Phase Formation in the Systems TiOCl₂—H₃PO₄—MF(HF)—H₂O (M = K, Rb, Cs)

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Abstract—From solutions containing 2–17 wt % TiO₂ at the molar ratios M/Ti = 1–4, F/Ti = 2–4, and PO₄³⁻/Ti = 0.5–10 under mild conditions, fluoro- and oxo(hydroxo) fluorophosphate titanates were isolated: crystalline M₂TiF₆ (M = K, Rb, Cs) and K₂Ti₂O₂·F₂PO₄·2H₂O, and amorphous K₃Ti₆O(OH)F₇(PO₄)₃·5H₂O, Cs₂Ti₂O₂F₂PO₄·6H₂O, and Cs₂Ti₂O₂F₂PO₄·3H₂O. In a mixture with M₂TiF₆ and KCl, phosphate-ion-containing crystalline phases of unidentified composition were detected. The phases were studied by elemental, crystal-optical, X-ray powder diffraction, thermal, IR spectroscopic, and electron microscopic analyses. Annealing fluorophosphate titanates gives a mixture of MTiOPO₄ and TiO₂. All the mentioned alkali metal fluorophosphates contain the tetrahedral ion PO₄³⁻ and titanium polyhedra with bonds Ti—F and Ti—O; some of them also contain bridging oxygen connecting titanium atoms: Ti—O—Ti; i.e., these substances are polymeric.

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There exist double titanium phosphates and oxophosphates [1, 2], which are isolated from solution in melt by spontaneous crystallization. Phosphates with lamellar structure are known to be ion exchangers [3]. They also have catalytic properties [4]. From solution in autoclave at 210°С, several types of layered fluorine-containing titanium phosphate were obtained, including TiIII⁴⁰F(TiO₂)₂·2H₂O [5] and Ti₂(OPO₄)₂F₂·N₂C₂H₄ [6]. In the latter compound, within layers, there are bonds between TiO₂F₂ octahedra and PO₄ tetrahedra, and Ti—F bonds are perpendicular to the layers. Under hydrothermal conditions, fluorophosphate titanates (NH₄)₃K₂(TiO₂F₂) [7] and (NH₄)₂₀K₁₈[Ti₂F₂(PO₄)₂·(PO₄OH)] have been found. The latter has unique layers consisting of PO₄³⁻ or PO₄OH tetrahedra and TiO₂F octahedra, and terminal atoms (F, O, or OH) form strong hydrogen bonds between the layers [8].

The purpose of this work was to study the possibility of the synthesis of alkali metal fluorophosphate titanates at room temperature.

EXPERIMENTAL

The initial medium was a TiOCl₂ solution containing 25.07 wt % TiO₂ and 20.60 wt % Cl⁻ (the molar ratio Cl⁻/Ti = 1.85). To the solutions diluted with water, one of the alkali metal fluoride and then phosphoric acid (85 wt %) were added at ~20°C while continuously stirring. The mixtures were kept at room temperature for ~7 days. The precipitate was filtered off, washed with water, water with alcohol, and alcohol, and then dried in air. The X-ray powder diffraction patterns were recorded with DRF-2 and DRON-2 devices (graphite monochromator, CuKα radiation). The crystal-optical measurements were performed using immersion liquids with a Leica DM 2500 P microscope. The elemental analysis was made according to standard procedures. Fluorine was determined after double distillation by potentiometry. The contents of the other components (K⁺, Rb⁺, Cs⁺, Ti(IV), PO₄³⁻) was found by X-ray spectroscopy with a Specroscan MAKC-GV spectrometer. The chemical composition of the amorphous phase sampled under the binocular microscope was determined with an MS 46 Cameca X-ray microanalyzer and also INCA Energy 400 instrument. The water content was determined from the weight loss after treating samples at 250°C and also by thermogravimetry with a Netzsch STA-409 simultaneous thermal analyzer in Pt—Rh crucibles containing 10% argon. In these measurements, differential scanning calorimetry curves were also recorded. The heating curves were also recorded in undried air with an HTP-70M with Pt/Pt–Rh thermocouples. The IR spectra within the range 400–3800 cm⁻¹ were recorded with a Nicolet 6700 FT-IR spectrometer. Samples for recording were prepared by compacting pellets with KBr. Scanning electron microscopy images were produced by a SEM LEO-420 scanning electron microscope.
RESULTS AND DISCUSSION

The isolated precipitates are extremely finely divided and poorly crystallized and are often a mixture of phases. Figure 1 schematically represents the fields of the formation of potassium fluorophosphate titanates. At low molar ratios F/Ti, X-ray amorphous phase VII is isolated (Table 1), and at high such ratios, hexafluorotitanates along with fluorophosphate titanates. At contents below 8 wt % TiO₂ and the molar ratio F/Ti = 3 in the absence of hydrofluoric acid and at F/Ti = 4 in the presence of HF, individual phase V forms. At high titanium contents (above 8 wt % TiO₂), KCl forms along with other phases.

The X-ray powder diffraction pattern of phase II shows that it is amorphized. Phases III, IV, and VIII crystallize in a mixture of hexafluorotitanates and/or KCl. Their presence was determined by X-ray powder diffraction patterns (Table 2).

Crystals of phase V form spherulite–like formations with refractive indices of N ₁ = 1.690 and N ₂ = 1.556. Their scanning electron microscopy images show peony–like particles with quasi–ordered structure and developed surface constituted by nanosized crystalline plates (Fig. 2). For phase V:

For K₂Ti₂O₂.5F₂PO₄⋅2H₂O anal. calcd., wt %: K⁺, 21.4; Ti(IV), 27.6; F⁻, 11.9; PO₄³⁻, 25.7; Σ(H₂O, OH), 10.4.

The differential thermal analysis curve during heating exhibits four significant endothermic events accompanied by weight loss (Fig. 3). The first two of them (at 96–192 and 478–494°C) characterize water removal, and the next two (at 549–616 and 726–753°C) are caused by salt perhydrolysis and, as can be judged from the weight loss in this range for the salt (NH₄)₀.₁₆K₁.₈₄[Ti₂F₂(PO₄)₂(PO₃OH)], by the release of OH, H₂O, F, HF, and F₂, individually fluorine-containing species [8]. The products of the decomposition of NH₄K₂Ti₂PO₄F₉ above 420°C are KTiOPO₄, K₂₆₆TiO₀₆F₅·₃₃ and TiO₂ [7]; (NH₄)₀.₁₆K₁.₈₄[Ti₂F₂(PO₄)₂(PO₃OH)] at ~1000°C — KTiOPO₄, TiO₂, and semi-amorphous phase. The content of titanium oxides is about a third of that of KTiOPO₄. Phase V is stable until ~400°C.

Phase VI is X-ray amorphous and was detected only in a mixture with KCl and K₂TiF₆⋅H₂O. Phase VII is also amorphous but was isolated as an individual phase. For phase VII:

For K₂Ti₂O(OH)F₆(PO₄)₂⋅5H₂O anal. calcd., wt %: K⁺, 13.80; Ti(IV), 22.55; F⁻, 15.65; PO₄³⁻, 33.53; H₂O,10.60.

1TG data taking into account the substitution of oxygen for fluorine.

Fig. 1. Fields of the formation of potassium fluorophosphate titanates at the molar ratios F/Ti = (a) >1 and (b) 1 and PO₄³⁻/Ti = (J) 1.5, (2) 4, and (3) 10. The circles represent experimental data. Phases: (I) K₂TiF₆, (II) K₂TiF₆⋅H₂O, (V) K₂Ti₂O₂.5F₂PO₄⋅2H₂O, (VII) K₂TiO(OH)F₆(PO₄)₂⋅5H₂O, and (IX) KCl. The compositions of phases III, IV, VI, and VIII were not determined.

Found, wt %: K⁺, 13.5; Ti(IV), 22.7; F⁻, 15.1(16.2); PO₄³⁻, 34.0; H₂O, 14.9(11.4).

The differential thermal analysis curve shows an endothermic event at 92–150°C, which is induced by the removal of most water, and an exothermic event at 572–595°C, which is caused by the crystallization of an intermediate product. The end product of heating (1000°C), as for phase V, is KTiOPO₄ with a small admixture of TiO₂; this product is represented in the X-ray powder diffraction pattern as the most intensive (for anatase) line at 3.55 Å.

Crystalline phase VIII was detected as an admixture to known phases I, II, and IX (Table 2). Phase VIII is fine-grained and weakly anisotropic with Nₘ = 1.617. Its average composition is KTiF₃PO₄⋅H₂O. The IR spectrum of this phase is similar to the spectrum of phase V (Table 3). The morphology of the