

Characterization of calcium phosphate ceramics obtained by chemical precipitation

D. N. UNGUREANU^{a*}, D. AVRAM^b, A. CATANGIU^a, F.V. ANGHELINA^a, V. DESPA^a

^a Valahia University of Targoviste, Faculty of Materials Engineering and Mechanics, Carol I Avenue, No. 2, 130024, Targoviste, Romania

^b Valahia University of Targoviste, Faculty of Environmental Engineering and Food Science, Carol I Avenue, No. 2, 130024, Targoviste, Romania

The aim of this paper was to obtain a hydroxyapatite powder by chemical co-precipitation process using calcium nitrate tetrahydrate and ammonium dihydrogen phosphate as starting reagents. Also, the results of thermal analysis, X-ray diffraction and scanning electron microscopy have been presented. DSC and DDSC analysis confirmed decomposition of nitrates from powders structure studied. X-ray diffraction reveals obtaining hydroxyapatite crystal size of 38nm, which will increase to 100 nm after thermal treatment at high temperature. Concerning the particle morphology, at low temperature, microparticles have an elongated (needle-like) aspect, which tends to become spherical after calcination at 1200°C.

(Received April 9, 2015; accepted June 24, 2015)

Keywords: Biomaterials, hydroxiapatite, Powders, Thermal analysis, Scanning electron microscopy

1. Introduction

Definition of the biomaterial given by the European Society for Biomaterials refers to any material used in a medical system capable of interacting with biological systems. This area of research is relatively new, appeared mainly after 1970.

In the last decades implants made of ceramic hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, have attracted more and more attention as an alternative to materials used in applications for bone repair and regenerative surgery. This material is considered the most important bioactive ceramics widely used in applications that include coating of orthopedic prostheses, dental implants, applications in maxillofacial surgery, reconstruction and growth of bone tissue affected by various diseases [1-4].

Methods for the synthesis of hydroxyapatite are multiple. Chemical coprecipitation method is most prevalent [5-7], along with hydrothermal methods [8-9], sol - gel synthesis [10-11], microwave irradiation [12-13], solvothermal method [14], solid state synthesis [15-16] etc. Obtaining of hydroxyapatite characterized by a high degree of crystallinity and purity depends on a number of factors involved in the synthesis of this biomaterial. In the case of chemical co-precipitation methods, synthesis temperature, pH of the reaction medium, starting materials (reagents) used or stirring speed of the reaction bath are parameters that leads to a product with optimal characteristics.

Chemical reagents most used are $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{NO}_3)_2$, CaCl_2 , as calcium precursors and H_3PO_4 , $(\text{NH}_4)_2\text{HPO}_4$, Na_2HPO_4 as phosphate precursors.

Regarding the synthesis conditions by chemical coprecipitation method, stoichiometric hydroxyapatite ($\text{Ca}/\text{P} = 1.67$) is obtained, where the synthesis temperature

is in the range of 25 - 75°C. Also, the pH of the bath shows high values ($\text{pH} = 10-11$) [17].

At the same time, there was a decrease of the powder particles size obtained from 3-5 μm to less than 1 μm , with increasing of synthesis temperature. Also, it was found to obtain hydroxyapatite particles less than 100 nm, when the synthesis was carried out at room temperature, and the reaction medium was stirred for 24 hours [17-19].

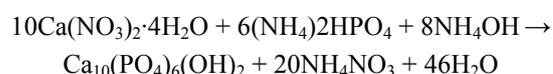
Another factor influencing the synthesis of hydroxyapatite is the pH of the reaction bath. The stability of hydroxyapatite powders increases with pH values. It has been observed conversion of hydroxyapatite in tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$), after heat treatment over 800°C, in the case of powders synthesized at $\text{pH}=8$. By increasing the pH values ($\text{pH} = 10-11$), allowed to obtain a stable hydroxyapatite at temperatures up to 1000°C [7, 17, 20].

2. Experimental part

2.1 Synthesis method

For this paper was obtained a hydroxyapatite powder synthesized by chemical co-precipitation process using 0.25 mol of calcium nitrate tetrahydrate and 0.15 mol of ammonium dihydrogen phosphate. After a method described in other papers [7, 21, 22].

The chemical reaction that describes this synthesis is presented below:



The precursors containing ions of calcium and phosphorus, respectively, 68.7wt% $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 23.2wt% $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in distilled water separately.

The solution containing ammonium hydrogen phosphate was added dropwise to the solution of calcium nitrate. The reaction bath was stirred intensely and the temperature therein was maintained at 60°C.

In order to obtain a precipitate with optimal characteristics, the pH of the solution was maintained at values ranging from 9.5 to 10.5 during the reaction by the addition of ammonium hydroxide.

The resulting gelatinous mixture was aged for 7 days at a temperature of 40°C, without stirring. The resulting precipitate was washed with deionized water.

In the next stage the precipitate filtration was performed using a Buchner funnel attached to a vacuum pump. The filtrate was dried for 24 hours at a temperature between 100 and 110°C. The resulting powder was ground in a mortar with pestle and calcined under 1200°C between 3 and 10 hours, depending on the heat treatment applied.

The method for obtaining hydroxyapatite powder according to the process technology described above is shown in Fig. 1.

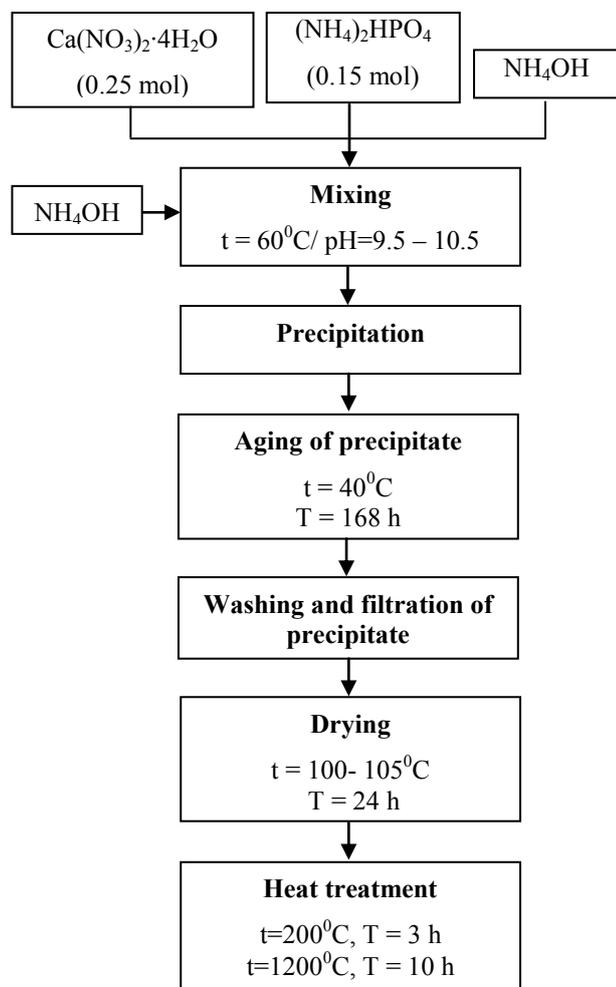


Fig. 1. Flow chart diagram for obtaining hydroxyapatite ceramic powder

2.2. Sample characterization

2.2.1 Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for bioceramic powder studied in this paper was achieved by using a simultaneous TGA / DTA / DSC thermal analyzer Netzsch STA 449 F3 JUPITER.

The device performs thermal analysis on all types of materials including heterogeneous substances. The temperature is in the range: -150°C ... + 2000°C for a heating rate between 0.1°C / min and 50°C / min., cooling time between 1500°C and 50°C is achieved in less than 30 minutes. The unit works in inert atmosphere or reducing gases, oxidative, static or dynamic.

2.2.2 X-ray diffraction analysis

X-ray diffraction analysis for phosphocalcic powders synthesized in this work was carried out by using a Bruker AXS D8 Advance diffractometer. The device is equipped with a copper anode tube ($\text{CuK}\alpha = 1.5405 \text{ \AA}$) and current parameters are: $U = 40 \text{ kV}$ and $I = 30 \text{ mA}$. Scanning was performed in (2θ) : $20^\circ - 60^\circ$ with a step of $0.04^\circ 2\theta/\text{s}$.

2.2.3 Scanning electron microscopy (SEM)

Morphological analysis of surface hydroxyapatite powders and other characteristics derived from this method of investigation was achieved by using a scanning electron microscope with field emission FE-SEM (Field Emission - Scanning Electron Microscope), Auriga model manufactured by Carl Zeiss. The device allows measurements to increasing order: $12\text{X} - 10^6\text{X}$, minimum resolution of 1 nm at 15 kV and 1.9 nm at 1 kV; accelerating voltage of 0.1 - 30 kV with steps of 10 V.

3. Results and discussion

3.1 Thermal analysis of hydroxyapatite powders

In case of hydroxyapatite obtained by the method above described, TGA / DTA / DSC analyzes performed on raw powders shows a thermal behavior described by the graph in Figure 2.

Thermogravimetric analysis (TG) shows a total weight loss of 6.37% in case of hydroxyapatite powder, after the heating cycle in the range of $25^\circ\text{C} - 1200^\circ\text{C}$.

Mass loss occurred in four stages: first from 25°C to 500°C , second between 500°C and 780°C , third between 780°C and 990°C and fourth from 990°C to 1200°C . In the first stage mass loss was 4.35%, it is associated phenomena of dehydration and loss of water adsorbed on the surface of hydroxyapatite powders [23].

This behavior is confirmed by derivative thermogravimetric analysis (DTG) by the presence of endothermic peak located at 127.7°C .

The last three stages of mass loss is relatively constant: 0.77% in the second stage, 0.57% in the third stage and 0.68% in the fourth stage. The loss in mass in the last three stages can be associated with removal of the water chemically bound to the hydroxyapatite crystal structure, decomposition of some compounds such as ammonium nitrate (NH_4NO_3) resulting from the synthesis

reaction and the loss of hydroxyl groups (dehydroxylation).

Nitrate decomposition from hydroxyapatite structure is evidenced by peaks located 601.1°C and 626.8°C and highlighted by analyzes of differential scanning calorimetry (DSC) and differential scanning calorimetry derived (DDSC).

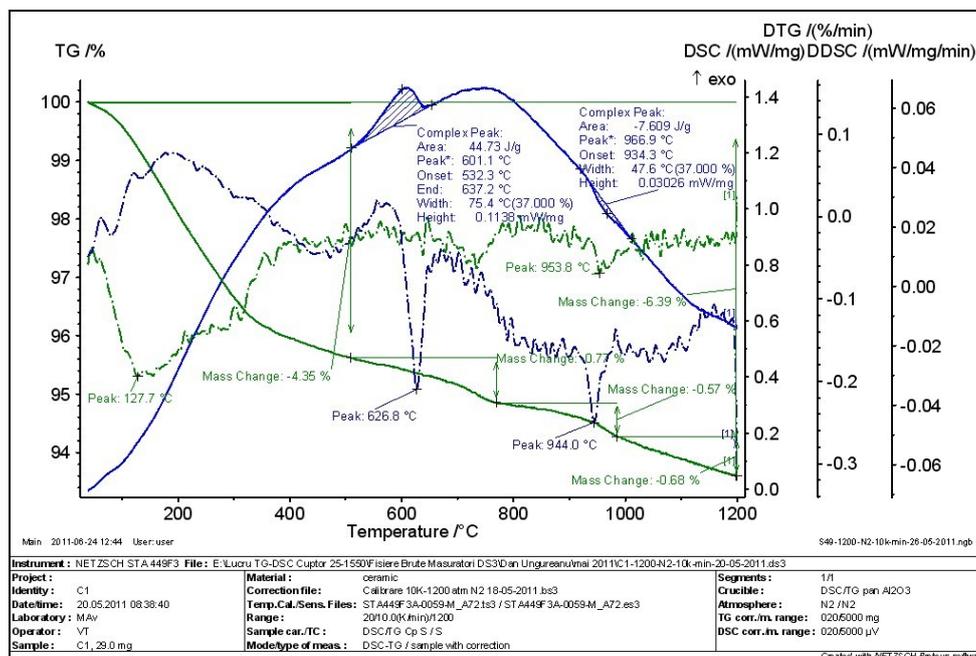
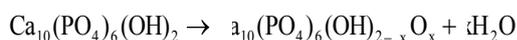


Fig. 2. Thermogravimetric analysis (TG) and calorimetric differential scanning (DSC) in the case of hydroxyapatite powders

The peaks shown by the three DTG thermal analysis, DSC and DDSC at temperature in the range of 944 to 966.9°C can be related to the phenomenon of dehydroxylation of hydroxyapatite and formation of oxy-hydroxyapatite phenomenon commonly encountered at temperatures above 800°C , and also mentioned in other papers [24]. The reaction of the loss of hydroxyl groups (OH) in the structure of hydroxyapatite is shown in next relation.



Decomposition and removing nitrates from hydroxyapatite structure is confirmed by X-ray diffraction analysis. After heat treatments performed up to 1200°C , there was no evidence other secondary crystalline phases phosphocalcic powder structure analysis.

3.2 XRD analysis

X-ray diffraction spectrums of hydroxyapatite synthesized according to the process technology presented in Figure 1 and heat-treated at 200°C and 1200°C is shown in Figure 3.

Regarding the composition of crystalline phases, in case of powders heat treated at low temperature ($t = 200^\circ\text{C}$), can be observed the presence of hydroxyapatite as the only phase in the calcium phosphate structure analyzed. The most important peaks characteristic of hydroxyapatite, are those at the angle 2θ : 25.80, 31.72, 32.08, 32.84, 34.03, 49.43 according to the following interplanar spacings: 3.44 \AA , 2.81 \AA , 2.78 \AA , 2.72 \AA , 2.63 \AA , 1.84 \AA .

The degree of crystallinity of the powders calculated in accordance with the method described in other papers was 65.8% [7]. The data regarding the average crystallite size is consistent with the results for the degree of crystallinity. In this case, was obtained an average crystallite size $\tau = 38 \text{ nm}$.

After heat treatment applied to hydroxyapatite powder at 1200°C , the degree of crystallinity was found to increase at 95%. Synthesized material has maintained stability in terms of phase composition. The conversion of hydroxyapatite in other compounds, based on calcium and phosphorous, has not been highlighted, after heat treatment performed at a high temperature. This is also confirmed by X-ray diffraction analysis, where hydroxyapatite is the only phase identified. The main

diffraction peaks are located at: 25.88 2θ ($d = 3.43 \text{ \AA}$), 31.78 2θ ($d = 2.81 \text{ \AA}$), 32.2 2θ ($d = 2.77 \text{ \AA}$), 32.93 2θ ($d = 2.71 \text{ \AA}$), 34.06 2θ ($d = 2.63 \text{ \AA}$), 39.82 2θ ($d = 2.26 \text{ \AA}$), 46.69 2θ ($d = 1.94 \text{ \AA}$), 49.48 2θ ($d = 1.84 \text{ \AA}$), 52.08 2θ

($d = 1.75 \text{ \AA}$) in accordance with standard ICDD - PDF 2: 00- 009 - 0432. Also, there has been found an increase of crystallite size at approx. 100 nm, after calcination of hydroxyapatite powders at 1200 $^{\circ}$ C.

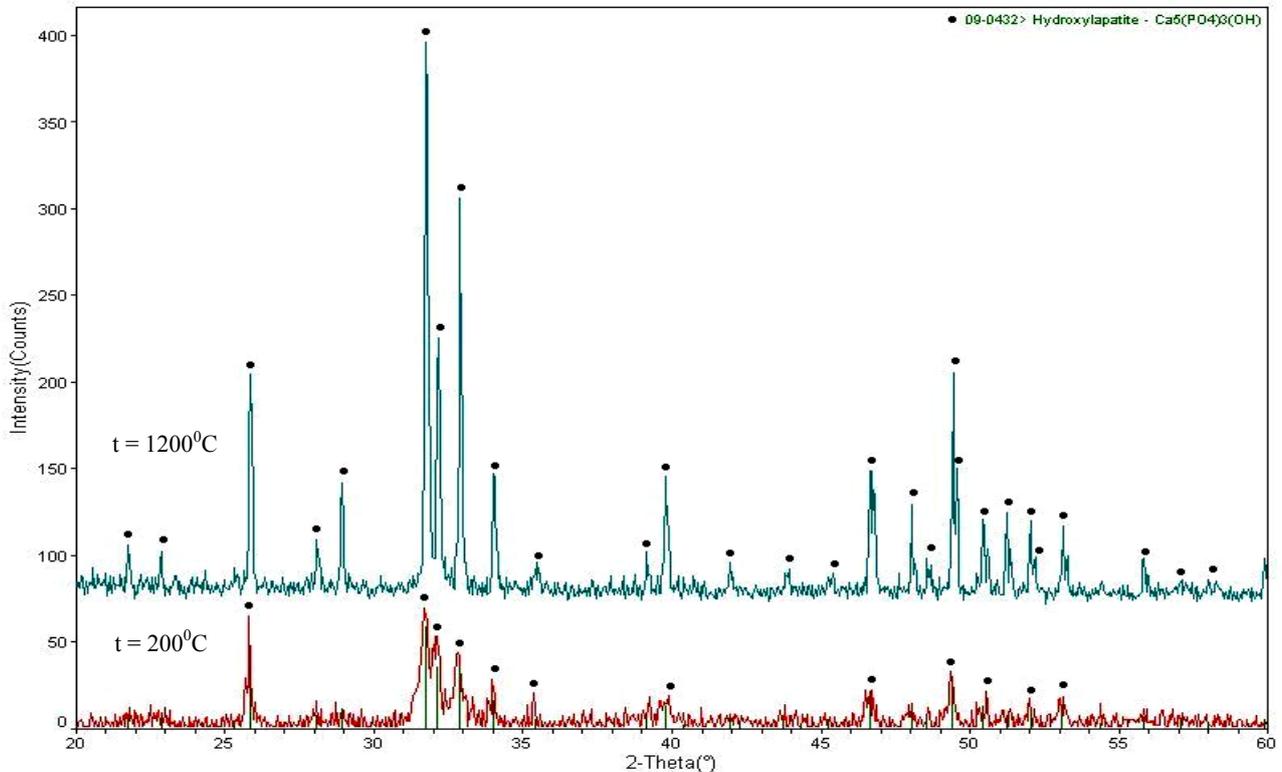
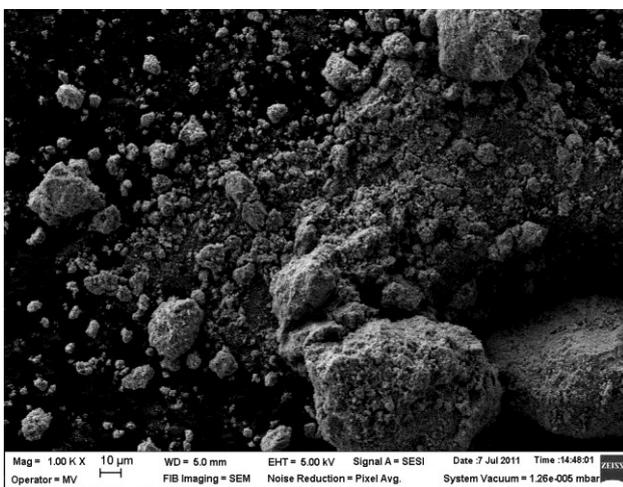


Fig. 3. X-ray diffraction spectrum of synthesized hydroxyapatite powders heat treated at 200 $^{\circ}$ C and 1200 $^{\circ}$ C

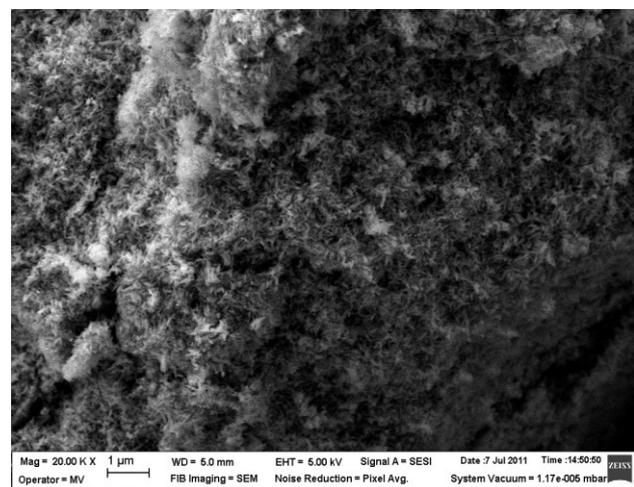
3.3 Hydroxyapatite SEM analysis

Fig. 4a shows the SEM micrograph of hydroxyapatite powder synthesized according to the technological process presented and thermal treated at 200 $^{\circ}$ C. One can see the appearance of irregular powder particles and unevenness

dimensions them. It is also obvious to the formation of clusters of particles, due to insufficient powder processing (crushing and grinding) in the subsequent stages of the synthesis.



(a)

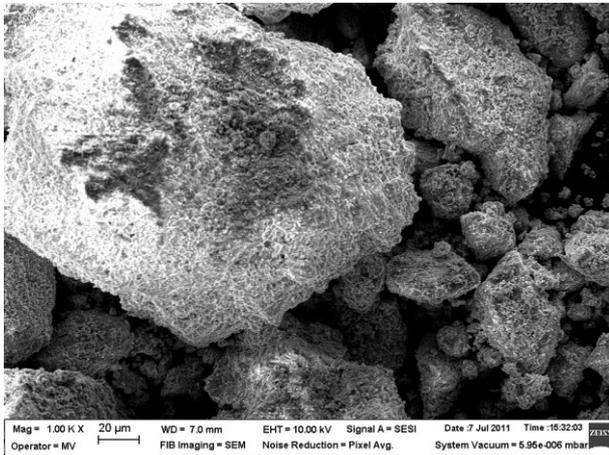


(b)

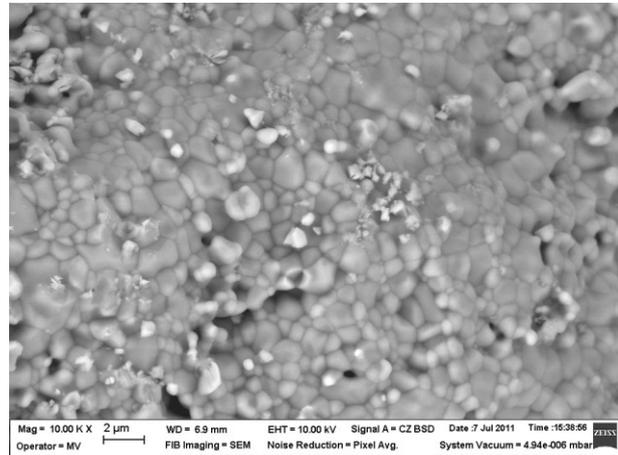
Fig. 4. SEM micrograph of the hydroxyapatite powder heat treated at 200 $^{\circ}$ C

In the case of hydroxyapatite powders analyzed at magnification of 20.000X and resolution 1 μ m (Fig. 4b) can be seen elongated ceramic particles and their relatively uniform distribution. The morphology of these particles has been influenced by the conditions of synthesis, particularly synthesis temperature and the pH of the reaction bath. Thus, a low temperature, in range of 40 to

60 $^{\circ}$ C leads to formation of elongated (needle-like) particles. At the same time, obtaining of hydroxyapatite with needle-like shape is influenced by the presence of aqueous alkaline reaction medium. An increase of apatite crystallites preferentially on direction of c-axis is possible in conditions of pH = 9 - 11.



(a)



(b)

Fig. 5. SEM micrograph of the hydroxyapatite powder heat treated at 1200 $^{\circ}$ C

After heat treatment of hydroxyapatite powders at 1200 $^{\circ}$ C can be observed synthesis of well-crystallized particles (Fig. 5.a). This phenomenon has been confirmed by the X-ray diffraction analysis. Also can notice the tendency to agglomerate microparticles, a consequence of the change of the specific surface area of powders, with increasing of heat treatment temperature. These issues are highlighted by SEM analysis (Fig. 5b) performed at magnification of 10,000 X and resolution of 2 μ m, where it is found obtaining of hydroxyapatite microparticles characterized by a high degree of packing, having variable dimensions, in some cases less than 1 μ m. Also, it can be seen a change in the morphology of ceramic micro particles with increasing of heat treatment temperature from 200 $^{\circ}$ C to 1200 $^{\circ}$ C, from an elongated (needle-like) in a hexagonal or rounded shapes. By increasing heat treatment temperature, specific surface area of powders will decrease, aspect highlighted by relatively smooth surface of calcined micro particles and an increase of their relative large size. All these aspects presented are prerequisites to obtain products with optimum characteristics after pressing and sintering processes.

4. Conclusions

Hydroxyapatite powders was synthesized from the two reagents based on calcium and phosphorus, such as: calcium nitrate tetrahydrate and ammonium dihydrogen phosphate. Control of acidity / basicity in reaction bath was carried out by using ammonium hydroxide in a concentration of 25%.

DSC and derived DSC analyzes (DDSC) showed decomposition of nitrate form hydroxyapatite powders structure analysis. In this regard were identified peaks located 601.1 $^{\circ}$ C and 626.8 $^{\circ}$ C. The possible formation of oxy - hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_x$), a phenomenon associated with loss of hydroxy groups in hydroxyapatite structure was revealed in case of powder analyzed, by the peaks located at 935 $^{\circ}$ C, by DTG, DSC and DDSC analysis.

Regarding the X-ray diffraction, it was found that hydroxyapatite is the only phase present in the raw powder structure analysis. The degree of crystallinity was 65.8%, and the crystallite size, 38 nm. After the heat treatment at high temperature, degree of crystallinity and crystallite size will increase to 95% respectively, at approx. 100nm.

Thermal stability of the powders analyzed was confirmed by the same analysis, after calcination at 1200 $^{\circ}$ C. Thus, the presence of crystalline phases such as: calcium oxide, β - tricalcium phosphate, α - tricalcium phosphate or tetracalcium phosphate, has not been confirmed by XRD analysis.

Powders synthesized according to technological process shows specific morphologies. Thus, at low temperature, micro particles have an elongated (needle-like) aspect due to conditions of synthesis, particularly synthesis temperature and the pH of the reaction bath. After heat treatment at high temperature can be observed well crystallized particles, characterized by a high degree of packing, having variable dimensions, in some cases less than 1 μ m. SEM analysis highlights a change regarding morphology of ceramic micro particles, from an elongated (needle-like) in hexagonal or rounded shapes.

Acknowledgements

The authors gratefully acknowledge Mrs. Violeta Tsakiris and Mr. Virgil Marinescu from National Institute for R&D in Electrical Engineering ICPE-CA Bucharest for their technical support regarding research facilities.

References

- [1] Y. Zhang, Y. Yokogawa, *J Mater Sci: Mater Med*, **19**, 623, (2008).
- [2] Y. Pan, D. Xiong, *JMEPEG*, **19**, 1037, (2010).
- [3] W.N. Capello, J.A. D'Antonio, M.T. Manley, J.R. Feinberg, *Seminars in Arthroplasty* **17**, 153, (2006).
- [4] N. Ohtsu, Y. Nakamura, S. Semboshi, *Surf. Coating Tech.*, **206**, 2616, (2012).
- [5] A. Lopez-Macipe, R. Rodriguez-Clemente, A. Hidalgo-Lopez, I. Arita, M. V. Garcia-Garduno, E. Rivera, V.M. Castano, *J. Mater. Synth. Process.*, **6**, 21, (1998).
- [6] V. P. Orlovskii, V. S. Komlev, S. M. Barinov - Hydroxyapatite and Hydroxyapatite - Based Ceramics, *Inorg. Mater.*, **38**, (2002).
- [7] N. Angelescu, D.N. Ungureanu, A. Catangiu, *Rev Chim-Bucharest*, **62**, 702, (2011).
- [8] Y.P. Guo, Y. Yao, C.Q Ning, Y.J. Guo, L.F. Chu, *Mater. Lett.*, **65**, 2205, (2011).
- [9] S. Jinawath, D. Pongkao, W. Suchanek, M. Yoshimura, *Int. J. Inorg. Mater.*, **3**, 997 (2001).
- [10] A. Bigi, E. Boanini, K. Rubini, *J. Solid State Chem.*, **177**(9), 3092 (2004).
- [11] A. Stoch, W. Jastrzebski, E. Długoń, W. Lejda, B. Trybalska, G.J. Stoch, A. Adamczyk, *J. Mol. Struct.*, **744–747**, 633 (2005).
- [12] J. Liu, K. Li, H. Wang, M. Zhu, H. Yan, *Chem. Phys. Lett.*, **396**, 429, (2004).
- [13] Y. Yang, J. L. Ong, J. Tian, *J. Mater. Sci. Lett.* **21**, 67, (2002).
- [14] Y.J. Wang, C. Lai, K. Wei, X. Chen, Y. Ding, Z. L. Wang, *Nanotechnology*, **17**, 4405, 2006.
- [15] R. R. Rao, H. N. Roopa, T. S. Kannan, *J Mater Sci: Mater Med*, **8**, 511, (1997).
- [16] X. Guo, H. Yan, S. Zhao, Z. Li, Y. Li, X. Liang, *Adv. Powder Technol.*, **24**(6), 1034, (2013).
- [17] E. B. Yarosh, B. A. Dmitrevskii, V. P. Naryzhnyi, S. K. Tsvetkov, *Russ. J. Appl. Chem.* **74**(6), 1058, (2001).
- [18] A.K. Nayak, *Int. J. Chem. Tech. Res.*, **2**, 903, (2010).
- [19] M.P. Ferraz, F.J. Monteiro, C.M. Manuel, *J. Appl. Biomater.*, **2**, 74, (2004).
- [20] W. Xia, K. Lin, Z. Gou, H. Engqvist, *Hydroxyapatite: Synthesis, Properties and Applications*, Nova Science Publishers, (2012).
- [21] I. Mobasherpour, M. Soulati Heshajin, A. Kazemzadeh, M. Zakeri, *J. Alloys Compd.* **430**, 330, (2007).
- [22] F. V. Anghelina, D. N. Ungureanu, V. Bratu, I.N. Popescu, C.O. Rusanescu, *Appl. Surf. Sci.*, **285**, 65, (2013).
- [23] C. Shu, W. Yanwei, L. Hong, P. Zhengzheng, Y. Kangde, *Ceram. Int.*, **31**, 135, (2005).
- [24] T. Wang, A. Dorner-Reisel, E. Müller, *J. Eur. Ceram. Soc.*, **24**, 693, (2004).

*Corresponding author: danungureanu2002@yahoo.com