

## Ceramics based on powder mixtures of $\beta$ -tricalcium phosphate and potassium hydrogen sulfate prepared under mechanical activation in acetone medium

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Powder mixtures of  $\beta$ -tricalcium phosphate  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and potassium hydrogen sulfate KHSO<sub>4</sub> homogenized under mechanical activation in acetone medium in a planetary mill were used for producing ceramics in the K<sub>2</sub>O-CaO-SO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> system. Powder mixtures were made at molar ratios of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/KHSO<sub>4</sub> established as 7/2, 4/2 and 1/2. According to XRD analysis data  $\beta$ -tricalcium phosphate  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was the main phase in all homogenized powder mixtures. After firing at 700-900 °C the phase composition of ceramic samples made from powder mixtures with molar ratios of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/KHSO<sub>4</sub>=7/2, 4/2 contained  $\beta$ -tricalcium phosphate  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, calciolangbeinite K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and potassium calcium phosphate Ca<sub>10</sub>K(PO<sub>4</sub>)<sub>7</sub>. Phase composition of ceramic samples from powder mixtures with a molar ratio of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/KHSO<sub>4</sub> established as 1/2 contained calciolangbeinite K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>,  $\beta$ -calcium pyrophosphate  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and potassium sulfate K<sub>2</sub>SO<sub>4</sub>. Ceramic materials containing the biocompatible phases mentioned above can be recommended for bone implants creation.

**Keywords:** tricalcium phosphate, potassium hydrogen sulfate, calciolangbeinite; potassium calcium phosphate; potassium sulfate; calcium pyrophosphate

### INTRODUCTION

There is nowadays demand to create new biocompatible and bioresorbable materials for development of regenerative medicine methods of bone defect treating [1]. It is impossible to create man-made analogues of natural bone. But it is possible to create close to perfect inorganic ceramic materials for compensation of bone defects of critical size for the period of its regeneration [2]. The mineral and chemical composition of the inorganic part of the bone can be a hint for implant material creation [3]. There is the list of phases of ceramics which can slowly dissolve and, therefore, can be gradually resorbed by the body, while releasing biocompatible ions and stimulate bone regeneration [4]. Some of these ions can be used as building materials for bone restoration and other can become a part of body fluids. It is worth mentioning the following biocompatible and bioresorbable ceramic phases:  $\beta$ -tricalcium phosphate  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, pyrophosphate Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, potassium-substituted tricalcium phosphate KCa<sub>10</sub>(PO<sub>4</sub>)<sub>7</sub>, potassium rhenanite KCaPO<sub>4</sub>, calcium sulfate anhydrite CaSO<sub>4</sub> and calciolangbeinite K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

The simple way to manage the rate of resorbability of ceramic composite material consists in an intentional combination in the microstructure

of different phases with different rates of solubility. The phase of calcium sulfate anhydrite in ceramic materials is introduced in order to control the limit and rate of resorption of the material intended for the treatment or temporary compensation of a bone defect during its restoration. The use of calcium sulfate anhydrite as a phase of a ceramic material for bone implants is of interest both by itself and in combination with other ceramic phases capable to be resorbed [5].

Different oxide systems were used for bioceramics creation up to nowadays. The most popular of them are CaO-P<sub>2</sub>O<sub>5</sub>, CaO-MgO-P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O-CaO-P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O-CaO-P<sub>2</sub>O<sub>5</sub>. Probably one attempt was made to create a ceramic composite in the K<sub>2</sub>O-CaO-SO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> oxide system [6] Ceramics containing tricalcium phosphate  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, potassium-substituted tricalcium phosphate Ca<sub>10</sub>K(PO<sub>4</sub>)<sub>7</sub> and calciolangbeinite K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> were created based on powder mixtures prepared from calcium hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> and potassium hydrogen sulfate KHSO<sub>4</sub> [6].

The aim of the present study consisted in creation of ceramic composites with biocompatible and bioresorbable phases in the K<sub>2</sub>O-CaO-SO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> system based on powder mixtures of  $\beta$ -tricalcium phosphate  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and potassium hydrogen sulfate KHSO<sub>4</sub>.

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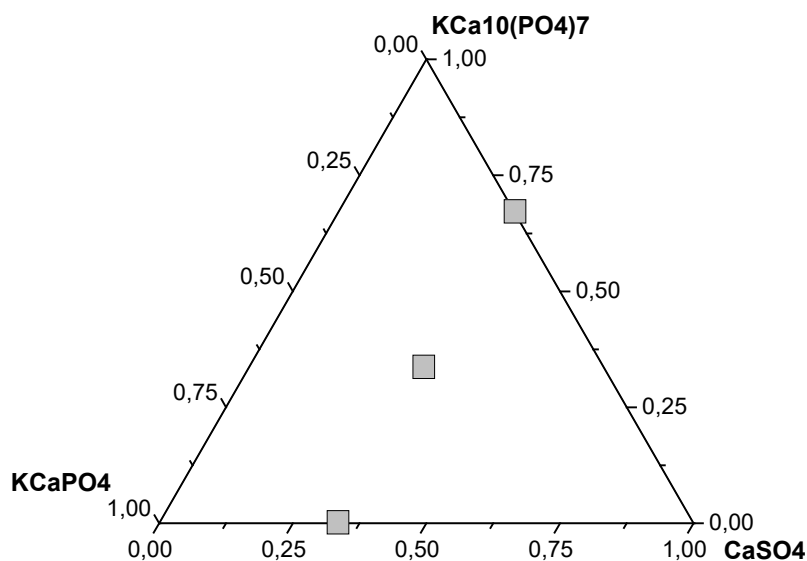
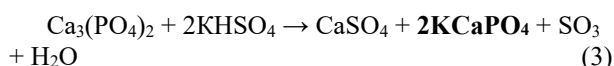
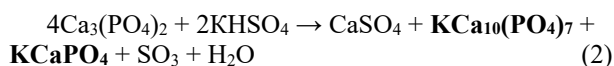
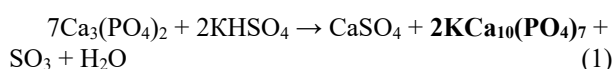


Fig. 1. Planned phase compositions of ceramic materials

#### EXPERIMENTAL

Planned phase compositions of ceramic samples are pointed in the diagram presented in Fig. 1. The following reactions (1-3) were used for calculation of the quantity of starting components (i.e.  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and potassium hydrogen sulfate  $\text{KHSO}_4$ ) of powder mixtures for preparation of ceramic samples with phase compositions pointed on the diagram (Fig. 1).



$\beta$ -Tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  (Sigma Aldrich, CAS # 7758-87-4, purum p.a.,  $\geq 96.0\%$ ) and potassium hydrogen sulfate  $\text{KHSO}_4$  (Russian Federation State Standard GOST 4223-75, CAS# 7646-93-7) were used for powder mixtures preparation. Powders of  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and potassium hydrogen sulfate  $\text{KHSO}_4$ , grinding media made of zirconium dioxide  $\text{ZrO}_2$ , and acetone (Russian Federation State Standard GOST 2603-79) were placed in containers made of agate. Then, the containers with powders,  $\text{ZrO}_2$ -grinding media, and acetone were fixed in a planetary mill. The planetary mill treatment of powder mixtures was conducted for 15 min at a rotation speed of 500 rpm and at ratio powder: grinding media = 1:5. Then, for acetone evaporation

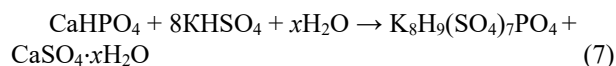
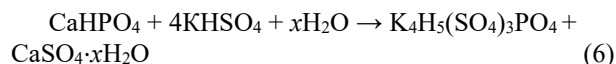
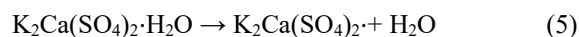
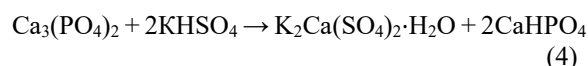
the powder mixtures were dried in air at ambient temperature for 2 h. After drying, the powder mixtures were passed through a sieve with mesh size of 200  $\mu\text{m}$ . Compact powder pre-ceramic samples in the form of disks of 12 mm in diameter and 2–3 mm thick were made from the prepared powder mixtures using a Carver laboratory press model C hand press at specific pressure of 100 MPa without any technological binder. The powder pre-ceramic samples were fired at 700, 800, 900  $^\circ\text{C}$  with a heating rate of 5 $^\circ\text{C}/\text{min}$  and holding time of 2 hours at the specified temperature.

Linear shrinkage and geometrical density of ceramic samples were determined by measuring their weight and size (with accuracy of  $\pm 0.05$  mm) before and after firing. X-ray powder diffraction (XRD) analysis of powder mixtures after treatment in the planetary mill and samples after firing was conducted on a Rigaku D/Max-2500 diffractometer with rotating anode (Japan) using  $\text{CuK}\alpha$  radiation. Phase analysis was performed using ICDD PDF2 database [1]. Synchronous thermal analysis was performed on a Netzsch STA 409 PC Luxx (Germany) thermal analyzer at a heating rate of 10 $^\circ\text{C}/\text{min}$ . Sample weight was at least 10 mg. The study of the composition of the gas phase resulting from sample decomposition was conducted with a Netzsch QMS 403C Aëolos (Germany) quadrupole mass spectrometer coupled with a Netzsch STA 409 PC Luxx thermal analyzer. Mass spectra were recorded for molecular weights 18 ( $\text{H}_2\text{O}$ ) and 64 ( $\text{SO}_2$ ). Microstructure of samples was studied by scanning electron microscopy using a Carl Zeiss

LEO SUPRA 50VP (Germany, auto emission source) at accelerating voltage of 3–20 kV in secondary electrons (SE2 detector). Samples were coated by chromium layer (up to 10 nm).

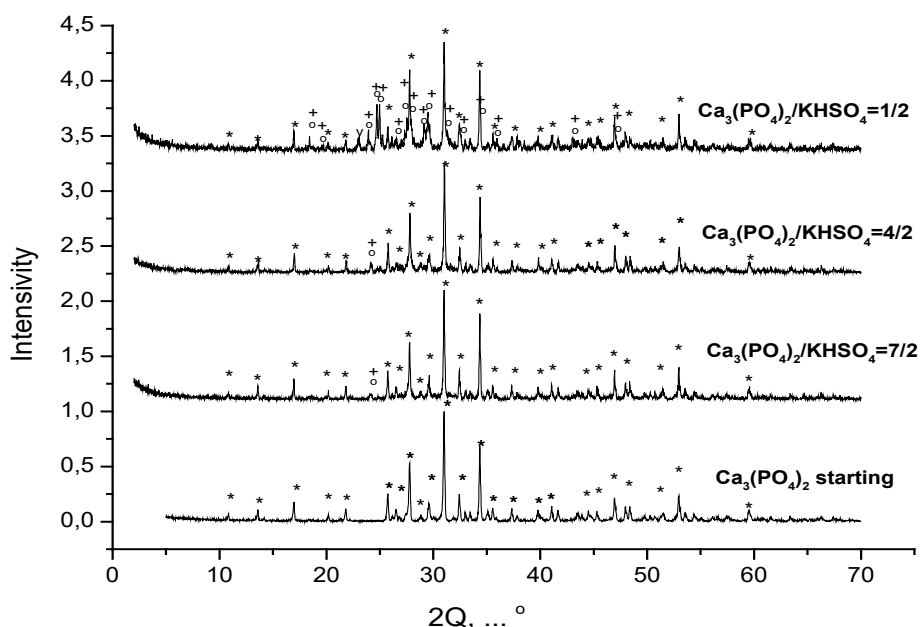
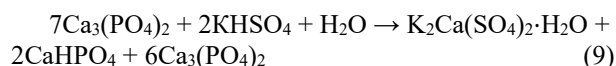
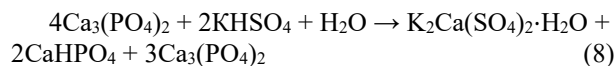
### RESULTS AND DISCUSSION

XRD data of powder mixtures of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  after mechanical activation in acetone medium are presented in Fig. 1. As we can see the phase composition of the powder mixtures did not change remarkably during homogenization. According to XRD analysis data  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  was the main phase in all powder mixtures after treatment in a planetary mill in acetone medium during 15 min. Only the powder mixture prepared at molar ratio of  $\text{Ca}_3(\text{PO}_4)_2 / \text{KHSO}_4 = 1/2$  with the biggest quantity of potassium hydrogen sulfate had small quantities of additional phases. Potassium hydrogen sulfate phosphates  $\text{K}_4\text{H}_5(\text{SO}_4)_3\text{PO}_4$  and  $\text{K}_8\text{H}_9(\text{SO}_4)_7\text{PO}_4$  were found additionally to  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  in the powder mixture with molar ratio of  $\text{Ca}_3(\text{PO}_4)_2 / \text{KHSO}_4 = 1/2$ . Presumably the following sequence of reactions could take place in case of local excess of potassium hydrogen sulfate  $\text{KHSO}_4$  in acetone medium:



Reflexes of phases of hydrated gypsum  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$  or syngenite  $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  were not found according to XRD data in the powder mixtures with a molar ratio of  $\text{Ca}_3(\text{PO}_4)_2 / \text{KHSO}_4 = 1/2$  after their treatment in a planetary mill in acetone medium presumably because of small quantities or due to their presence in quasi-amorphous form.

To keep in mind molar ratios of starting components in powder mixtures we can rewrite reaction (4) for the molar ratio of  $\text{Ca}_3(\text{PO}_4)_2 / \text{KHSO}_4 = 4/2$  (reaction 8) and for the molar ratio of  $\text{Ca}_3(\text{PO}_4)_2 / \text{KHSO}_4 = 7/2$  (reaction 9) as follows:



**Fig. 2.** XRD data of powder mixtures of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  after mechanical activation in acetone medium.  
\* -  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ , PDF-Card 9-169; o -  $\text{K}_8\text{H}_9(\text{SO}_4)_7\text{PO}_4$ , PDF-Card 48-709; + -  $\text{K}_4\text{H}_5(\text{SO}_4)_3\text{PO}_4$ , PDF-Card 48-710; v -  $\text{KHSO}_4$ , PDF-Card 11-649

This formal presentation of possible processes can help to understand the dominant presence of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and absence of reflexes of acidic

potassium hydrogen sulfate phosphates at XRD graphs for powder mixtures with molar ratios of  $\text{Ca}_3(\text{PO}_4)_2 / \text{KHSO}_4 = 4/2$  and  $\text{Ca}_3(\text{PO}_4)_2 / \text{KHSO}_4 =$

7/2 because potassium hydrogen sulfate was taken in quantities that were lower than it was necessary for development of reaction (4).

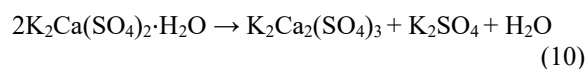
Comparison of the microstructures of the prepared powder mixtures (Fig. 3) allows us to make a conclusion about a slight difference of particle dimensions of different powder mixtures. The higher the content of potassium hydrosulfate powder the lower is the particle dimension.

Thermal analysis data indicate a decrease in the mass of the powder mixtures during heating (Fig. 4 a). The higher the content of calcium hydrosulfate in the initial mixtures, the greater is the change of the mass of the powders. DSC data are presented in Fig. 4 b.

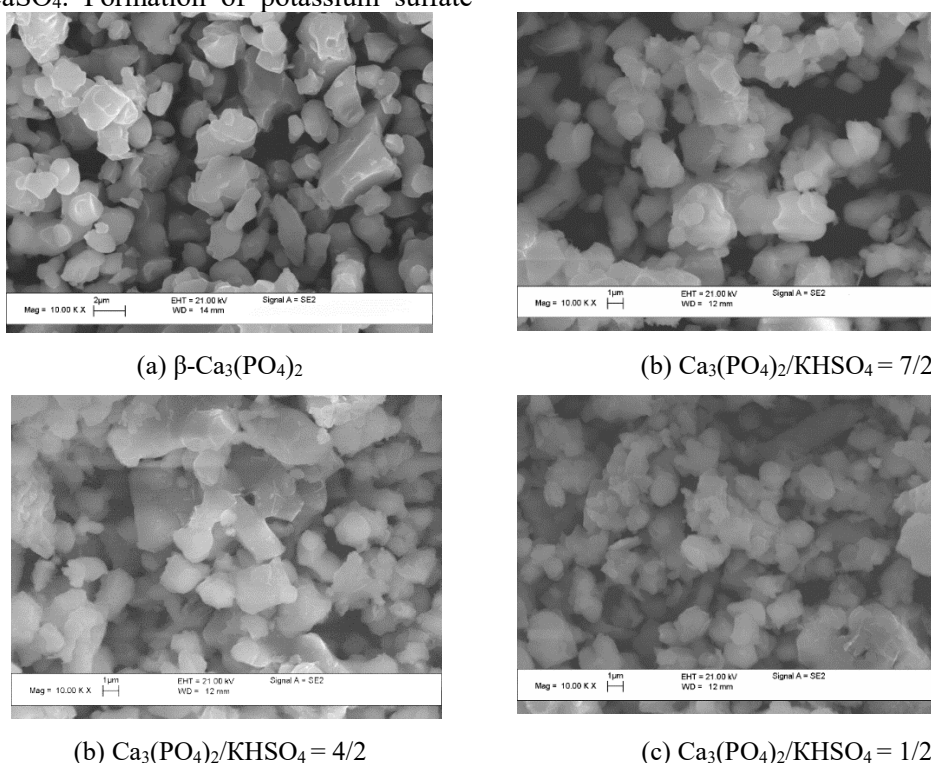
One can see two endothermic peaks at 210 °C and at 868 °C on the DSC curve for powder mixture prepared at molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  established as 1/2. The first peak can be attributed to a process of salts decomposition and water release (Fig. 5 a).

The second peak can be attributed to eutectic melting point (867 °C [8]) present in the system  $\text{K}_2\text{SO}_4 - \text{CaSO}_4$ . Formation of potassium sulfate

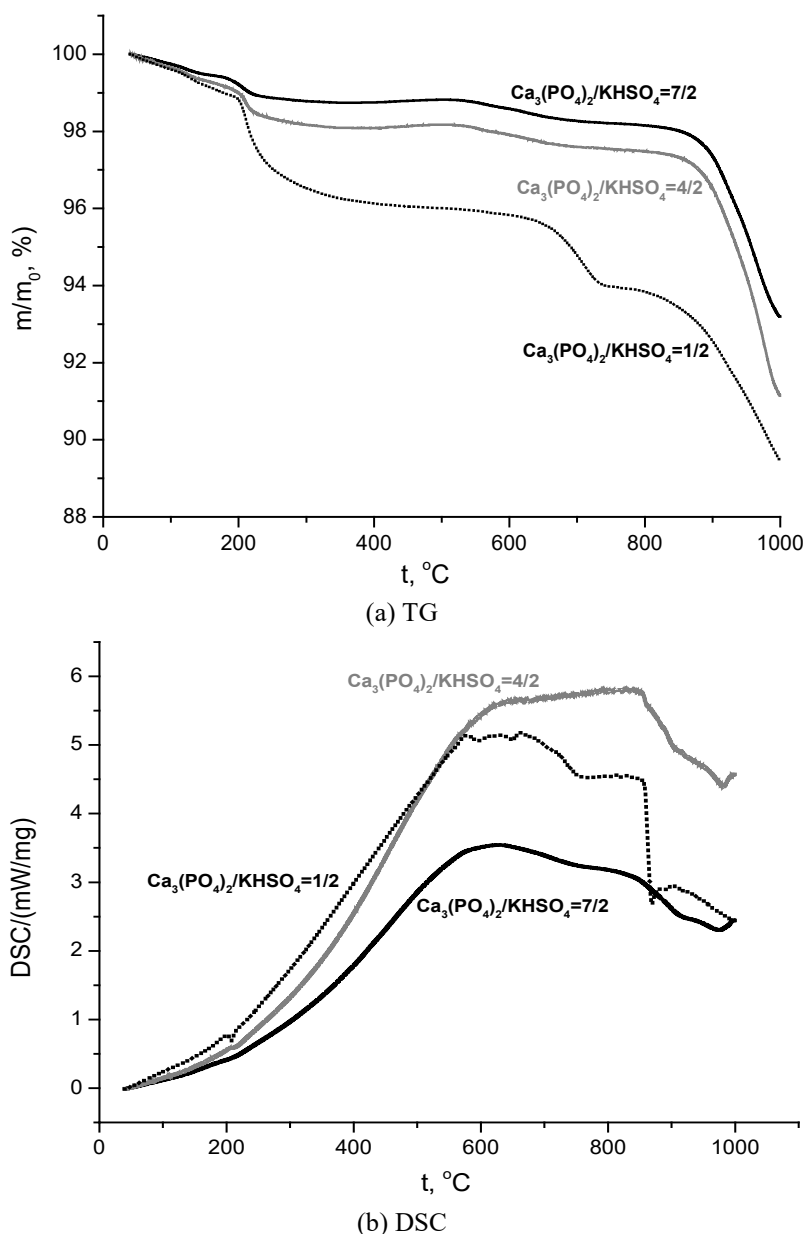
$\text{K}_2\text{SO}_4$  can take place due to formation of calciolangbeinite (potassium calcium double sulfate)  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$  from syngenite  $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  (reaction 10) [9]:



The higher the content of calcium hydrosulfate in the initial mixtures, the greater is the change of the mass of the powders. The mass spectrometry data for  $m/Z=18$  (Fig. 5 a) reflect the release of water from the studied powder mixtures. The change of the powder mixture masses takes place due to the release of physically bound water at a temperature about 100 °C. The change of the powder mixture masses takes place due to decomposition of different hydrated salts in the range about 200-500 °C for all powder mixtures. The change of the powder mixture masses due to water release takes place in the range of 500 - 800 °C for powder mixtures with molar ratio  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$  and 4/2; and in the range of 550-600 °C for the mixture with molar ratio  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 1/2$ .



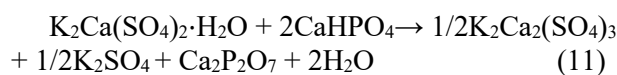
**Fig. 3.** Microstructure of starting powder of  $\beta$ -tricalcium phosphate  $\beta\text{-Ca}_3(\text{PO}_4)_2$  (a) and powder mixtures after mechanical activation in acetone medium prepared at molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  established as 7/2 (b), 4/2 (c) and 1/2 (d).

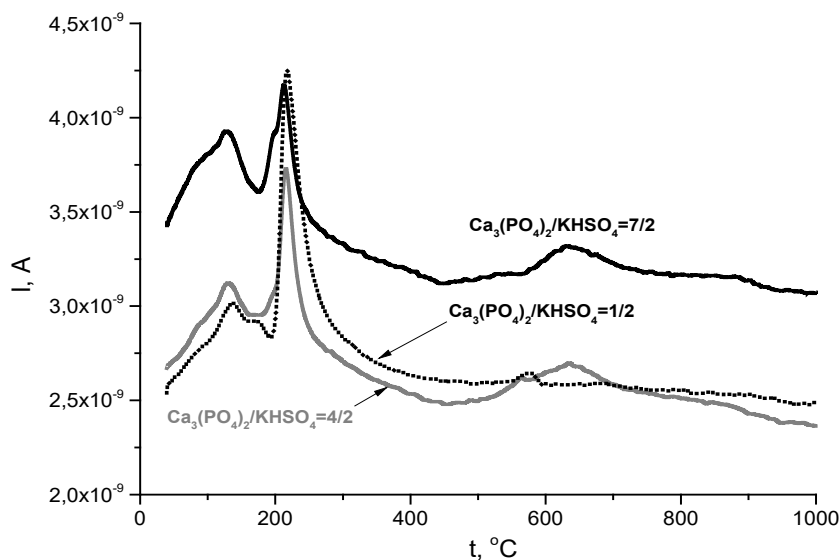


**Fig. 4.** Thermal analysis data for powder mixtures prepared from  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  using mechanical activation treatment: TG (a); DSC (b).

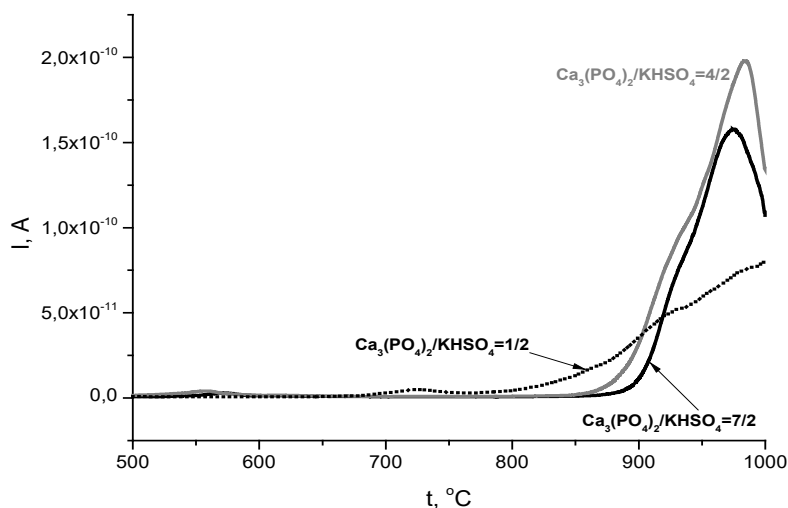
The mass spectrometry data for  $m/Z=64$  reflect the release of sulfur oxide  $\text{SO}_2$  from the studied powder mixtures. Sulfur oxide  $\text{SO}_2$  evolution from powder mixture prepared at molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  established as 1/2 started at 670 °C; from powder mixture prepared at molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  established as 4/2 started at 850 °C and from powder mixture prepared at molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  established as 7/2 started at 880 °C. At 1000 °C  $\text{SO}_2$  evolution process for powder mixtures with molar ratios  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$  and 4/2 had the tendency to finish. For powder mixture with molar ratio  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 1/2$  the change in the mass of the samples due to the release

of sulfur oxide took place without any tendency to finish up to 1000 °C. The higher the content of potassium hydrogen sulfate in the initial mixture, the more noticeable is the contribution of this process to the change in the mass of powder mixtures. We assume that  $\text{SO}_2$  evolution can be due to formation of potassium substituted tricalcium phosphate from potassium sulfate and calcium phosphates. For powder mixture with molar ratio  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 1/2$  with reference to reaction 4 the following reactions during heating can be suggested:





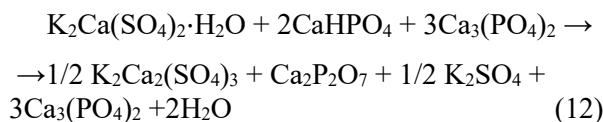
(a) MS\_18\_H2O



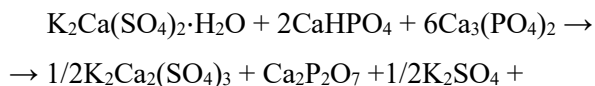
(b) MS\_64\_SO2

**Fig. 5.** Thermal analysis data for powder mixtures prepared from  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  using mechanical activation treatment: MS\_18\_H2O (a); MS\_64\_SO2 (b).

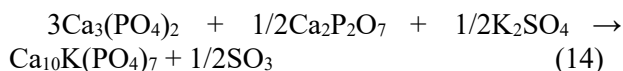
For a powder mixture with molar ratio  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 4/2$  with reference to reaction 8 the following reaction during heating can be suggested:



For powder mixture with molar ratio  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$  with reference to the reaction 9 the following reaction during heating can be suggested:



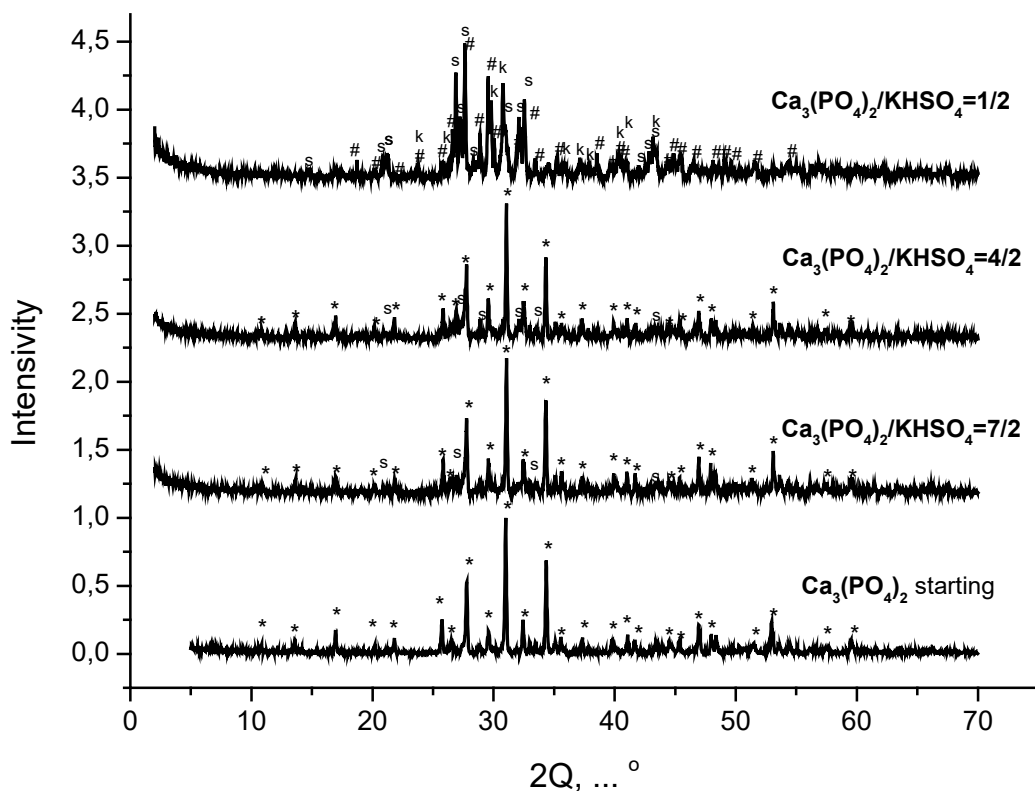
Formation of potassium substituted tricalcium phosphate can be described by reaction (14).



Reactions 11-14, written taking into account the data of XRD of powder mixtures after treatment under conditions of mechanical activation and thermal analysis and the keeping in mind of the molar ratio of K/Ca/S/P in starting powder mixtures give us opportunity to expect the following phase composition in ceramic materials presented in Table 1.

**Table 1.** Possible phase composition of ceramic materials based of powder mixture of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$

Molar ratio of $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$	$\beta$ - $\text{Ca}_3(\text{PO}_4)_2$	$\text{K}_2\text{Ca}_2(\text{SO}_4)_3$	$\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$	$\text{K}_2\text{SO}_4$	$\text{Ca}_{10}\text{K}(\text{PO}_4)_7$
7/2	+	+	+	-	+
4/2	-	+	+	-	+
1/2	-	+	+	+	-



**Fig. 6.** XRD data of ceramic samples based on powder mixtures of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  prepared under mechanical activation after firing at  $900^\circ\text{C}$  (2 hours).

# -  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ , PDF-card 9-346; k -  $\text{K}_2\text{SO}_4$ , PDF-card 5-613; s -  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ , PDF-card 20-867;

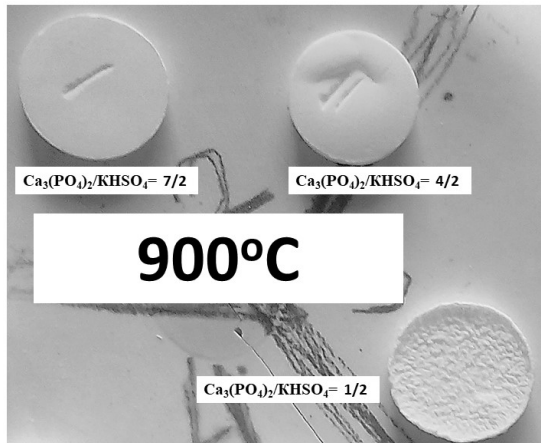
\* -  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ , PDF-card 45-138; \* -  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ , PDF-Card 9-169;

We can see from the table that all ceramic samples could include calciolangbeinite  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$  and  $\beta$ -pyrophosphate  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ . In ceramic samples based on powder mixtures with the biggest quantity of  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  in the starting powder mixture ( $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$ )  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  could be in the phase composition. Potassium substituted tricalcium phosphate could be in the ceramics based on the powder mixtures with  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$  and  $4/2$ . And potassium sulfate could be in the phase composition of ceramic samples based on powder mixture with  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 1/2$ .

XRD data of ceramic samples based on powder mixtures of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  prepared under mechanical activation after firing at  $900^\circ\text{C}$  are presented in Fig. 6.

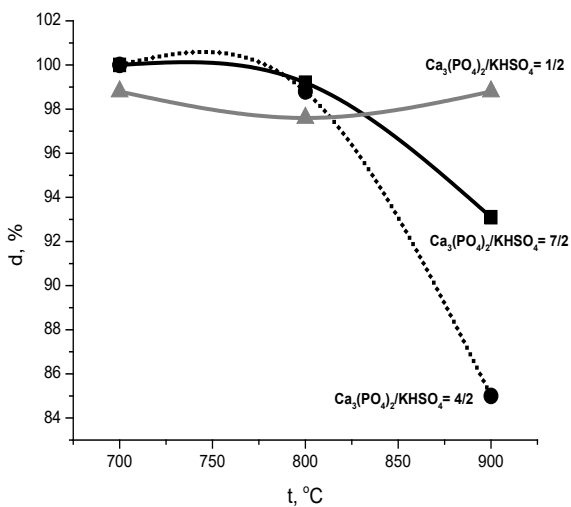
According to XRD data (Fig. 6) calciolangbeinite  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$  was found in the phase composition of all ceramic samples after firing at  $900^\circ\text{C}$ . XRD reflexes of  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and potassium-substituted tricalcium phosphate  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  are very close. Those reflexes were found in ceramics based on a powder mixture with molar ratio  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$  and  $4/2$ . The phase composition of ceramics based on a powder mixture with a molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 1/2$  also included  $\beta$ -pyrophosphate  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and potassium sulfate  $\text{K}_2\text{SO}_4$ . Phase compositions of ceramic samples found using XRD data are in good correlation with expected phase composition of ceramics suggested in table 1. Only  $\beta$ -pyrophosphate  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  was not found by means XRD in ceramic samples based on powder mixture with a molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$ .

Phone photo shows the apparent difference between ceramic samples after firing at 900 °C (Fig. 7).



**Fig. 7.** Phone photo of ceramic samples after firing at 900 °C (2 hours).

The maximum density ( $\sim 2 \text{ g/cm}^3$ ) and maximum linear shrinkage (16%) were observed for a sample based on a powder mixture with molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 4/2$  (Figs. 8 and 9).



**Fig. 8.** Dependence of the diameter of ceramic samples obtained from powder mixtures prepared under mechanical activation conditions in acetone at molar ratios  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2, 4/2, 1/2$  on firing temperature.

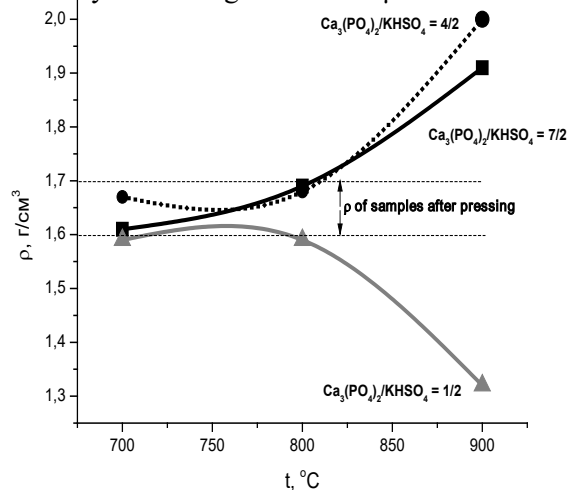
Micrographs of cross-sections and surfaces of ceramic samples after firing at 900°C prepared based on powder mixtures of  $\beta\text{-Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  mechanically activated in acetone medium at molar ratios of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  established as 7/2, 4/2 and 1/2 are presented in Fig. 10.

Microstructure of ceramic sample with a molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  specified as 7/2 (Fig. 10 a,b)

looks undersintered, the diameter of the sampleremains practically the same as before firing. The grain size can be estimated as 2-4  $\mu\text{m}$ .

The microstructure of a ceramic sample with a molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  specified as 1/2 also looks undersintered. One can see microcracks in the cross-section. The grain size can be estimated as 0.5-3  $\mu\text{m}$ .

The microstructure of a ceramic sample with a molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  specified as 4/2 looks better than others. The grain size is preferably in the range of 0.3-1.5  $\mu\text{m}$ .

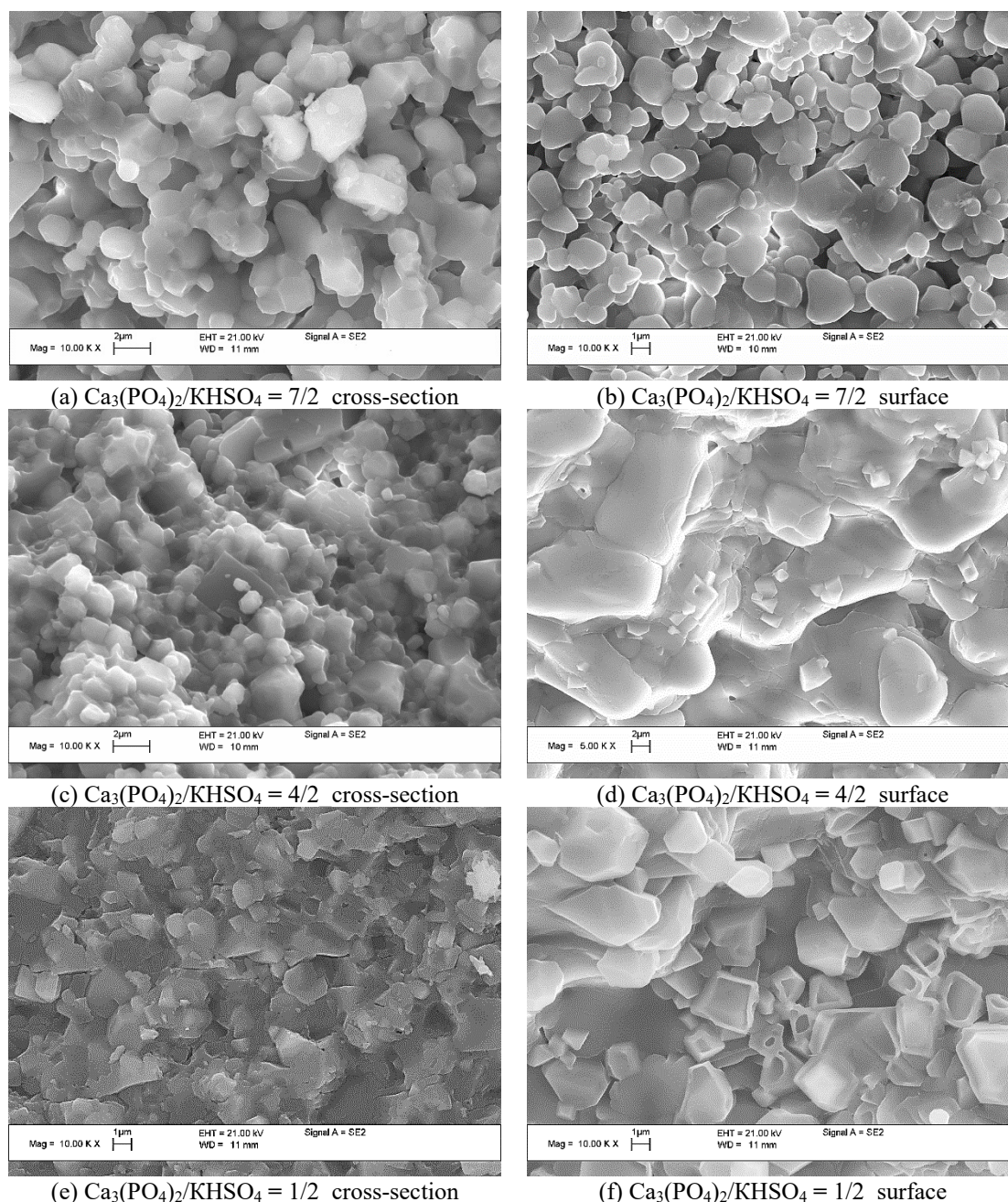


**Fig. 9.** Dependence of density of ceramic samples obtained from powder mixtures prepared under mechanical activation conditions in acetone at molar ratios  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2, 4/2, 1/2$  on firing temperature.

## CONCLUSIONS

Powder mixtures of  $\beta$ -tricalcium phosphate  $\beta\text{-Ca}_3(\text{PO}_4)_2$  and potassium hydrogen sulfate  $\text{KHSO}_4$  were homogenized in acetone medium under conditions of mechanical activation using a planetary mill at molar ratios established as 7/1, 4/1 and 2/1.  $\beta$ -Tricalcium phosphate  $\beta\text{-Ca}_3(\text{PO}_4)_2$  was the main phase in all prepared powder mixtures. Only the powder mixture with the highest content of potassium hydrogen sulfate  $\text{KHSO}_4$  (molar ratio  $\beta\text{-Ca}_3(\text{PO}_4)_2/\text{KHSO}_4=1/2$ ) additionally had small quantities of potassium hydrogen sulfate phosphates such as  $\text{K}_8\text{H}_9(\text{SO}_4)_7\text{PO}_4$  and  $\text{K}_4\text{H}_5(\text{SO}_4)_3\text{PO}_4$ . It was the first time when we observed the formation of acidic potassium sulfate phosphates in the powder systems based on  $\beta\text{-Ca}_3(\text{PO}_4)_2$  and potassium hydrogen sulfate  $\text{KHSO}_4$  during mechanical activation.





**Fig. 10.** Micrographs of ceramic samples after firing at  $900^\circ\text{C}$  prepared based on powder mixtures of the  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KHSO}_4$  mechanically activated in acetone medium at molar ratios of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4$  established as 7/2 (a, b), 4/2 (c, d) and 1/2 (e, f); cross-sections (a, c, e) and surfaces (b, d, f).

After firing at  $900^\circ\text{C}$  the phase composition of all ceramic samples contained phase of calciolangbeinite  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ . Reflexes of  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ , potassium-substituted tricalcium phosphate  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  were found in ceramics based on powder mixtures with molar ratios  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 7/2$  and  $4/2$ . The phase composition of ceramics based on a powder mixture with a molar ratio of  $\text{Ca}_3(\text{PO}_4)_2/\text{KHSO}_4 = 1/2$  also included  $\beta$ -pyrophosphate  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and potassium sulfate  $\text{K}_2\text{SO}_4$ .

The results of this study allow us to consider the possibility of creating new ceramic composite

materials for the treatment of bone tissue defects, which, in addition to calcium phosphate phases such as  $\beta$ -tricalcium phosphate  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  and  $\beta$ -pyrophosphate  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ , include potassium-substituted tricalcium phosphate  $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$  and calciolangbeinite  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$  as a possible new resorbable phase of the ceramic material containing  $\beta$ -calcium pyrophosphate  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ .

It should be noted that formation of calciolangbeinite  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$  in the powder system containing calcium phosphate and potassium hydrogen sulfate forced the formation of calcium phosphate during heating with lower calcium to

phosphorus ratio than starting calcium phosphate had.

The results of the present investigation can be taken into account when creating resorbable ceramic materials in the  $K_2O$ - $CaO$ - $SO_3$ - $P_2O_5$  system for bone defect treating, with biocompatible and bioresorbable phases such as tricalcium phosphate  $Ca_3(PO_4)_2$  and calciolangbeinite (potassium calcium double sulfate)  $K_2Ca_2(SO_4)_3$ .

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