Sol-Gel Synthesis of Ca₃(PO₄)₂ and Ca_{3 - x}Na_{2x}(PO₄)₂ Powders for the Fabrication of Bioceramics by 3D Printing

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Abstract—We report techniques for the synthesis of microcrystalline powders of tricalcium phosphate (TCP) $(\beta$ -Ca₃(PO₄)₂) and phase A (Ca_{2.5}Na(PO₄)₂, an ordered solid solution based on Ca_{3 - x}Na_{2x}(PO₄)₂ α -rhenanite), by the Pechini sol-gel process. The phosphorus-containing reagents used are triethyl phosphate $PO(OC_2H_5)_3$, ethylenediamine(tetramethylenephosphonic (EDTMP), (TEP), and acid) $(H_2O_3PCH_2)_2N(CH_2)_2N(CH_2PO_3H_2)_2$. We analyze the phase composition, micromorphology, and sintering behavior of the synthesized powders. The use of TEP as a phosphorus-containing reagents leads to a change in Ca/P ratio (stoichiometry) in the final product as a result of TEP vaporization during gel polycondensation and the formation of a mixture of hydroxyapatite $(Ca_{10}(OH)_2(PO_4)_6)$ and calcium oxide. If EDTMP is used, the stoichiometry remains unchanged owing to Ca^{2+} chelating by the complexone: in TCP synthesis, gel thermolysis at temperatures from 750 to 1000°C leads to β -TCP crystallization (with an average particle size of 1 μ m); in the synthesis of phase A, gel thermolysis at temperatures from 500 to 800°C leads to the formation of a mixture of β -TCP, β -CaNaPO₄, and phase A (average particle size of 250 nm in the range 500– 700°C). According to dilatometry data, the synthesized powders can be densified more rapidly in comparison with powders prepared by ceramic processing route. The present results suggest that sol-gel processing with the use of EDTMP can be recommended for the synthesis of powders of resorbable phosphates, such as TCP and $Ca_{3-x}Na_{2x}(PO_4)_2$, suitable for stereolithographic fabrication of osteoconductive bioceramics.

Keywords: calcium sodium mixed phosphates, tricalcium phosphate, sol-gel synthesis, complexone, sintering, bioceramics, 3D printing

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INTRODUCTION

The current approach to biomaterials engineering for bone tissue replacement relies on the use of resorbable and osteoconductive implants that temporarily fill bone defects and ensure conditions for stimulating natural bone regeneration processes [1–3]. Suitable basic components for the fabrication of such materials are calcium phosphates, namely, tricalcium phosphate (TCP) (Ca₃(PO₄)₂) and Ca_{3 – x}Na_{2x}(PO₄)₂ mixed sodium phosphates (so-called sodium rhenanites), owing to their biocompatibility and substantial resorbability [4].

One important requirement for the structure of implants is the presence of a system of pores at least 200 μ m in diameter [2], which enable bone and vascular tissue ingrowth and improve the osteoconductive properties of the material. An intended system of pores and complex architecture of a material can be reproduced using stereolithographic 3D printing, a method offering high spatial resolution [5, 6]. To employ this method, and improve implant resorbability, it is nec-

essary to use fine powders (with a particle size in the range 100-500 nm) [7].

TCP and rhenanites are typically prepared by solid-state synthesis [8] because these phosphates cannot be obtained via precipitation from aqueous solutions as a consequence of hydrolysis and precipitation of phosphates more stable under synthesis conditions, for example, hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$. High firing temperatures, an inherent feature of solid-state synthesis, lead to rapid sintering and the formation of large particle agglomerates with a broad size distribution. In connection with this, it is necessary to find an alternative approach to the synthesis of such powders.

Reports in the literature describe in more or less detail a number of techniques for the synthesis of some calcium phosphates via precipitation from nonaqueous (methanol and ethylene glycol) solutions [7, 9], examine the use of hydrothermal treatment [10–12], and present sol–gel synthesis of HA [13–16], but there is little data on such syntheses in the case of TCP [17] and no data for rhenanites. A citrate version of sol-gel synthesis, the so-called Pechini process, offers considerable potential for the preparation of finely dispersed phosphate powders. It takes advantage of polycondensation reaction between metal citrate complexes and ethylene glycol (EG), which leads to the formation of polyester chains in solution [18, 19]. Previously, we proposed techniques for the synthesis of TCP and sodium-substituted rhenanites via precipitation and sol-gel processing in EG, but the results showed that the techniques should be improved because of the deviations from the required Ca/Na ratio during the synthesis of rhenanites via precipitation in EG and the systematic presence of calcium oxide impurities in the case of the Pechini process [20], similar to what was obtained in early studies concerned with the sol-gel synthesis of phosphates, for example, by Jillavenkatesa and Condrate [13].

The main difficulty with the use of the sol-gel approach to the synthesis of TCP and rhenanites is proper selection of the phosphorus-containing reagent. It should be nonreactive with calcium salts in the initial stage of synthesis in order to avoid formation and precipitation of poorly soluble phosphates [21]. This requirement is met by organic esters of phosphoric acid, namely, by $PO(RO)_{3-n}(OH)_n$ (n = 0, 1, 1) 2) alkyl phosphates, which are nonreactive with calcium salts under ordinary conditions because of the low hydrolysis rate [22]. Other suitable reagents are phosphonate complexones, including ethylenediamine(tetramethylenephosphonic acid) (EDTMP), $(H_2O_3PCH_2)_2N(CH_2)_2N(CH_2PO_3H_2)_2$, used in this work, which is capable of acting as not only a phosphorus source but also a chelating agent, together with citric acid, typically used in the Pechini process.

The objectives of this work were to develop and test a sufficiently versatile sol-gel process for the synthesis of fine, highly sinterable powders of TCP and sodiumcontaining mixed phosphates (rhenanites) for subsequent use as starting materials for the fabrication of macroporous ceramic and composite implants by stereolithographic 3D printing.

EXPERIMENTAL

TCP synthesis with the use of triethyl phosphate (TEP). The phosphorus-containing reagent used was TEP (Sigma-Aldrich, no. 216003-500G, d = 1.068– 1.069 g/mL), and the calcium source used was calcium nitrate predehydrated at 250°C (RusKhim, analytical grade). Calcium nitrate and an excess of citric acid (Sigma-Aldrich, no. 27487-250G-F) were dissolved in EG (Sigma-Aldrich, no. 293237-1L, d = 1.11 g/mL), following which an appropriate volume of TEP was added. After stirring for some time, the resultant solution was heated to 70°C over a period of 2 h and boiled down for several hours at this temperature, which caused a considerable decrease in volume and

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gelation (the formation of transparent, very viscous resin). If the heating rate was too high, the solution became turbid.

The resultant gel was dried at 130°C and then heattreated at a temperature of 1000°C:

$$\operatorname{Ca}(\operatorname{NO}_3)_2 + \operatorname{C}_6\operatorname{H}_8\operatorname{O}_7 \leftrightarrow \operatorname{Ca}(\operatorname{C}_6\operatorname{H}_6\operatorname{O}_7) + 2\operatorname{HNO}_3, (1)$$

$$3Ca(C_6H_6O_7) + 2PO(OC_2H_5)_3 + 65/2O_2$$

$$t = Ca_3(PO_4)_2 + 30CO_2 + 24H_2O.$$
(2)

TCP synthesis with the use of EDTMP. The phosphorus-containing reagent used was EDTMP (Reakhim no. 1088-70, pure grade), which was prerecrystallized via preparation of a solution saturated at 60°C, filtration on filter paper, boiling down, and filtration at reduced pressure. The calcium source used was dehydrated calcium nitrate. Appropriate amounts of EDTMP and calcium nitrate, an excess of citric acid, and EG were dissolved in water on a magnetic stirrer. The resultant solution was heated to 80°C over a period of 2 h and slowly boiled down until gelation (2-3 h):

$$6Ca (C_6H_6O_7) + C_6H_{20}N_2P_4O_{12} + 39O_2$$

t = 2Ca₃ (PO₄)₂ + 42CO₂ + 28H₂O + 2NO₂. (3)

The resultant gel was dried at 130°C and then heat-treated at 750 and 1000°C.

 $Ca_{2.5}Na(PO_4)_2$ (phase *A*) synthesis. EDTMP and sodium hydroxide (Labtekh no. 4328-77, analytical grade) as a sodium source were dissolved in water on a magnetic stirrer. To the resultant solution were added calcium nitrate, an excess of citric acid, and EG. The solution was heated to 70°C over a period of 2 h and slowly boiled down until gelation (3 h):

$$C_{6}H_{20}N_{2}P_{4}O_{12} + 2NaOH$$

= Na₂(C₆H₁₈N₂P₄O₁₂) + 2H₂O, (4)

$$Na_{2} (C_{6}H_{18}N_{2}P_{4}O_{12}) + 5Ca (C_{6}H_{6}O_{7}) + 69/2O_{2} = (t) 2Ca_{2.5}Na (PO_{4})_{2} (5) + 36CO_{2} + 24H_{2}O + 2NO_{2}.$$

The resultant gel was dried at 130°C and then heattreated at 510, 610, 680, and 800°C.

X-ray diffraction characterization was carried out on a Rigaku D/Max-2500 rotating-anode diffractometer (Japan). Intensity data were collected in reflection (Bragg–Brentano) geometry with Cu K_{α} radiation ($\lambda_{av} = 1.54183$ Å) using quartz sample holders. In qualitative analysis of the X-ray diffraction data, we used WinXPOW software and PCPDF ICDD PDF-2 database resources. In quantitative X-ray diffraction analysis, the weight fraction of a component was evaluated by the Chang method [23] using the following relation:

$$\omega(A) = \frac{I_i(A) / (I / I_{\rm cor}(A) I_i^{\rm rel}(A))}{\Sigma(N) I_j(N) / (I / I_{\rm cor}(N) I_j^{\rm rel}(N))}, \qquad (6)$$

where $I_i(A)$ is the measured intensity of the ith reflection from the phase of interest; $I_j^{rel}(A)$ is the relative intensity of this reflection in the above-mentioned database; $I/I_{cor}(A)$ is the corundum number of the phase; and $I_j(N)$, $I_j^{rel}(N)$ and $I/I_{cor}(N)$ are the respective parameters for all the components of the mixture under investigation (including A).

Thermogravimetry (TG) and differential thermal analysis (DTA). The materials were characterized by TG and DTA using an STA 409 PC Luxx top-loading simultaneous thermal analysis system (Netzsch, Germany). The measurements were performed in air in the temperature range from 40 to 1000°C at a heating rate of 10°C/min.

The particle size distribution was determined using dynamic light scattering with a Zetasizer Nano ZS instrument in the range 0.2 to $100 \,\mu$ m.

Scanning electron microscopy (SEM) characterization was carried out on a LEO SUPRA 50VP field emission scanning electron microscopes (Carl Zeiss, Germany). Specimens were attached to a copper substrate with conductive adhesive carbon tape, without additional sputtering. The accelerating voltage of the electron gun was 1-21 kV. Images were obtained in secondary electron mode at magnifications of up to $10000/25000 \times$ using an SE2 or InLens detector.

Dilatometric analysis was carried out using a DIL 402 C horizontal dilatometer (Netzsch, Germany). Specimens were heated at a rate of 52°C/min to temperatures between 1000 and 1200°C and held there for 6 h.

The geometric density of ceramic disks prepared by sintering in the range $800-1000^{\circ}$ C for 2 h was determined by measuring their mass (with an accuracy of 10^{-4} g) and linear dimensions (with an accuracy of 10 µm, using a micrometer).

RESULTS AND DISCUSSION

TCP and $Ca_{2.5}Na(PO_4)_2$ (phase *A*) were prepared by sol-gel synthesis via the Pechini process in ethylene glycol and water-ethylene glycol mixed solutions using citric acid as a gelation agent (and a chelating agent). We carried out several experiments with different phosphorus-containing reagents—TEP and EDTMP. Their amounts were adjusted so as to obtain the ratio Ca/P = 1.5 in the final product. The choice of the phosphorus sources was dictated by the necessity to prevent their premature interaction with calcium salts, which otherwise might have led to the formation of poorly soluble phosphates. We tested previously reported sol-gel processes with the use of ammonium hydrogen phosphates [17], but unsuccessfully, because precipitation occurred even before the onset of gelation processes during heating of the solution. It seems likely that the complex-forming effect of citric acid is insufficient for preventing interaction of calcium ions with phosphate anions. The calciumcontaining reagent used was calcium nitrate, readily soluble in water and moderately soluble in EG. As a result, the system contained nitric acid, which acted as an additional oxidizer in subsequent steps of synthesis and speeded up thermolysis processes. If water—ethylene glycol mixtures were used, the molar ratio of citric acid to EG was chosen to be 1 : 1, which was thought to be sufficient for the gelation process to occur [16].

TCP synthesis with the use of TEP. Calcium nitrate, citric acid, and TEP were dissolved in EG to give concentrations of 0.5, 1, and 0.33 M, respectively. The dissolution and the boiling down of the resultant solution took a long time (3-4 h). Reaction (1) yielded calcium citrate complexes, which interacted with EG molecules through a polycondensation reaction to form ester bonds. The dried gel was heat-treated at 1000°C, which led to destruction of the organic matrix and interaction of its components, resulting in the formation of phosphates according to scheme (2).

According to X-ray diffraction data (Fig. 1a), gel thermolysis led to the formation of a mixture of HA and calcium oxide, which points to a change in Ca/P ratio during synthesis: it exceeds 1.67, which means that there is phosphorus deficiency relative to the intended TCP composition. This leads us to conclude that the boiling point of TEP (289°C) is lower than the onset temperature for its interaction with the calciumcontaining reagent. In the alternative technique, TEP was added after gel formation and cooling. An attempt to keep the reagent in the polymer network, preventing its rapid vaporization, was unsuccessful.

According to thermal analysis data (Fig. 2a), exothermic peaks begin to emerge at 320°C (presumably, this event is vaporization of the phosphorus-containing reagent). The most active heat release is observed at a temperature near 500°C. It seems likely that the processes that occur under these conditions are oxidative pyrolysis of the organic matrix and phosphate crystallization.

TCP synthesis with the use of EDTMP. EDTMP was dissolved in water (the process took a considerable time, but could be accelerated by heating) to give a 0.03 M solution, following which we added calcium nitrate, citric acid (to give concentrations of 0.18 and 0.3 M, respectively), and EG (so that the EG : citric acid molar ratio was 1 : 1). Prolonged boiling down led to gelation, and the resultant gel was heat-treated (reaction (3)).

To find suitable conditions for heat treatment of the gel, we carried out thermal analysis (Fig. 2b), which showed that the largest exothermic peak,



Fig. 1. X-ray diffraction patterns of samples obtained via TCP synthesis with the use of TEP after firing of the gel at 1000° C (a) and with the use of EDTMP after firing of the gels at 750 and 1000° C (b) and via synthesis of phase *A* after firing of the gels in the range $510-800^{\circ}$ C (c).

accompanied by a sharp weight loss and carbon dioxide and nitrogen(II) oxide release, was located at a temperature of 720°C. Therefore, the processes that occurred in this step were the decomposition of organic components and crystallization of the synthesis products. A weaker exothermic peak was observed at a temperature of 1000°C.

Using reference and literature data [24, 25] on the stability constants of calcium complexes with citric acid and EDTMP, we analyzed ionic equilibria in solution at various component concentrations (Fig. 3). The conclusion was drawn that, in an acid medium, citric acid was a stronger complexing agent than was EDTMP, so it was citric acid that bound calcium cations in the initial stages of the synthesis. It is worth noting however that, for pH > 4, EDTMP also exists in solution in the form of some complexes with calcium ions (for example, CaH₃EDTMP³⁻); that is, the phosphate component already contains strong Ca-(O-P-) bonds. It seems likely that this prevents pyrohydrolysis of the phosphate component during subsequent firing and deviations from stoichiometry in the final product. This is confirmed by experimental data: according to X-ray diffraction results (Fig. 1b, Table 1), the products of gel thermolysis at 750 and 1000° C consist of phase-pure β -TCP.

 $Ca_{2.5}Na(PO_4)_2$ (phase *A*) synthesis. EDTMP and sodium hydroxide were dissolved in water to give concentrations of 0.1 and 0.2 M, respectively (owing to the formation of a soluble salt by reaction (4), the dissolution time of the acid was considerably shorter). To the resultant solution we added calcium nitrate and citric acid to give concentrations of 0.5 and 1 M and EG to a concentration of 1 M. After boiling-down the solution, the resultant gel was fired.

Heat treatment temperatures were chosen using thermal analysis data (Fig. 2c), with allowance for the largest exothermic peaks. The highest heat release rate, with a sharp weight loss, was observed at a temperature of 600°C. A comparable exothermic peak was observed at a temperature of 550°C.

According to X-ray diffraction data (Fig. 1c), heat treatment at 800°C led to the formation of a mixture consisting of β -TCP, β -CaNaPO₄, and phase *A* (reaction (5)). Since phase *A* is an ordered high-temperature solid solution, according to the phase diagram of



Fig. 2. TG and DTA data for TCP synthesis with the use of TEP (a), TCP synthesis with the use of EDTMP (b), and synthesis of phase A (c).



Fig. 3. Effect of pH on the content of predominant species in solution for the (a) Ca^{2+} -EDTMP-cit³⁻ and (b) Ca^{2+} -PO₄³⁻ - *cit*³⁻ systems (*cit*³⁻ = citrate anion).

the $Ca_3(PO_4)_2$ —CaNaPO₄ system it should decompose eutectoidally below 980°C to form TCP and rhenanite in the weight ratio 1 : 1 [26]. It is worth noting that the sol—gel-derived powders annealed below the eutectoid temperature contained a metastable phase,

A (the formation of metastable phases is rather typical of sol-gel synthesis). According to quantitative X-ray diffraction data, the $Ca_3(PO_4)_2$: $CaNaPO_4$: $Ca_{2.5}Na(PO_4)_2$ weight ratio in our syntheses was 2.42 : 2.26 : 1 (Table 1). Firing at other temperatures in the

Synthesis	Weight fraction				
	$Ca_3(PO_4)_2$	Ca ₁₀ (PO ₄) ₆ (OH) ₂	CaNaPO ₄	CaO	Ca _{2.5} Na (PO ₄) ₂
TCP from TEP	0	0.71	0	0.29	0
TCP from EDTMP	1	0	_	0	_
Phase A	0.43	0	0.40	0	0.17

Table 1. Quantitative X-ray diffraction results for the synthesis products

range $550-800^{\circ}$ C yielded materials with a similar phase composition.

Analysis of the micromorphology of the synthesized TCP and phase *A* powders by SEM (Figs. 4, 5) showed that high thermolysis temperatures (above 700°C) led to the formation of large particles more than 1 μ m in diameter. Active recrystallization of the material, evidenced by the growth and coalescence of primary particles, suggests that the synthesized powders exhibit activity in sintering processes, which potentially allows one to produce dense and, hence, high-strength ceramics from them. This is of special importance in the fabrication of macroporous materials by 3D printing techniques, where high porosity (above 80%) leads to strength loss. The particles obtained at lower firing temperatures $(500-700^{\circ}C)$ have a rounded shape, characteristic of sol-gel synthesis, and a considerably smaller diameter, in the range 200–500 nm, acceptable for synthesis.

Dynamic light scattering data (Fig. 6) confirm the particle size inferred from micrographs of the powder. The results for the macrocrystalline samples obtained at high temperatures demonstrate the presence of particles 2 μ m and more in diameter. In the powders prepared at temperatures from 500 to 680°C, the average particle size is 250 nm. The presence of modes corresponding to diameters of 1 and 5 μ m in the particle size distribution can be accounted for by the formation of agglomerates.



Fig. 4. Micromorphology of the powders obtained through the synthesis of phase A via gel thermolysis at (a, b) 610, (c) 680, and (d) 800°C.

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Fig. 5. Micromorphology of the powders obtained through TCP synthesis via gel thermolysis at (a) 750 and (b) 1000°C.



Fig. 6. Dynamic light scattering data: comparison of the particle size of powders of phase *A* after firing at (a) 510, 550, 610, (b) 680, and 800°C and comparison of the particle size of TCP powders after firing at (c) 750 and 1000°C.

According to dilatometry data (Fig. 7), shrinkage of compacted sol-gel-derived powders begins at substantially lower temperatures in comparison with a mechanical mixture of β -TCP and β -CaNaPO₄ and is larger. At temperatures above 1000°C, we observed effects corresponding to secondary crystallization: an increase in the linear size of the samples and an increase in the size of some grains to above 50 μ m. This suggests that the sintering temperature should not exceed 1000°C, unlike in the case of powders prepared

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Fig. 7. Dilatometry data for the powders of phase *A*: shrinkage of compacts prepared from a mechanical mixture of β -TCP and β -CaNaPO₄ (ceramic history) (*1*) and by sol–gel processing at 610 (*2*) and 510°C (*3*).

by ceramic processing route, where the single-step isothermal sintering temperature, for example, in the CaNaPO₄–CaKPO₄ system, is from 1200 to 1300°C [27].

CONCLUSIONS

We have proposed techniques for the synthesis of TCP and calcium sodium mixed phosphate powders based on the citrate Pechini process, with the use of EDTMP as a phosphorus source.

Citric acid and EDTMP can act as chelating agents and prevent precipitation f crystalline calcium phosphates from solution, which makes them suitable reagents for use in the sol-gel synthesis of TCP and sodium calcium mixed phosphates (rhenanites). Low EDTMP solubility makes it difficult to use it in aqueous and water-ethylene glycol media, but in the case of synthesis of compounds with a rhenanite composition (including phase A, Ca_{2.5}Na(PO₄)₂) this problem disappears owing to the formation of a readily soluble sodium salt.

The use of alkyl phosphates in the sol-gel synthesis of TCP entails a change in Ca/P ratio and, hence, in the stoichiometry of the material during heat treatment of the gel because of the removal of the phosphorus-containing reagent from the reaction zone. If EDTMP is used, phosphorus losses can be avoided, presumably, owing to the partial binding of EDTMP by calcium cations.

Heat treatment of the gels at 1000°C led to the formation of large particles several microns in diameter, suggesting that the synthesized powders exhibited activity in sintering processes. Heat treatment in the temperature range 500–700°C led to the formation of particles with an optimal size, 200–500 nm, which met requirements for stereolithographic 3D printing. Appreciable densification of such powders began at temperatures 300°C lower in comparison with powders prepared by ceramic processing route.

The present results demonstrate that sol-gel processing with EDTMP as a phosphorus source can be used for synthesis of resorbable phosphate materials, such as TCP and rhenanites, and is potentially attractive for further investigation, modification, and use in the fabrication of bioceramics and filling of composites.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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