



Calcium phosphate bioceramics prepared from wet chemically precipitated powders[#]

Kristine Salma, Liga Berzina-Cimdina, Natalija Borodajenko

Riga Biomaterials Innovation and Development Centre, Riga Technical University, Pulka Str. 3/3, Riga, LV-1007, Latvia

Received 16 December 2009; received in revised form 26 March 2010; accepted 1 April 2010

Abstract

In this work calcium phosphates were synthesized by modified wet chemical precipitation route. Contrary to the conventional chemical precipitation route calcium hydroxide was homogenized with planetary mill. Milling calcium oxide and water in planetary ball mill as a first step of synthesis provides a highly dispersed calcium hydroxide suspension. The aim of this work was to study the influence of main processing parameters of wet chemical precipitation synthesis product and to control the morphology, phase and functional group composition and, consequently, thermal stability and microstructure of calcium phosphate bioceramics after thermal treatment. The results showed that it is possible to obtain calcium phosphates with different and reproducible phase compositions after thermal processing (hydroxyapatite [HAp], β -tricalcium phosphate [β -TCP] and HAp/ β -TCP) by modified wet-chemical precipitation route. The β -TCP phase content in sintered bioceramics samples is found to be highly dependent on the changes in technological parameters and it can be controlled with ending pH, synthesis temperature and thermal treatment. Pure, crystalline and highly thermally stable (up to 1300°C) HAp bioceramics with homogenous grainy microstructure, grain size up to 200–250 nm and high open porosity can be successfully obtained by powder synthesized at elevated synthesis temperature of 70°C and stabilizing ending pH at 9.

Keywords: calcium phosphates, hydroxyapatite, β -tricalcium phosphate, wet chemical precipitation synthesis

1. Introduction

Calcium phosphates are chemical compounds of special interest in many interdisciplinary fields of science, including geology, chemistry, biology and medicine [1]. Calcium phosphate with an apatitic structure occurs naturally in the human body and can be described as a calcium deficient carbonate-hydroxylapatite. The chemical similarity of hydroxylapatite to the bone mineral suggests an intrinsic biocompatibility [2]. Due to excellent biocompatibility with living body and bioactivity, calcium phosphate (CaP) ceramics are widely used as biomedical implant materials. Biomaterials and bioceramics made of calcium phosphates are produced in different forms: granules, blocks (dense or porous),

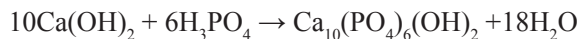
injectable compositions, self-hardening cements, coatings on metallic implants, composites from polymers, and so forth [3]. Bioceramics made of dense hydroxylapatite [HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] would be a good example of a bioactive material, while porous scaffolds made of biphasic calcium phosphates [BCP, β -TCP + HAp] or bone grafts made of β -tricalcium phosphate [β -TCP, $\text{Ca}_3(\text{PO}_4)_2$] appear to be the examples of bioresorbable materials [2]. Various synthesis routes, including wet chemical synthesis (such as precipitation, hydrothermal, hydrolysis and sol-gel techniques) have been developed for the preparation of calcium phosphate powders, which have to present desirable characteristics, such as, crystallinity, stoichiometry, morphology, surface area and particle size for specific applications [4]. All these properties are dependent on synthesis method and its conditions. Physico-chemical characteristics of synthesized calcium phosphates have significant effect on the final material quality (phase composition,

[#]Paper presented at 8th Students' Meeting, SM-2009, Processing and Application of Ceramics, Novi Sad, Serbia, 2009

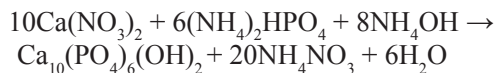
* Corresponding author: tel: +371 670 89 605

fax: +371 670 89 619, e-mail: kristine.salma@rtu.lv

density, thermal stability, microstructure, mechanical properties, dissolution behaviour and cellular response in living body) after thermal treatment. Methods based on precipitation from aqueous solution are most suitable for preparation of large amounts of hydroxyapatite. The difficulty with most of the conventional precipitation methods used is the synthesis of well-defined and reproducible calcium orthophosphates [5]. Problems can arise due to lack of precise control on the factors governing the precipitation, pH, temperature, Ca/P ratio of reagents, which can lead to products with differences in stoichiometry, crystallinity, morphology, that contribute to the different *in vivo/in vitro* behaviours [5]. Wet chemical precipitation from solution is the most common synthesis route to prepare calcium phosphates, generally hydroxyapatite and involves chemical reaction of inorganic oxide solutions [6,7]. The two most popular ways of precipitating CaP were based on the methods developed by Rathje in 1939 and Hayek and Newesely in 1963 [7]. Rathje's method consisted of dropwise addition of phosphoric acid to a stirring suspension of calcium hydroxide according to the reaction given below:



Hayek and Newesely's method consisted of reaction between calcium nitrate and ammonium phosphate with added ammonium hydroxide according to the reaction given below:



Other synthesis reactions include solid-state reactions, hydrothermal techniques, hydrolysis of other calcium phosphates and sol-gel methods [8]. In this

work calcium phosphates were synthesized by modified wet chemical precipitation route using nonstoichiometric concentrations of starting reagents such as $\text{Ca}(\text{OH})_2$ and H_3PO_4 (usually 0.3 M for H_3PO_4 solution and 0.5 M for $\text{Ca}(\text{OH})_2$ solution) [9–11]. Contrary to the conventional chemical precipitation route calcium hydroxide was homogenized with planetary mill. Milling calcium oxide and water in planetary ball mill as a first step of synthesis provides a highly dispersed calcium hydroxide suspension. This method has advantages, such as: simple processing route, large yield (87%), it is suitable for an industrial production, it requires inexpensive reagents and CaP products with variable phase composition can be obtained. The main disadvantage of this method is that multiple process parameters that can significantly change properties of synthesis product must be controlled. That is the reason for which the correlation between the precipitation conditions and properties of the powder has been investigated by several researchers [12]. The aim of this work was to study the influence of main processing parameters in used wet chemical precipitation. This parameters included temperature of synthesis (20°C, 45°C and 70°C) and ending pH value of synthesis (6, 7, 9 and 11). Besides various sintering temperature were used to study thermal stability. In this regards microstructure and morphology of CaP bioceramics were examined after heating at 1000 to 1300°C.

II. Experimental procedure

Calcium phosphates were prepared by a precipitation reaction between calcium hydroxide suspension (CaO , Riedel-de Haën®, Germany) and orthophosphoric acid solution (H_3PO_4 , 85%, Sigma-Aldrich, Germany). Nature, purity and concentration of reagents are

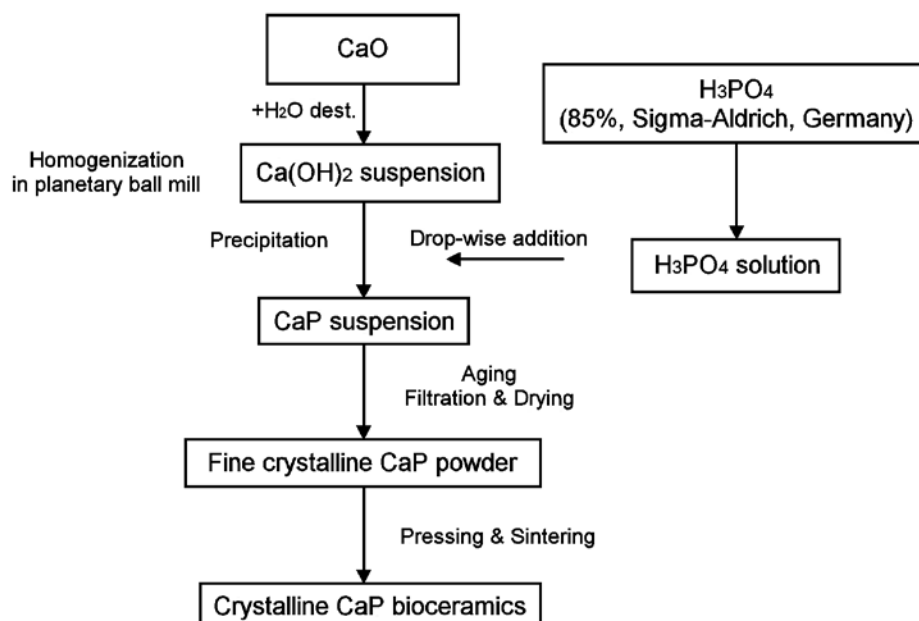


Figure 1. Modified wet chemical precipitation route for CaP synthesis

important factors for production of homogeneous material. The detailed procedure of modified wet chemical precipitation route of CaP powder is given in Fig. 1.

Calcium oxide was suspended in distilled water and milled at rotation speed of 300 rpm with a Pulversette 5 planetary mill (Fritsch, Idar-Oberstein Germany) to obtain homogenous calcium hydroxide suspension. The precipitation reaction took place in a 2 l reactor, equipped with stirrer, electrical heater with thermostat, combined pH electrode and Titronic® system for acid solution addition. Acid solution was added to the calcium hydroxide suspension with slow addition rate ~ 0.75 ml/min under vigorous stirring. The temperature of suspension during synthesis (T_s) was 20°C, 45°C or 70°C. The ending pH value of the suspension was stabilized in the range of 6–11 for 1 h.

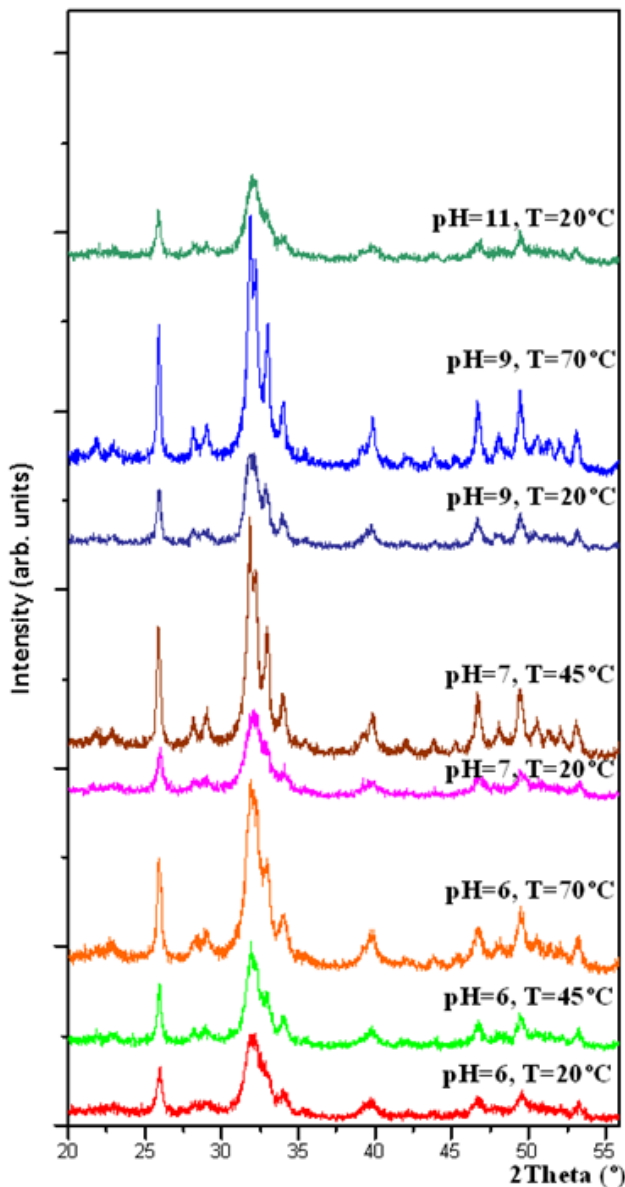


Figure 2. X-ray diffraction patterns of as-synthesized calcium phosphate powders ($T_s=20^\circ$, 45° , 70°C , pH=6, 7, 9, 11) dried at 105°C for 24 h

The suspension was aged for 20 hours at room temperature. After aging the suspension was filtrated in a Buchner funnel, dried at 105°C and ground in a mortar. Synthesized powders were uniaxially pressed (5 kN) in cylindrical tablets ($\phi 10$ mm) and sintered at temperatures ranging from 1000 to 1300°C for 1 h.

Fourier-transform infrared spectroscopy (FT-IR, Scimitar Series model Varian 800) was used to determine the various functional groups in the synthesized and sintered calcium phosphate samples in the $4000\text{--}400$ cm^{-1} range. All IR measurements were carried out at room temperature using the KBr pellet technique. X-ray diffractometry (XRD, X'Pert PRO PAN Analytical diffractometer) was used to analyse phase composition, thermal stability, crystallinity of synthesized and bioceramics samples using CuK_α radiation in the 2θ range between 20° and 90° at room temperature. The morphology of the synthesized powders and microstructure of sintered bioceramics samples were studied with field emission scanning electron microscopy (FE-SEM, Tescan Mira/LMU). Sintering was investigated with heating microscope (Hesse Instruments).

III. Results and discussion

The effect of synthesis temperature and ending pH of synthesis was examined and X-ray diffraction patterns of as-synthesized calcium phosphates are shown in Fig. 2. All as-synthesized powders are fine-crystalline with apatite structure [13]. It can be seen that the diffraction peaks become narrower and sharper with increasing the synthesis temperature. This indicates that the crystallinity and crystallite size of the of precipitated apatites increase when synthesis temperature

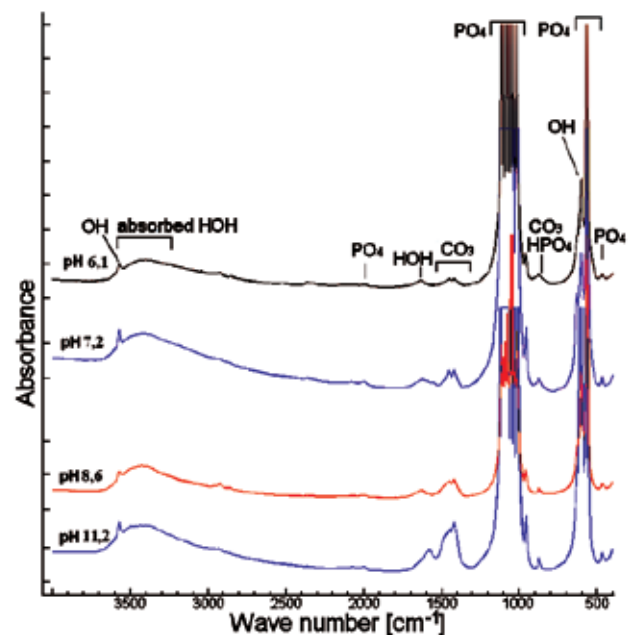


Figure 3. IR spectra of as-synthesized calcium phosphate powders ($T_s=70^\circ\text{C}$, pH=6, 7, 9, 11) dried at 105°C for 24 h

Table 1. Vibrational bands in as-dried CaP powders determined by FT-IR spectroscopy

Groups	Wavenumber [cm ⁻¹]	Groups	Wavenumber [cm ⁻¹]
PO ₄ v ₁	962	CO ₃ v ₃	1482, 1424
PO ₄ v ₂	469	CO ₃ v ₂ , HPO ₄	875
PO ₄ v ₃	1088, 1046	OH v _s , v _L	3571, 632
PO ₄ v ₄	599, 560	HOH	3700-3100, 1637

is increased from 20°C to 70°C at all ending pH values investigated.

FTIR spectra of calcium phosphate powders are shown in Fig. 3. It was found that all as-dried CaP samples, synthesized with different ending pH values (from 6 to 11) and temperatures (in the range from 20°C to 70°C), show phosphate, carbonate and hydroxyl vibrational bands in IR spectra, as summarized in Table 1. The broad absorption band between 3700 and 3100 cm⁻¹ assigned to the O-H stretch vibration of hydrogen bonded OH groups, together with the absorption peak at 1637 cm⁻¹ ascribed to O-H bending mode, are evidence of the presence of absorbed water in the synthesis products that disappeared after thermal treatment at 1000°C. The two sharp peaks observed at 3571 and 632 cm⁻¹, are attributed to the characteristic stretching and vibrational modes of structural OH groups [14,15]. The main characteristic bands of PO₄ tetrahedral apatite's structure are clearly observed in Fig. 3. The peak at 469 cm⁻¹ is attributed to PO₄ v₂, the double peak at 599, 560 cm⁻¹ belongs to PO₄ v₄, 962 cm⁻¹ for PO₄ v₁ and the peaks at 1088 and 1046 cm⁻¹ for PO₄ v₃. The absorption bands at 1482, 1424 and 875 cm⁻¹ confirm the presence of carbonate group, respectively CO₃ v₃ and CO₃ v₂. The carbonate bands for CaP prepared with pH 11 have showed stronger peaks than syntheses with the pH value in the range of 6–9. Also, increasing ending pH induced the substitution of PO₄ groups with CO₃

groups. Slow acid addition rate (0.75 ml/min) leads to an incorporation of carbonate in apatite structure, but prevent formation of Ca-deficient apatite phase [16]. These results clearly indicate the formation of a typical apatite structure for all synthesized powders. A weak band near 875 cm⁻¹ can be attributed to HPO₄ groups, which are more clearly observed in IR spectra of CaP by pH = 6 (Fig. 3). From literature this band can be associated with Ca-deficient apatite (CDAp) and decomposition of CDAp after thermal treatment lead to formation of β-tricalcium phosphate (β-TCP) or biphasic calcium phosphates (BCP) [7,17,18]. These results of FTIR spectra for sintered CaP bioceramic samples show that after heating the carbonate contents in HAp decreases.

FE-SEM micrographs of the as-dried CaP powders show strong agglomerated primary nano-size synthesis products (Fig. 4). Precipitation conditions have shown significant effect on crystal size and morphology. FE-SEM micrograph (Fig. 4a) of the as-dried CaP powder synthesized at pH = 6 and 70°C shows small agglomerated circular crystals of about 100 nm. FE-SEM micrograph (Fig. 4b) of the sample synthesized at pH = 6 and T_s = 20°C shows agglomerated needle-like morphology of about 50–100 nm. Crystals prepared at high temperature are more rounded. FE-SEM investigations of synthesized CaP powders showed, that the lower synthesis temperature gave smaller morphology of crystals

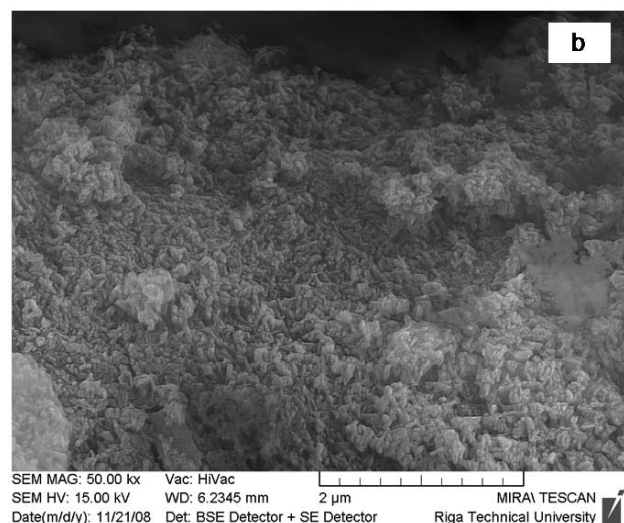
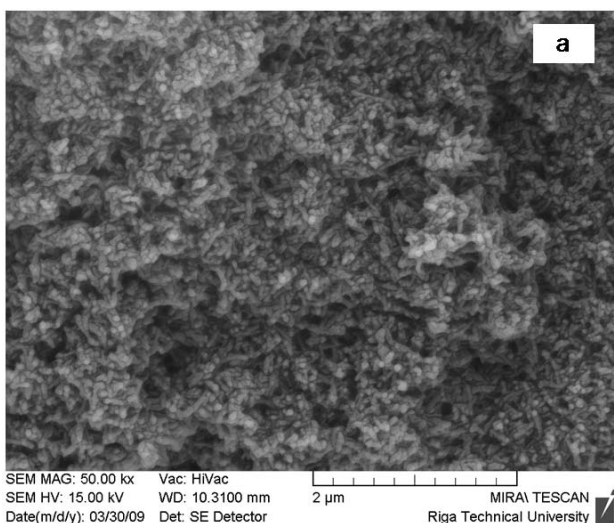


Figure 4. FE-SEM micrographs of as-dried CaP powders synthesized at: a) T_s=70°C, pH 6 and b) T_s=20°C, pH 6

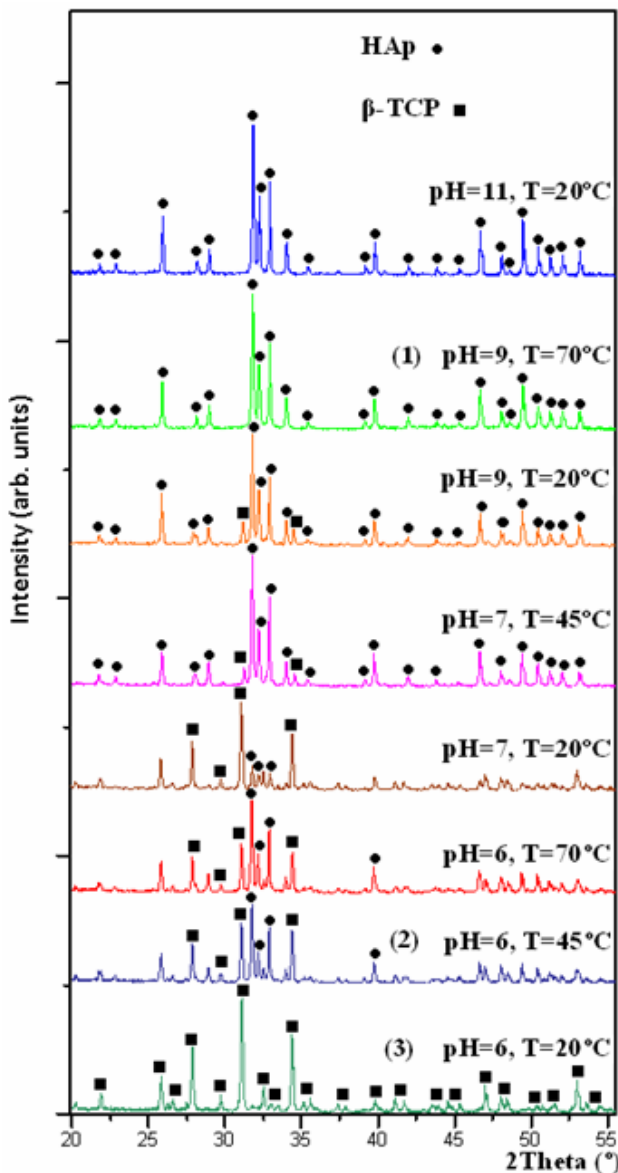


Figure 5. X-ray diffraction patterns of different calcium phosphate phase compositions; (HAp) pH 9, $T_s=70^\circ\text{C}$; (HAp/ β -TCP) $T_s=45^\circ\text{C}$, pH 6; (β -TCP) pH 6, $T_s=20^\circ\text{C}$, sintered at 1000°C for 1 h

with needle-like morphology and increasing of synthesis temperature lead to formation of more circular crystals with larger size.

After thermal treatment at 1000°C XRD patterns of the CaP bioceramics samples show significant changes in phase composition and crystallinity in dependence on synthesis conditions (Fig. 5). Pure, crystalline and highly thermally stable (up to 1300°C) HAp phase can be successfully synthesized by elevating synthesis temperature to 70°C and stabilizing ending pH = 9 (Fig. 5, pattern 1). The XRD pattern of sample synthesized at pH = 6 (Fig. 5, pattern 2) shows that this sample is a biphasic mixture of hydroxyapatite and β -TCP (HAp/ β -TCP ratio 57/43 by half quantitative method). The XRD pattern of the pellet prepared from the CaP powder synthesized at pH = 6 and $T_s = 20^\circ\text{C}$ (Fig. 5, pattern 3) con-

sists of pure β -TCP phase. After XRD investigations of CaP bioceramics samples it was found that higher pH values (pH = 9 and 11) favours formation of HAp phase in sintered samples, whereas lower pH values (pH = 6) increase stability of β -TCP phase. Influence of temperature is also important as at the same ending pH value stability of HAp phase in the sintered sample increases with temperature. Thus, sample with pure HAp phase was obtained from powder synthesized at pH = 11 ($T_s = 20^\circ\text{C}$) and pH = 9 ($T_s = 70^\circ\text{C}$), but sample with pure β -TCP was prepared from the powders synthesized at pH = 6 ($T_s = 20^\circ\text{C}$). All other bioceramics are biphasic with variable HAp and β -TCP phase ratio.

After thermal treatment at 1200°C XRD patterns of the CaP bioceramics samples show significant changes in phase composition, respectively, the content of minor biphasic calcium phosphates phase decreases with decreasing sintering temperature. The crystallinity of CaP bioceramics samples increases (diffraction peaks become sharper) with an increase of sintering temperature up to 1200°C .

FE-SEM micrographs (Fig. 6) of the sintered CaP bioceramics samples show significant differences in ceramics microstructure depending on the phase composition. The homogenous fine grained microstructure of HAp bioceramics with small grain size of about 100–150 nm is shown in Fig. 6a. An increase in grain size and density is observed with an increase in the sintering temperature. The sintering of HAp improves the crystallinity and density as well. For biphasic systems HAp/ β -TCP, CaP microstructure depended on the amount of β -TCP. The microstructure of HAp/ β -TCP samples (up to 20 wt.% of β -TCP) is close to that of pure HAp microstructure with enlarged grains exhibiting a regular shape and strongly bonded ones with the others. In Fig. 6b is shown FE-SEM micrograph of HAp/ β -TCP sample with grain size of about 200–250 nm. On the opposite, FE-SEM micrograph of β -TCP bioceramics sample shows fine microstructure of small circular grains (Fig. 6c). At temperature higher than 1000°C grain growth is observed in sintered CaP samples. Due to the grain growth the diffraction peaks in XRD are sharper at 1200°C . During sintering, the minor phase slows down the sintering of the biphasic calcium phosphates. The microstructure and sinterability of the biphasic CaP ceramics depend on the proportions of these two phases.

IV. Conclusions

The results show that it is possible to obtain calcium phosphates with different and reproducible phase compositions (HAp, β -TCP and HAp/ β -TCP) by modified wet-chemical precipitation route.

This study shows that the technological parameters considerably influence composition of synthesized powder and formation of hydroxyapatite and β -tricalcium phosphate phase during sintering.

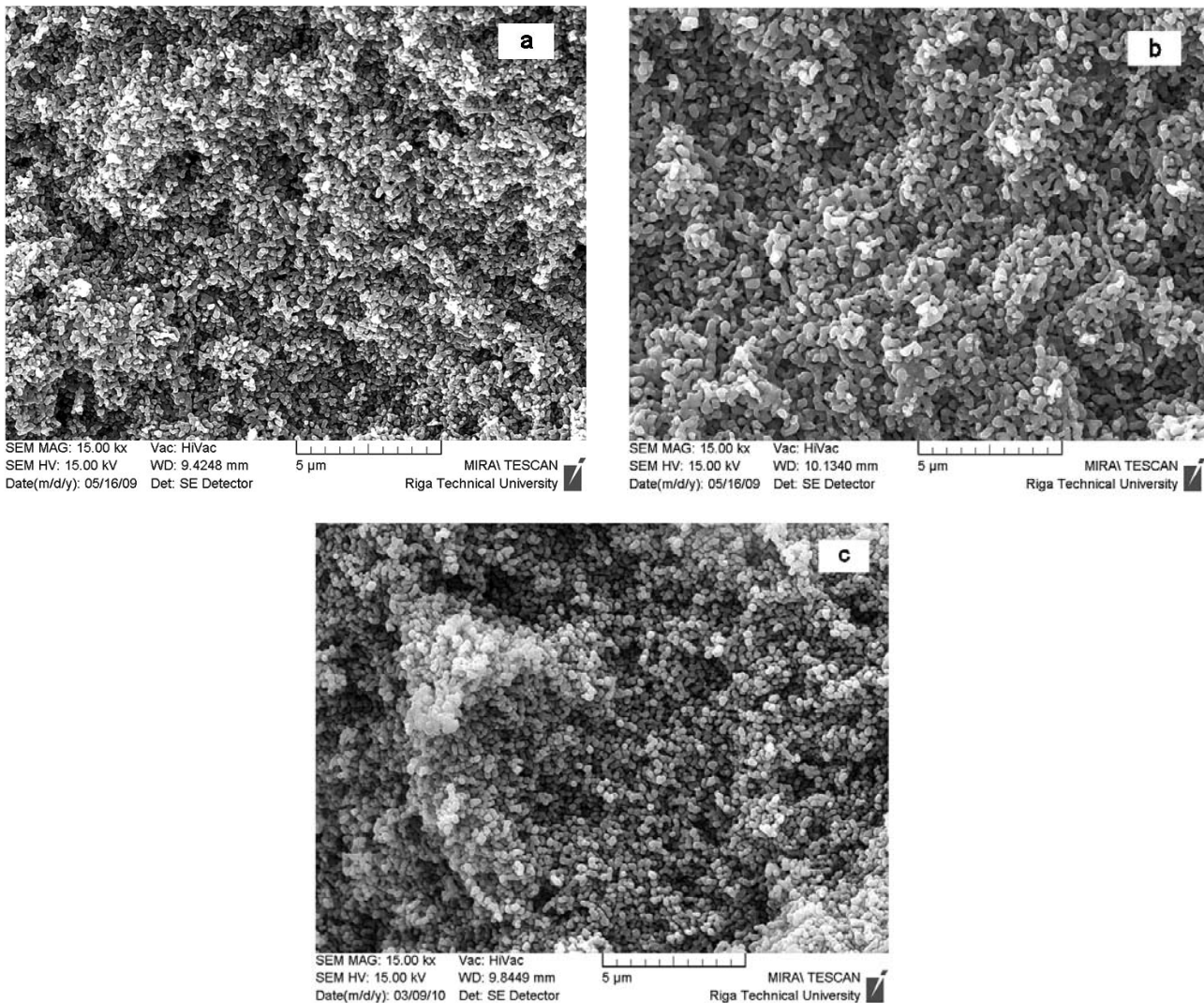


Figure 6. FE-SEM micrographs of CaP bioceramic samples (sintered at 1000°C for 1h) with different phase composition, corresponding to XRD patterns: 1 (a), 2 (b) and 3 (c) presented in Fig. 5

Pure, crystalline and highly thermally stable (up to 1300°C) HAp bioceramics with homogenous microstructure and grain size up to 200–250 nm was obtained from powders synthesized at elevated synthesis temperature (70°C), stabilizing ending pH 9 and after aging of suspension for 20 h.

Acknowledgement This work has been supported by the European Social Fund within the project: „Support for the implementation of doctoral studies at Riga Technical University”.

References

1. S.V. Dorozhkin, “Calcium Orthophosphates in Nature, Biology and Medicine”, *Materials*, **2** (2009) 399–498.
2. S.M. Best, A.E. Porter, E.S. Thian, J. Huang, “Bioceramics: Past, present and for future”, *J. Eur. Ceram. Soc.*, **28** (2008) 1319–1327.
3. R.Z. LeGeros, J.P. LeGeros, “Calcium phosphate bioceramics: past, present, and future”, *Key Eng. Mater.*, **240-242** (2003) 3–10.
4. A. Bianco, I. Cacciotti, M. Lombardi, L. Montanaro, “Thermal stability and sintering behavior of hydroxyapatite nanopowders”, *J. Therm. Anal. Cal.*, **88** [1] (2007) 237–243.
5. M. Vallet-Regí, J.M. González-Calbet, “Calcium phosphates as substitution of bone tissues”, *Prog. Solid State Chem.*, **32** (2004) 1–31.
6. E. Bouyer, F. Gitzhofer, M.I. Boulos, “Morphological study of hydroxyapatite nanocrystal suspension”, *J. Mater. Sci. - Mater. Med.*, **11** (2000) 523–31.
7. L.L. Hench, J. Wilson, *An introduction to bioceramics*, World Scientific, Singapore 1993.
8. M.P. Ferraz, F.J. Monteiro, C.M. Manuel, “Hydroxyapatite nanoparticles: A review of preparation methodologies”, *J. Appl. Biomater. Biomech.*, **2** (2004) 74–80.
9. S. Raynaud, E. Champion, D. Bernache-Assollant, “Calcium phosphate apatites with variable Ca/P atomic ratio I. Synthesis, characterization and thermal stability of powders”, *Biomaterials*, **23** (2002) 1065–1072.

10. S. Raynaud, E. Champion, D. Bernache-Assollant, “Calcium phosphate apatites with variable Ca/P atomic ratio II. Calcination and sintering”, *Biomaterials*, **23** (2002) 1073–1080.
11. S. Raynaud, E. Champion, J.P. Lafon, D. Bernache-Assollant, “Calcium phosphate apatites with variable Ca/P atomic ratio III. Mechanical properties and degradation in solution of hot pressed ceramics”, *Biomaterials*, **23** (2002) 1081–1089.
12. M.R. Saeri, A. Afshar, M. Ghorbani, N. Ehsani, C.C. Sorrell, “The wet precipitation process of hydroxyapatite”, *Mater. Lett.*, **57** (2003) 4064–4069.
13. P.W. Brown, B. Constanz, *Hydroxyapatite and related materials*, CRC Press, United States of America 1994.
14. S.M. Barinow, J.V. Rau, S. Nunziante Cesaro, J. Āurišin, I.V. Fadeeva, D. Ferro, L. Medvecky, G. Trionfetti, “Carbonate release from carbonated hydroxyapatite in the wide temperature range”, *J. Mater. Sci. - Mater. Med.*, **17** (2006) 597–604.
15. J. Qian, Y. Kang, W. Zhang, Z. Li, “Fabrication, chemical composition change and phase evolution of biomorphic hydroxyapatite”, *J. Mater. Sci. - Mater. Med.*, **19** (2008) 3373–3383.
16. J. Marchi, P. Greil, J.C. Bressiani, F. Müller, “Influence of synthesis conditions on the characteristics of biphasic calcium phosphate powders”, *J. Appl. Ceram. Technol.*, **6** [1] (2009) 60–71.
17. Z.Z. Zyman, M.V. Tkachenko, D.V. Polevodin, “Preparation and characterization of biphasic calcium phosphate ceramics of desired composition”, *J. Mater. Sci. - Mater. Med.*, **19** (2008) 2819–2825.
18. N. Rameshbabu, K. Prasad Rao, “Microwave synthesis, characterization and in-vitro evaluation of nanostructured biphasic calcium phosphates”, *Curr. Appl Phys.*, **9** (2009) S29–S31.

