Ceramics Based on Brushite Powder Synthesized from Calcium Nitrate and Disodium and Dipotassium Hydrogen Phosphates

T. V. Safronova*, V. I. Putlyaev, Ya. Yu. Filippov, T. B. Shatalova, and D. S. Fatin

Moscow State University, Moscow, 119991 Russia *e-mail: t3470641@yandex.ru Received April 25, 2017

Abstract—Brushite (CaHPO₄ · 2H₂O) powder has been synthesized in aqueous 1.0 M solutions of calcium nitrate dipotassium hydrogen phosphate, and disodium hydrogen phosphate at a Ca/P ratio of unity, without adjusting the pH of the reaction. After synthesis and drying, the fraction of a reaction by-product (NaNO₃, KNO₃, or their mixture) in the powder was about 20 wt %. After firing at temperatures from 800 to 1000°C, the ceramics prepared using the powder synthesized from Ca(NO₃)₂ and Na₂HPO₄ consisted of β -Ca₂P₂O₇ and β -NaCaPO₄. After firing at temperatures from 900 to 1100°C, the ceramics prepared using the powder synthesized of Ca₁₀K(PO₄)₇ and CaK₂P₂O₇. The ceramic composites produced in this study can be recommended as materials for resorbable bone implants.

Keywords: synthesis, calcium nitrate, brushite, reaction by-product, sodium nitrate, potassium nitrate, bioceramics, composite, calcium pyrophosphate, rhenanite, potassium-substituted tricalcium phosphate, potassium calcium double pyrophosphate

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INTRODUCTION

The inorganic component of bone tissue consists predominantly of carbonate hydroxyapatite [1, 2]. For this reason, calcium phosphates are employed in the fabrication of ceramic materials for bone implants [3]. Regenerative treatment techniques include the use of bone implants from resorbable materials [4]. There are two approaches for improving resorbability (solubility) of calcium phosphate-based ceramic materials. One of them is to improve calcium phosphate solubility (compared to hydroxyapatite (HA)) by varying the lattice parameters of the material through aliovalent substitutions (for example, Na⁺ ions for Ca²⁺ ions or CO_3^{2-} carbonate ions for PO_4^{3-} phosphate ions). A more radical approach to controlling the resorbability (solubility) of materials is to produce composite materials whose structure includes phases with a far better resorbability [5]. The list of highly resorbable phases is rather long. It includes calcium phosphates with a Ca/P ratio smaller than that in HA (Ca/P = 1.67) [6], as well as double phosphates of calcium and alkali metals with biocompatible cations (Na⁺ and K⁺) [7, 8]. The following ceramic phases offer better resorbability than does HA: tricalcium phosphate (TCP), $Ca_3(PO_4)_2$ (Ca/P = 1.5); calcium pyrophosphate (CPP), $Ca_2P_2O_7$ (Ca/P = 1.0); tromelite, $Ca_4P_6O_{19}$ (Ca/P = 0.66); calcium polyphosphate; sodium- and potassium-substituted TCP; sodium and potassium rhenanite, MPO₄ (M = Na and K); and calcium sodium and calcium potassium double pyrophosphates, $CaM_2P_2O_7$ (M = Na and K).

Ceramic composites with such a phase composition can be produced from both a powder mixture containing direct precursors of the phases of interest and a powder mixture whose components enter a heterogeneous reaction on heating [9].

There are relatively few examples of the use of a single-source precursor for the fabrication of multiphase ceramics. In particular, TCP/CPP ceramic composites were produced from octacalcium phosphate (OCP), $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, which has an intermediate Ca/P molar ratio: 1.33 [10]. X-ray amorphous ortho- and pyrophosphate powders with a variable Ca/P ratio can also be thought of as single-phase and suitable for the fabrication of ceramic calcium phosphate composites [11]. In most cases, physical homogenization (mixing) of powder precursors to the phases of interest is used in the fabrication of ceramic canceramic composites [12].

One type of the physical homogenization of powder mixtures in the fabrication of such ceramic composites is the disaggregation of calcium phosphate powder synthesized through precipitation from solution when the precipitate contains a reaction by-prod-

Expected phase composition of the powder	
on of the powder	
KNO ₃	

Table 1. Powder synthesis conditions

* Na_2HPO_4 suspension in an aqueous Na_2HPO_4 solution.

uct [13]. On heating, reaction by-products, such as alkali metal salts (potassium or sodium nitrates, chlorides, and acetates) persisting in the composition of the calcium phosphate precipitate, react with the phosphate or its thermal conversion product to form resorbable phases: calcium alkali metal double phosphate salts.

The purpose of this work was to prepare ceramic composite materials from calcium phosphate powders synthesized in aqueous calcium nitrate and disodium and/or dipotassium hydrogen phosphate solutions at Ca/P = 1, without adjusting the solution pH. After synthesis, such powders will contain not only the calcium phosphate but also sodium and potassium nitrates as partially removable reaction by-products. On heating, the nitrates will react with the calcium phosphate to form biocompatible and bioresorbable phases.

EXPERIMENTAL

Calcium phosphate powders were synthesized using calcium nitrate (Ca(NO₃)₂, Ruskhim, Premium grade, Russian Federation Purity Standard TU 2143-017-77381580-1212), disodium hydrogen phosphate (Na₂HPO₄ · 12H₂O, Sigma Aldrich, puriss. p.a., \geq 99.0%), and dipotassium hydrogen phosphate (K₂HPO₄ · 3H₂O, Sigma Aldrich, puriss. p.a., \geq 99.0%). The concentrations of the solutions used in our syntheses are indicated in Table 1. The amounts of the starting chemicals were calculated for the following reaction schemes:

$$Ca(NO_3)_2 + Na_2HPO_4 + 2H_2O$$

= CaHPO₄ · 2H₂O + 2NaNO₃, (1)

$$Ca(NO_{3})_{2} + \frac{1}{2}K_{2}HPO_{4} + \frac{1}{2}Na_{2}HPO_{4} + 2H_{2}O$$

$$= CaHPO_{4} \cdot 2H_{2}O + NaNO_{3} + KNO_{3},$$
(2)

$$Ca(NO_3)_2 + K_2HPO_4 + 2H_2O$$

= CaHPO_4 \cdot 2H_2O + 2KNO_3. (3)

A disodium and/or dipotassium hydrogen phosphate solution (250 mL) was rapidly added to an aqueous calcium nitrate solution (250 mL) with constant stirring. The resultant brushite suspensions in the mother liquor were then stirred at room temperature for 15 min. The precipitates were separated from the mother liquor in a Buchner funnel without washing, placed in open plastic containers, and dried in air for a week. The powders were disaggregated by grinding in a planetary mill for 15 min at a rotation rate of 7000 rpm, using zirconia grinding media and acetone as a disaggregation medium. The powder-to-ball weight ratio was 1:5. After disaggregation, the powders were dried in air at room temperature for 2 h. Next, the dried powders were passed through a polyester sieve with a nominal aperture size of 200 µm. The powders were then pressed at 100 MPa into disk-shaped compacts 12 mm in diameter and 2-3 mm in thickness on a Carver manual press (USA). The reaction by-product (presumably, NaNO₃ and/or KNO₃) acted as a temporary process binder (plasticizer). The green powder compacts were fired in a furnace at different temperatures in the range 800–1100°C (heating rate of 5°C/min, holding at the required temperature for 2 h) and then furnacecooled.

The variation of the pH in the reaction zone on the addition of 150 mL of a Na_2HPO_4 and/or K_2HPO_4 solution to 100 mL of a $Ca(NO_3)_2$ solution was calculated by modeling ionic equilibria in solution using the Visual MINTEQ 3.1 program [14]. The concentration of the solutions and precipitation temperature were taken to be 0.1 M and 25°C, respectively. As the likely solid phases present, we considered $Ca_{10}(PO_4)_6(OH)_2$, $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, and $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$.

The linear shrinkage and geometric density of the ceramic samples were determined by measuring their mass and dimensions (with an accuracy of ± 0.05 mm) before and after firing.

The phase composition of the as-prepared and disaggregated powders and heat-treated samples was determined by X-ray diffraction on a Rigaku D/Max-2500 rotating-anode diffractometer (Japan) with CuK_{α}

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Fig. 1. Calculated variation in solution pH on the addition of 150 mL of a 0.1 M Na_2HPO_4 or K_2HPO_4 solution to 100 mL of an aqueous 0.1 M $Ca(NO_3)_2$ solution.

radiation. The phases present were qualitatively identified using ICDD PDF2 database resources [15].

The samples were characterized by simultaneous thermal analysis at a heating rate of 10° C/min, using a Netzsch STA 409 PC Luxx thermoanalytical system (Netzsch, Germany). The composition of the vapor phase resulting from the decomposition of the samples was determined using a QMS 403C Aëolos quadrupole mass spectrometer (Netzsch, Germany), combined with the Netzsch STA 409 PC Luxx thermoanalytical system. Mass spectra were taken for the mass numbers 18 (H₂O), 46 (NO₂), and 30 (NO).

The microstructures of the samples were examined by scanning electron microscopy (SEM) on a LEO SUPRA 50 VP electron microscope (Carl Zeiss, Germany; field emission source) at accelerating voltages from 3 to 20 kV in secondary electron imaging mode (SE2 detector). A chromium layer (≤ 10 nm in thickness) was grown on the sample surface by sputter deposition.

RESULTS AND DISCUSSION

The plot of the calculated pH in the reaction zone as a function of the volume of the Na₂HPO₄ or K₂HPO₄ solution added to the aqueous Ca(NO₃)₂ solution (Fig. 1) indicates that, under given synthesis conditions (room temperature, reaction until the ratio Ca/P = 1 is reached), the pH of the solution will lie in the range 4.25–4.75. This pH range corresponds to preferential formation of brushite, CaHPO₄ · 2H₂O [reactions (1)–(3)]. The experimentally determined values for the solution during precipitation, pH 4-5, agree with the calculation results.

The reason for this unusual behavior of the solution pH is that the first drop of the M_2HPO_4 added to the Ca(NO₃)₂ solution causes apatite precipitation according to the reaction scheme

$$10Ca(NO_3)_2 + 10M_2HPO_4 + 2H_2O$$

= Ca₁₀ (PO₄)₆ (OH)₂ \ +20MNO_3 + 4H_3PO_4. (4)

The formation of the acid instantaneously reduces the pH of the solution and prevents apatite precipitation. Calculation for the 0.1 M solutions indicates that the supersaturation with respect to apatite is at a level of zero, whereas that with respect to brushite is about -0.2 to -0.3. In a real system, a tenfold increase in concentration results in a positive supersaturation with respect to brushite. Brushite crystallization requires lower supersaturation levels in comparison with HA. Such supersaturation will be sufficient for brushite crystallization. After complete brushite precipitation (the added volume of the solution is 100 mL on the horizontal axis in Fig. 1), the solution pH increases because HPO_4^{2-} ions begin to accumulate in solution, and their hydrolysis results in an alkaline medium. It is important to note that, if the solutions are poured together in the opposite order, there is no sharp drop in pH, and the major phase is HA. Heat treatment of a powder system containing HA and sodium and/or potassium nitrate yields a material containing calcium-enriched phases (CaO and



Fig. 2. X-ray diffraction patterns of the powders after synthesis and drying.

 $Ca_4P_2O_9$), which attack living tissue because their hydrolysis leads to highly alkaline pH values.

According to the X-ray diffraction data in Fig. 2, indeed the phase composition of the as-synthesized powders includes only brushite. Weighing the synthesized powders after synthesis and drying showed that, in all cases, the weight of the powders exceeded the calculated one by about 20%. At the same time, according to the X-ray diffraction data, peaks of NaNO₃ (expected by-product of reaction (1) and, in part, of reaction (2)) were only detected in the case of the "Na" powder. It is the presence of by-products-NaNO₃ in the "Na" powder, KNO₃ in the "K" powder, and a NaNO₃ + KNO₃ salt mixture in the "NaK" powder-which is responsible for the excess weight of the powders relative to the calculated one. Given that the weight of the powder is 20% higher than the weight calculated for brushite, the sodium nitrate content of the "Na" powder can be estimated at 29 mol %, and the potassium nitrate content of the "K" powder, at 25 mol %.

Micrographs of powders synthesized in aqueous 1 M Ca(NO₃)₂ and Na₂HPO₄ and/or K₂HPO₄ solutions at Ca/P = 1 (Fig. 3) demonstrate that the powders consist of platelike particles on the order of 10 to 20 μ m in lateral size. The platelets in the "Na" powders are 0.3 to 1 μ m in thickness, and those in the "K" powders are 1 to 2 μ m in thickness. The "K" and "KNa" powders can be seen to contain particles that

seem to be fragments of brushite plates. Thus, the X-ray diffraction data for the as-synthesized and dried powders are consistent with the electron microscopy results. Note that the nature of the cation in the phosphate used is seen to influence the thickness of the brushite plates.

Thermal analysis and mass spectrometry data are presented in Fig. 4. The total weight loss of each powder at 1000°C is 27–29%. The adsorbed water loss in all of the powders can be estimated at 5%. The characteristic step at 200°C in the thermogravimetry curves of the powders, which amounts to 12-13% (Fig. 4b), and the mass spectrometry data for m/Z = 18 (Fig. 4a) demonstrate that the conversion of brushite to monetite [reaction (5)] takes place in all of the powders:

$$CaHPO_4 \cdot 2H_2O = CaHPO_4 + 2H_2O.$$
 (5)

At the same time, the characteristic step in the thermogravimetry curve at 400°C, corresponding to the conversion of monetite to calcium pyrophosphate [reaction (6)], was not detected, Nevertheless, the possibility that reaction (6) takes place should not be completely ruled out:

$$2CaHPO_4 = Ca_2P_2O_7 + H_2O.$$
 (6)

It seems likely that the presence of reaction byproducts (NaNO₃ and KNO₃) in the synthesized powders under investigation changes the typical stepwise path of the thermal conversion of brushite, with characteristic temperatures of 200 and 400°C:

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Fig. 3. Micromorphology of the powders synthesized from (a) calcium nitrate $(Ca(NO_3)_2)$ and disodium hydrogen phosphate (Na_2HPO_4) , (b) calcium nitrate $(Ca(NO_3)_2)$ and disodium and dipotassium hydrogen phosphates (Na_2HPO_4) , and (c) calcium nitrate $(Ca(NO_3)_2)$ and dipotassium hydrogen phosphate (K_2HPO_4) .

$$CaHPO_4 \cdot 2H_2O$$

$$\xrightarrow{200^{\circ}C} CaHPO_4 \xrightarrow{400^{\circ}C} Ca_2P_2O_7.$$

According to reference data, the melting point of NaNO₃ is $t_m = 307^{\circ}$ C and that of KNO₃ is $t_m = 335^{\circ}$ C. The salts decompose markedly above 400°C. Note also that the NaNO₃–KNO₃ system has the lowest melting point, $t = 222^{\circ}$ C, and 47.7% NaNO₃ [16]. Indeed, it can be seen in Fig. 4b that the weight loss curve of the "NaK" powder shows monotonic behavior starting at a temperature (195°C) 10°C lower than that in the case of the "Na" and "K" powders (205°C). Ionic sodium nitrate or potassium nitrate melts will inevitably react with monetite, a hydrous calcium phosphate, to form calcium sodium or calcium potassium double phosphates.

The mass spectrometry data for m/Z = 30 (corresponds to NO and replicates the shape of the curve for NO₂) lead us to assume that the evolution of nitrogen oxides (NO₂ and NO) in a wide temperature range (220–650°C) is due to both the interaction of molten sodium and potassium nitrates, presumably according to the reaction schemes (7) and (8), and the salt decomposition proper (peritectic melting) when the

decomposition temperature is reached [reactions (9) and (10)]. Differential thermal analysis (DTA) curves have a very broad endothermic peak in this temperature range:

$$4\text{CaHPO}_{4} + 4\text{NaNO}_{3}(l) \rightarrow 4\text{NaCaPO}_{4} + 2\text{H}_{2}\text{O} + 4\text{NO}_{2} + \text{O}_{2},$$
(7)

$$4CaHPO_4 + 4KNO_3(l) \rightarrow 4KCaPO_4 + 2H_2O + 4NO_2 + O_2,$$
(8)

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2, \tag{9}$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2. \tag{10}$$

According to reference data, NaNO₂ has $t_m = 284^{\circ}$ C, and KNO₂ melts incongruently at $t_m = 440^{\circ}$ C. The NaNO₂-KNO₂ system has the lowest melting point, $t_m = 224^{\circ}$ C, at 65.25% NaNO₂ [17]. Sodium and potassium nitrites also react with monetite, according to schemes (11) and (12):

$$2CaHPO_4 + 2NaNO_2(l) \rightarrow 2NaCaPO_4$$

$$+ H_2O + NO_2 + NO,$$
(11)

$$2\text{CaHPO}_{4} + 2\text{KNO}_{2}(l) \rightarrow 2\text{KCaPO}_{4} + \text{H}_{2}\text{O} + \text{NO}_{2} + \text{NO}.$$
(12)



Fig. 4. Simultaneous thermal analysis of the powders synthesized from $Ca(NO_3)_2$ and Na_2HPO_4 ("Na"), $Ca(NO_3)_2$ and Na_2HPO_4/K_2HPO_4 ("NaK"), and $Ca(NO_3)_2$ and K_2HPO_4 ("K"): (a) ion current as a function of temperature (mass spectrometry data) for m/Z = 18 (water) and m/Z = 30 (nitric oxide); (b) TG and DSC curves.

Reactions (6)–(12) constitute an overall process in which monetite reacts with a nitrate melt in the temperature range 220–650°C to form solid double phosphates, nitrogen(II) and nitrogen(IV) oxides, oxygen, and water vapor. The weight losses associated with the course of the monetite/melt interaction reactions and by-product decomposition reactions in this temperature range are comparable for the powders under consideration: 12% for the "Na" powder, 11% for the "K" powder, and 12.5% for the "NaK" powder. The sample weight was observed to stop varying at 510°C for the "Na" powder, and 545°C for the "NaK" powder. Thus, the formation of the double phosphates reaches completion at 600°C.

This is, in principle, consistent with previous work [8], where the formation temperature of double phosphates in $Ca_2P_2O_7 + M_2CO_3$ (M = Na, K) mixtures under isothermal conditions was also estimated at 600°C.

The powder preparation stage for the fabrication of ceramics includes disaggregation, which is typically performed in a liquid with a low surface tension and relatively low boiling point. In this study, we used acetone, which contained trace amounts of water because of its hygroscopicity.

It can be seen from the X-ray diffraction data in Fig. 5 that disaggregation in acetone leads to changes in the phase composition of some of the powders. In



Fig. 5. X-ray diffraction data for the powders after disaggregation.

the "Na" powder, brushite converted into monetite [reaction (6)]. In the "K" powder, brushite did not convert into monetite, despite the effects of a hygroscopic medium (acetone) and mechanical activation. In the "NaK" powder, both brushite and monetite were present. In addition, the X-ray diffraction data for all of the powders indicated the presence of sodium and potassium nitrates as reaction by-products. Since we used acetone containing a slight amount of water, the possibility of detecting by-products by X-ray diffraction was most likely due to the fact that there was a dissolution/crystallization process, which led to an increase in the particle size of the salts. That brushite converted into monetite in the presence of NaNO₃ and persisted in the presence of KNO₃ is most likely due to the higher solubility of NaNO₃ in water (91.2 g for 100 mL at 20°C) in comparison with KNO₃ (31.6 g for 100 mL at 20°C) [18]. In such a situation, NaNO₃ acts as an additional hygroscopic (drving) substance. which takes up water from brushite [reaction (5)].

The micrographs in Fig. 6 point to significant changes in the morphology of "Na" powder particles (Fig. 6a), which transformed as a result of the disaggregation in acetone from platelets into particles with a planar needle-like (lamellar) morphology, characteristic of monetite crystals. The "NaK" and "K" powder particles (Figs. 6b, 6c) retained, for the most part, their platelike morphology, but the longitudinal size of the plates decreased. In the "NaK" powder, we observe not only plates but also separate needle-like particles. The plates in the "K" powder are seen to have a tendency toward splitting. In the "K" and "KNa" powders, the amount of particles that were assumed to be fragments of brushite plates considerably increased. It seems likely that the thicker brushite plates obtained in the case of dipotassium hydrogen phosphate have low strength and readily break up in various directions.

The relative density of the green compacts was 54– 59% (Table 2). This relatively low green density of the compacts is due to both the small particle size of the powders and their inherent morphology (plates or needles).

According to the X-ray diffraction data in Table 3 and Fig. 7, the phase composition of the ceramics prepared from the "Na" powder by firing in the range $800-1000^{\circ}$ C includes β -NaCaPO₄ and β -Ca₂P₂O₇. The phase composition of the ceramics prepared from the "K" powder by firing in the range $900-1100^{\circ}$ C includes the K-substituted TCP Ca₁₀K(PO₄)₇ and the potassium calcium double pyrophosphate K₂CaP₂O₇. The phase composition of the "NaK" ceramics includes all of the above-mentioned high-temperature phases.



Fig. 6. Micromorphology of the powders disaggregated in acetone after synthesis from (a) calcium nitrate $(Ca(NO_3)_2)$ and disodium hydrogen phosphate (Na_2HPO_4) , (b) calcium nitrate $(Ca(NO_3)_2)$ and disodium and dipotassium hydrogen phosphates (Na_2HPO_4) , and (c) calcium nitrate $(Ca(NO_3)_2)$ and dipotassium hydrogen phosphate (K_2HPO_4) .

Analysis of the variation in the phase composition of the "Na" powder indicates that, according to the Na₂O-CaO-P₂O₅ phase diagram [19], a representative point would move along the Ca₂P₂O₇-Na₂O join from Ca₂P₂O₇ through NaCaPO₄. The X-ray diffraction data confirm this trajectory of the representative point: the phase composition of the ceramics prepared from the "Na" powder comprises β -NaCaPO₄ and β -Ca₂P₂O₇. Analysis of the variation in the phase composition of the "K" powder indicates that, according to the K₂O–CaO–P₂O₅ phase diagram [20], a representative point would move along the Ca₂P₂O₇–K₂O join across the Ca₂P₂O₇–Ca₃(PO₄)₂–K₂CaP₂O₇ region. The X-ray diffraction data confirm this direction of motion, which terminated on the Ca₃(PO₄)₂–K₂CaP₂O₇ join, because the phase composition comprises K₂CaP₂O₇ and the K-substituted TCP Ca₁₀K(PO₄)₇, which is similar in structure to Ca₃(PO₄)₂.

Notation	Geometric density, g/cm ³	Composition of the powder used for compaction	Calculated density*, g/cm ³	Relative density	
Na	1.26	CaHPO ₄ , NaNO ₃	2.36	54%	
NaK	1.35	CaHPO ₄ · 2H ₂ O, NaNO ₃ , KNO ₃	2.28	59%	
К	1.33	CaHPO ₄ · 2H ₂ O, KNO ₃	2.27	59%	

 Table 2. Density of the green compacts

* The density was calculated by an additive method with allowance for the estimated synthesis product yield (120%), thermal analysis data, and density data for brushite (CaHPO₄ · 2H₂O, 2.3 g/cm³, PDF card no. 9-77), monetite (CaHPO₄, 2.9 g/cm³, PDF card no. 9-80), NaNO₃ (2.26 g/cm³, PDF card no. 36-1474), and KNO₃ (2.1 g/cm³, PDF card no. 71-1558).

Notation	Composition of the powder used for compaction	Firing temperature, °C			
		800°C	900°C	1000°C	1100°C
Na	CaHPO ₄ , NaNO ₃	β-Na	β -NaCaPO ₄ , β -Ca ₂ P ₂ O ₇		
NaK	CaHPO ₄ · 2H ₂ O, NaNO ₃ , KNO ₃	-	$\begin{array}{c} \beta \text{-NaCaPO}_4, \beta \text{-Ca}_2 P_2 O_7 \\ \text{KCa}_{10}(\text{PO}_4)_7, \text{K}_2 \text{CaP}_2 O_7 \end{array}$		
К	$CaHPO_4 \cdot 2H_2O, KNO_3$	—	KCa ₁₀ (PO ₄) ₇ , K ₂ CaP ₂ O ₇		

 Table 3. Phase composition of the ceramics after firing

Figure 8 shows the linear shrinkage and density of the ceramic samples after firing. The shrinkage and density curves of the "Na" samples have a maximum after firing at 900°C, where the shrinkage is 30% and the density is 2.7 g/cm³. The noticeable shrinkage of the samples from the "Na" powder after firing at 900°C is due to the presence of a melt in the Na₂O– CaO–P₂O₅ system at temperatures above 780°C. For example, the β -NaCaPO₄ and β -Ca₂P₂O₇ phases detected by X-ray diffraction in the composition of the ceramics prepared from the "Na" powder form a eutectic at t = 1202°C and about 30 wt % NaCaPO₄. Moreover, the NaCaPO₄–Ca₂P₂O₇–Na₂CaP₂O₇ composition triangle, which has the NaCaPO₄– Ca₂P₂O₇ join as one of its sides, contains a ternary eutectic with $t = 780^{\circ}$ C. There are also binary eutectics in the NaCaPO₄- Na₂CaP₂O₇ system, with $t = 800^{\circ}$ C, and in the Ca₂P₂O₇-Na₂CaP₂O₇ system, with $t = 803^{\circ}$ C [19]. The observed decrease in the density of the samples after firing at a temperature of 1000°C is most likely due to the accumulation of the melt (with a descending baseline of the DTA curve) and the release of volatile gaseous components (nitrogen and phosphorus oxides) from it.

The "K" samples have a relatively low shrinkage, just 5% at 1100°C. After firing at temperatures from 900 to 1100°C, their density is near 1 g/cm³. The shrinkage and density curves of the "NaK" samples also have a maximum, after firing at 1000°C, where their shrinkage is 23% and their density is 2.2 g/cm³.



Fig. 7. X-ray diffraction data for the ceramic samples prepared by firing at 1000°C.

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Fig. 8. (a) Linear shrinkage and (b) density of the samples as functions of firing temperature.

The insignificant shrinkage of the ceramic prepared from the "K" powder is due to the higher melting points of possible eutectics in the $Ca_2P_2O_7$ - $Ca_3(PO_4)_2-K_2CaP_2O_7$ system, which contains its phase composition. This region has a ternary eutectic with $t = 1038^{\circ}$ C. The $Ca_3(PO_4)_2-K_2CaP_2O_7$ system has a eutectic with $t = 1140^{\circ}$ C, and the $Ca_2P_2O_7-K_2CaP_2O_7$ system has a eutectic with $t = 1040^{\circ}$ C [20]. Thus, equilibrium melting in the potassium system begins at temperatures above 1000° C; that is, the amount of the melt is far smaller than that in the sodium system at comparable temperatures, and densification is essentially due to solid-state sintering. The low diffusion mobility of the potassium cation compared to the sodium cation and the well-known poor solid-state sinterability of pyrophosphate ceramics [7, 21] lead to a very small densification of the ceramic samples containing only potassium.

Figure 9 illustrates the microstructure of the ceramics prepared from the "Na" powder. After firing at 800°C (Fig. 9a), the ceramic is poorly sintered and has a porous, permeable structure. The grain size is 0.5 to 1 μ m. After firing at 900°C (Fig. 9b), the microstructure of the ceramic prepared from the "Na" powder is formed by grains ranging in size from 0.5 to 20 μ m. After firing at 1000°C (Fig. 9c), the microstructure of the ceramic prepared from the "Na" powder is formed by grains ranging in size from 0.5 to 20 μ m.



Fig. 9. Microstructure of the ceramics prepared from the "Na" powders after firing at (a, b) 800, (c, d) 900, and (e, f) 1000°C.

scatter in grain size attests to secondary recrystallization, which is due to the presence of a melt. After firing at 900 and 1000°C, the ceramics prepared from the "Na" powder had a considerable porosity. The pore size was $3-10 \,\mu\text{m}$ after firing at 900°C and $10-40 \,\mu\text{m}$ after firing at 1000°C. We believe that the spherical shape of the pores was a consequence of the coalescence of melt droplets, whose viscosity prevented gas bubbles from leaving the droplets.

Figure 10 illustrates the microstructure of the ceramic samples prepared from powders synthesized from different pairs of precursors, after firing at

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1000°C for 2 h. The ceramics prepared from the "Na" and "NaK" powders have considerable porosity and range in pore size from 10 to 40 μ m. In micrographs of fracture surfaces of the "NaK" ceramics, the grain size is difficult to determine. We observe a conchoidal transgranular fracture, which also points to liquid-assisted sintering. After firing at 1000°C, the microstructure of the ceramics prepared from the "K" powders corresponds to the initial stage of sintering (consolidation of the particles): grains 1–3 μ m in size are separated by a connected pore system.



Fig. 10. Microstructure of the ceramics prepared from the (a, c) "NaK" and (b, d) "K" powders after firing at (a, b) 1000 and (c, d) 1100°C.

CONCLUSIONS

Reactions between aqueous 1.0 M solutions of calcium nitrate and disodium and/or dipotassium hydrogen phosphates at room temperature, without adjusting the solution pH, ensure the preparation of calcium phosphate powders whose phase composition includes brushite (CaHPO₄ \cdot 2H₂O) and the corresponding reaction by-product. Disaggregation in acetone does not influence the Ca/P ratio in the powders, but changes their phase composition: their X-ray diffraction patterns show peaks of NaNO₃ and KNO₃ as reaction by-products. In the presence of NaNO₃, disaggregation leads to the conversion of brushite to monetite, changing the morphology of the particles. According to X-ray diffraction data, the presence of potassium nitrate does not favor the conversion of brushite to monetite. The phase composition of the ceramics after firing is a consequence of the reaction between brushite (or monetite) and the reaction by-product on heating. From the powder consisting of monetite and sodium nitrate, we obtained a β -Ca₂P₂O₇/ β -CaNaPO₄ composite; from the powder consisting of brushite and potassium nitrate, we obtained a $Ca_{10}K(PO_4)_7/K_2CaP_2O_7$ composite; and finally from the powder consisting of brushite, monetite, sodium nitrate, and potassium nitrate, we obtained a ceramic composite containing phases detected in the ceramics produced from the powders containing either sodium nitrate, or potassium nitrate, namely, β -Ca₂P₂O₇, β -CaNaPO₄, Ca₁₀K(PO₄)₇, and K₂CaP₂O₇. The ceramic composites based on calcium phosphates prepared from synthetic powders and containing bioresorbable and biocompatible phases can be recommended for the fabrication of bone implants.

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