a solid-state reaction and a flux growth technique.

In the first step, a mixture of 3 g $CsPO_3$ (14.15 mmol), 0.850 g TiO_2 (10.62 mmol) and 0.142 g MgO (3.54 mmol) was grinded, placed into a platinum crucible, and then 0.5 ml of 80 mass% solution of H_3PO_4 (7.08 mmol) was added to the reagents. The mixture prepared was gradually heated at a heating rate 25 K h^{-1} up to 1073 K to decompose the orthophosphate acid and to evaporate water. In the second step, the sintered mixture was grinded again to achieve better reactivity of the components and was heated up to 1420 K for 3 h to obtain a flux. To crystallize (I) in a single phase the resulted flux was cooled at a rate 20 K h^{-1} down to 1173 K and finally quenched to room temperature. After that, the colorless needle-like crystals of (I) were separated from the flux by washing in boiling water.

Table 1
Crystal Data and Refinement of $Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$

	$Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$	
Crystal data		
Crystal system	Triclinic	
Space group	$P-1$	
Cell parameters (Å, °)	$a = 6.3245(4)$	$\alpha = 72.760(4)$
	$b = 9.5470(4)$	$\beta = 85.689(5)$
	$c = 15.1892(9)$	$\gamma = 73.717(4)$
V (Å^3)	840.75(8)	
Z	1	
$\rho_{calc.}$ (g/cm^3)	3.39	
Crystal dimensions (mm)	0.15 × 0.05 × 0.05	
Data collection		
Wavelength (Å)	0.71073	
Monochromator	Graphite	
Scan mode	φ and ω	
μ (mm^{-1})	5.879	
Absorption correction	multiscan	
T_{min}, T_{max}	0.5653, 0.6832	
Number of reflections	17522	
Independent reflections	4872	
Reflections with $>2\sigma(I)$	4066	
$R_{int.}$	0.0298	
Theta max. (°)	30	
$h=$, $k=$, $l=$	$-8\rightarrow8;-12\rightarrow13;-21\rightarrow21$	
$F(0\,0\,0)$	799.7	
Solution and refinement		
Primary solution method	Direct	
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.0261P)^2+3.9590P]$ where $P=(F_o^2+2F_c^2)/3$	
R_1(all)	0.0454	
wR_2	0.0761	
S	1.051	
Number of parameters	321	
Number of restraints	3	
Extinction coeff.	0.0021(3)	
$(\Delta\rho)_{max,\ min}$ (e Å^{-3})	2.544, −2.742	

2.2. Analytical procedure

The analysis of the elements Cs, Ti, Mg and P was performed by energy dispersive spectroscopy using a Link Isis analyzer mounted on a Philips XL 30 FE 6 scanning electron microscope. The atomic ratio of the elements in (I) was found to be 3.7:5.8:0.6:10. The measurements were made on the same sample as for X-ray investigations. Additional ICP determination of the Cs, Ti and Mg amounts in (I) was performed on "Spectroflame Modula ICP" ("Sectro", Germany) instrument. The atomic ratio which was found is close to those found by energy dispersive spectroscopy and equal to 3.67:5.75:0.65.

The powder X-ray diffraction (DRON-3 with monochromatized Cu$K\alpha_1$ radiation $\lambda = 1.54056$) confirmed that the obtained polycrystalline sample of (I) is well crystallized and single phased. The X-ray powder diffraction patterns of the powder samples coincide with the generated from the single-crystal structural data. The impurities were not detected by the powder XRD. Non-crystalline impurities were not found by the optical microscopy.

As the sample is colorless it was supposed that obtained compound contains no titanium (III). To check this we performed EPR investigations at 70 and 298 K. The titanium (III) was not detected.

2.3. X-ray data collection and crystal data

For single crystal X-ray diffraction colorless needle crystal of (I) was selected. X-ray experiment was performed on Oxford-Diffraction XCalibur 3 diffractometer. Multi-scan absorption correction was applied to the obtained data [33]. An experiment was performed at 295 K. Cell parameters and space group were determined by 450 reflections ($15^\circ < \theta < 25^\circ$). Crystal data and experimental conditions for intensity measurements and refinement are listed in Table 1.

The structure was solved with direct method using SHELXS-97 [34] and refined anisotropically using

Table 2
Atomic coordinates and U_{eq} for $Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$

Atom	Occupancy	x	y	z	U_{eq}
Cs1	0.885(2)	0	1	0.5	0.02819(16)
Cs2*A*	0.915(3)	0.05175(9)	0.73172(6)	0.27267(8)	0.04219(18)
Cs2*B*	0.085(3)	0.0721(10)	0.7507(6)	0.2348(7)	0.04219(18)
Cs3*A*	0.1850(9)	0.1663(4)	0.83197(19)	−0.02167(11)	0.0281(3)
Cs3*B*	0.1356(12)	−0.0143(4)	0.8201(3)	−0.03112(15)	0.0281(6)
Cs3*C*	0.0864(11)	0.0691(9)	0.8349(5)	−0.0132(3)	0.0281(6)
Ti1/Mg1	0.9254(10)/0.0746(14)	0.37966(10)	0.08127(7)	0.25264(4)	0.00801(13)
Ti2	1	0.71202(10)	0.52626(7)	0.12783(4)	0.00971(12)
Ti3/Mg3	0.9626(17)/0.037(2)	0.28519(10)	0.57631(7)	0.63060(4)	0.00877(13)
Mg4	0.187(6)	0.0050(13)	0.9639(7)	−0.0050(6)	0.015(2)
P1*A*	0.5	0.5895(4)	0.9047(2)	0.09659(13)	0.0147(4)
P1*B*	0.5	0.4553(4)	0.8910(2)	0.09348(13)	0.0155(4)
P2	1	0.25707(14)	0.43878(10)	0.10462(6)	0.00979(16)
P3	1	0.26791(14)	0.31080(10)	0.39673(6)	0.00905(16)
P4	1	0.50308(14)	0.74436(10)	0.43532(6)	0.00842(16)
P5	1	0.83800(14)	0.17352(10)	0.25424(6)	0.00974(16)
O1	1	0.4336(4)	0.8872(3)	0.35605(18)	0.0175(5)
O2	1	0.3116(4)	0.1920(3)	0.34610(18)	0.0165(5)
O3	1	0.0746(4)	0.0721(3)	0.25704(17)	0.0127(5)
O4	1	0.3133(4)	0.2685(3)	0.15812(18)	0.0179(5)
O5	1	0.4501(6)	0.9618(4)	0.1672(2)	0.0301(7)
O6	1	0.6128(6)	0.7453(3)	0.1035(2)	0.0310(7)
O7*A*	0.5	0.8120(10)	0.9244(8)	0.0998(4)	0.0303(14)
O7*B*	0.5	0.2296(11)	0.8785(8)	0.0859(5)	0.0331(15)
O8	1	0.5	1	0	0.0427(13)
O9	1	0.0232(4)	0.5207(3)	0.12567(18)	0.0146(5)
O10	1	0.2796(4)	0.4549(3)	0.00193(17)	0.0159(5)
O11	1	0.4106(4)	0.5152(3)	0.13434(17)	0.0143(5)
O12	1	0.0261(4)	0.3900(3)	0.39962(18)	0.0143(5)
O13	1	0.3441(4)	0.2146(3)	0.50105(17)	0.0140(5)
O14	1	0.3984(4)	0.4270(3)	0.36422(17)	0.0125(5)
O15	1	0.3108(4)	0.7055(3)	0.49238(17)	0.0143(5)
O16	1	0.6477(4)	0.6119(3)	0.40596(19)	0.0176(5)
O17	1	0.7956(4)	0.2302(3)	0.33973(17)	0.0139(5)
O18	1	0.7988(4)	0.3057(3)	0.16594(18)	0.0150(5)
O19	1	0.6862(4)	0.0724(3)	0.25684(18)	0.0137(5)
O20	1	0.7160(4)	0.5223(3)	0.25375(17)	0.0137(5)

SHELXL-97 [34]. After the refinement of the basic model and the accurate definition of positions Cs1, Cs2 and Cs3, some more Fourier-peaks with high electronic density was determined: one and three near to the Cs2 and Cs3 atoms position, respectively. Taking into account a local coordination environment of these peaks and chemical analysis data, it is supposed that near to the Cs2 position there is an extra position of caesium, whereas the three peaks close to Cs3 refer to the two positions of caesium atoms and the one position of magnesium atom, accordingly. The occupancy of positions Ti1, Ti2, Ti3 and Mg1, Mg2 and Mg3 as positions corresponding to the titanium ones was refined by using linear free variable restraints (SUMP) [34] with regard to the compound electroneutrality. A considerable value of U_{eq}(O8) for position O8 and high values of U_{eqs} for both P1*A* and P1*B* positions concern with the origin of the diphosphate group which adopt the atoms. As the diphosphate group is disordered and equiprobably orientated in two opposite directions, so the P1*A* and P1*B* positions are half occupied. The occupancy of caesium sites was refined using equivalent atomic displacement parameters constrains (EADP) [34] for different types of the caesium. Total occupancy of the Cs3*A*, Cs3*B*, Cs3*C* and Mg4 sites is less then 1.

The atomic coordinates, occupancies and U_{eq} are listed in Table 2.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-416666.

3. Results and discussion

3.1. Crystal structure

The projection of the structure of (I) along *a* (Fig. 1) shows the three-dimensional character of the $[Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2]_\infty$ framework forming large tunnels running along *a*, where the Cs^+ cations are located. The framework built up of four sorts of units sharing their apices: $[PO_4]$ tetrahedra, diphosphate groups $[P_2O_7]$, octahedral $[TiO_6]$ and bioctahedral units $[Ti_2O_{11}]$. The mixed titanophosphate three-dimensional framework of (I) delimits one six-side (1) and two different five-side (2, 3) separated open tunnels.

The six-side tunnel is formed by two $[TiO_6]$ octahedra interlinked with two eclipsed $[P_2O_7]$ groups (Fig. 1 marked 1). The first five-side tunnel (Fig. 1 marked 2) is formed by the $[Ti_2O_{11}]$ bioctahedron connected with two $[PO_4]$ tetrahedra of different diphosphate groups and one $[TiO_6]$ octahedron. The second five-side tunnel (Fig. 1 marked 3) is formed by isolated $[TiO_6]$ octahedron and one of $[TiO_6]$ octahedron belonging to $[Ti_2O_{11}]$ bioctahedron which are connected with isolated orthophosphate tetrahedron and eclipsed $[P_2O_7]$ group. Cs1, Cs2 and Cs3 atoms

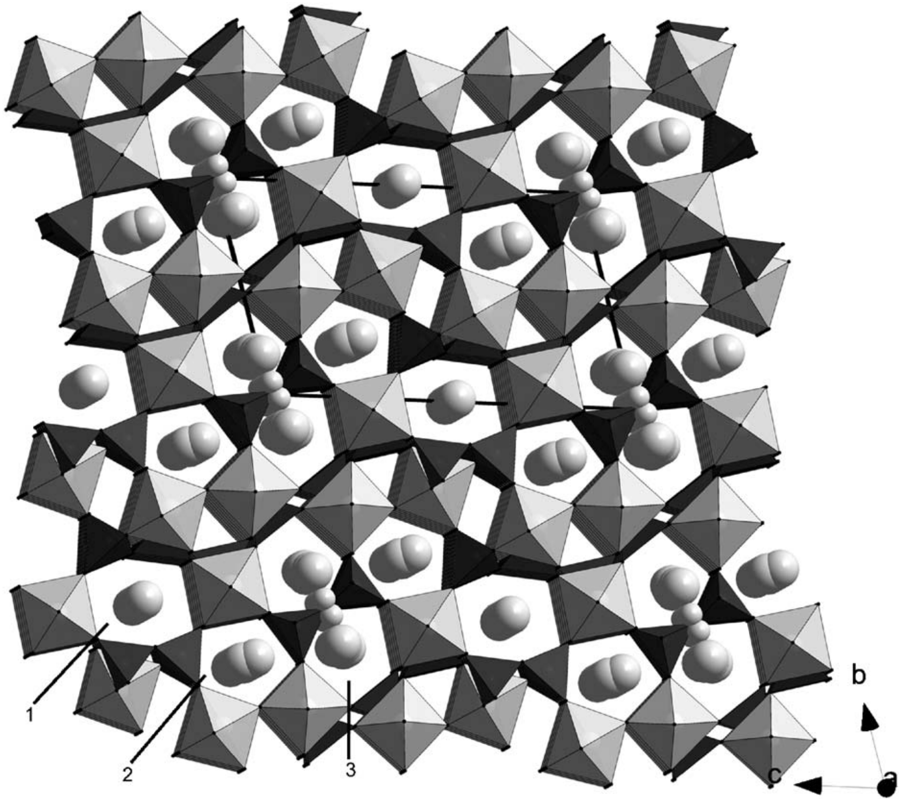

Fig. 1. Projection of $Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$ on the *bc* plane. Metal octahedra are shown with light gray shading, PO_4 tetrahedra with dark gray shading, Mg atoms are small light gray circles and Cs atoms are large light gray circles.

Table 3
Selected bond distances (Å) and angles (deg) for $Cs_{3.70}Mg_{0.60}Ti_{2.78}(TiO)_3(P_2O_7)_4(PO_4)_2$

Ti1–O4	1.892(3)	P1*A*–O6	1.460(3)
Ti1–O5^{v}	1.920(3)	P1*A*–O5	1.470(3)
Ti1–O19	1.922(2)	P1*A*–O7*A*	1.477(6)
Ti1–O3	1.951(2)	P1*A*–O8	1.5316(19)
Ti1–O2	1.965(3)		
Ti1–O1^{v}	2.004(3)	P1*B*–O6	1.439(4)
		P1*B*–O5	1.465(3)
Ti2–O20	1.904(3)	P1*B*–O7B	1.481(6)
Ti2–O10^{iv}	1.924(3)	P1*B*–O8	1.5519(19)
Ti2–O11	1.932(2)		
Ti2–O6	1.935(3)	P2–O10	1.521(3)
Ti2–O18	1.936(3)	P2–O9	1.526(3)
Ti2–O9^{viii}	1.952(2)	P2–O11	1.529(3)
		P2–O4	1.538(3)
Ti3–O20^{i}	1.730(3)		
Ti3–O17^{i}	1.951(3)	P3–O2	1.504(3)
Ti3–O16^{i}	1.961(3)	P3–O12	1.508(3)
Ti3–O12^{ii}	1.971(2)	P3–O14	1.511(2)
Ti3–O14^{i}	1.999(2)	P3–O13	1.610(3)
Ti3–O15	2.117(3)		
		P4–O16	1.503(3)
		P4–O15	1.507(2)
Mg4–O7*B*	1.889(10)	P4–O1	1.508(3)
Mg4–O7*A*^{iii}	1.944(10)	P4–O13^{i}	1.612(3)
Mg4–O7*B*^{vii}	1.975(10)		
Mg4–O7*A*^{viii}	2.020(10)		
		P5–O18	1.524(3)
		P5–O17	1.527(3)
		P5–O19	1.532(2)
		P5–O3^{viii}	1.533(3)
		P1*A*–O8–P1*B*^{viii}	146.01(10)
		P3–O13—P4^{i}	125.63(16)

Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) $-x$, $1-y$, $1-z$; (iii) $x-1$, y, z; (iv) $1-x$, $1-y$, $-z$; (v) x, $y-1$, z; (vi) $1+x$, y, z; (vii) $-x$, $2-y$, $-z$; (viii) $1-x$, $2-y$, $-z$.

occupies sites in (1), (2) and (3) tunnels, respectively. The occupancy of Cs1 is 0.885(2). The Cs2 atoms are disordered between two sites Cs2*A* and Cs2*B* with occupancy of 0.915(3) and of 0.085(3), respectively. The Cs3 atoms are disordered between three sites Cs3*A*, Cs3*B* and Cs3*C* which occupancies are 0.1850(9), 0.1356(12) and 0.0864(11).

There are three types of $[TiO_6]$ octahedra in (I). Octahedra $[Ti1O_6]$ are isolated, while octahedra $[Ti2O_6]$ and $[Ti3O_6]$ are linked via O20 atom forming $[O_5Ti2O20Ti3O_5]$ bioctahedron.

A wide range of Ti–O distances [1.730(3)–2.117(3) Å] are observed in (I). The titanium octahedra are distorted according to bonds lengths and angles analysis. Selected bond lengths are listed in Table 3. $[Ti1O_6]$ and $[Ti2O_6]$ octahedra are slightly distorted. An axial bond Ti1–O4 is the shortest and Ti1–O1 is the longest. Another binding character is observed for the $[Ti2O_6]$ octahedron. This octahedron is squeezed along the O20–Ti2–O10 axis. $[Ti3O_6]$ polyhedron has the highest distortion degree. A shape of the Ti3 oxygen environment is close to that in $[Ti1O_6]$, where one bond is short and the opposite is long.

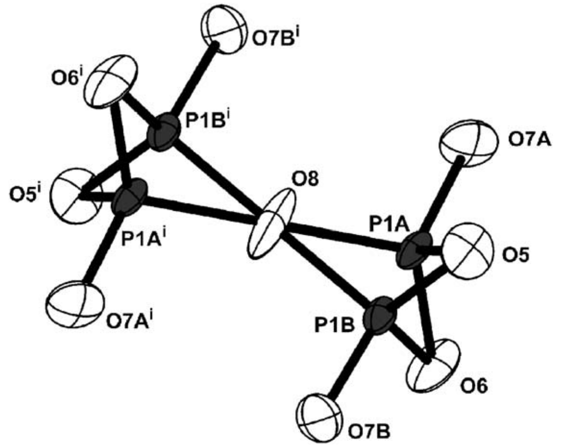

Fig. 2. View of disordered $[O_3P1AOP1BO_3]$ diphosphate group (50% probability displacement ellipsoids). Symmetry codes: (i) $1-x$, $2-y$, $-z$.

We indicated a rather short distance between bridging O20 atom and Ti3 atom with the value of 1.730(3) Å assigning as multiple one (Ti–O bond valence is 1.258). The refined value of the Ti3–O20 distance is comparable with those found in the structure of $KTiOPO_4$ [35]. The terminal titanyl distances in $KTiOPO_4$ [35] have values of 1.717(4) Å for Ti1–O and 1.738(4) Å for Ti2–O. Mg(1) and Mg(3) atoms adopt Ti1 and Ti3 sites with occupancies 0.0746(14) and 0.037(2), accordingly. The distortion degree of $[TiO_6]$ octahedrons effects significantly on the occupation of Ti position with Mg, and $[Ti_2O_{11}]$ bioctahedron can be considered as a less favorable unit for Mg inclusion.

There are two independent orthophosphate $[P2O_4]$ and $[P5O_4]$ groups and two types of diphosphate $[O_3P3OP4O_3]$ and $[O_3P1AOP1BO_3]$ groups in (I). The interatomic distances and angles (listed in Table 3) show that the $[PO_4]$ tetrahedra, are almost regular with classical P–O bonds ranging from 1.439(4) to 1.612(3) Å [36]. Bonds between bridging oxygen atom and phosphorus atoms are longer with a value near 1.6 Å in diphosphate groups. Both diphosphates have eclipsed conformation. For $[O_3P1AOP1BO_3]$ diphosphate group orientation disorder is observed (Fig. 2).

Mg4 atoms, split by the two positions with 0.187(6) site occupancy and interatomic distances equated to 0.733(13) Å, are coordinated by four oxygen atoms belonging to two diphosphate groups and forming distorted planoquadratic environment with the Mg4–O bond lengths of 1.889(10), 1.944(10), 1.975(10) and 2.020(10) Å. Two configurations (1) or (2) for $[P1_2O_7]$ groups are possible depending on the atoms situated between the groups i.e. Cs3*A*, Cs3*B* and Cs3*C* or Mg4 (Fig. 3). Distances between Cs3 and Mg4 sites are in range of 1.456(8)–2.302(9) Å. According to this fact both Cs3 and Mg4 atoms cannot occupy their positions at the same time. The concurrent filling of the Cs3*A*, Cs3*B*, Cs3*C* and Mg4 position is observed in (I).

Cs3 position splitting gives three sites Cs3*A*, Cs3*B* and Cs3*C* with the general occupancy equal to 0.407. The

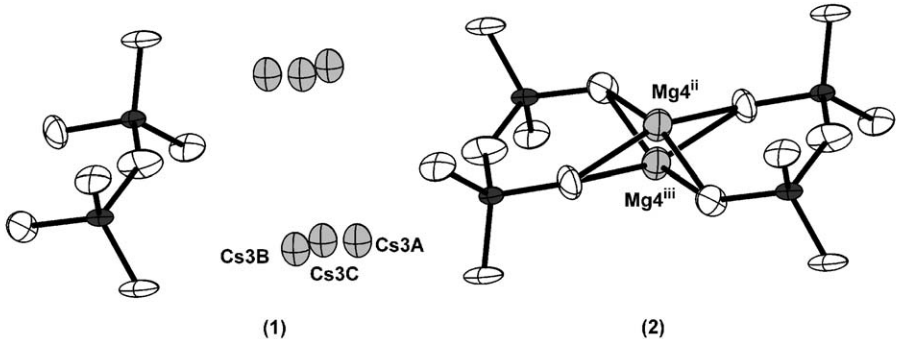

Fig. 3. Two possible configurations (1) or (2) for [$P1_2O_7$] diphosphate group (50% probability displacement ellipsoids). Symmetry codes: (ii) $-1-x$, $2-y$, $-z$; (iii) $-1+x$, y, z.

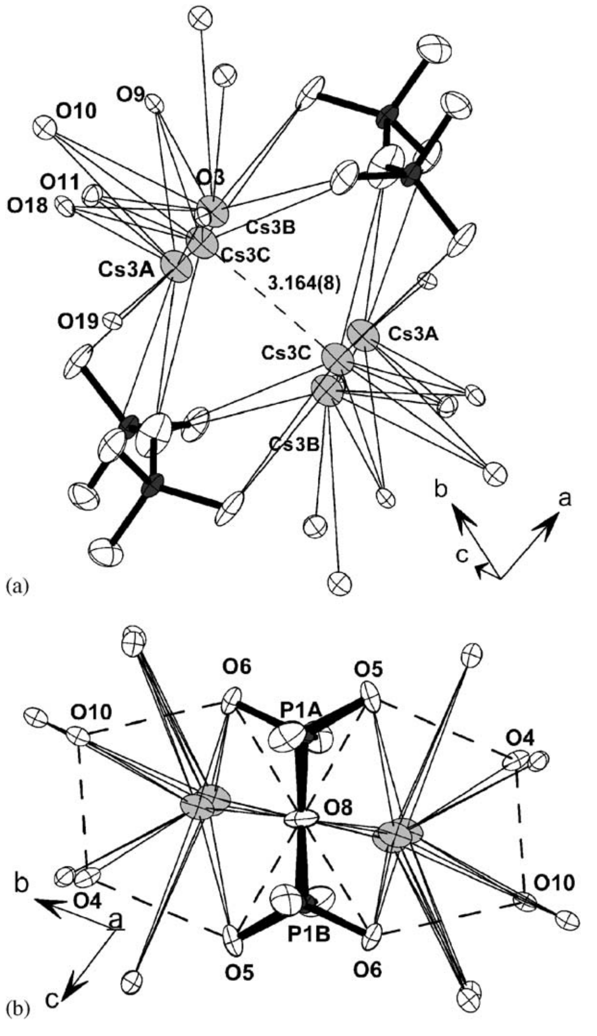

Fig. 4. View of oxygen environment of Cs3 atoms. Allocation of Cs3 atoms in five side tunnel (3). (50% probability displacement ellipsoids). White ellipsoids are oxygen atoms, light gray—caesium atoms, dark gray—phosphorus atoms. (a) Best view of oxygen environment of Cs3 atoms. (b) View along axis *a*. The dashed line limits the tunnel shape.

splitting of the Cs3 position shows the banana like shape. Such shape fits to the shape of tunnel. Cs3–O7A(O7B) interatomic distances are close to 2 Å that has no physical reason. As the diphosphate group which coordinates Cs3 atoms is disordered then the caesium atoms can occupy sites only in configuration 1 (Fig. 3). In this case the Cs3 atom has no contacts with the O7A, O7B and Mg4 atoms. Banana like shape of the Cs3 position splitting can be explained by the existing of the free interatomic space (exchanging space between two tunnels) between the nearest Cs3*A*(Cs3*B*, Cs3*C*) and Cs3*A*(Cs3*B*, Cs3*C*) sites. The shortest contact between Cs3*C* and Cs3*C* positions is equal to 3.164(8) Å. From the other side, the Cs3 oxygen environment (O3, O9, O10, O11, O18 and O19) belongs to Ti1 and Ti2 polyhedra (a part of the hard framework). Cs3 atoms trying to fill its open polyhedra deeply insert between two diphosphate groups (Fig. 4).

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