

## REDOX-EFFECTS AT FORMATION OF FRAME MATRIXES OF PHOSPHATES IN HYDROTHERMAL CONDITIONS

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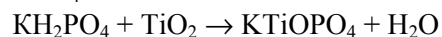
**Key words:** phosphates, hydrothermal synthesis, KTP

Use of methods of hydrothermal interaction allows to synthesize and raise the monocrystals of complex phosphates having applied value. In particular, double phosphate of potassium-titan  $\text{KTiOPO}_4$  (KTP) possesses unique nonlinear-optical properties and of interest for laser technics. Partial replacement of positions of the titan in  $\text{KTiOPO}_4$  other tetravalent metals or alloying REE considerably is changed with nonlinear-optical characteristics KTP [1,2]. At the same time, there are open questions alloying  $\text{KTiOPO}_4$  various ions in conditions of its hydrothermal synthesis.

We investigate processes of phase formation complex phosphates for systems  $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}-\text{TiO}_2-\text{M}_2\text{O}_3$  ( $\text{M}^{3+} = \text{Al}, \text{Fe}$ ) in conditions of isothermal hydrothermal interaction – temperature 450-460 °C, pressure 1000-1100 atm, time of interaction 120-140 hour. Experiments carried out with use ampoules method (copper ampoules) in steel autoclaves. As initial components used  $\text{KH}_2\text{PO}_4$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3$ . In an autoclave filled sated solution  $\text{KH}_2\text{PO}_4$ . The received phases washed water or 5 %-s' solution HCl.

The phase structure of the synthesized phosphates is established by a method of X-ray powders ( $\text{CuK}\alpha$ -radiation). Connections also investigated spectral methods – IR-spectroscopy (a range of frequencies of 1500-400  $\text{cm}^{-1}$ ), an electronic paramagnetic resonance (a spectrometer “PS 100.X”), electronic spectroscopy (spectrometer UV-VIS "Specord" I-40, frequencies of 12000-30000  $\text{cm}^{-1}$ ).

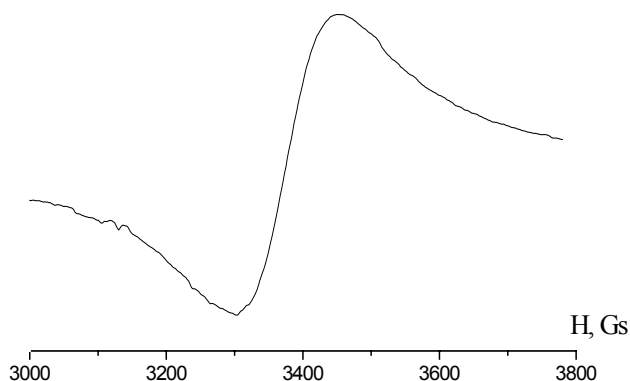
Molar ratio  $(\text{Ti}+\text{M}^{\text{III}})/\text{P}$  in systems varied from 0,1 up to 1,0 for fixed value  $\text{K}/\text{P} = 1$ . Thus a ratio of  $\text{M}^{\text{III}}/\text{Ti}$  set in limits from 0 up to 0,20. For initial system  $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}-\text{TiO}_2$  ( $\text{M}^{\text{III}}/\text{Ti} = 0$ ) in all a range of ratio  $\text{Ti}/\text{P}$  formation  $\text{KTiOPO}_4$  is fixed:



Entering into system aluminium or iron oxides results in reception of the polycrystalline painted phases. Thus, with growth in system of an initial ratio of  $\text{M}^{\text{III}}/\text{Ti}$  from 0,05 up to 0,15 transition from light blue up to intensively dark blue color is observed. At the same time, calculation of roentgenograms has shown isomorphism the synthesized connections. For all received phosphates parameters of crystal cells are close and insignificantly differ from parameters of cell  $\text{KTiOPO}_4$  (space group  $\text{Pna}2_1$ ;  $a = 1,281$ ,  $b = 1,062$ ,  $c = 0,604$  nm,  $V = 0,8217$   $\text{nm}^3$ ).

Research of the synthesized connections by methods EPR and electronic spectroscopy has allowed to establish unequivocally presence in their structure of the trivalent titan. It is necessary to note, that chromophore  $[\text{Ti}^{3+}\text{O}_6]$  it is not fixed in samples for which phase formation passed in absence in system of aluminium or iron.

Spectrum EPR at 20 °C is submitted as symmetric singlet with  $g = 2,001$  and  $\Delta H = 110$  Gs (Fig). It is caused by presence at samples of ions  $\text{Ti}^{3+}$  in deformed oxygen octahedral an environment. In turn,



to presence of the trivalent titan testifies and the widened line of absorption in electronic spectra in the field of 17200-18200  $\text{cm}^{-1}$  that corresponds with one-electronic transition  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$  in chromophore  $[\text{Ti}^{3+}\text{O}_6]$ . For ferriferous connections two strips of absorption are fixed also at 23600 and 19000  $\text{cm}^{-1}$  which are caused by presence chromophore  $[\text{Fe}^{3+}\text{O}_6]$ . It specifies simultaneous presence in structure of the received phosphates as different-valent the titan, and trivalent metal.

IR-spectra of the received connections of structure  $K_{1+x}M_{x-y}^{III}Ti_y^{III}Ti_{1-x}^{IV}OPO_4$  ( $0 < x < 0,2$ ;  $0 < y < 0,1$ ) are identical to IR-spectrum  $KTiOPO_4$  and are characterized by the following set of strips of absorption: valent asymmetric fluctuations of phosphatic group correspond with three doublets 1125, 1105, 1050, 1035, 1015, 1000  $cm^{-1}$ . Valent symmetric fluctuation of connection P-O is answered with an intensive strip of absorption at 980  $cm^{-1}$ . Deformation fluctuations of phosphatic group and fluctuation in octahedrons of connections Ti-O,  $M^{III}$ -O are located in the field of 640-400  $cm^{-1}$ .

Thus, phase formation crystal matrix KTP it is accompanied by partial reduction  $Ti^{4+} \rightarrow Ti^{3+}$ . Thus, the general structure of the received connections is described with formula  $K_{1+x}M_{x-y}^{III}Ti_y^{III}Ti_{1-x}^{IV}OPO_4$  ( $0 < x < 0,2$ ;  $0 < y < 0,1$ ). The synthesized complex phosphates can be submitted as firm solutions with a crystal framework such as  $KTiOPO_4$  for which positions of atoms of the tetravalent titan are in part replaced with aluminium or iron and the titan 3+. Thus the total charge of crystal framework  $[TiOPO_4]^-$  grows. Its indemnification occurs due to additional potassium ions which enter into vacant positions of cavities of a framework.

The observable redox-effect at formation of double phosphates in hydrothermal conditions is fixed for the first time. Earlier partial reduction  $Ti^{4+} \rightarrow Ti^{3+}$  it was marked at a melted solution crystallization in systems  $K_2O-P_2O_5-TiO_2-M^{III}_2O_3$  ( $M^{III} - Al, Fe, Cr, Sc, In$ ) with phase formation phosphates of general formula  $K_{1+x}M_{x-y}^{III}Ti_y^{III}Ti_{2-x}^{IV}(PO_4)_3$  ( $0 < x \leq 1$ ) [3-5]. In work [3], on an example isostructural to langbeinite phases  $K_{1+x}Al_{x-y}Ti_y^{III}Ti_{2-x}^{IV}(PO_4)_3$  ( $0 < x \leq 1$ ), process of alloying initial phosphate  $KTi_2(PO_4)_3$  by trivalent elements is in details investigated. Being based on results of researches of electronic structure of some connections by methods of x-ray photoelectronic spectroscopy, the x-ray fluorescent analysis and EPR-spectroscopy, authors offer the mechanism phase formation a phosphatic framework and redox-effects are considered. It has been shown, that at the first stage aluminium enters in crystallography positions not the titan, and potassium agrees principle  $Al^{3+} \rightarrow 3K^+$ . As the result, arises significant localization of a positive charge in cationic sub lattice. Pressure arising in structure result to homolitic break of connection Ti-O and downturn of cationic and anionic sub lattice charge. Further there is an occurrence of aluminium in structure formed octahedrons of the titan to simultaneous filling cationic vacancies of potassium atoms.

For hydrothermal conditions of synthesis realization of the specified mechanism passes with phase formation crystal framework  $[TiOPO_4]^-$ . Thus, at formation complex oxide frameworks in hydrothermal conditions including at mineral formation, it is necessary to take into account interference of polyvalent metals and opportunities of course of oxidation-reduction processes.

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21) 2003  
 Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003  
 URL: [http://www.scgis.ru/russian/cp1251/h\\_dgggms/1-2003/informbul-1\\_2003/hydroterm-2e.pdf](http://www.scgis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/hydroterm-2e.pdf)  
 Published on July 15, 2003

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