

Synthesis and Structural Relationship of Complex Tantalum Phosphates in the Flux System $K_2O-P_2O_5-Ta_2O_5-MoO_3$

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Abstract. Single crystals of $K_2Ta_4O_{11}$ (**I**), $K(TaO_2)_2PO_4$ (**II**) and $K_3Ta_5O_{11}(PO_4)_2$ (**III**) were synthesized by flux-aided method in the pseudo-quaternary system $K_2O-P_2O_5-Ta_2O_5-MoO_3$. Tight interrelation of their crystal structures has been found via X-ray diffraction study. Experimental solid-state band gap measurements revealed its semiconductor nature corroborated with DFT calculations. Local structure of PO_4 groups in (**II**) and (**III**) compounds was probed with ^{31}P MAS NMR spectroscopy.

Key words: tantalum, phosphate, intergrowth structures, x-ray diffraction, solid state NMR, density functional theory.

I. INTRODUCTION

From the point of view of “structure-properties” relationship rigid tetrahedral geometry of $[XO_4]$ ($X = Si, P, S, V, As, Se$) anions should preserve certain configuration of $[M^VO_6]$ (where $M = Nb$ or Ta). From the other hand, cations of Nb^V and Ta^V usually form highly polarisable bonds due to the second-order Jahn-Teller (SOJT) effect leading to set of useful macroscopic properties [1]. Therefore, various topologically distinct combinations of tilted oxo-octahedra with rigid symmetrical tetrahedra may be considered as pathways to compounds with either electrophysical or optical properties at the first stage. It is probable that new materials are based on it. Conventional “waterline” group of compounds bearing features of oxides and complex salts (so-called phosphate bronzes) may be considered. Reveau and co-workers reported a number of representatives [2] of this class classifying them into groups upon topological principle with relation to the types of tungsten bronzes (TB), namely, tetragonal (TTB) and hexagonal (HTB) ones. The latter can be regarded as ionic conductors, thermo- and electrochromic, charge density wave (CDW) materials [3]. The recent rise of active research on oxide semiconductor photocatalytic materials attracts more attention to this class of compounds due to their high crystallinity, stability and photocatalytic activity [4]. However, in our opinion, an absence of an appropriate synthetic approach disables an embodiment of potential solutions to this problem.

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Here is reported an episode of systematic study on complex phosphates based on Vb group of metals.

II. EXPERIMENTAL SECTION

Compounds (**I**), (**II**) and (**III**) were synthesized by flux-aided ($K_2Mo_2O_7$) melts in spontaneous regime of crystallization in a range of $K/P \leq 1$ and $Ta/P = 0.22-1.39$. Single diffraction experiments were performed on Agilent XCalibur Ruby and XCalibur Sapphire 3 diffractometers. Bulk polycrystalline samples were checked for purity with Shimadzu XRD-6000 diffractometer (Bragg-Brentano $\theta-2\theta$ diffraction geometry, secondary graphite monochromator, Cu-anode tube) and Huber G670 Guinier camera (IP cylindrical detector, germanium primary monochromator, Cu-anode). Thermoanalytical study was carried out on a simultaneous analyzer (STA 409C, Netzsch, Pt/Rh crucibles, thermocouple type S, heating/cooling rate 30 K/min). Measurements were conducted in flowing argon atmosphere (120 mL/min). Solid state ^{31}P -NMR experiments were performed with Bruker Avance III 400 WB spectrometer. Powder second-harmonic generation (SHG) tests on **II** were carried out by conventional Kurtz-Perry method described elsewhere [5, 6]. About 100 mg of powder was pressed into a pellet, which was then irradiated with a pulsed IR beam (10 ns and 10 kHz) produced by a Q-switched Nd:YAG laser of wavelength 1064 nm. Polycrystalline α - SiO_2 was used as a standard for measurements.

III. RESULTS AND DISCUSSION

A. Crystal structure

All reported compound belong to trigonal crystal system (Table 1).

(**I**) crystallizes isotypically to natrotantite ($A_2M_4O_{11}$), where $A = Na, Ag^I$; $M = Nb^V, Ta^V$ [7-8]. Its framework consists of successive stacking of Ta_2O_5 (U_3O_8 –topology) and $KTaO_3$ layers along the [001] axis. Otherwise, $[Ta_7O_{30}]$ building units (BU) are recognized. Potassium atoms are comprised within a cage which is delimited with two adjacent BU 's. Upon inclusion of $[PO_4]$ tetrahedra, structure of (**II**) turns to heterodesmic framework consisting of $[Ta_4P_2O_{23}]$. The latter are shared exclusively via common oxygen vertices. Potassium atoms are strongly differentiated by their location: K1 (symmetry $D3$) is surrounded with six O atoms to produce trigonal-prismatic environment, while partially filled K2 (symmetry $C1$) is being in strongly distorted six-fold environment. The structure of (**III**) has the same structural features as parental (**I**) and (**II**) revealing its inter-growth nature.

B. Solid state band gap measurements and DFT calculations

Experimental band gaps for **I-III** were estimated experimentally as 4.06(1), 3.29(1) and 3.71(1) eV respectively. Their theoretically calculated counterparts agree well at chosen level of theory (generalized gradient approximation on Perdew-Burke-Ernzerhof parameterization as implemented in DMol³ code [9]). **I** was found to be a wide direct band gap semiconductor (3.8 eV), while **II** and **III** are in-direct one (3.0 and 3.5 eV, respectively).

Table 1. Summary of crystallographic data on I-III

	I	II	III
Empirical formula	K ₂ Ta ₄ O ₁₁	K(TaO ₂) ₂ PO ₄	K ₃ Ta ₅ O ₁₁ (PO ₄) ₂
<i>M_r</i>	978.00	559.97	1388
<i>T</i> (K)	293(2)	293(2)	293(2)
Crystal system	Trigonal		
Space group	R-3c	R32 (155)	R-3c
Unit cell dimensions (<i>a</i> , <i>c</i> in Å)			
	36.8575(13)	10.31740(1)	53.546(3)
Volume (Å ³)	1256.11(7)	1594.02(2)	7782.8(11)
Formula units (<i>Z</i>)	6	9	18
Density (calculated) (g·cm ⁻³)	7.758	5.250	5.331
Radiation	CuKα	MoKα	MoKα
Absorption coefficient, (mm ⁻¹)	103.248	31.686	32.515
<i>F</i> (000)	2508	2196	10872
<i>θ</i> Range (°)	7.21-64.95	3.05-45.71	3.06-30.54
Data/restraints/parameters	1628/0/29	3029/0/65	5149/0/137
Goodness-of-fit on <i>F</i> ²	1.162	1.071	1.023
Final <i>R</i> indices	<i>R</i> ₁ = 0.024,	<i>R</i> ₁ =0.021,	<i>R</i> ₁ =0.046,
[<i>F</i> ₀ ² >2σ(<i>F</i> ₀ ²)] ^a	w <i>R</i> ₂ = 0.058	w <i>R</i> ₂ =0.048	w <i>R</i> ₂ =0.094

C. ³¹P Solid State NMR probing

³¹P NMR MAS shows low-field shift of a signal ascribed to a single non-equivalent phosphorus in (**II**) to its counterpart in (**III**). This fact could be explained with the increase of local distortion of [PO₄] tetrahedra from C₂ to C₁ symmetry of oxygen environment (Fig. 2).

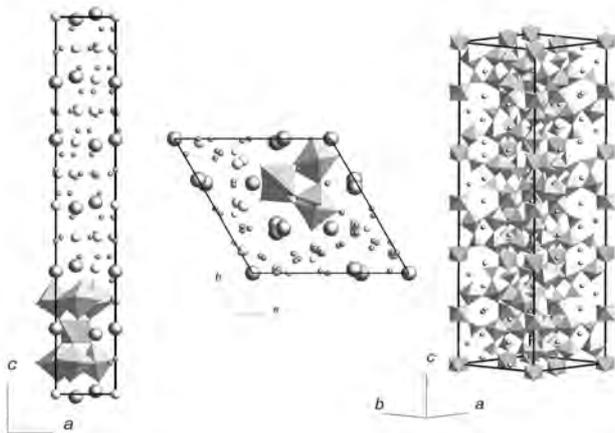


Fig. 1. View of unit cells for I (left), II (middle) and III (right). BU's are emphasized with polyhedral presentation (see description in the text).

D. Non-linear optical properties

Compound **II** crystallizes in non-centrosymmetrical space group R32. Preliminary estimate of the second harmonic response for this double phosphate gives 22.2 (a.u.) intensity relatively to polycrystalline α-SiO₂.

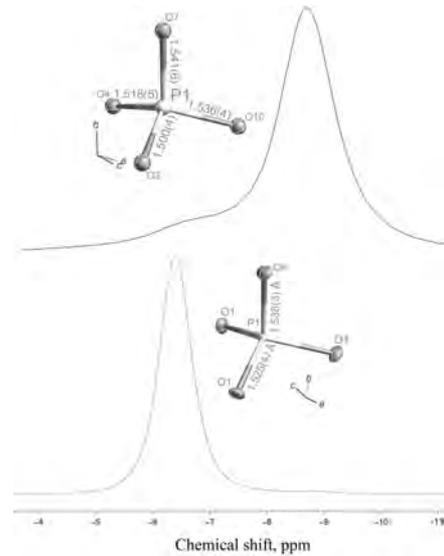


Fig. 2. Plot of ³¹P MAS NMR signals for (II) and (III).

IV. CONCLUSIONS

This study has revealed the subtle relationship of pure metal-containing oxide phases with tetrahedral oxoanionic salts though the formation of intergrowth structures. This approach might be useful for design of “easy-to-tune” materials.

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