

## Crystallization of complex phosphates based on titanium and bivalent or trivalent metals from cesium and rubidium phosphate self-fluxes

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The particularities of phase formation in the self-flux  $\text{Cs}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2$  system were investigated at molar ratios of  $\text{Cs}/\text{P} = 0.9-1.2$ , and  $\text{Ti}/\text{P} = 0.3$  over a temperature range of  $1000-550^\circ\text{C}$ . The formation conditions of the complex phosphates  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  (at  $\text{Cs}/\text{P} = 1.0$ ) and  $\text{CsTiOPO}_4$  (at  $\text{Cs}/\text{P} = 1.2$ ) were established. It was found that the addition of bi- and trivalent metals oxides into the self-flux  $\text{M}^{\text{I}}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2-\text{M}^{\text{III}}_2\text{O}_3$  ( $\text{M}^{\text{I}}\text{O}$ ) ( $\text{M}^{\text{I}} - \text{Cs}$ ,  $\text{Cs}/\text{Rb}$ ,  $\text{M}^{\text{I}} - \text{Co}$ ,  $\text{Ni}$ ,  $\text{M}^{\text{III}} - \text{Fe}$ ,  $\text{Mn}$ ) system (at molar ratios of  $\text{M}^{\text{I}}/\text{P} = 1.0$  and  $1.2$ ,  $\text{Ti}/\text{P} = 0.3$ ,  $\text{Ti}/\text{M}^{\text{III}} = 1.0$  and  $\text{Cs}/\text{Rb} = 1.0$ ) caused the formation of  $\text{M}^{\text{I}}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  and  $\text{M}^{\text{I}}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $\text{M}^{\text{I}} - \text{Cs}$ ,  $\text{Cs}/\text{Rb}$ ) ( $0.3 \leq x \leq 0.5$ ) phosphates which belong to a cubic system, space group  $Fd-3m$ . The obtained phosphates were characterized by the powder X-ray diffraction, FTIR spectroscopy, TG/DTA and elemental analysis.

**Keywords:** cesium, titanium, complex phosphates, FTIR spectroscopy, powder X-ray diffraction.

Закономірності фазоформування в розчинах-розплавах системи  $\text{Cs}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2$  досліджено у розрізах мольних співвідношень:  $\text{Cs}/\text{P} = 0.9-1.2$ ,  $\text{Ti}/\text{P} = 0.3$  в інтервалі температур  $1000-550^\circ\text{C}$ . Установлено умови кристалізації фосфатів:  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  (при  $\text{Cs}/\text{P} = 1.0$ ) і  $\text{CsTiOPO}_4$  (при  $\text{Cs}/\text{P} = 1.2$ ). Для розчинів-розплавів систем  $\text{M}^{\text{I}}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2-\text{M}^{\text{III}}_2\text{O}_3$  ( $\text{M}^{\text{I}}\text{O}$ ) ( $\text{M}^{\text{I}} - \text{Cs}$ ,  $\text{Cs}/\text{Rb}$ ,  $\text{M}^{\text{I}} - \text{Co}$ ,  $\text{Ni}$ ,  $\text{M}^{\text{III}} - \text{Fe}$ ,  $\text{Mn}$ ) (в розрізах мольних співвідношень:  $\text{M}^{\text{I}}/\text{P} = 1.0$  і  $1.2$ ,  $\text{Ti}/\text{P} = 0.3$ ,  $\text{Ti}/\text{M}^{\text{III}} = 1.0$  і  $\text{Cs}/\text{Rb} = 1.0$ ), встановлено, що внесення оксиду двох- або тривалентного металу в розплав сприяє формуванню фосфатів:  $\text{M}^{\text{I}}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  і  $\text{M}^{\text{I}}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $\text{M}^{\text{I}} - \text{Cs}$ ,  $\text{Cs}/\text{Rb}$ ) ( $0.3 \leq x \leq 0.5$ ), які належать кубічній сингонії (пр. гр.  $Fd-3m$ ). Синтезовані фосфати охарактеризовані з використанням методів порошкової рентгенографії, ІК спектроскопії, ТГ/ДТА і елементного аналізу.

**Кристалізація складних фосфатів на основі титану та дво- і тривалентних металів з цезій- та рубідійфосфатних розчин-розплавів.** *Н.Ю.Струтинська, М.С.Слободяник, Ю.О.Тітов, Т.Ю.Слива, Я.А.Краєвська.*

Закономірності фазоформування у розчин-розплавах системи  $\text{Cs}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2$  досліджено у розрізах мольних співвідношень:  $\text{Cs}/\text{P} = 0.9-1.2$ ,  $\text{Ti}/\text{P} = 0.3$  в інтервалі температур  $1000-550^\circ\text{C}$ . Встановлено умови кристалізації фосфатів:  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  (при  $\text{Cs}/\text{P} = 1.0$ ) та  $\text{CsTiOPO}_4$  (при  $\text{Cs}/\text{P} = 1.2$ ). Для розчин-розплавів систем  $\text{M}^{\text{I}}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2-\text{M}^{\text{III}}_2\text{O}_3$  ( $\text{M}^{\text{I}}\text{O}$ )

(M<sup>I</sup> — Cs, Cs/Rb, M<sup>II</sup> — Co, Ni, M<sup>III</sup> — Fe, Mn) (у розрізах мольних співвідношень: M<sup>I</sup>/P = 1.0 і 1.2, Ti/P = 0.3, Ti/Mn<sup>II</sup> = 1.0 та Cs/Rb = 1.0), встановлено, що додавання оксиду дво- чи тривалентного металу сприяє формуванню фосфатів: M<sup>I</sup><sub>1+2x</sub>Ti<sub>1-x</sub>M<sup>II</sup><sub>x</sub>OPO<sub>4</sub> і M<sup>I</sup><sub>1+x</sub>Ti<sub>1-x</sub>M<sup>III</sup><sub>x</sub>OPO<sub>4</sub> (M<sup>I</sup> — Cs, Cs/Rb) (0.3 ≤ x ≤ 0.5), що належать до кубічної сингонії (пр. гр. *Fd-3m*). Синтезовані фосфати досліджені методами порошкової рентгенографії, ІЧ-спектроскопії, ТГ/ДТА та елементного аналізу.

## 1. Introduction

Significant interest in complex phosphates of alkali and polyvalent metals is caused by a large variety of their structural types (NASICON, langbeinite, olivine, alluaudite, zeolite, etc.), which suggest the presence of different useful functional properties for use in various industries. Thus, the NASICON-related complex phosphates are promising for the creation of modern solid electrolytes [1–3], while the compounds belonging to alluaudite, zeolite and olivine structural types are important in the development of cathode materials, catalysts and phosphors [4–14]. High chemical resistance of langbeinite type phosphates to aggressive environments and radiations allows them to be considered as a matrix for the disposal of radioactive waste [15]. It is important to find out the possible factors for influencing on the formation of complex phosphates with different structures and properties.

For the complex phosphates based on Ti–M<sup>II</sup> or Ti–M<sup>III</sup> pairs, the formation of compounds which belong to different structure types takes place depending on the alkali metal nature. Thus, sodium-containing phosphates belong to the NASICON structural type (trigonal system, space group *R-3c*) [16–19], while potassium phosphates [20, 21] and rubidium-containing phosphates [22–27] crystallize in a cubic system, space group *P2<sub>1</sub>3* (langbeinite-related). Thus, the effect of the alkali metal nature on the formation peculiarities of crystalline frames of complex phosphates based on pairs Ti–M<sup>II</sup> or Ti–M<sup>III</sup> is observed.

Previously, for complex cesium-containing phosphates, a significant influence of cesium cations on the peculiarities of the phosphate structure was found [28, 29]; and in some cases, the formation of compounds with a peculiar type of the frame was also revealed [30–32]. Taking into account the above facts and the lack of information on the formation peculiarities of the Cs–Ti–M<sup>II</sup> (M<sup>III</sup>) based phosphates the following studies were carried out.

This paper is devoted to the results of determination the formation of complex phosphates in the multi-component self-flux system of M<sup>I</sup><sub>2</sub>O–P<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub>–M<sup>III</sup><sub>2</sub>O<sub>3</sub> (M<sup>II</sup>O)

(M<sup>I</sup> — Cs, Cs/Rb, M<sup>II</sup> — Co, Ni, M<sup>III</sup> — Fe, Mn) at molar ratios of M<sup>I</sup>/P = 1.0 and 1.2, Ti/P = 0.3, Ti/M<sup>n</sup> = 1.0 and Cs/Rb = 1.0, including a simpler system of Cs<sub>2</sub>O–P<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub> (Cs/P = 0.9–1.2, Ti/P = 0.3) over the temperature range of 1000–550°C. The synthesized phosphates were characterized using the methods of powder X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric (TG) and differential thermal analysis (DTA), and elemental analysis.

## 2. Experimental

The peculiarities of the complex phosphates formation in the self-fluxes M<sup>I</sup><sub>2</sub>O–P<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub>–M<sup>III</sup><sub>2</sub>O<sub>3</sub> (M<sup>II</sup>O) (M<sup>I</sup> — Cs, Cs/Rb) and Cs<sub>2</sub>O–P<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub> systems were studied at fixed contents of polyvalent metals: Ti/P = 0.3, Ti/M<sup>III</sup> (M<sup>II</sup>) = 1.0, while the molar ratios were varied: Cs/P = 0.9, 1.0 and 1.2. As initial components, CsH<sub>2</sub>PO<sub>4</sub>, RbH<sub>2</sub>PO<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, MgO, CoO, CuO, Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> materials of an analytical grade were used.

The experimental procedure included the preparation of homogeneous melts at 1000°C and their further gradual cooling to 850–550°C for crystallization of complex phosphates. The final temperature depended on the initial M<sup>I</sup>/P ratio in the melt. To create the required molar ratio of Cs/P < 1.0 or Cs/P > 1.0, the calculated amounts of H<sub>3</sub>PO<sub>4</sub> or Cs<sub>2</sub>CO<sub>3</sub>, respectively, were added to the mixture of CsH<sub>2</sub>PO<sub>4</sub> + TiO<sub>2</sub> + M<sup>III</sup><sub>2</sub>O<sub>3</sub> (M<sup>II</sup>O). The dissolving of oxides in the phosphate melts takes place during heating of the systems under isothermal conditions at a temperature of 1000°C for 2 h (for the melts with Cs/P = 0.9) or 30 min. (for the melts with Cs/P = 1.2). After that, the temperature was lowered at a rate of 25–50°/h, and when the formation of the crystals began, a periodic sampling of the melt was carried out. When the viscosity of the melt changed sharply, the cooling was stopped and the system was kept under isothermal conditions for 1 h. The crystalline phases were washed from the residues of the melt with distilled water, dried and analyzed.

The phase compositions of the obtained phosphates were determined by powder X-ray

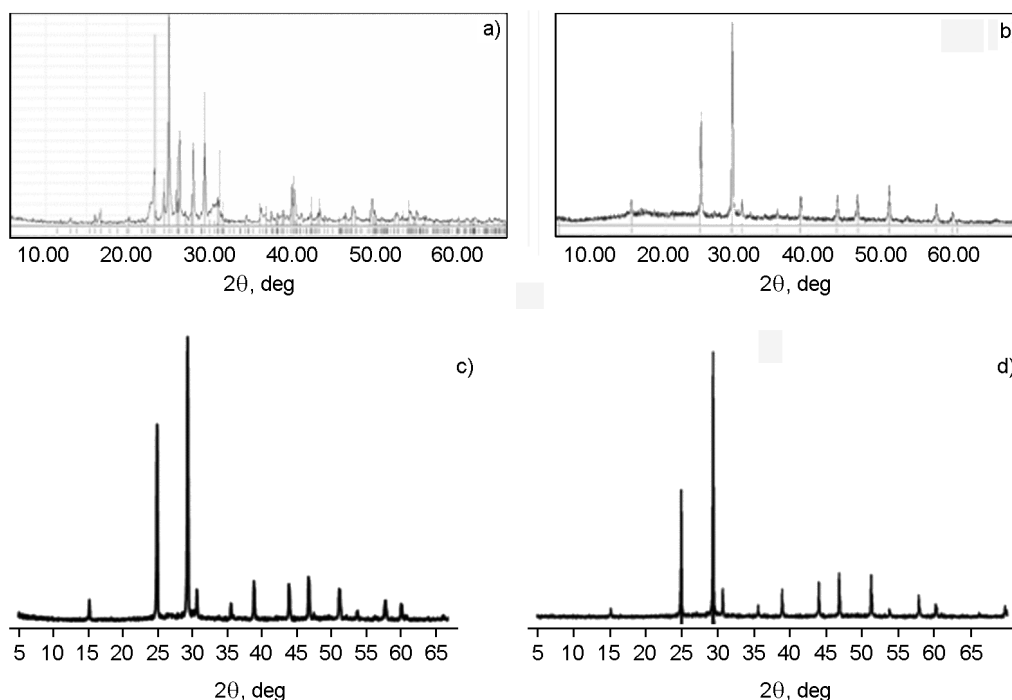


Fig. 1. XRD patterns for prepared compounds:  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  (ICDD #00-081-1303) — a,  $\text{CsTiOPO}_4$  (ICDD #00-048-0017) — b, and new phosphates:  $\text{Cs}_{1.3}\text{Ti}_{0.7}\text{Co}_{0.3}\text{OPO}_4$  — c,  $\text{Cs}_{1.5}\text{Ti}_{0.5}\text{Fe}_{0.5}\text{OPO}_4$  — d.

diffraction (XRD). A Shimadzu XRD-6000 diffractometer with  $\text{Cu-K}\alpha$  radiation was used. The data were collected over the  $2\theta$  range of  $5.0\text{--}70.0^\circ$  with steps of  $0.02^\circ$  and counting time of 2 s. The program Fullprof was used for calculation of lattice parameters.

The type of phosphate anions in the composition of the prepared compounds was identified using a FTIR spectroscopy method. Fourier transform infrared spectra (FTIR) were obtained using a PerkinElmer Spectrum BX spectrometer in the range of  $400\text{--}4000\text{ cm}^{-1}$  (at the resolution of  $1\text{ cm}^{-1}$ ) for the samples pressed into the pellets of KBr.

The elemental compositions of the samples were investigated by X-ray fluorescence method (Elvax Light spectrometer). The thermal behavior of the prepared new complex phosphates was studied using a Shimadzu simultaneous TG/DTA analyzer DTG-60H. The samples were heated in a platinum crucible in air from the room temperature to  $1000^\circ\text{C}$  with a rate of  $10^\circ\text{C}/\text{min}$ .  $\alpha\text{-Al}_2\text{O}_3$  was used as a standard sample.

### 3. Results and discussion

At the first step, the crystallization of the self-flux  $\text{Cs}_2\text{O-P}_2\text{O}_5\text{-TiO}_2$  system at the molar ratios of  $\text{Cs}/\text{P} = 0.9, 1.0$  or  $1.2$  and with fixed contents of  $\text{TiO}_2$  ( $\text{Ti}/\text{P} = 0.3$ ) was investigated. It was found, that in the

$\text{P}_2\text{O}_5$ -rich region ( $\text{Cs}/\text{P} = 0.9$ ) the solidification of the melts without formation of crystal phases took place. The increasing of the  $\text{Cs}/\text{P}$  molar ratio led to formation of different complex phosphates:  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  (at  $\text{Cs}/\text{P} = 1.0$ ) and  $\text{CsTiOPO}_4$  (at  $\text{Cs}/\text{P} = 1.2$ ). These results show that as the content of Cs cations increases in the melt, they begin to influence on the phase formation; this is manifested in the depolymerization of phosphate chains and formation of  $\text{CsTiOPO}_4$  with isolated phosphate tetrahedra  $\text{Cs}/\text{P} = 1.2$  in the cross-section. According to the X-ray powder diffraction data,  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  belongs to orthorhombic system (space group  $P2_12_12_1$ ), and the calculated lattice parameters:  $a = 13.595(4)$ ,  $b = 7.283(2)$ ,  $c = 9.473(6)\text{ \AA}$  are close to the corresponding data from ICDD #00-081-1303 (Fig. 1a). The obtained  $\text{CsTiOPO}_4$  phosphate crystallizes in a cubic system (space group  $Fd\text{-}3m$ ) with the calculated lattice parameter  $a = 10.074(1)\text{ \AA}$  (ICDD #00-048-0017) (Fig. 1b). Taking into account that for the simpler  $\text{Cs}_2\text{O-P}_2\text{O}_5\text{-TiO}_2$  system the formation of complex phosphates takes place only at the molar ratio of  $\text{Cs}/\text{P} \geq 1.0$ , we studied the peculiarities of phase formation in the melts containing the  $\text{M}^{\text{II}}$  or  $\text{M}^{\text{III}}$  cations for the  $\text{Cs}_2\text{O-P}_2\text{O}_5\text{-TiO}_2\text{-M}^{\text{III}}_2\text{O}_3$  ( $\text{M}^{\text{II}}\text{O}$ ) systems with two ratios of  $\text{Cs}/\text{P} = 1.0$  and  $1.2$  and the

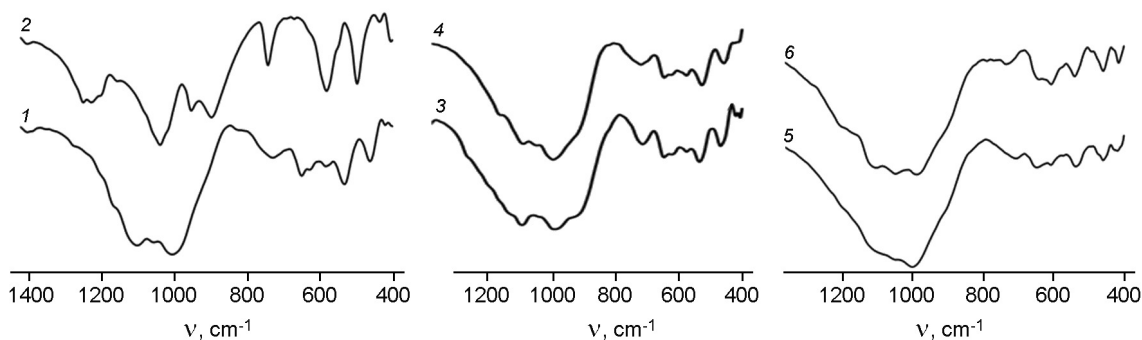


Fig. 2. FTIR-spectra of obtained phosphates:  $\text{CsTiOPO}_4$  (curve 1),  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  (curve 2),  $\text{Cs}_{1.3}\text{Ti}_{0.7}\text{Co}_{0.3}\text{OPO}_4$  (curve 3),  $\text{Cs}_{1.5}\text{Ti}_{0.5}\text{Fe}_{0.5}\text{OPO}_4$  (curve 4),  $(\text{Cs/Rb})_{1.3}\text{Ti}_{0.7}\text{Co}_{0.3}\text{OPO}_4$  (curve 5),  $(\text{Cs/Rb})_{1.5}\text{Ti}_{0.5}\text{Fe}_{0.5}\text{OPO}_4$  (curve 6).

fixed contents of polyvalent metals:  $\text{Ti/P} = 0.30$  and  $\text{Ti/M}^n = 1.0$  ( $\text{M}^n - \text{M}^{\text{II}}$  or  $\text{M}^{\text{III}}$ ).

The results of the phase analysis for the synthesized phosphates showed that the composition of the obtained phosphates does not depend on the molar ratio of Cs/P in the initial melts. According to the X-ray powder diffraction data, the complex phosphates  $\text{Cs}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$  ( $\text{M}^{\text{II}} - \text{Co}, \text{Ni}$ ) and  $\text{Cs}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $\text{M}^{\text{III}} - \text{Fe}, \text{Mn}$ ) belong to a cubic system (space group  $Fd-3m$ ) (Fig. 1c–d). Analysis of the calculated lattice parameters for the prepared compounds and their comparison with the corresponding a value for the known  $\text{CsTiOPO}_4$  phosphate ( $a = 10.074(1) \text{ \AA}$  [33]) indicates the partial heterovalent substitution of titanium atom by bi- or trivalent metal:

$\text{Ti}^{4+} \rightarrow \text{M}^{2+} + 2\text{Cs}^+$  and  $\text{Ti}^{4+} \rightarrow \text{M}^{3+} + \text{Cs}^+$ . In the case of Fe- and Mn-containing phosphates, the ionic radii of these cations are the same ( $0.645 \text{ \AA}$  for a coordination number of 6) [34], thus, the calculated lattice parameters are similar (see Table); that indicates a similar substitution degree of Ti. This fact is additionally confirmed by the elemental analysis data that indicate the formation of  $\text{Cs}_{1.5}\text{Ti}_{0.5}\text{M}^{\text{III}}_{0.5}\text{OPO}_4$  compounds.

The obtained results were analyzed and compared with data [25, 26] on the studying the interaction of  $\text{TiO}_2 + \text{M}^{\text{III}}_2\text{O}_3$  or  $\text{TiO}_2 + \text{M}^{\text{II}}\text{O}$  oxide mixtures with  $\text{Rb}_2\text{O}-\text{P}_2\text{O}_5$  melts; a significant difference between the results was established. In the case of the Rb-containing system, the langbeinite-related  $\text{Rb}_2\text{FeTi}(\text{PO}_4)_3$  [25] and  $\text{Rb}_{1.5}\text{Ni}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$  [26] phases (cubic system, space group  $P2_13$ ) were obtained; while in the Cs-containing systems, the  $\text{Cs}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$  and  $\text{Cs}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  phases (cubic system, space group  $Fd-3m$ ) were formed. This indicates the influence of the alkali metal

Table. The unit cell parameters for new phosphates  $\text{Cs}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$  and  $\text{Cs}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $0.3 < x < 0.5$ ) (cubic system, space group  $Fd-3m$ )

Complex Phosphate			
$\text{Cs}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$		$\text{Cs}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$	
$\text{M}^{\text{II}}$	$a, \text{ \AA}$	$\text{M}^{\text{III}}$	$a, \text{ \AA}$
Co	10.092(2)	Fe	10.088(1)
Ni	10.086(5)	Mn	10.089(8)

nature on the phase formation peculiarities in multi-component melts of the  $\text{M}^{\text{II}}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2-\text{M}^{\text{III}}_2\text{O}_3$  ( $\text{M}^{\text{II}}\text{O}$ ) system.

To establish the features of the influence of alkali metal pairs present in the melts on the crystallization peculiarities of the complex phosphates, the mixed alkali metal-phosphate  $\text{Cs}_2\text{O}-\text{Rb}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2-\text{M}^{\text{III}}_2\text{O}_3$  ( $\text{M}^{\text{II}}\text{O}$ ) systems at molar ratios of  $(\text{Cs} + \text{Rb})/\text{P} = 1.0$ ,  $\text{Cs/Rb} = 1.0$ ,  $\text{Ti/P} = 0.30$  and  $\text{Ti/Mn} = 1.0$  were studied. The key role of cesium cations in the formation of complex phosphates with a  $[(\text{Ti/Mn})\text{OPO}_4]$  ( $\text{M}^n - \text{M}^{\text{II}}, \text{M}^{\text{III}}$ ) crystalline lattice including both alkali metal cations was established. This influence of the alkali metal cations with a larger ionic radius on the phase crystallization process in the multi-component systems and the formation of the typical crystalline frameworks were also observed in the case of the mixed sodium-potassium [35] and potassium-rubidium [36] phosphate systems.

The FTIR spectra of the synthesized phosphates are shown in Fig. 2. The relative intensities and positions of the vibration modes in the spectra of the new  $\text{M}^{\text{II}}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$  and  $\text{M}^{\text{II}}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $\text{M}^{\text{II}} - \text{Cs}, \text{Rb/Cs}$ ) phosphates are similar to the known  $\text{CsTiOPO}_4$ : in the frequency region of  $1100-980 \text{ cm}^{-1}$ ,

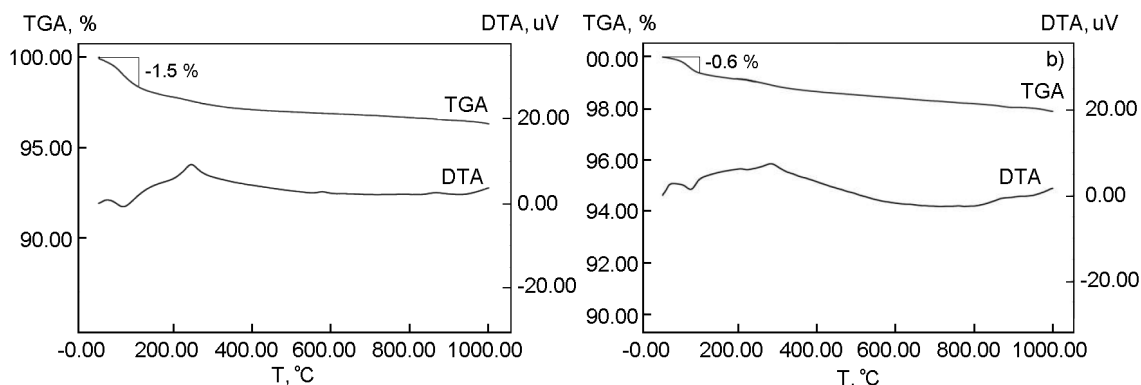


Fig. 3. Thermogravimetric and differential thermal analysis for new obtained phosphates:  $\text{Cs}_{1.5}\text{Ti}_{0.5}\text{Fe}_{0.5}\text{OPO}_4$  — a and  $(\text{Cs/Rb})_{1.3}\text{Ti}_{0.7}\text{Co}_{0.3}\text{OPO}_4$  — b.

the bands correspond to symmetric and asymmetric ( $\nu_s$  and  $\nu_{as}$ ) P–O vibrations of the  $\text{PO}_4$  tetrahedron, while at  $720\text{ cm}^{-1}$ , the (Ti–O) vibrations are observed. In the  $\text{Cs}_2\text{TiOP}_2\text{O}_7$  spectrum (Fig. 2), in the frequency region of  $1200\text{--}920\text{ cm}^{-1}$  the bands are a superposition of asymmetric and symmetric vibrations of  $\text{PO}_3$  groups; the vibrations near  $900\text{ cm}^{-1}$  correspond to asymmetric  $\nu_{as}$  (P–O–P), and at  $720\text{ cm}^{-1}$  these are symmetric  $\nu_s$  (P–O–P) of the  $\text{P}_2\text{O}_7$  group.

The TG/DTA results for the new prepared  $\text{M}^{\text{I}}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$  and  $\text{M}^{\text{I}}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $\text{M}^{\text{I}} - \text{Cs, Cs/Rb}$ ) ( $0.3 \leq x \leq 0.5$ ) phosphates showed that their melting points are higher than  $1000^\circ\text{C}$  (Fig. 3), and the phase transitions in the temperature range of  $25\text{--}1000^\circ\text{C}$  are absent. The general nature of TG and DTA curves for all the phosphates is similar, that's why only the  $\text{Cs}_{1.5}\text{Ti}_{0.5}\text{Fe}_{0.5}(\text{PO}_4)_3$  and  $(\text{Cs/Rb})_{1.3}\text{Ti}_{0.7}\text{Co}_{0.3}(\text{PO}_4)_3$  derivatograms were presented for example (Fig. 3). The mass losses during the heating of the phosphates from  $25$  to  $1000^\circ\text{C}$  were  $0.6\text{--}1.5\text{ wt. \%}$ , which is due to the removal of absorbed water. It should be noted that in the phosphates containing a pair of alkali metal cations, the content of the absorbed water was larger.

Thus, the investigation the Cs-containing multi-component melts and mixed alkali metal phosphate systems has revealed an important role of cesium cations in the formation of high-symmetric  $[(\text{Ti/Mn})\text{OPO}_4]$  frames (cubic system), while the rubidium cations promote the formation of the langbeinite-related  $[(\text{Ti/M}^{\text{n}})_2(\text{PO}_4)_3]$  phosphates [22–26].

#### 4. Conclusions

The formation peculiarities of complex phosphates in the  $\text{M}^{\text{I}}_2\text{O}\text{--}\text{P}_2\text{O}_5\text{--}\text{TiO}_2\text{--}\text{M}^{\text{III}}_2\text{O}_3(\text{M}^{\text{II}}\text{O})$  ( $\text{M}^{\text{I}} - \text{Cs, Cs/Rb}$ ,  $\text{M}^{\text{II}} - \text{Co, Ni}$ ,  $\text{M}^{\text{III}} - \text{Fe, Mn}$ ) systems at molar ratios of  $\text{M}^{\text{I}}/\text{P} = 1.0$ ,  $\text{Cs/Rb} = 1.0$ ,  $\text{Ti/P} = 0.30$  and  $\text{Ti/M}^{\text{n}} = 1.0$  were investigated using the high temperature crystallization method over the temperature range of  $1000\text{--}650^\circ\text{C}$ . It was found that the addition of bi- or tri-valent metal oxides to the self-flux  $\text{Cs}_2\text{O}\text{--}\text{P}_2\text{O}_5\text{--}\text{TiO}_2$  system expands the region of formation of phosphates with a  $[(\text{Ti/M}^{\text{n}})\text{OPO}_4]$  crystalline frame (cubic system) based on both the polyvalent metals in the molar ratio region of  $\text{Cs/P} = 1.0\text{--}1.2$ . For mixed systems of alkali metals,  $(\text{Cs/Rb})_2\text{O}\text{--}\text{P}_2\text{O}_5\text{--}\text{TiO}_2\text{--}\text{M}^{\text{III}}_2\text{O}_3(\text{M}^{\text{II}}\text{O})$ , the key role of cesium cations in the formation of  $(\text{Cs/Rb})_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$  and  $(\text{Cs/Rb})_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $0.3 \leq x \leq 0.5$ ) phosphates was established, while in rubidium-containing systems, the formation of langbeinite-related  $\text{Rb}_2\text{FeTi}(\text{PO}_4)_3$  and  $\text{Rb}_{1.5}\text{Ni}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$  complex phosphates was observed. According to the TG/DTA data, new synthesized  $\text{M}^{\text{I}}_{1+2x}\text{Ti}_{1-x}\text{M}^{\text{II}}_x\text{OPO}_4$  and  $\text{M}^{\text{I}}_{1+x}\text{Ti}_{1-x}\text{M}^{\text{III}}_x\text{OPO}_4$  ( $\text{M}^{\text{I}} - \text{Cs, Cs/Rb}$ ) ( $0.3 \leq x \leq 0.5$ ) phosphates have melting temperatures above  $1000^\circ\text{C}$ . The obtained results indicate the key role of cesium cation in the formation of complex phosphates with the  $[(\text{Ti/M}^{\text{n}})\text{OPO}_4]$  frame based on the pair of  $\text{Ti}\text{--}\text{M}^{\text{n}}$  where  $\text{M}^{\text{n}}$  are  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$ .

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