

Amorphous calcium phosphate powder synthesized from calcium acetate and polyphosphoric acid for bioceramics application



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ABSTRACT

Amorphous hydrated calcium phosphate powder was synthesized at room temperature from aqueous solutions of polyphosphoric acid and calcium acetate with addition of ammonia water solution. Synthesized powder remains amorphous after heat in the temperature range 200–500 °C. Phase composition of powder and compacted powder samples after firing at 800 °C consists of calcium polyphosphate (β -Ca(PO₃)₂), tromelite (Ca₄P₆O₁₉) and calcium pyrophosphate (β -Ca₂P₂O₇). Synthesis of amorphous hydrated calcium phosphate powder with the ion-exchange stage for preparing an aqueous solution of polyphosphoric acid can be recommended as a simple way of production of powdered precursor for biocompatible bioresorbable phosphate ceramics containing calcium polyphosphate, tromelite and calcium pyrophosphate.

1. Introduction

Modern medicine development demands creation of new materials which can be used for treatment of injured bone. The modern regeneration approach of injured bone treatment can be extended if a variety of bioresorbable ceramic materials based on calcium phosphates is available. The implanted biomaterial should be gradually replaced by natural bone tissue, serving as a source of elements such as calcium and phosphorus for the tissue regeneration. The ability to be resorbed is strongly related to solubility of the implanted material. The lower is the calcium to phosphorus (Ca/P) molar ratio in a calcium phosphate material, the higher is its ability to be dissolved and, hence, to be resorbed. Calcium phosphates with $0.5 \leq \text{Ca/P} \leq 1.5$ have been recognized as bioresorbable and biocompatible materials. Calcium polyphosphate (Ca(PO₃)₂)_n [hereafter, designated as Ca(PO₃)₂ for short] has the lowest possible Ca/P molar ratio, 0.5. Therefore, ceramics based on calcium polyphosphate or containing this phase are promising biomaterials for regenerative medicine applications. Ceramics based on calcium polyphosphate has already been produced, investigated, and tested in vitro [1,2] and in vivo [3,4].

Special-purpose ceramic materials are usually prepared from fine-powder precursors. Various synthetic routes have been investigated to obtain powders applied for fabrication of calcium phosphate ceramics, precipitation from aqueous solutions being the most popular one. Aqueous solutions of soluble ortho- or pyrophosphates have been used

for precipitation of various calcium phosphates [5,6]. Majority of the wet-precipitated powder precursors of calcium phosphate ceramics are hydrated acidic or basic salts. In view of this, powders with the molar ratio Ca/P=0.5 can be used for creation of the calcium polyphosphate phase in ceramics. A number of compounds meeting this demand have been reported: Ca(H₂PO₄)₂ and Ca(H₂PO₄)₂·H₂O [7,8], CaH₂P₂O₇ [9], CaH₂P₂O₇·H₂O, [10], CaNH₄HP₂O₇ [11], Ca(NH₄)₂P₂O₇·H₂O [12], CaNH₄HP₂O₇, Ca₂NH₄H₃(P₂O₇)₂·H₂O, Ca₂NH₄H₃(P₂O₇)₂·3H₂O [13], and CaH₂(HPO₃)₂ [14]. The desired calcium polyphosphate phase of a ceramic material can be formed via thermal treatment of powders of the above-listed salts.

The most well studied and widely used compound of the hydrated acidic calcium phosphate type is Ca(H₂PO₄)₂·H₂O; it has been used for preparation of Ca(PO₃)₂ powder, further applied in manufacturing of porous bioceramics [3,4]. Glassy or crystalline powders of Ca(PO₃)₂ [15] have been synthesized from Ca(H₂PO₄)₂·H₂O via thermal treatment. Powder of calcium polyphosphate polymorph stable up to 690 °C (γ -Ca(PO₃)₂) has been synthesized from an acidic flux prepared of phosphoric acid (H₃PO₄, 85 wt%) and calcium hydroxide (Ca(OH)₂) [16].

According to the phase diagram [17], any calcium phosphate phase can be formed in a ceramic material via heterogeneous heat-induced reaction in a properly homogenized mixture of a calcium- and phosphorus-containing powders, provided that the precursors are taken in stoichiometric ratio. Examples of preparation of the desired

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calcium phosphate phases can be found in Refs. [18–20].

An attempt to prepare sodium calcium polyphosphate via the interaction of calcium chloride and sodium polyphosphate has been reported in Ref. [21]. However, sodium calcium polyphosphate cannot serve as a precursor of pure calcium phosphate-based ceramics; instead, ceramics containing sodium phosphates or sodium calcium polyphosphates are thus formed.

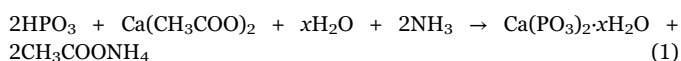
Pyrophosphoric, metaphosphoric, and polyphosphoric acids as well as ammonium pyrophosphate and polyphosphate can be hardly found as commercially available reagents. Compounds containing condensed phosphate anion can be synthesized via heating of orthophosphoric acid [22]. However, generally this method yields a mixture of phosphate anions with different condensation degree rather than a single-phase product. Methods taking advantage of ion exchange are far more attractive for synthesis of the acids containing condensed phosphate anions [23].

This work aimed to elaborate a convenient procedure to prepare a powdered precursor of calcium polyphosphate ceramic phase via the interaction of calcium acetate and polyphosphoric acid in the aqueous solution in presence of ammonia aqueous solution. In particular, we report a simple yet versatile method to synthesize a powder precursor of calcium polyphosphate phase from aqueous solutions of calcium acetate and polyphosphoric acid, the latter being prepared from NaPO_3 via ion exchange. We would like to underscore the choice of calcium acetate as a calcium ions source. The presence of ammonium acetate and/or acetic acid (the by-products) in the synthesized powder leads to the formation of uniformly distributed carbon in the prepared powder of calcium phosphates after its thermal treatment at relatively low (about 800 °C) temperatures [24]. The presence of such carbon phase in the inorganic powder can (1) afford the ultrafine grained microstructure of the ceramics, (2) yield a gaseous porogen if irregular porous structure should be formed in the ceramics in the presence of inorganic melt, (3) serve as a coloring agent thus improving the printing quality (if stereolithography is used for molding of prefabricated unit of porous ceramic material with regular architecture from suspension of the inorganic powder in a mixture of UV-curable monomers).

2. Experimental

2.1. Powder synthesis and samples preparation

Calcium phosphate powder was fabricated via conventional wet-precipitation technique according to formal reaction (1), from 0.5 M. aqueous solution of polyphosphoric acid and 0.5 M. aqueous solution of calcium acetate anhydrate (GOST R 54537-2011, Labteh, Russia).



In turn, polyphosphoric acid was prepared via ion exchange technique from aqueous solution of sodium hexametaphosphate (NaPO_3)₆ (crystalline, +200 mesh, 96%, Aldrich) using KU-2–8 ion exchange resin (GOST 202 98-71, “AZOT”, Cherkassy, Ukraine) in the H^+ -form. The ion exchange resin was taken in excess (by mass) with respect to sodium hexametaphosphate. The scheme of calcium phosphate powder preparation is presented in Fig. 1.

After addition of a stoichiometric (according to Eq. (1)) amount of aqueous solution of $\text{Ca}(\text{CH}_3\text{COO})_2$ to an aqueous solution of polyphosphoric acid, followed by addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$ to pH =9, white precipitate was formed. Its suspension in the mother liquor was matured for 15 min at room temperature, and then the product was filtered off and dried in air during 48 h (no washing of the precipitate was performed). The dried powder was disaggregated in a ball mill for 3 min in acetone medium at the liquid (acetone): powder: grinding media(ZrO_2) ratio equal to 2:1:5 (w/w/w).

The so processed powder was sieved (Saatile HiTech™ polyester fabrics, 200 μm) and uniaxially compacted portionwise (0.5 g) in a stainless steel disc-shaped mold (diameter 12 mm) at 50 MPa using Carver laboratory press model C (USA). Paraffin wax (melting point 53–57 °C, Aldrich) was used as the plasticizer (10% of the calcium phosphate mass). Small batches of the non-compacted product after drying and disaggregation were annealed at different temperatures (2 h, 200–800 °C, step 100 °C). The compacted specimens were annealed at different temperatures (2 h, 400–1000 °C, step 100 °C) as well.

2.2. Samples characterization

Density of the green compacts and sintered samples was calculated from the measured mass and geometry dimensions of the specimens. Phase composition of the prepared powders and compacted samples after the heat treatment was examined by means of X-ray diffraction (XRD) (2θ 5–70°, Cu K_α radiation, Rigaku D/MAX 2500 with rotating anode, Japan). The phases were identified using ICDD PDF2 database [25]. Fourier transform infrared spectra (FTIR) were recorded in the 520–4000 cm^{-1} range using a Spectrum One FTIR spectrometer (PerkinElmer, USA). Thermal analysis (TA) was performed using an STA 409 PC Luxx thermal analyzer (NETZSCH, Germany) during heating in air (10 °C/min, 40–1000 °C), the specimen mass being at least 10 mg. The evolved gases composition was simultaneously monitored during the TA experiment using a coupled QMS 403 C Aeolos quadrupole mass spectrometer (NETZSCH, Germany). The mass spectra were registered for the species with following m/z values: 18 (corresponding to H_2O), 44 (corresponding to CO_2), 30 (corresponding to NO), and 12 (corresponding to C). The specimens microstructure was studied using a SUPRA 50 VP scanning electron microscope (Carl Zeiss, Germany); the imaging was performed in a low vacuum mode at an accelerating voltage of 21 kV (VPSE secondary electron detector) or of 3–21 kV (SE2 detector). The absorption spectra (λ 200–700 nm) of the heat-treated samples (400–600 °C, disc-shaped, diameter 10–11 mm) were recorded using a Lambda 35 UV/VIS spectrophotometer (PerkinElmer, USA). Degradation of ceramic samples after the heat treatment at 700, 800 and 900 °C was estimated according to ISO 10993, part 14 “Identification and quantification of degradation products from ceramics” [26]. Briefly, 1 g of crushed and sieved (315 μm mesh) sample of the ceramic material was placed in a plastic container, and 20 mL of citric buffer solution (pH 3) was added; mass loss was measured after 120 h keeping of the specimen of ceramic material at 37.5 °C.

3. Results and discussion

According to XRD data (Fig. 2), the as-synthesized powder as well as the powder heat-treated at 200–500 °C were amorphous (the formation of $\gamma\text{-Ca}(\text{PO}_3)_2$ was not detected in after annealing over that temperature range). It should be noted that when a different synthesis procedure had been used, $\gamma\text{-Ca}(\text{PO}_3)_2$ was formed already at 250 °C, and $\beta\text{-Ca}(\text{PO}_3)_2$ appeared at 600 °C [27]; alternatively, $\gamma\text{-Ca}(\text{PO}_3)_2$ was formed at T 250–400 °C, being transformed into calcium polyphosphate glass upon further heating up to 550 °C [16].

According to the FTIR data for the powder after synthesis (Fig. 3), the bands with maximum at 3200 and 1651 cm^{-1} were assigned to O–H/ H_2O vibrations, the band with maximum at 2366 cm^{-1} was assigned to $\text{CO}_2/\text{CO}_3^{2-}$, a group of bands in the 2500–4000 cm^{-1} range were assigned to $\text{NH}_3/\text{NH}_4^+$, and the bands at 1300–1600 cm^{-1} were assigned to carboxylic groups. Finally, we were able to identify the 1700–4000 cm^{-1} range as containing the bands of different forms of adsorbed byproducts (including O–H/ H_2O , $\text{CO}_2/\text{CO}_3^{2-}$, $\text{NH}_3/\text{NH}_4^+$, and –C–OH) formed via the reaction (1). The FTIR spectrum at 500–1500 cm^{-1} was similar (except for slight shift of the peaks) to those for amorphous calcium polyphosphate reported in Refs. [28,29]. The

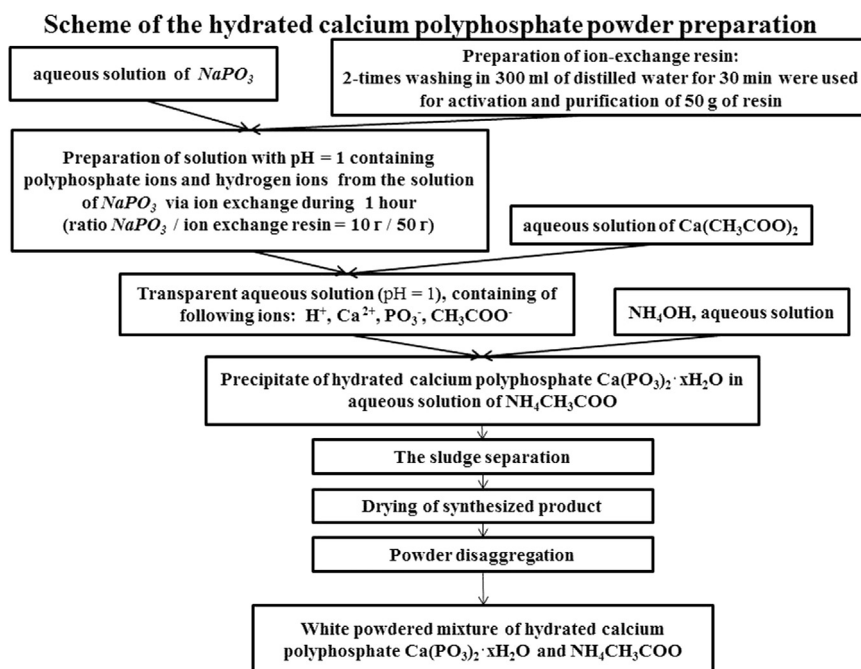


Fig. 1. Scheme of the hydrated calcium polyphosphate powder preparation.

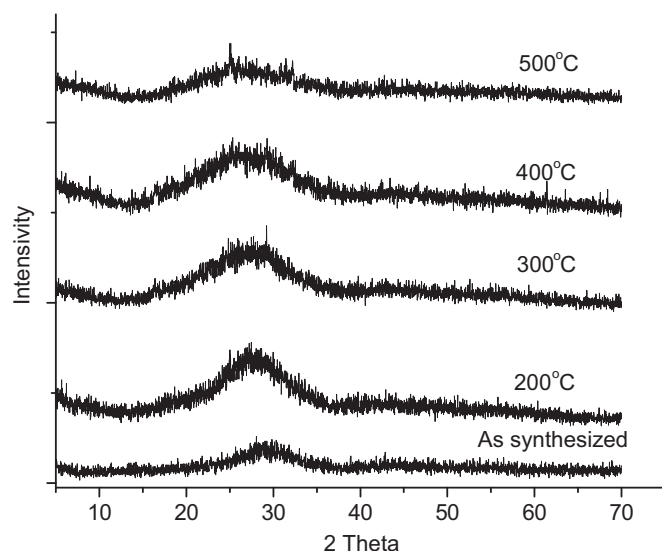


Fig. 2. XRD patterns of the as-prepared powder and the samples after 2 h heat treatment at different temperatures (200–500 °C with the of 100 °C step).

bands in that range could be assigned to stretching of different phosphate units in polyphosphate anion: 1236 ($\nu_{\text{as}}(\text{PO}_2)^-$), 1114 ($\nu_{\text{as}}(\text{PO}_3)^-$ and $\nu_{\text{s}}(\text{PO}_3)^-$), 911 ($\nu_{\text{as}}(\text{P}-\text{O}-\text{P})$), 731 ($\nu_{\text{s}}(\text{P}-\text{O}-\text{P})$), and 541 ($\nu_{\text{as}}(\text{P}-\text{O}=\text{P})$) cm^{-1} .

The collected TA data revealed that total mass loss when heating up to 1000 °C equaled 21–22% (Fig. 4a). According to the simultaneously recorded MS profiles, H_2O evolution gave the major contribution to the mass loss (Fig. 4b), with three maximums observed at 120, 255, and 640 °C. The first maximum evidently corresponded to evaporation of the physically adsorbed water; the second maximum was assigned to dehydration of the $\text{Ca}(\text{PO}_3)_2 \cdot x\text{H}_2\text{O}$ crystal hydrate, and the third maximum was associated with elimination of the strongly bound (structural) water, being retained in the sample at heating up to fairly high temperatures. The x value in the product formula, $\text{Ca}(\text{PO}_3)_2 \cdot x\text{H}_2\text{O}$, was estimated as of 0.6 basing on the TA data. It should be noted that the presence of the structural water will strongly affect the phase

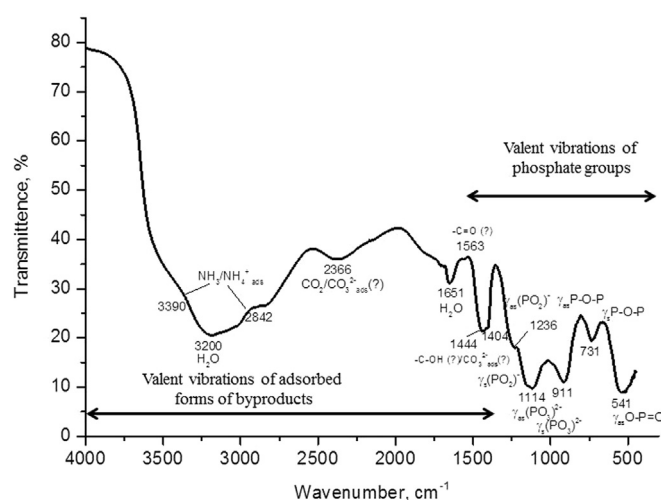
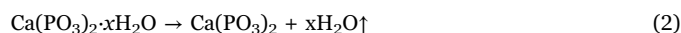


Fig. 3. FTIR of the as-prepared powder.

composition of ceramics manufactured from the studied powder, since heat-induced hydrolysis of calcium polyphosphate is possible if water is retained in its structure up to sufficiently high temperature.

XRD patterns of the powder and compacted specimens heat-treated at 600–900 °C are presented in Figs. 5 and 6, respectively, and their phase composition is summarized in Tables 1, 2. According to the XRD data, both samples after heat treatment at 600 °C consisted of β - $\text{Ca}(\text{PO}_3)_2$ (PDF C79-700). Taking into account chemical composition of precursors of the synthesized powder (Fig. 1) and phase composition of the powder and compacted powder samples after heat treatment at 600 °C, we suggested that chemical composition of the synthesized calcium phosphate was $\text{Ca}(\text{PO}_3)_2 \cdot x\text{H}_2\text{O}$. Therefore, its thermal decomposition at 100–600 °C could be expressed by the general reaction (2).



Profiles of carbon dioxide (m/z 44, Fig. 3d) and carbon (m/z 12, Fig. 4e) evolution were very similar in shape and reflected the contribution of ammonium acetate ($\text{CH}_3\text{COONH}_4$) decomposition to the heat-induced mass loss of the studied powder. Ammonium acetate

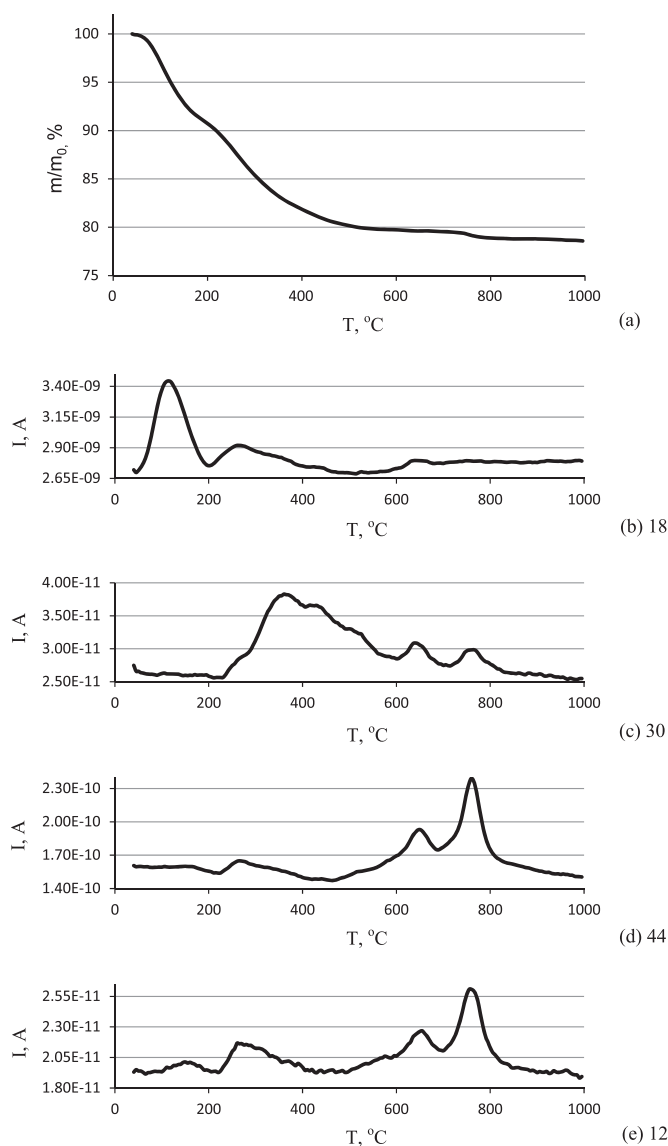


Fig. 4. TA of the as-prepared powder sample (a) and simultaneously detected evolution of the gaseous decomposition products: MS profiles for m/z 18 (b), 30 (c), 44 (d), and 12 (e).

could be adsorbed at the powder surface from the mother liquor during synthesis. Decomposition of ammonium acetate yielded various carbonaceous solids and carbon, their ratio being changed during heating at 400–800 °C. The presence of carbonaceous species and carbon in the solid residue was confirmed by the observed change of the sample color during heating (Fig. 7); in detail, the initially white powder turned sequentially light grey (400 °C), almost black (500 °C), and light grey again (600–800 °C). The evolution of adsorption spectra of the compacted samples upon heat treatment at different temperatures (Fig. 8) was in agreement with visual observations (Fig. 7a) as well as the TA and MS data (Fig. 4d and e). According to the experimental data, decomposition of ammonium acetate with formation of nitrogen oxides took place over the 225–960 °C range (in this work we report the results for NO, m/z 30). The NO evolution profile (Fig. 4c) exhibited several temperature points corresponding to the local concentration maximums: 260, 355, 435, 510, 650, and 765 °C. Indeed, decomposition of ammonium salts in the presence of oxygen is a complex multistage process. It should be noted that the presence of nitrogen compounds in the structure of calcium phosphate powder after the heat treatment has been demonstrated earlier [30]. Let us mention that some of the maximums in the “ m/z 30” curve coincided

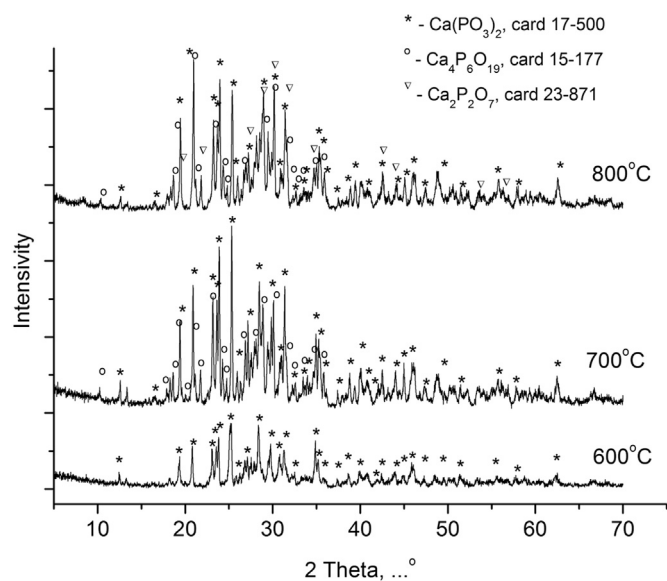


Fig. 5. XRD patterns of the synthesized powder after heat treatment at different temperatures (2 h, 600–800 °C with the of 100 °C step). Reference XRD patterns for selected calcium phosphates are given for comparison.

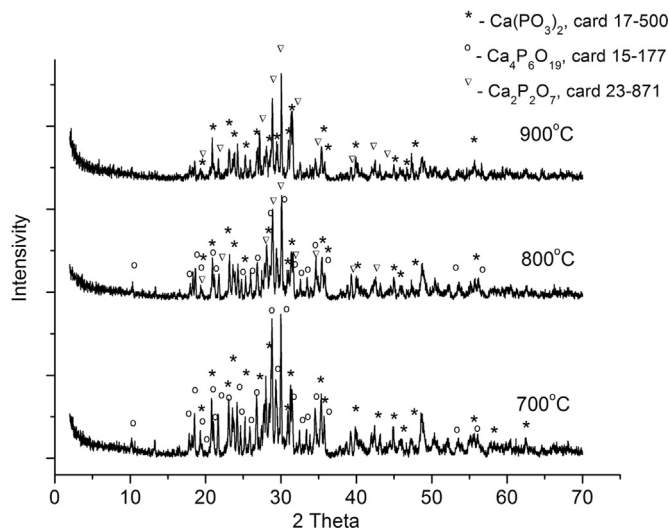


Fig. 6. XRD patterns of the ceramic specimens fabricated from the synthesized powder after heat treatment at different temperatures (2 h, 700–900 °C with the of 100 °C step).

Table 1

Phase composition of synthesized powder after heat treatment at different temperatures in interval of 200–800 °C.

Temperature of heat treatment of synthesized powder, °C						
200	300	400	500	600	700	800
Amorphous				β -Ca(PO ₃) ₂	β -Ca(PO ₃) ₂	β -Ca(PO ₃) ₂
					Ca ₄ P ₆ O ₁₉	Ca ₄ P ₆ O ₁₉
						β -Ca ₂ P ₂ O ₇

with those in the “ m/z 18” one, while other peaks corresponded to those in the “ m/z 44” and “ m/z 12” ones. Therefore, different stages of NO evolution were accompanied by formation of H₂O, CO₂, or C species, and the overall mass loss was a result of several simultaneously occurring multistage processes involving both calcium phosphate species and ammonium acetate.

SEM images of the studied powder after 2 h heat treatment at

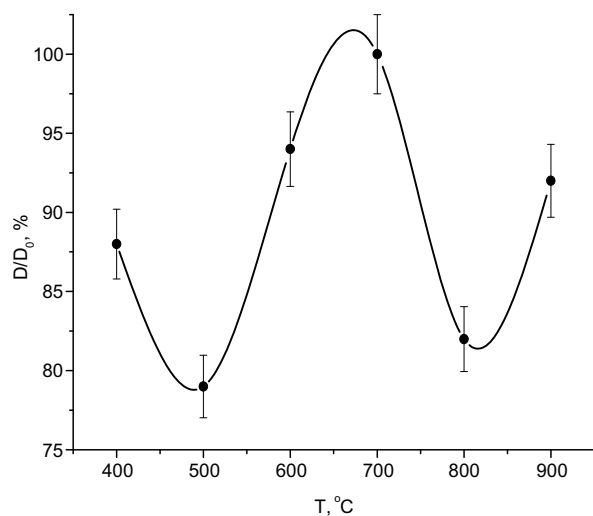
Table 2

Phase composition of ceramic samples after heat treatment at different temperatures in interval of 600–1000 °C.

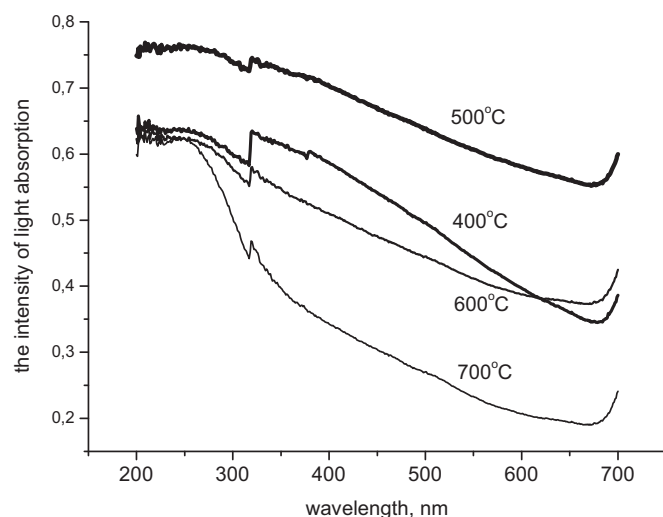
Temperature of heat treatment				
600 °C	700 °C	800 °C	900 °C	1000 °C
β -Ca(PO ₃) ₂	β -Ca(PO ₃) ₂ Ca ₄ P ₆ O ₁₉	β -Ca(PO ₃) ₂ Ca ₄ P ₆ O ₁₉ β -Ca ₂ P ₂ O ₇	β -Ca(PO ₃) ₂ β -Ca ₂ P ₂ O ₇	melt



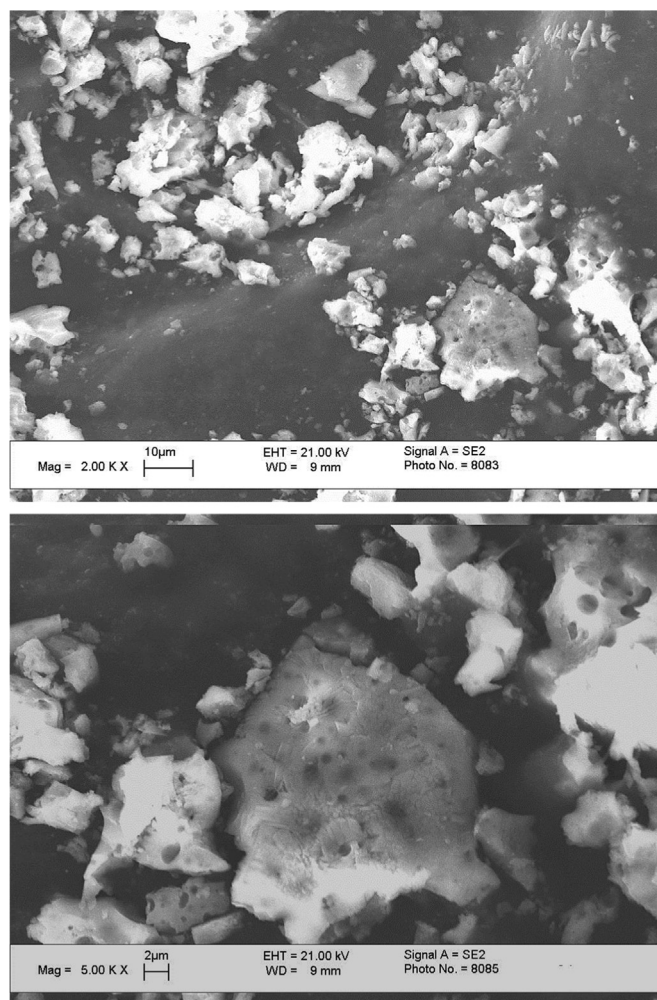
a)



b)

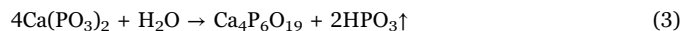
Fig. 7. View of the samples after heat treatment at different temperatures (a) and relative diameter of the ceramic samples as a function of the heat treatment temperature (b).**Fig. 8.** UV-Vis absorption spectra of the compacted samples after heat treatment at different temperatures.

600 °C are presented in Fig. 9. The annealed sample consisted of fairly big blocks (1–12 μm) and a fraction of smaller particles. The big blocks were porous (pore size of about 1 μm) and were in turn built of smaller

**Fig. 9.** SEM images of the synthesized powder after heat treatment (2 h, 600 °C).

rectangular 500–1000 μm crystallites. The pores formation could be explained by evolution of gaseous products in the course of the pristine powder heat-induced decomposition (cf. the gases evolution curves in Fig. 4).

Phase composition analysis of powder and compacted powder samples after annealing at 700 °C revealed that they consisted of calcium polyphosphate β -Ca(PO₃)₂ and tromelite Ca₄P₆O₁₉ (Tables 1, 2, Figs. 5 and 6). Synthesis of tromelite from calcium oxide and phosphorous acid HPO₃ via the two stage-heating under nitrogen (at 497 °C and then at 897 °C, the latter stage being necessary for red phosphorus evaporation) has been earlier reported [31]. Tromelite formula Ca₄P₆O₁₉ could be alternatively written as [Ca₂P₂O₇ + 2Ca(PO₃)₂]; its formation in the powder systems studied in this work could be a result of the process expressed by reaction (3):



The starting components of the reaction (3) were present in the studied powder system at 600 °C, as confirmed by the XRD and TA/MS data. Tromelite presence in the sample after the heat treatment was confirmed by means of XRD. Formation of HPO₃ during heat-induced hydrolysis of Ca(PO₃)₂ was not directly confirmed in this work; however, the possibility of HPO₃ formation during decomposition of calcium hydrogen phosphate has been stated earlier [32]. In detail, investigation of calcium hydrogen phosphate pyrolysis has shown that dehydration of phosphorous acid or its acid salts is not a simple process, and the presence of water favors formation of HPO₃ from calcium pyro- or polyphosphates at high temperature.

The powder and compacted powder samples after annealing at 800 °C consisted of calcium polyphosphate β - $\text{Ca}(\text{PO}_3)_2$, tromelite $\text{Ca}_4\text{P}_6\text{O}_{19}$, and β - $\text{Ca}_2\text{P}_2\text{O}_7$ phases (Tables 1, 2, Figs. 6 and 7). Hence, the XRD data evidenced development of heat-induced hydrolysis of calcium phosphates containing condensed, preferably polyphosphate, anion with the increasing temperature via reactions (3) and (4).



It has been reported that $\text{Ca}(\text{PO}_3)_2$ and $\text{Ca}_2\text{P}_2\text{O}_7$ can be formed upon heating of compound $\text{CaH}_2(\text{HPO}_3)_2$ with molar ratio $\text{Ca}/\text{P}=0.5$ [14]. In this work, we demonstrated the formation of calcium phosphates with molar ratio $\text{Ca}/\text{P}=0.67$ (tromelite $\text{Ca}_4\text{P}_6\text{O}_{19}$) and $\text{Ca}/\text{P}=1$ (β -calcium polyphosphate β - $\text{Ca}(\text{PO}_3)_2$) from the synthesized $(\text{Ca}(\text{PO}_3)_2 \cdot x\text{H}_2\text{O})$ powder ($\text{Ca}/\text{P}=0.5$) upon heating at 700–900 °C were established in present work. The phenomenon was in agreement with the earlier presented data on the phase transformation of calcium phosphate (molar ratio $\text{Ca}/\text{P}=0.5$) during heating in the presence of H_2O [14].

According to the available phase diagram [31], troemilite phase can exist between the $\text{Ca}(\text{PO}_3)_2$ ($T_{\text{melt}} = 980$ °C) and $\text{Ca}_2\text{P}_2\text{O}_7$ ($T_{\text{melt}} = 1350$ °C) ones, at 914–984 °C. According to the data of this work, troemilite was found in powder and ceramic samples after the heat treatment at 700 and 800 °C. This seeming disagreement can be rationalized as follows. When plotting a phase diagram, the phase composition corresponding to a certain point in the diagram field is conventionally determined for the samples obtained by cooling of the superheated melt. On the other hand, the ceramics technology based on fine synthetic inorganic powders with small particle size implies that the powder system is heated from the ambient to the higher temperature. Hence, the data of this work in comparison with the reference data manifest the “composition – structure – dispersion – properties” relationship proposed by I.V. Tananaev; in particular, the powder system of particles with smaller dimension demonstrates lower temperature of a phase transition [33].

Relative diameter (with respect to that of the compacted sample before the heat treatment) and relative density (with respect to the theoretical value) of the ceramic sample as functions of the heat treatment temperature are presented in Figs. 7b and 10, respectively. The relative diameter dependence was non-monotonous, exhibiting two minimums at 500 and 800 °C. The highest relative diameter of the sample (100%) and the lowest relative density (28%) were observed for the sample heat-treated at 700 °C. That temperature was marked by evolution of CO_2 , NO, and a minor fraction of H_2O (Fig. 4). Relative

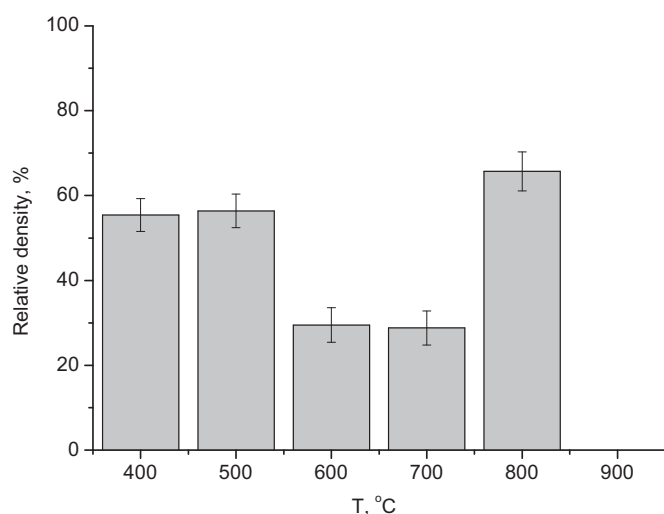


Fig. 10. Relative density of the ceramic samples as a function of the heat treatment temperature. 100% corresponds to density of β - $\text{Ca}(\text{PO}_3)_2$ (2.873 g/cm³, PDF card C79-700).

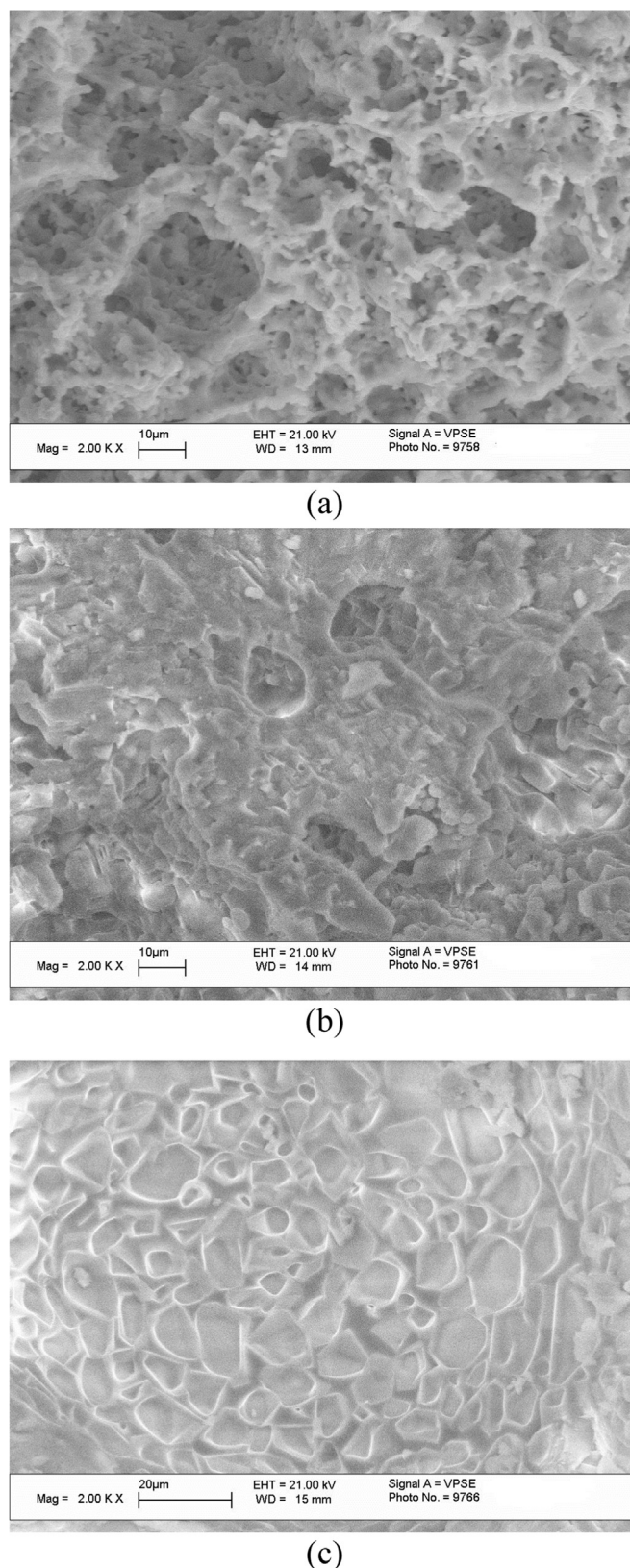


Fig. 11. SEM images of the ceramics manufactured from the synthesized powder, after 2 h heat treatment at 700 (a), 800 (b), and 900 °C (c).

diameter of the ceramic sample after annealing at 800 °C was about 82%, and its relative density was about 67%. The 960–968 °C temperature range corresponds to the liquidus temperature near vertical line of $\text{Ca}(\text{PO}_3)_2$ in the CaO – P_2O_5 phase diagram [17]. Visual

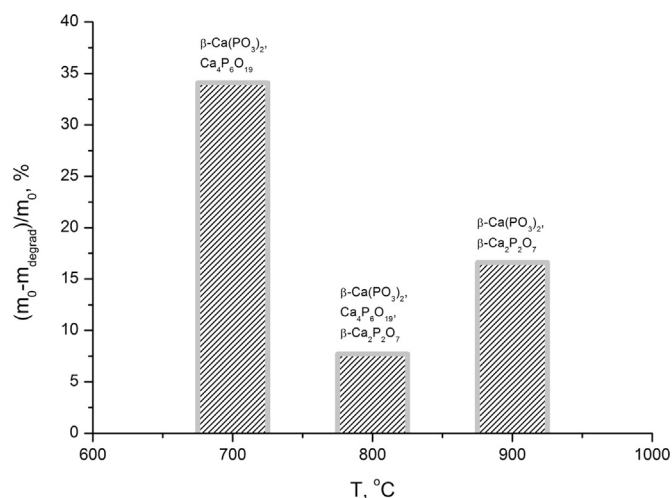


Fig. 12. Degradation of ceramic samples in acidic solution after firing at different temperatures.

appearance and microstructure of the ceramic samples after the heat treatment at 900 °C (Fig. 11c) revealed the melt formation. Therefore, the increase in the sample relative diameter at 900 °C (Fig. 7b) could be due to its melting, melt spreading, and evaporation [34]. The somewhat lower temperature of the studied samples melting as compared with that of Ca(PO₃)₂ in the CaO–P₂O₅ phase diagram could possibly arise from the presence of Na⁺ ions which could be preserved in the prepared powder due to certain features of ion exchange process in the aqueous solution. Density of the ceramic sample after heat treatment at 900 °C could not be measured.

Microstructure of the ceramic materials after annealing at 700–900 °C (Fig. 11) coincided with the temperature dependences of the relative diameter and density. The ceramics treated at 700 °C exhibited porous structure with bigger pores of 5–20 μm and smaller pores of 1–2 μm (Fig. 11a). Density of that sample equaled 0.83 g/cm³ (28% of the theoretical density). The ceramics treated at 800 °C consisted of fairly uniform 2–4 μm grains and 10–15 μm isolated pores (Fig. 11b). Density of that sample equaled 1.89 g/cm³ (65% of the theoretical density). It is worth notice that density of the compacted powder before the heat treatment equaled 1.4–1.5 g/cm³ (≈50% of 2.873 g/cm³, density of β-Ca(PO₃)₂). The ceramics treated at 900 °C consisted of grains with broad size distribution, from relatively small (4–6 μm) to quite big (10–12 μm). The microstructure reflected the process of liquid-phase sintering via dissolution-crystallization mechanism, when the bigger grains grew further, the smaller grains being dissolved in the calcium phosphate melt. Microstructure of the samples after annealing at 1000 °C could not be examined because of complete specimen melting.

The data on degradation of ceramic samples after the heat treatment at 700, 800, and 900 °C when soaked with aqueous solution of citric acid (pH=3) during 120 h is shown in Fig. 12. The most prominent mass loss (about 34%) was found for the ceramics after the heat treatment at 700 °C. That could be related to the feature of phase composition of the ceramics consisting of β-Ca(PO₃)₂ and Ca₄P₆O₁₉ as well as the fact that sintering process was not developed at 700 °C. The ceramics treated at 800 °C demonstrated the smallest mass loss (about 8%). That ceramics also exhibited the strongest shrinkage and could be regarded as the most sintered and dense one (Figs. 7 and 10). Phase composition of the ceramics included the Ca₄P₆O₁₉ and β-Ca₂P₂O₇ phases, i.e. those with higher Ca/P ratio as compared to β-Ca(PO₃)₂. Assuming that formation of calcium pyrophosphate occurred in the studied ceramic materials due to thermal hydrolysis and loss of polyphosphoric acid, it was reasonable to expect that the Ca/P ratio in the samples after the treatment at 900 °C was somewhat lower than that for the samples treated at 800 °C. However,

the ceramics after heat treatment at 900 °C demonstrated the mass loss of 16%, slightly higher than that for the sample fired at 800 °C. That discrepancy might be due to the fact that the samples of ceramics after firing at 900 °C exhibited significant porosity. The values of mass loss during the degradation of the ceramics samples heat-treated at 800 and 900 °C and exposed to an acidic solution resulted from the fact that the Ca/P ratio in those samples was fairly close because the structure of tromelite could be regarded as a combination of polyphosphate and pyrophosphate structures.

4. Conclusion

Amorphous hydrated calcium phosphate powder has been prepared via wet-precipitation route from aqueous solutions of calcium acetate and polyphosphoric acid, the latter being obtained via ion exchange. Heat treatment of the synthesized powders and powder compacts at 700–900 °C has led to the products containing exclusively the biocompatible phases: calcium polyphosphate, tromelite, and calcium pyrophosphate. The heat treatment at 500–700 °C has afforded black- or grey-colored carbon-containing powders. Colored inorganic powders have been recognized as suitable components of suspensions to be used in high-quality streolithographic printing of prefabricated unit of porous ceramic material with regular architecture. It has been shown that the presence of carbon in the preheated powder does not influence the phase composition of the ceramic annealing products. Therefore, the discussed method can be recommended as a process stage for production of resorbable phosphate bioceramics.

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References

- [1] A. Balamurugan, K.E. Mabrouk, S. Pina, M.M. Bousmina, J.M. Ferreira, Melt-derived condensed polymorphic calcium phosphate as bone substitute material: an in vitro study, *J. Am. Ceram. Soc.* 94 (9) (2011) 3023–3029.
- [2] F.M. Wang, K. Qiu, T. Hu, C.X. Wan, X.D. Zhou, J.L. Gutmann, Biodegradable porous calcium polyphosphate scaffolds for the three-dimensional culture of dental pulp cells, *Int. Endod. J.* 39 (6) (2006) 477–483.
- [3] R.M. Pilliar, M.J. Filiaggi, J.D. Wells, M.D. Grynpas, R.A. Kandel, Porous calcium polyphosphate scaffolds for bone substitute applications – in vitro characterization, *Biomaterials* 22 (9) (2001) 963–972.
- [4] R.M. Pilliar, R.A. Kandel, M.D. Grynpas, J. Theodoropoulos, Y. Hu, B. Allo, A. Changoor, Calcium polyphosphate particulates for bone void filler applications, *J. Biomed. Mater. Res. B: Appl. Biomater.* (2016). <http://dx.doi.org/10.1002/jbm.b.33623>.
- [5] T.V. Safronova, A.V. Kuznetsov, S.A. Korneychuk, V.I. Putlyayev, M.A. Shekhirev, Calcium phosphate powders synthesized from solutions with [Ca²⁺]/[PO₄³⁻]=1 for bioresorbable ceramics, *Cent. Eur. J. Chem.* 7 (2) (2009) 184–191.
- [6] T.V. Safronova, V.I. Putlyayev, K.A. Bessonov, V.K. Ivanov, Ceramics based on calcium pyrophosphate nanopowders, *Process. Appl. Ceram.* 7 (1) (2013) 9–14.
- [7] G. MacLennan, C.A. Beevers, The crystal structure of monocalcium phosphate monohydrate, Ca(H₂PO₄)₂·H₂O, *Acta Crystallogr.* 9 (2) (1956) 187–190.
- [8] B. Boonchom, C. Danvirutai, The morphology and thermal behavior of calcium dihydrogen phosphate monohydrate (Ca (H₂PO₄)₂·H₂O) obtained by a rapid precipitation route at ambient temperature in different media, *J. Optoelectron. Biomed. Mater.* 1 (2009) 115–123.
- [9] L.E. Jackson, A.J. Wright, A new synthetic route to calcium polyphosphates, *Key Eng. Mater.* 284 (2005) 71–74.
- [10] J. Trommer, M. Schneider, H. Wozzala, A.N. Fitch, Structure determination of CaH₂P₂O₇ from in situ powder diffraction data, *Mater. Sci. Forum* 321 (2000) 374–379.
- [11] E.H. Brown, W.E. Brown, J.R. Lehr, J.P. Smith, A.W. Frazier, Calcium ammonium pyrophosphates, *J. Phys. Chem.* 62 (3) (1958) 366–367.
- [12] Y.V. Subbarao, R. Ellis, Reaction products of polyphosphates and orthophosphates with soils and influence on uptake of phosphorus by plants, *Soil Sci. Soc. Am. J.* 39 (6) (1975) 1085–1088.
- [13] E.H. Brown, J.R. Lehr, J.P. Smith, A.W. Frazier, Fertilizer materials, preparation and characterization of some calcium pyrophosphates, *J. Agric. Food Chem.* 11 (3) (1963) 214–222.

- [14] D. Zobel, N. Ba, Untersuchungen zur phosphitpyrolyse; reaktionen beim erhitzen von $\text{CaH}_2(\text{HPO}_3)_2 \cdot \text{H}_2\text{O}$ in abwesenheit von sauerstoff, *Z. Chem.* 9 (11) (1969) 433.
- [15] P. Prokupkova, P. Mošner, L. Koudelka, M. Vlček, Preparation and study of $\text{Ca}_{1-x}\text{Mg}_x(\text{PO}_3)_2$ glassy and crystalline phases, *J. Mater. Sci.* 33 (3) (1998) 743–748.
- [16] L.E. Jackson, B.M. Kariuki, M.E. Smith, J.E. Barralet, A.J. Wright, Synthesis and structure of a calcium polyphosphate with a unique criss-cross arrangement of helical phosphate chains, *Chem. Mater.* 17 (18) (2005) 4642–4646.
- [17] W.L. Hill, G.T. Faust, D.S. Reynolds, *Am. J. Sci.* 242 (9) (1944) 457–477.
- [18] C.K. Hsu, A study on thermal behavior of uncalcined $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and CaCO_3 mixtures, *Thermochim. Acta* 392 (2002) 157–161.
- [19] T.V. Safronova, V.I. Putlyaev, V.K. Ivanov, A.V. Knot'ko, T.B. Shatalova, Powders Mixtures Based on Ammonium Hydrophosphate and Calcium Carbonate for Preparation of Biocompatible Porous Ceramic in the $\text{CaO}-\text{P}_2\text{O}_5$ System, *Refract. Ind. Ceram.* 56 (5) (2016) 502–509.
- [20] T. Safronova, V. Putlayev, M. Shekhirev, Resorbable calcium phosphates based ceramics, *Powder Metall. Met. Ceram.* 52 (5–6) (2013) 357–363.
- [21] H. Zhou, S. Kong, S.B. Bhaduri, L. Deng, Preparation of calcium phosphates with negative zeta potential using sodium calcium polyphosphate as a precursor, *Mater. Lett.* 156 (2015) 9–81.
- [22] N.A. Pinchukova, A. Ju Voloshko, L.V. Gudzenko, S.M. Desenko, V.A. Chebanov, O.V. Shishkin, Method of producing polyphosphoric acid, Patent RU 2415807, 10.04, 2011.
- [23] T.V. Safronova, V.I. Putlyaev, S.A. Kurbatova, T.B. Shatalova, D.S. Larionov, D.A. Kozlov, P.V. Evdokimov, Properties of amorphous calcium pyrophosphate powder synthesized via ion exchange for the preparation of bioceramics, *Inorg. Mater.* 51 (11) (2015) 1177–1184.
- [24] T.V. Safronova, V.I. Putlyaev, G.K. Kazakova, S.A. Korneichuk, Biphasic $\text{CaO}-\text{P}_2\text{O}_5$ ceramic based on powder synthesized from calcium acetate and ammonium hydrophosphate, *Glass Ceram.* 70 (1–2) (2013) 65–70.
- [25] ICDD, PDF-4+2010 (Database), in: Dr. Soorya Kabekkodu (Ed.) International Centre for Diffraction Data, Newtown Square, PA, USA, 2010 (<http://www.icdd.com/products/pdf2.htm>).
- [26] ISO 10993-14. Biological evaluation of medical devices — Part 14: Identification and quantification of degradation products from ceramics. <https://www.iso.org/obp/ui/#iso:std:iso:10993:-14:ed-1:v1:en>.
- [27] M. Weil, M. Puchberger, J. Schmedt auf der Guenne, J. Weber Synthesis, Crystal structure, and characterization (vibrational and solid-state ^{31}P MAS NMR Spectroscopy) of the high-temperature modification of calcium catena-polyphosphate (V), *Chem. Mater.* 19 (21) (2007) 5067–5073.
- [28] W.E.G. Müller, E. Tolba, H.C. Schröder, S. Wang, G. Glaßer, R. Muñoz-Espí, Th. Link, X. Wang, A new polyphosphate calcium material with morphogenetic activity, *Mater. Lett.* 148 (2015) 163–166.
- [29] H. Zhou, S. Kong, Z. Liu, Y. Pan, Y. Liu, M. Luo, L. Deng, Fabrication and evaluation of calcium alginate/calcium polyphosphate composite, *Mater. Lett.* 180 (2016) 184–187.
- [30] M. Gafurov, T. Biktairov, B. Yavkin, G. Mamin, Y. Filippov, E. Klimashina, S. Orlinskii, Nitrogen-containing species in the structure of the synthesized nano-hydroxyapatite, *JETP Lett.* 99 (4) (2014) 196–203.
- [31] H.A. Höpfe, Synthesis, crystal structure, and vibrational spectra of $\text{Ca}_4\text{P}_6\text{O}_{19}$ (Trömelite) – a catena – hexaphosphate, *Z. für Anorg. und Allg. Chem.* 631 (6–7) (2005) 1272–1276.
- [32] D. Grant, D.S. Payne, S. Skledar, The pyrolysis of inorganic phosphites, *J. Inorg. Nucl. Chem.* 26 (12) (1964) 2103–2111.
- [33] I. Tananaev, V. Fedorov, E. Kalashnikov, The physical chemistry of energy-saturated media, *Russ. Chem. Rev.* 56 (2) 107–120.
- [34] N.M. Pavlushkin, *Khimicheskaya tekhnologiya stekla i sitallov* (Chemical technology of glass and glass-ceramics), Stroyizdat, Moscow, 1983, p. 432 (in Russian).