

## Studies on sintering process of synthetic hydroxyapatite\*

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**In this study the effect of sintering process in different temperatures on microstructure and morphological properties of sintered hydroxyapatite (HAp) was investigated. HAp powder was prepared by wet precipitation method from following reagents:  $\text{Ca}(\text{OH})_2 + \text{H}_3\text{PO}_4$  in an alkaline conditions. Thermal analysis (TA), X-Ray diffraction method (XRD), FT-IR spectrometry (FT-IR) and scanning electron microscopy (SEM) were used to elaborate the phase composition and properties of sintered HAp samples and raw HAp powder as well. The total and apparent density and total porosity of sintered compacts, shrinkage and weight loss during the sintering were also measured. The results show that there is a difference in sintering behavior of synthetic hydroxyapatites depending on sintering temperature. The main differences refer to the loss of mass, shrinkage, changes in porosity and density of the investigated materials.**

**Key words:** calcium phosphates, hydroxyapatite, sintering process, wet synthesis

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### INTRODUCTION

Being the main inorganic constitution of hard tissues (bone and teeth), calcium phosphates have been applied in medical and dental applications in hard tissue repair. Hydroxyapatite (HAp) ceramics have attracted attention because of their excellent osteoconductive and bioactive properties. Such materials are biocompatible, bioactive, osteoconductive, nontoxic, noninflammatory and have an ability to form strong bonds with the living hard tissue (Sopyan *et al.*, 2007; Fathia *et al.*, 2008; Lee *et al.*, 2010; Zhang *et al.*, 2011). From all the synthetic materials applied in medicine and dentistry hydroxyapatite bioceramic shows the biggest similarity in structure and chemical composition to the bone mineral. This resemblance gives hydroxyapatite numerous advantages advisable in biomedical application with the high biocompatibility, bioactivity and osteoconductivity being the most important (Sobczak & Kowalski, 2007; Sobczak *et al.*, 2011). Hydroxyapatite is composed of ions (mainly  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$ ) that naturally occur in tissue and, thus, HAp do not have the biotoxic properties and can be safely introduced to human body (LeGeros, 2008; Malina *et al.*, 2011). HAp bioceramics play a significant role in bone loss filling, paradentosis treatment, broken bones consolidation and stabilization, spinal column surgery and in otolaryngology. Hydroxyapatite is widely used in dental implants, as drug carrier, scaffolds for tissue engineering and coatings covering the surface of implants made of other biomaterials (Joschek *et al.*, 2000; Fathia *et al.*, 2008; Malina *et al.*, 2011).

Thermal stability of hydroxyapatite bioceramic is an important issue since the implants are usually prepared by high-temperature sintering of pressed powders of hydroxyapatite. Stea and coworkers reported that sintered HAp forms very tight bonds with the bone tissue (Prokopiev & Sevostianov, 2006). The temperature and time of thermal treatment are the most important parameters influenced on HAp properties. During sintering, two separate processes affecting the morphology of solids occur: densification and grain growth (Gu *et al.*, 2002). Two of them are thermally activated, but only the densification is desired. In the first step of sintering process (in temperature below 750°C) the internal powder expansion is observed. Subsequently, in higher temperature compaction process is initiated and leads to remove pores from the material. Finally, the sample shrinks and reaches its maximum density in sintered form. Sintering is conducted so as to achieve the highest density while reducing grain growth (Champion, 2013).

In this study the dependence of microstructural and morphological properties of heat treatment hydroxyapatite on the sintering temperature was investigated. Raw hydroxyapatite powder obtained by wet precipitation methods was sintered in a wide range of temperatures and examined using thermal analysis (TA), X-Ray diffraction analysis (XRD), FT-IR spectrometry (FT-IR) and scanning electron microscopy (SEM) to elaborate the phase composition and properties of sintered HAp. Due to the fact that changes in the mechanical properties and microstructure of the sintered HAp specimens correlate with grain sizes, density of the specimen and porosity, the density and porosity of sintered compacts, shrinkage and weight loss during the sintering were also measured.

### MATERIALS AND METHODS

**Chemicals.** All chemicals used in experiments were of reagent grade and used as received. Calcium carbonate precipitated, orthophosphoric acid 85% and ammonia solution 25% were purchased from POCh (Poland). For obtain  $\text{Ca}(\text{OH})_2$  as a source of calcium in HAp, calcium carbonate was calcined at 950°C for 3 hours and then resultant calcium oxide was mixed with water. Distilled water was used to prepare all of the solutions.

**Hydroxyapatite synthesis and sintering procedure.** Hydroxyapatite powder was prepared by precipitation method using  $\text{Ca}(\text{OH})_2$  as calcium source and  $\text{H}_3\text{PO}_4$  as

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**Abbreviations:** FT-IR, FT-IR spectrometry; TA, thermal analysis; XRD, X-Ray diffraction analysis; SEM, scanning electron microscopy

phosphorus source in alkaline environment. Ca/P molar ratio was 1.67. Firstly, calculated amount of aqueous solution of calcium hydroxide was poured into a beaker and ammonia solution was added to maintain pH greater than 9 throughout the synthesis process. Secondly, aqueous solution of  $\text{H}_3\text{PO}_4$  was added dropwise into a mixture under continuous stirring with a magnetic stirrer. An alkaline environment is needed to preserve the crystallization process of the apatite, therefore addition of ammonia can maintain these conditions after dropping of phosphoric acid. The HAp synthesis was performed at room temperature. Obtained slurry was stirred for 1 hour at room temperature, then left to mature for the next 24 hours. After that the precipitate was filtered off through Büchner funnel. The filter cake was washed with distilled water and left to dry at room temperature. Resultant HAp powder was uniaxially compacted by hydraulic press into cylindrical specimens and then sintered in different temperatures ranging from 800°C to 1400°C for 2 h in a programmable furnace.

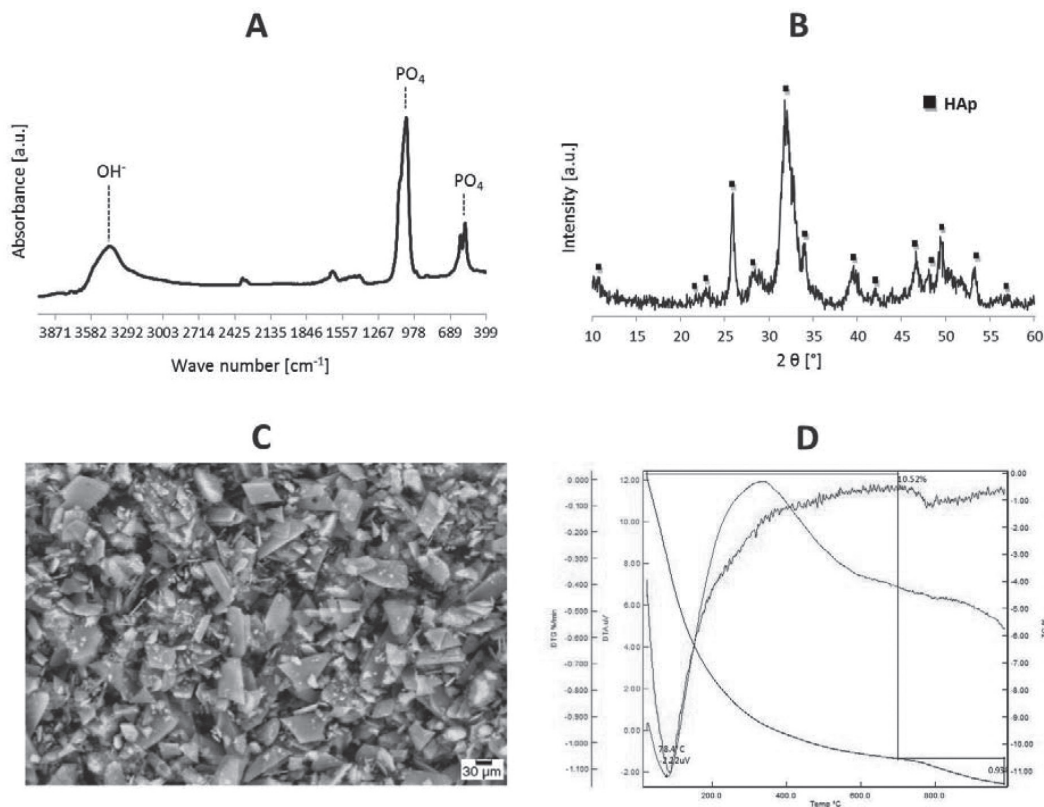
**Characterization techniques.** The as-produced sintered bodies and raw HAp powder were investigated with following characterization techniques. To characterize the crystallized solids chemical analyses, powder X-ray diffraction (XRD), FT-IR spectroscopy, thermal analysis and SEM methods were applied. Philips X'pert XRD equipment with a graphite monochromator (PW 1752/00), Cu K $\alpha$ , ( $\lambda = 0.15418$  nm) radiation, a Ni filter in 2 $\times$  range of 10 to 60 degrees at 30 kV, 30 mA was used. FT-IR Spectrometer of Scimitar Series FTS 2000 produced by the Digilab company within the basic wavenumber range of 400–4000  $\text{cm}^{-1}$  was used to record IR spectra

(1.0 mg of sample in 0.2 g KBr pressed pellet). Thermal decomposition was investigated using a TGA-DTA (simultaneous Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) fully automated system (Universal V2.3C TA Instruments) with 20 deg/min heating rate. The SEM images were obtained using JEOL JSM 7500F: the samples were adhesive on carbon tape sliiced to a copper holder coated with chromium film. The total and apparent density and total porosity of sintered compacts, shrinkage and weight loss during the sintering were also measured. Total density was determined by simple pycnometric method using a glass flask with a close-fitting ground glass stopper with a capillary hole through it. Hydrostatic weighing (HW) uses the Archimedes principle was used to calculate apparent density of sintered specimens. The procedure of HW involves using the following three measurable values: the weight of the body outside the water, the weight of the completely immersed body and the density of the water. The value of total and apparent density is needed to evaluate the percentage of total material porosity (P) according to the equation:

$$P = \left(1 - \frac{\text{apparent density } \text{g/cm}^3}{\text{total density } \text{g/cm}^3}\right) * 100 \%$$

## RESULTS

**Characterization of raw hydroxyapatite.** FT-IR spectrum of raw synthetic hydroxyapatite shown in Fig. 1A indicates the presence of characteristics bands corresponding to  $\text{PO}_4$  group. The band within wave num-



**Figure 1. Characterization of raw hydroxyapatite:** (A) FT-IR spectrum; (B) XRD pattern; (C) SEM image; (D) Thermal analysis curves.

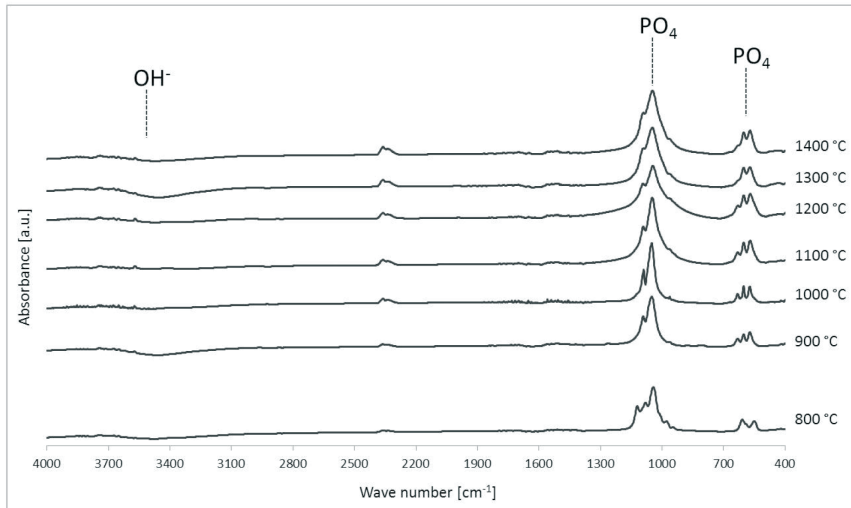


Figure 2. FT-IR spectra of HAp sintered at different temperatures.

ber range  $605\text{--}560\text{ cm}^{-1}$  is assigned to asymmetric deformation of O-P-O vibrational mode while the most intensive absorption band in the region of  $1200\text{--}1000\text{ cm}^{-1}$  corresponds to asymmetric stretching band P-O mode. The broad band with an average intensity within high wave number range ( $3550\text{--}3350\text{ cm}^{-1}$ ) is typical of OH<sup>-</sup> group in HAp and indicates the presence of water in HAp structure. Fig. 1B presents X-ray diffraction pattern of synthetic HAp. XRD analysis showed that hydroxyapatite is the only crystalline phase identified in the material. However, extended, not visibly separated peaks with lower intensity indicate a low degree of crystallinity. These features are characteristic for hydroxyapatites precipitated from aqueous solutions.

The microstructure of HAp was examined using scanning electron microscope (Fig. 1C). HAp grains with flakes-like shape are quite diversified both in shape and size and not combine in large agglomerates. It can be concluded that the small size of crystallites affect the thermal stability of the powder. HAp is thermally stable

up to  $700^\circ\text{C}$ , TG curve runs uniformly to this temperature and then at  $800^\circ\text{C}$  a mild weight loss is observed (Fig. 1D). The first break of the curve with 10.52% weight loss associates with a partial desorption of water and dehydroxylation of HAp. The second break corresponds to the thermal decomposition of HAp. The total weight loss is 11.46%.

**Characterization of sintered hydroxyapatite.** The heat treatment was carried out in temperature from  $800$  to  $1400^\circ\text{C}$ . Infrared analysis indicate the presence of phosphate groups in all tested materials over the range of sintering temperatures. The intensity of bands assigned to PO<sub>4</sub> increases with increasing sintering temperature to about  $1000^\circ\text{C}$ , whereas decreases in higher temperatures and peaks are extended with lower resolution. Simultaneously, with increase of sintering temperature, the intensity of bands corresponded to OH<sup>-</sup> group is reduced and total disappearance of the OH<sup>-</sup> band at  $633\text{ cm}^{-1}$  is observed at  $800^\circ\text{C}$ . Peaks at  $1121\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$  were observed in samples sin-

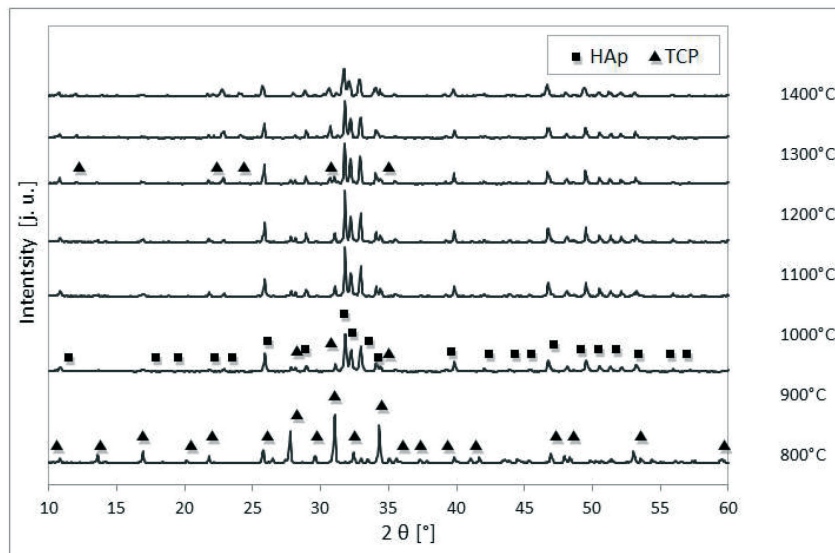
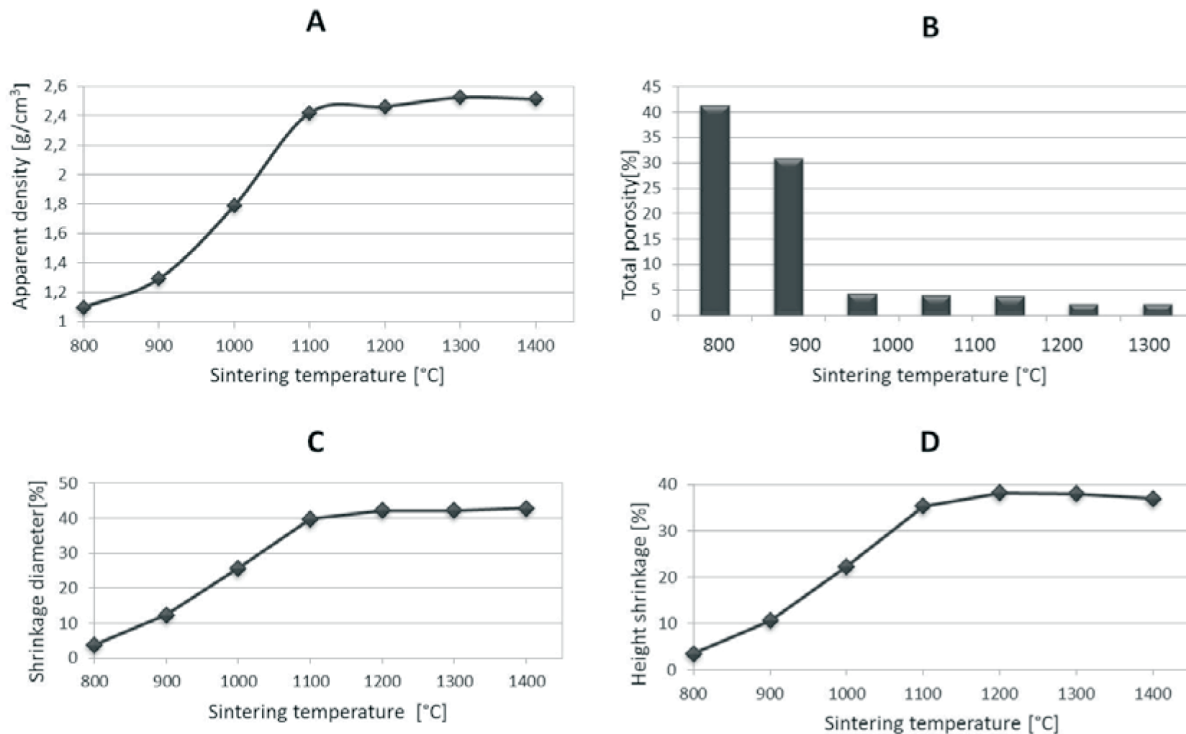


Figure 3. XRD patterns of HAp sintered at different temperatures.



**Figure 4. Influence of HAp sintering temperature on:** (A) Apparent density; (B) Total porosity; (C) Shrinkage diameter; (D) Height diameter.

tered at 800°C, at higher temperatures they disappears. Figure 2 presents FT-IR spectra of sintered HAp.

After sintering, specimens that had been crushed were again examined by X-ray diffraction method. The X-ray pattern for the HA sintered indicated low thermal stability. The reflections from TCP phase are already recorded in the lowest sintering temperature used in experiment. At 800°C the only product of sintering is TCP, whereas HAp is totally decomposed. However, in higher sintering temperatures both phases are observed: HAp and TCP. Reappearance of HAp phase at 900°C is a probably consequence of the reaction proceeded during sintering cooling and it leads to partial restore of HAp (TCP → HAp). Sintering process in higher temperatures (above 1000°C) do not lead to further transformations. The presence of two phases is constantly observed: starting material (HAp) and its partial degradation product (TCP). The share of second product increases at 1200°C.

Effect of sintering temperature on the apparent density of sintered synthetic HAp is shown on Fig. 4A. The consequence of temperature rising is an increase the apparent density of the sintered material and a decrease in porosity. Initiation of compressing process designated by abrupt increase in apparent density is already observed at 800°C and could begin initiated at temperatures lower than used in this study. According to literature, a high calcination temperature leads to improved packing of HAp grains and, consequently, to higher material density. In contrast, this relation runs differently during sintering. Calcining process causes a delay of sintering initiation therefore it is necessary to use higher temperatures to achieve high density (Juang & Hon, 1996). Based on the present graph, it can be concluded that the grains compaction is the most intense in the temperature range 900–1100°C. Sintering process in higher temperatures re-

sults in a slight increase in density (*plateau* of the curve) and unlimited grain growth. It is commonly known that the compaction of the material is associated with a decrease in porosity (Fig. 4B). The porosity represents one of the main factors defining bioactivity. Implants with low porosity have lower osteoconductivity since they less support bone ingrowth and formation of the bonds with the living tissues (Prokopiev & Sevostianov, 2006). At a temperature of 900–1000°C a rapid decrease of sintering porosity from 31.00% to 4.44% is observed. These changes determine temperatures at which intense concentration is occurred. In the next step, weight loss during sintering process and shrinkage of linear dimensions were measured. The general trend of increasing mass loss with increasing sintering temperature is clearly visible. Weight loss is proceeded rapidly and at final sintering temperature reaches 13.21%. Nevertheless, synthetic HAp shows deviation from this dependence at 1300°C — in this case, a decrease of weight loss is observed. The slope of the curves showing the dependence of the sintering shrinkage dimensions are presented in Fig. 4C and D. The relative shrinkage of the sintering rises steeply as temperature increases up to 1100°C and then remains without significant changes. The final shrinkage diameter of sintering is 42.89%, which is associated with significant weight loss during sintering. Since HAp was prepared from aqueous solutions without initially thermal treatment, this material loses large quantities of water and noticeably shrinks.

## DISCUSSION

The work presents significant impact of many factors on sintering process of synthetic hydroxyapatite prepared



by precipitation method. Sintering is a purposeful procedure conducted in to improve the overall characteristics of the starting materials (Juang & Hon, 1996; Gibson *et al.*, 2001). The desired degree of crystallinity of hydroxyapatite is obtained by the calcination in a temperature ranging from 600 to 1300°C, wherein the sintering process occurs simultaneously and as a result the particle size increases.

The stoichiometry of raw products plays the key role during sintering due to its influence on physicochemical properties and thermal stability of HAp (Lazić *et al.*, 2001). In terms of thermal treatment, stoichiometry hydroxyapatite with molar ratio Ca/P 1.67 exactly, is the most desired parameter because of great sinterability and stability in high temperatures. It could be concluded that synthetic HAp remains thermally stable in lower temperatures (below 800°C) than natural, bone-derived HAp (Sobczak-Kupiec & Wzorek, 2012). XRD analysis showed thermal partial decomposition of raw HAp into two phases: TCP (tricalcium phosphate) and HAp in temperature 900°C and higher. Based on these results it is shown that during cooling process inverse phase change (TCP → HAp) and partial reconstruction of HAp have occurred. As (Raynaud *et al.*, 2002) reported, the necessary condition for the occurrence of these changes is the presence of moisture in the atmosphere during cooling of sinters. Sintering process in temperatures higher than 1200°C caused an increase of tricalcium phosphate content in sintering products demonstrated by the presence of additional reflections on XRD patterns attributed to TCP. From this temperature, a decrease in the compaction speed of sintered HAp presented as *plateau* on the curve illustrated the dependence of the apparent density of sintering temperature. With an increase of TCP phase content, the effectiveness of sintering hydroxyapatite materials decreases, as a result obtained ceramic is characterized by an inhibition of compaction at high temperatures and reduced density. During sintering, the agglomerates can produce the empty spaces increasing the susceptibility to cracking of the material. It is a consequence of the difference in the shrinkage of the agglomerates and the surrounding single particles of powder. The pores created by the irregular powder particles cannot be completely removed during the rapid growth in the sintering temperature they exist in the material in the form of closed pores, reducing the density of sinters (Thangamani *et al.*, 2002).

The observed differences of HAp during sintering process confirmed an influence of synthesis and HAp production processing on sintering and characterization of the final products. The exact information about the

influence of sintering conditions on the properties of as-produced HAp bioceramics is the issue of great importance to the further development of HAp biomaterials.

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