

SYNTHESIS AND STRUCTURE OF DOUBLE PHOSPHATES OF TITANIUM AND ALKALI METALS

Natalya CHUDINOVA and Elena MURASHOVA

Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskij prospekt 31, Moscow, Russia

Received 8 October 1999

Abstract. Interaction of powdered titanium with the polyphosphoric acid melt containing cations of alkali metals was studied at 350 °C. For the first time double condensed phosphates of titanium and alkali metals with a composition $\text{Na}_3\text{Ti}^{\text{III}}\text{P}_8\text{O}_{23}$ and $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$ were obtained and studied by XRD. Ultraphosphates $\text{Na}_3\text{Ti}^{\text{III}}\text{P}_8\text{O}_{23}$ with framework structure contain cage-type anions. Tetraphosphate $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$ is of a layer structure.

Key words: phosphates, crystal structure.

INTRODUCTION

The chemistry of condensed phosphates as a branch of modern science evolved in the second half of the 20th century [1]. Estonian chemists G. Tammann and J. Kurrol stood at its very source [2]. Our contemporary Academician M. Veiderma and his school in Tallinn Technical University have successfully taken part in its formation and development [3–7].

Syntheses of new compounds with oligomeric and polymeric anions are among the important tasks of the chemistry of condensed phosphates. Many compounds of this group of phosphates have been obtained in the course of systematic studies on the interaction of metal oxides with polyphosphoric acid (PPA) melts initiated by Academician I. Tananaev in the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. As a result it was shown that in the same conditions various metal cations form in the melt of PPA phosphates with different types of anions [8]. As a rule the most complicated

anions form when several metal cations with different charge, size, and structure of the electron shell are used in combination. In particular by this way condensed phosphates of alkali and trivalent metals (Al, Ga, V, Cr, Mn, Fe) with unknown or unusual forms of anions such as cyclooctaphosphates $M_2^I M_2^{III} P_8 O_4$ ($M^I = K, Rb$), cyclododecaphosphates $M_3^I M_3^{III} P_{12} O_{36}$ ($M^I = Cs, Rb$), ultra-phosphates $Na_3 M^{III} P_8 O_{27}$, and others were obtained [9–11].

The study on the conditions of formation, composition, and structure of condensed phosphates of Group IV elements was the next stage of research. The study reported here was aimed at the synthesis of double phosphates of titanium and alkali metals and the determination of their crystal structure. So far only polyphosphate $Ti^{III}(PO_3)_3$ [12] and some diphosphates $Ti^{IV}P_2O_7$ [13], $M^I Ti^{III} P_2 O_7$ [14, 15], where M^I is an alkali metal, and $BaTi_2^{III}(P_2O_7)_2$ [16] have been described in the literature.

EXPERIMENTAL

In the present research interaction of metallic titanium with phosphoric acid containing cations of alkali metals (Na, K, Rb, Cs) at 350°C was studied. Carbonates and nitrates of alkali metals, phosphoric acid (85%), and powdered metallic titanium were used as initial materials. The use of TiO_2 is not appropriate due to its inactivity with respect to the PPA melt. A mixture of the mentioned components with an atomic ratio $M^I:P:Ti = 7.5:15:1$ was put into a glass carbon crucible and then heated in a muffle furnace at 350°C during 7 days. When the powdered titanium had dissolved the melt acquired a pale blue colour, which stayed for some days. Later the melt became colourless. The reduced crystals were washed with cold water from the excess of phosphoric acid and then dried in the air. The obtained compounds were studied by phase and X-ray analyses.

In the PPA melts containing sodium and titanium cations two compounds formed: $Ti^{IV}P_2O_7$ in the form of a white powder and $Na_3Ti^{III}P_8O_{23}$, a double ultraphosphate, as pale blue crystals. In the presence of potassium and rubidium only $Ti^{IV}P_2O_7$ crystallized. From the melt containing caesium cations the colourless $Cs_2Ti^{IV}P_4O_{13}$ precipitated immediately.

The composition and structure of $Na_3Ti^{III}P_8O_{23}$ and $Cs_2Ti^{IV}P_4O_{13}$ were established by X-ray analysis. Experimental conditions of taking diffractograms, main crystallographic parameters, and the results of the determination of the structure are presented in Table 1, coordinates of atoms and thermal parameters in Table 2. The coordinates of the atoms in the structure of $Na_3Ti^{III}P_8O_{23}$ were specified by the least squares method (LSM) with the use of anisotropic approximation by the program SHELX76 [17]. The positions of the atoms in the structure of $Cs_2Ti^{IV}P_4O_{13}$ were found from the Patterson function and specified by LSM with the use of anisotropic approximation by the program SHELXL93 [18].

Table 1. Main crystallographic parameters, experimental conditions, and parameters of the structure adjustment

Parameter	Na ₃ Ti ^{III} P ₈ O ₂₃ Cubic	Cs ₂ Ti ^{IV} P ₄ O ₁₃ Triclinic
a, Å	11.968(4)	5.1162(8)
b, Å		7.9407(8)
c, Å		15.714(2)
α, °		84.16(1)
β, °		83.92(2)
γ, °		80.64(1)
Space group	P4 ₃ 2	P $\bar{1}$
Z	4	2
V, Å ³	1714.2(9)	624.0(1)
ρ _{calc.} , g/cm ³	2.839	3.432
μ, mm ⁻¹	1.46	7.00
2θ _{max.} , °	70	56
Crystal size, mm	0.2 × 0.2 × 0.2	0.1 × 0.2 × 0.2
Diffractometer*	Syntex P2 ₁	Enraf-Nonius CAD-4
Scanning	ω/2θ	ω/2θ
N _a **	1007	2309
N _o **	640	2058
N _p **	55	181
wR2, R1		0.128, 0.045
R, wR	0.033, 0.036	
Gof	1.27	1.05
w	1/σ ² (F)	1/σ ² (F ²)

* γMoK_α; graphite monochromator; ψ-correction of reflections.

** N_a = number of observed reflections;

N_o = number of independent reflections with I > 2σ(I);

N_p = number of adjusted parameters.

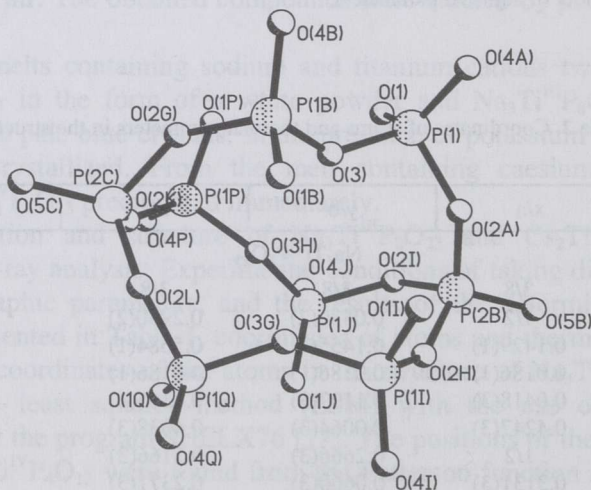
Table 2. Coordinates of atoms and thermal parameters in the structures

Atom	x/a	y/b	z/c	B _{eq.} , Å ²
Na ₃ Ti ^{III} P ₈ O ₂₃				
Ti(1)	3/8	3/8	3/8	0.62(1)
Na(1)	1/2	0.0430(2)	0.2930(2)	1.49(4)
P(1)	0.1429(1)	0.1455(1)	0.5684(1)	0.68(2)
P(2)	0.0186(1)	0.0186(1)	0.0186(1)	0.64(1)
O(1)	0.0418(3)	0.1197(3)	0.6365(3)	1.13(6)
O(2)	0.4247(3)	0.0064(3)	0.4038(3)	1.14(6)
O(3)	1/2	0.2666(3)	0.5166(3)	1.11(7)
O(4)	0.3131(3)	0.0660(3)	0.2371(3)	1.08(6)
O(5)	0.0892(2)	0.0892(2)	0.0892(2)	1.04(5)

Table 2 continued

Atom	x/a	y/b	z/c	B _{eq.} , Å ²
$\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$				
Cs(1)	0.3257(1)	0.2562(1)	0.01154(3)	1.81(2)
Cs(2)	0.7334(1)	0.7014(1)	0.47003(3)	1.91(2)
Ti(1)	0.5547(2)	0.9422(2)	0.7395(1)	0.74(2)
P(1)	0.1239(3)	0.7796(2)	0.6479(1)	0.82(3)
P(2)	0.3318(3)	0.5933(2)	0.8045(1)	0.85(3)
P(3)	0.6855(3)	0.3272(2)	0.7126(1)	0.82(3)
P(4)	0.9789(3)	0.0989(2)	0.8369(1)	0.86(3)
O(1)	0.2910(9)	0.9144(6)	0.6661(3)	1.05(8)
O(2)	0.213(1)	0.6986(7)	0.5677(3)	1.65(9)
O(3)	0.149(1)	0.6364(6)	0.7284(3)	1.39(8)
O(4)	-0.1693(9)	0.8583(6)	0.6544(3)	1.20(8)
O(5)	0.486(1)	0.4070(6)	0.7885(3)	1.14(8)
O(6)	0.185(1)	0.5818(7)	0.8898(3)	1.9(1)
O(7)	0.538(1)	0.7144(6)	0.7922(3)	1.12(8)
O(8)	0.566(1)	0.1749(6)	0.6908(3)	1.08(8)
O(9)	0.943(1)	0.2536(6)	0.7598(3)	1.26(8)
O(10)	0.743(1)	0.4508(6)	0.6405(3)	1.47(9)
O(11)	0.881(1)	0.1644(8)	0.9208(4)	1.9(1)
O(12)	1.2758(9)	0.0319(6)	0.8267(3)	1.01(8)
O(13)	0.8199(9)	-0.0359(6)	0.8125(3)	1.12(8)

X-ray analysis showed that $\text{Na}_3\text{Ti}^{\text{III}}\text{P}_8\text{O}_{23}$ is an ultraphosphate with a cage structure of the anion. The whole compound has a framework structure. The insulate anion $\text{P}_8\text{O}_{23}^{6-}$ can be represented as a ring of six PO_4 tetrahedrons with a bridge of two PO_4 tetrahedrons (Fig. 1). It is bound with TiO_6 octahedrons by common oxygen corners. Sodium atoms occupy holes in the octahedron.

Fig. 1. Structure of the cage-type anion P_8O_{23} .

$\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$ is a double tetrphosphate with a layer structure. The layers are perpendicular to the direction coincident with the parameter c and consist of P_4O_{13} anions and TiO_6 octahedrons. Distances between the neighbouring layers make up $1/2C = 7.886 \text{ \AA}$. The anions consist of four PO_4 tetrahedrons linked by common oxygen corners forming thus short chains. In the anions three different P–O bond distances were fixed. The longest, $1.576\text{--}1.639 \text{ \AA}$, belongs to the bridge oxygen atoms and the medium, $1.515\text{--}1.547 \text{ \AA}$, to the end oxygen atoms coordinated by titanium atoms. The shortest P–O distance, $1.460\text{--}1.473 \text{ \AA}$, belongs to the end oxygen atoms incoming to the coordination sphere of caesium atoms. The distances Ti–O in the octahedron are equal to one another. The caesium atoms are disposed between the layers $[\text{TiP}_4\text{O}_{13}]$ and surrounded by six nearest oxygen atoms at a distance of $3.027\text{--}3.384 \text{ \AA}$ (Fig. 2). It should be mentioned that the coordination number 6 is rarely met in oxygen compounds of caesium. Apparently in this case the number is conditioned by the requirements of the structural frame.

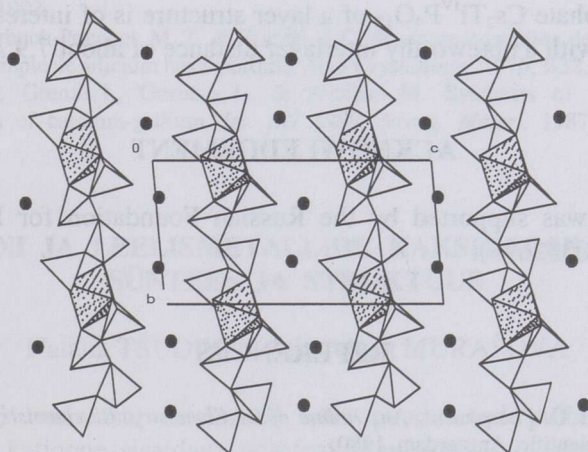


Fig. 2. Projection of the $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$ structure along $[100]$.

DISCUSSION

The experiments showed that by the interaction of powdered titanium with the PPA melt its oxidation occurs, first into cations Ti^{III} (formation of a pale blue melt) and afterwards into Ti^{IV} , which precipitate as corresponding phosphates. The composition and structure of the obtained compounds are defined by the nature of the alkali metal cation and titanium oxidation number. With the sodium cation ultraphosphate of trivalent titanium $\text{Na}_3\text{Ti}^{\text{III}}\text{P}_8\text{O}_{23}$ (with a low admixture of $\text{Ti}^{\text{IV}}\text{P}_2\text{O}_7$) and with the caesium cation tetrphosphate of quadrivalent titanium $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$ forms. The former compound is analogical to ultraphosphates of trivalent metals $\text{Na}_3\text{M}^{\text{III}}\text{P}_8\text{O}_{23}$ synthesized by us earlier [10], and the latter to

$(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ [19]. Titanium does not form double phosphates with potassium and rubidium and it precipitates in the form of $\text{Ti}^{\text{IV}}\text{P}_2\text{O}_7$, although with other trivalent metals we have obtained in the same conditions double cycloocta- $\text{M}_2^{\text{I}}\text{M}_2^{\text{III}}\text{P}_8\text{O}_{24}$ and cyclododecaphosphates $\text{M}_3^{\text{I}}\text{M}_3^{\text{III}}\text{P}_{12}\text{O}_{36}$ [9]. Probably the absence of such compounds with titanium can be explained by the kinetics of the processes in the melt. Our earlier studies showed that the above-mentioned double cycloocta- and cyclododecaphosphates crystallize from the PPA melts extremely slowly (during several weeks) in contrast to ultraphosphates $\text{Na}_3\text{M}^{\text{III}}\text{P}_8\text{O}_{23}$, which crystallize within 2–3 days [20]. Therefore, in the presence of sodium cations Ti^{III} formed in the melt has time to evolve to the solid phase in the form of a double ultraphosphate while in the presence of potassium, rubidium, and caesium cations the oxidation of Ti^{III} to Ti^{IV} proceeds more rapidly than the evolution of cyclophosphates of trivalent titanium and leads to the precipitation of phosphates of quadrivalent titanium $\text{Ti}^{\text{IV}}\text{P}_2\text{O}_7$ and $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$. All the obtained phosphates are compounds that are stable in the air, do not dissolve in water, and dissolve with difficulty in acids. The obtained cyclotetraphosphate $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$ of a layer structure is of interest as a potential ion exchanger with a noteworthy interlayer distance of about 7.9 Å.

ACKNOWLEDGEMENT

This study was supported by the Russian Foundation for Basic Research (project No. 980332695).

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TITAANI JA LEELISMETALLIDE KAKSIKFOSSAATIDE SÜNTEES JA STRUKTUUR

Natalia TŠUDINOVA ja Jelena MURAŠOVA

On esitatud uurimuste tulemused, mis puudutavad pulbrilise titaani ja leelismetallide katioone sisaldava polüfosforhappe sulami vahelisi reaktsioone 350°C juures. Esmakordselt on sünteesitud titaani ja leelismetallide kondenseeritud kaksikfosfaadid valemiga $\text{Na}_3\text{Ti}^{\text{III}}\text{P}_8\text{O}_{23}$ ja $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$. Röntgen-difraktsioonanalüüsi abil on kindlaks tehtud, et $\text{Na}_3\text{Ti}^{\text{III}}\text{P}_8\text{O}_{23}$ on srestikuline ultrafosfaat, mis sisaldab ümbrisstruktuuriga anioone, ja $\text{Cs}_2\text{Ti}^{\text{IV}}\text{P}_4\text{O}_{13}$ on kihilise struktuuriga tetrafosfaat.