Thermal stability of chemically precipitated hydroxyapatite nanopowders

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Abstract— In this paper we present a synthesis method for obtaining hydroxyapatite nanopowders by chemical precipitation. As the starting reagents, analytical grade $Ca(OH)_2$, H_3PO_4 and NH_4OH were used. The proposed method led to obtaining a hydroxyapatite with a high degree of crystallinity and purity.

The crystallinity degree was great than 90%, in case of sample thermal treated at 1200^0C. Also, the resulting hydroxyapatite powder exhibits an average crystallites size of about 28 to 47 nm, after heat treatment at 1200^0C. All hydroxyapatite nanopowder samples obtained were thermally stable up to 1200^0C. The XRD patterns presented did not reveals the transformation of hydroxyapatite in secondary phases, such as: α – tricalcium phosphate, β – tricalcium phosphate, after heat treatment at 800^0C and 1200^0C. A small amounts of calcium oxide has been or CaO Moreover, the products was characterized by a good stoichiometry.

The synthesized samples were characterized by X-ray diffraction (XRD), Fourier transformed-infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and other techniques.

Keywords—chemical recipitation, hydroxyapatite, thermal treatment, x - ray methods

I. INTRODUCTION

Hydroxyapatite is a major mineral component of bone tissue. HA is biocompatible with the human organism and is capable of integrating biologically into bone tissue [1].

Hydroxyapatite belong to the apatite family. Apatite is the name given to a group of crystals of the general chemical formula $M_{10}(XO_4)_6Z_2$, where M = Ca^{2+}, Sr^{2+}, Ba^{2+}, Na^+, Pb^{2+}, La^{3+}, and many rare earth elements; XO_4 = PO_4^{3-}, VO_4^{3-}, SiO_4^{4-}, AsO_4^{3-}, CO_3^{2-}; Z = OH^-, Cl^-; F^-; CO_3^{2-} [2]

The molar ratio of calcium to phosphorus Ca/P varies from 1.2 to almost 2 in hydroxyapatite. The stoichiometric molar ratio of hydroxyapatite is 1.67; however, this is not the value observed in the organism because small amounts of other materials incorporated (carbonates, fluorine, chlorine, magnesium ions etc.) [3].

Chemical stability of apatites is influenced by the apatite composition and synthesis method which also affects crystal size and composition. Solubility of this material is affected by the substitutions in the apatite structure [4]. For example, compared with unsubstituted apatites prepared by precipitation or hydrolysis method, strontium, magnesium or carbonate substitution causes an increase in solubility while fluoride substitution causes a decrease in solubility [4] - [7].

This biomaterial is widely used to repair, fill, extend and reconstruct damaged bone tissue [8, 9]. It can also be used in soft tissue. Hydroxyapatite can be manufactured synthetically by using a number of different methods. The processes for the preparation of hydroxyapatite and any other calcium phosphate powders may be classified under two main headings: synthesis from mammal bones or coral and in the lab, in this case it can be synthesized by reactions in solid state [10], coprecipitation [11, 12], hydrothermal methods [13], sol-gel process [14], microwave processing [15], among others [16].

The most popular methods are chemical coprecipitation from water solutions containing the ions Ca^{2+}, PO_4^{3-}, and OH^-, which in conditions of pH > 7, form primary crystallites of insoluble hydroxyapatite [17]. There are typically two types of process in the wet method: one involves the reaction of calcium salts and phosphate salts [3]

$$10(CaNO_3)_2\cdot 4H_2O + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 46H_2O$$

and, the other involves the neutral reaction of acid and alkaline solutions, as we described in this paper.

The objective of this work is hydroxyapatite powders synthesis by coprecipitation method. The thermal treated powders were characterized by X-ray diffraction in order to identify the phase composition and crystallinity. For estimation of hydroxyapatite powder quality has been used Fourier transformed infrared spectroscopy (FTIR) tehniques, the morphology of synthesized powders has been studied by scanning electron microscopy (SEM), chemical composition of hydroxyapatite powders thermal treated at 200^0C was determinated by energy-dispersive X-ray spectroscopy (EDS), measurement of hydrodynamic sizes of well dispersed particles was archived by using dynamic light scattering technique (DLS), as well rheological properties has been studied .

II. EXPERIMENTAL PROCEDURE

A. *Hydroxyapatite Synthesis*

Hydroxyapatite was synthesized via the chemical precipitation method. Flow chart of this synthesis is chematically illustrated in Figure 1.

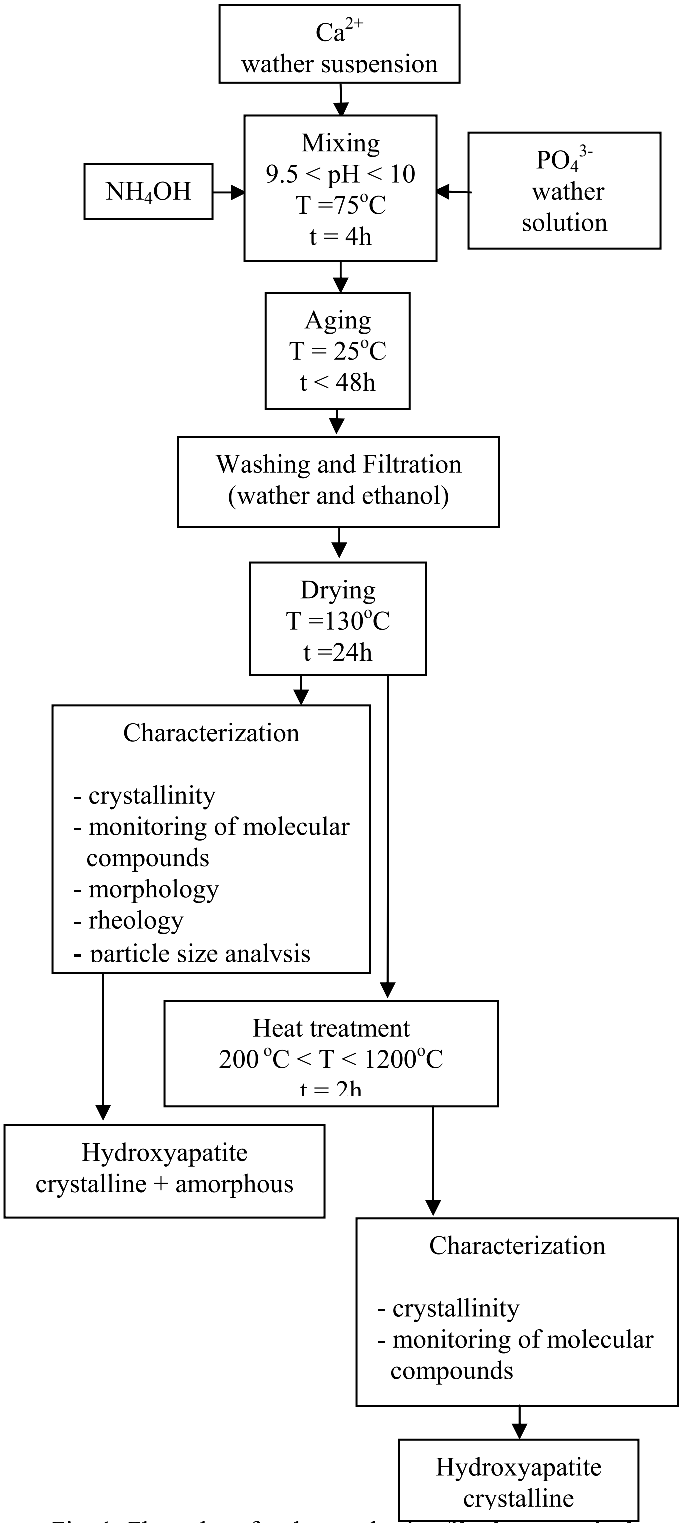


Fig. 1. Flow chart for the synthesis of hydroxyapatite by precipitation process

As the starting reagent, analytical grade $Ca(OH)_2$, H_3PO_4 and NH_4OH were used. Properties of the chemicals used to produce hydroxyapatite powders are summarized in Table I.

Table I. Raw materials used for the processing of hydroxyapatite ceramics

Name	Features		Producer
	Chemical formula	Purity/ Solution in water, %	
Calcium nitrate tetrahydrate	$Ca(OH)_2$	99	Acros Organics, Belgia
Ammonium hydroxide	NH_4OH	28	
Orthophosphoric acid	H_3PO_4	86.14	Fisher Chemical, S.U.A

The chemical equation that describes the reaction is:

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$$

Chemical precipitation is performed by preparing a suspension consist in 75 g calcium hydroxide, $CaOH_2$, in 510 mL distilled water and a solution of 40 ml ortophosphoric acid, H_3PO_4, in 200 ml distilled water.

In order to obtain a hydroxyapatite slurry, H_3PO_4 suspension was added by dropwise, for 3 hours over the alkaline solution based on $Ca(OH)_2$, in conditons of intense stirring.

During the addition the pH was kept at 9.5 – 10, by using concentrated aqueous ammonia solution, NH_4OH, in order to obtain a stoichiometric hydroxyapatite (Ca/P = 1.67).

After the complete addition, the reaction mixture were kept during 48 hours for aging. In order to remove any impurities, the precipitate was separated from the suspension by vacuum filtration, washed with distilled water and ethanol. The filtered cake was oven dried at 130^0C for 24 hours and then ground to a powder in an mortar and pestle.

In the next step, hydroxyapatie powders was heat treated at 200^0C, 600^0C, 800^0C and 1200^0C for 2 hours. Finally, powders were then ball milled, using a porcelain mill pot with tungsten carbide balls, for 1hour. The procedure for preparing hydroxyapatite powder, in agreement with procedure above mentionated, is schematically illustrated in Fig. 1.

B. *Characterization Techniques*

The structural characterization was carried out by X-ray diffraction using a Bruker AXS D8 ADVANCE diffractometer with $Cu_{k\alpha} = 1.5405Å$ radiation generated at a voltage of 40 kV and a curent of 30 mA. Data were collected in the 2θ range of 20–60°, with a step size of 0.04° 2θ. X-ray analysis was used to assess the present phases, the degree of crystallinity and size of crystallites, in case of hydroxyapatite studied.

Identification of phases was achieved by comparing the diffraction patterns of hydroxyapatie obtained in laboratory with ICDD – PDF2 (The International Centre for Diffraction Data - Powder Diffraction File 2) standards.

Table II. Phases identifications present in samples obtained by chemical precipitation

Calcium phosphate compound and their chemical formula	PDF files
Hydroxyapatite - $Ca_{10}(PO_4)_6(OH)_2$	00-009-432
Calcium Phosphate - β-Ca3(PO4)2	00-009-169
Calcium Phosphate - α-Ca3(PO4)2	00-009-348
Tetracalcium phosphate - $Ca_4(PO_4)_2O$	00-025-1137
Calcium Oxide - CaO	00-037-1497

The fraction of crystalline phase (Xc) of the hydroxyapatite powders was evaluated by the following equation [18]

$$X_C = 100 \cdot \frac{I_{300} - V_{112/300}}{I_{300}}, [\%] \qquad (1)$$

where I_{300} is the intensity of (300) diffraction peak and $V_{112/300}$ the intensity of the hollow between (112) and (300) diffraction peaks of hydroxyapatite.

The crystallite size, τ, of hydroxyapatite powder has been calculated based on Scherrer`s equation [19]:

$$\tau = \frac{K \cdot \lambda}{W \cdot \cos(\theta)}, [nm] \qquad (2)$$

where: K = constant dependent on crystallite shape, 0.8 < K < 1.1; K = 0.94 for FWHM of spherical crystals with cubic symmetry; λ is the wavelength of monochromatic radiation ($\lambda_{\alpha 1}$ = 1.5405Å). w is defined as the full width of peack from the intensity distribution pattern measured at half of the maximum intensity value. This value is the difference between two 2 theta values, in radians; and θ is the Bragg angle, in degree.

The chemical characteristics of powders, after heat treatment at different temperatures were analyzed by FTIR absorption spectroscopy within the range between 4000 and 600 cm^{-1}, by using a Fourier transformed infrared spectrometer (FTIR- Spectrum GX Perkin Elmer), equipped with ATR (attenuated total reflectance) crystal. The sample was placed over the ATR crystal to cover the crystal surface.

Scans in the range of 600– 4000 cm^{-1} were accumulated for each spectrum at a spectral resolution of 4 cm^{-1}. Morphology of the hydroxyapatite powders was studied using scanning electron microscopy (SEM) on Philips XL-30-ESEM TMP (accelerating voltage, 25–30 kV), equipped with EDS detector.

The dispersibility of the hydroxyapatite powders was evaluated form the dispersed particle size, which was measured in isopropyl alcohol medium by dynamic light scattering by using a model 90 plus Zeta Sizer (Brookhaven Inc.)

The rheological characteristics in the sens of determination of flow rate of hydroxyapatite powders were determined in accordance with ASTM B213-03.

Thermal treatment of hydroxyapatite powders was achived in a high temperature furnace model Naberherm HT 04/17, equipped with molybdenum disilicide ($MoSi_2$) elements, and are available for a max. chamber temperature of 1750^0C. The maximum furnace chamber temperature relates to operation in air conditions.

Heat treatment schedule in case of hydroxyapatie powders calcined at 1200^0C and the furnace are presented in figure 2.

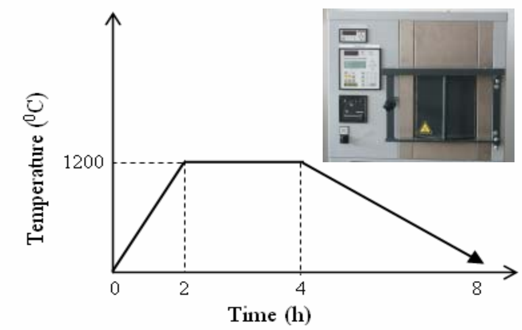


Fig.2. Graphic display of thermal treatment scheme for hydroxyapatite powders at 1200^0C

After program start the furnace heats linearly from the ambient temperature of the furnace to 1200^0C within 2 hours at a rate of 9^0C/min. On reaching 1200^0C, the temperature is maintained for 2 hours and, then the furnace cools down linearly to 40^oC within 4 hours.

III. RESULTS AND DISCUSSION

A. X – Ray Diffraction (XRD)

Fig. 3 show the X - ray diffraction pattern for a commercial hydroxyapatie sample.

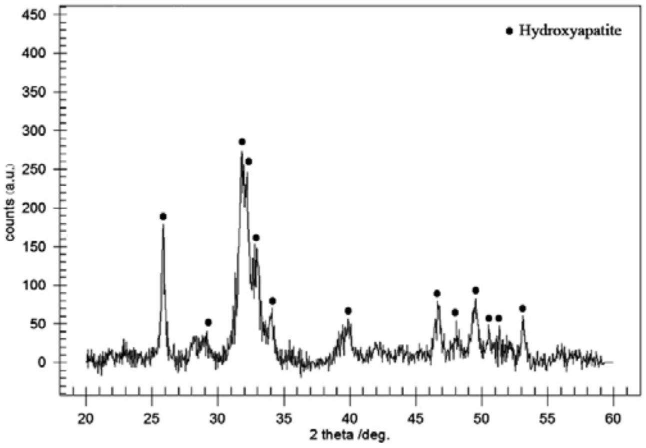
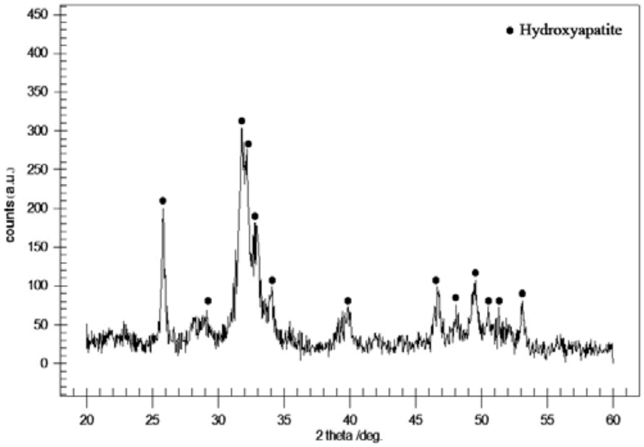


Fig. 3. XRD pattern of commercial hydroxyapatite (Acros Organics, Be)

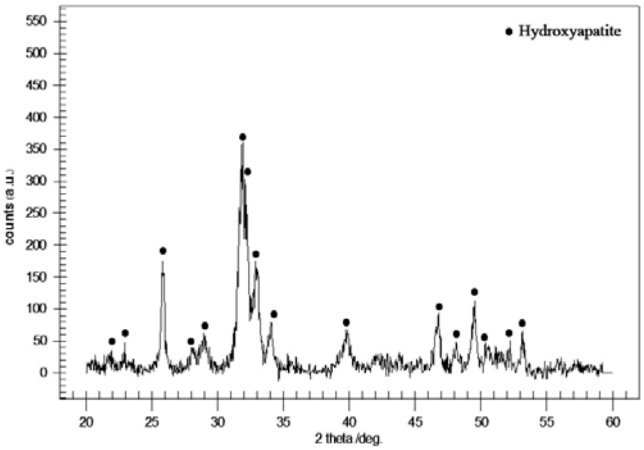
All XRD patterns shows diffraction lines characteristic of hydroxyapatite, both present in standards and in literature.

The major phase, as expected, is hydroxyapatite, which is confirmed by comparing data obtained with the ICDD - PDF2 card: 00-009-0432.

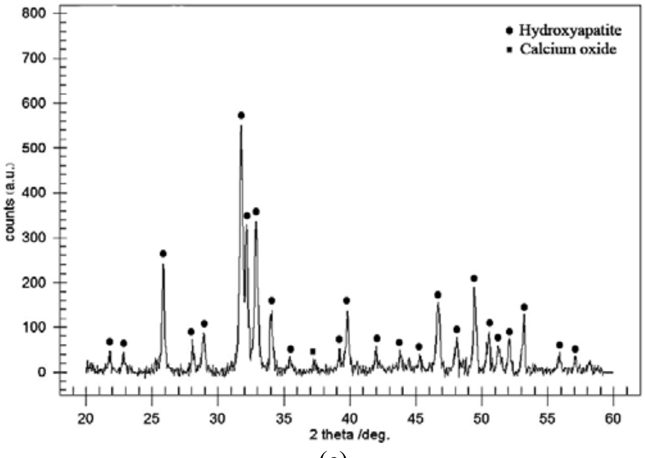
In case of sample heat treated at 200^0C, XRD pattern revealed the presence of an important amorphous phase. The proportion of amorphous phase decreases with increasing of heat treatment temperature.



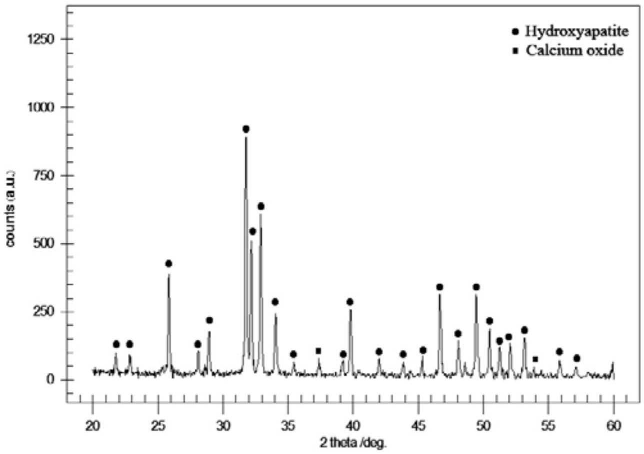
(a)



(b)



(c)



(d)

Fig. 4. X- ray diffraction patterns of hydroxyapatite powders: samples thermal treated at (a) 200^0C; (b) 600^0C; (c) 800^0C; (d) 1200^0C

When the temperature was increased, the hydroxyapatite peaks became sharper, due to crystal growth. An estimation related to crystallites size for hydroxyapatite powders, according to Scherrer`s formula reveals a proportional increase of crystallite size from 28 nm to 47 nm with increasing of the heat treatment temperature from 200 – 1200^0C.

The estimated crystallites size of hydroxyapatie are in according with data obtained regarding the crystallinity degree.

The crystallinity degree increases from 26% to 38% and 96% with increasing of heat treatment temperatures from 200^0C to 600^0C, respectively, 1200^0C.

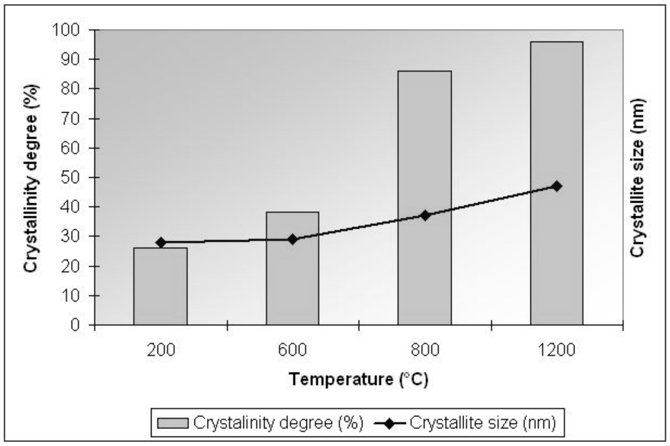


Fig. 5. Effect of thermal treatment on the crystallinity degree and crystallite size of hydroxyapatite powders

The XRD patterns of samples heat treated above 800^oC shows that only secondary phase present is calcium oxide (CaO), identified at 37.37 and 53.86 (2θ).

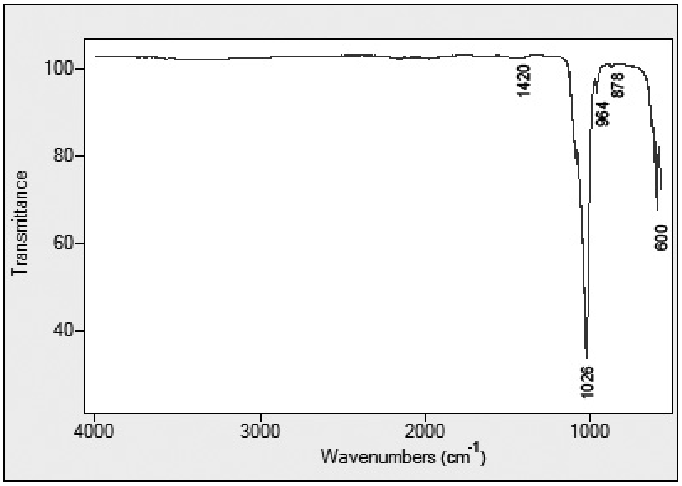
B. *FTIR Spectrometry*

The FTIR spectra of commercial hydroxyapatite and thermal treated hydroxiapatite, obtained in according with procedure presented in Fig. 1, are shown in Figure 6 (a, b, c).

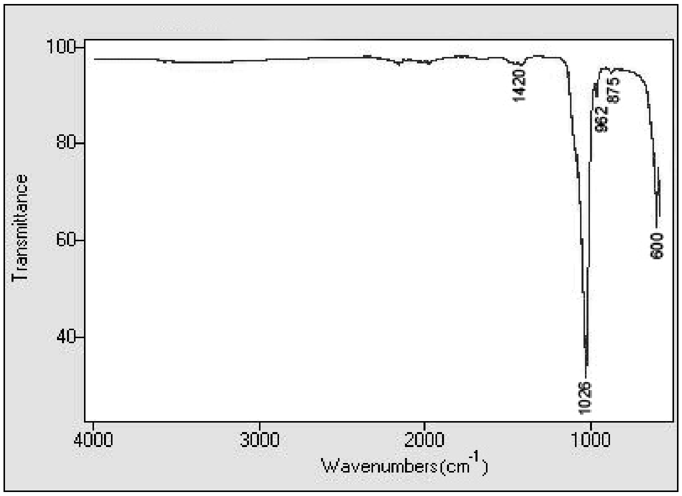
In case of spectrum presented in figure 4a and 4b, the absorption bands at 1420 cm^{-1}, 875 cm^{-1} and 878 cm^{-1} suggest the presence of CO^{3-} in hydroxyapatite structure [20, 21]. The absorption bands at 1026, 962 and 600 cm^{-1} detected in the spectra are attributed PO_4^{3-} groups [22]-[24].

After heat treatment at 1200^{o}C, no peak related to CO_3^{2-} group (1420 cm^{-1}, 875 cm^{-1}) was not detected, as shown in figure 4b. Synthesis of hydroxyapatite is revealed by the absence of large peak located at 3550 cm^{-1}, assigned to the crystallization water, i.e. water molecules trapped in the apatite unit cell [25, 26]. Generally, stoichiometric hydroxyapatite cannot contain water molecules in its unit cell while nonstoichiometric can contain some water molecules [25, 27].

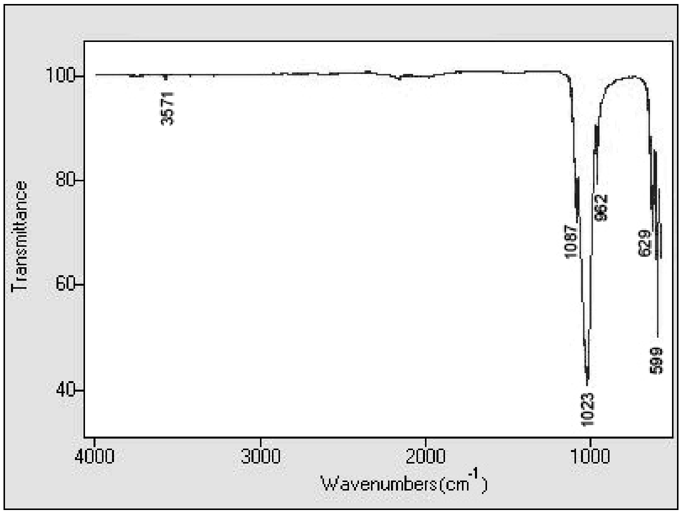
The presence of hydroxyl ion in the apatite lattice are confirmed by absorption bands at 3571 cm^{-1} and 629 cm^{-1}, attributed to the stretching and flexural modes of hydroxyl (OH^{-}) group [28]. The characteristic bands of the PO_4^{3-} groups is observed



(a)



(b)



(c)

Fig. 6. FTIR spectra of (a) commercial hydroxyapatite and synthesized in according with procedure above mentionated and heat treated at (b) 200^{0}C and (c) 1200^{0}C

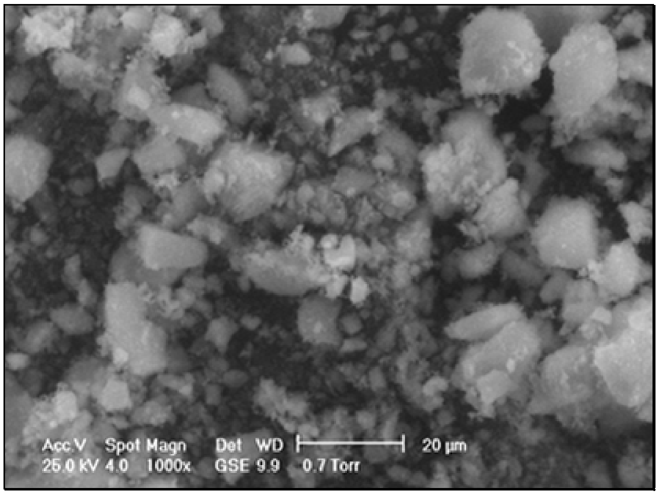
C. *Scanning electron microscopy*

The morphologies of the co-precipitated produced powders, heat treated at 200^{o}C, observed by SEM, are shown in Fig. 7.

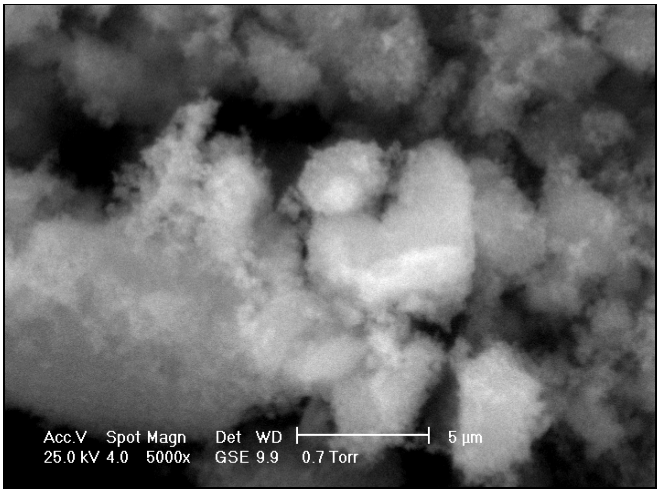
This sample mostly consists of the particles with fine grain, homogeneous and uniform distribution of components. Spherical particles obtained will allow a high degree of packing, otherwise most particles are submicron size, as shown in Fig. 7a and 7b, while figure 7c reveals presence of nanometric particles.

Fig. 7a and 7b reveals microstructural aspects of the sample analyzed at magnifications of 1000x, respectively 5000x. Figure 5a shows a cluster with various sizes and preferentially associated. High resolution image (10000X) provides details of constituent structure in which particles are mostly spheroidal shape and homogeneous distributed.

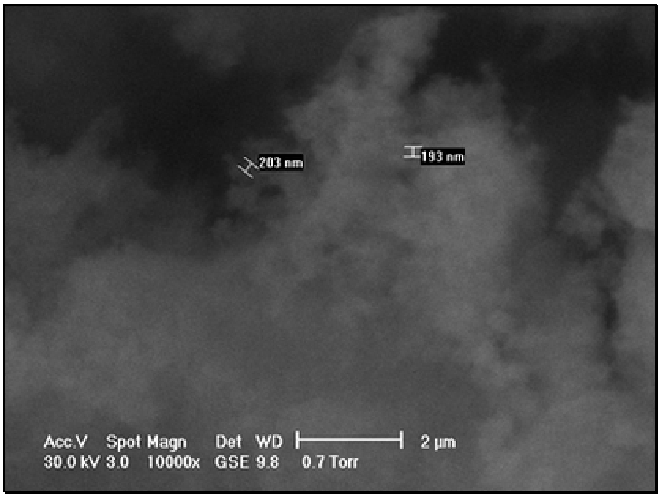
A qualitative analysis recorded magnification of 10000X reveals the microstructure of two individual particles with average diameter of 203 and 193 nm.



(a)



(b)



(c)

Fig. 7. SEM images of hydroxyapatite powders heat treated at 200^{0}C (a), (b) low magnification; (c) high magnification

EDS spectrum of hydroxyapatite powders thermal treated at 200^{0}C is presented in Fig. 8.

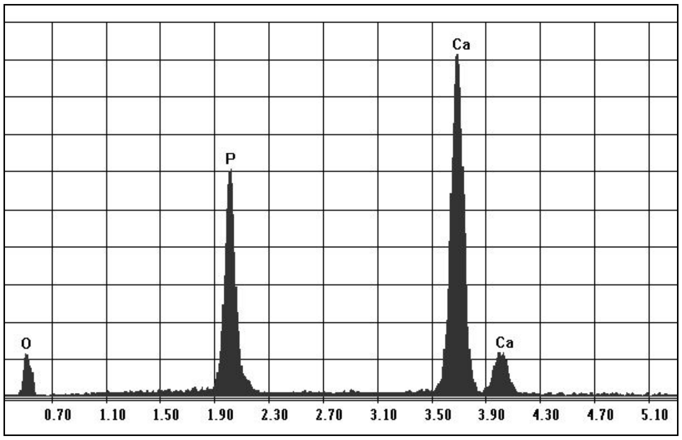


Fig. 8. EDS spectrum of hydroxyapatite powders heat treated at 200^{0}C.

EDS spectrum of hydroxyapatite sample thermal treated at 200^{0}C shows the presence in composition of oxygen, phosphorus and calcium which are the chemical elements of the powder mixture.

Chemical analysis of hydroxyapatie powders is presented in Table III.

Table III. Chemical composition of hydroxyapatite powders thermal treated at 200^{0}C

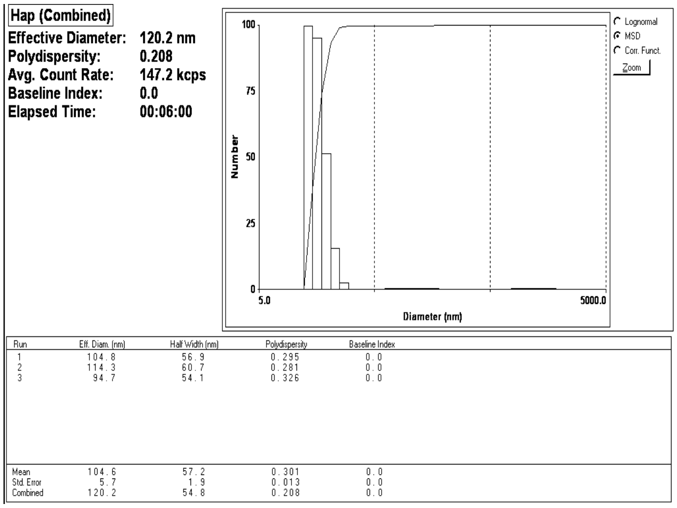
Chemical element	In weight %	In atomic %
O	41.5	61.9
P	18.62	14.34
Ca	39.89	23.75
Total	100	100

Elemental identification by EDS was used to provide information about the Ca/P ratio.

The composition of stoichiometric hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is 39.89% Ca and 18.5% P (wt.%).

The results of semi quantitative chemical analysis achieved by EDS technique for the hydroxyapatite powder derived from sample heat treated at 200^{0}C shown that the Ca and P contents in the powder were 39.89 and 18.62 wt.%, witch corresponds to a Ca/P ratio 1.656, very close to stoichiometric value, 1.67.

Particle size distribution of hydroxyapatite powders termal treated at 200^{0}C, determined by dynamic light scattering, is presented in Fig. 9



Hap (Combined)
Effective Diameter: 120.2 nm
Polydispersity: 0.208
Avg. Count Rate: 147.2 kcps
Baseline Index: 0.0
Elapsed Time: 00:06:00

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	104.8	56.9	0.295	0.0
2	114.3	60.7	0.281	0.0
3	94.7	54.1	0.326	0.0
Mean	104.6	57.2	0.301	0.0
Std. Error	5.7	1.9	0.013	0.0
Combined	120.2	54.8	0.208	0.0

Fig. 9. Particle size distribution of hydroxyapatite nanopowders analyzed by DLS method

The values recorded for the hydroxyapatite sample, reveals an average particle size of approx. 120 nm with unimodal distribution of particles, as we present in Fig. 9.

Other techniques, as atomic force microscopy (AFM) could reveal a rough surface architecture for HA, the predominant size of grains being in the range of 90-100 nm [29]. At higher temperature the deagglomeration of bulk phases and agglomeration of nano phases leads to the nano crystalline hydroxyapatite. As a conclusion, the crystal size distribution depends on the size of the critical nucleus under the super saturation condition.

D. *Rheological study*

The ability of hydroxyapatite powder to flow depends on a number of factors, such as: powders density, particle size distribution, specific surface area, particle shape etc. The flow rate decrease with the increasing of moisture in the powder, specific surface and fractions with low average diameter. Since powder particles is considered very small (0.47 ±0.01 μm), they do not have gravity, which leads to the conclusion that ultrafine powders have high specific surface which will lead to increasing packing and an advanced densification.

IV. CONCLUSIONS

The proposed method for the synthesis of hydroxiapatite powders led to obtaining a product with a high degree of crystallinity and purity. The crystallinity degree was greater than 95%, in case of all samples heat treated at 1200^{o}C. The X – ray diffraction analysis reveal the presence of insignificant amounts of calcum oxide as secondary phases, less than 2%. The IR spectrum confirm the formation of hydroxyapatite. Scanning electron microscopy reveals synthesis of spherical particles hydroxyapatite with fine grain, homogeneous and uniform distribution. The results of semi quantitative chemical analysis achieved by energy-dispersive X-ray spectroscopy (EDS) reveals a synthesized hydroxyapatite with good stoechiometry, close to theoretical value, Ca/P = 1.67. Particle size distribution of hydroxyapatite powders derived from dynamic light scattering analysis reveals an average particle size of approx. 120 nm with unimodal distribution of particles. Rheological study leads to conclusion that ultrafine powders have high specific surface, therefore an advanced densification.

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Professor Nicolae Angelescu is the holder of many awards and international recognition.

Zorica Bacinschi was born in Baia-Mare (Maramures County, Romania), on 21st July, 1952. She graduated in Metallurgical Engineering field in 1977 at the University “Politehnica” of Bucharest, Romania. In 1997, she received her Ph.D. in Metallurgy (Material Science and Engineering field) from the same University “Politehnica” of Bucharest (UPB) - Thesis Research regarding influence of manufacture and processing parameteres on the physico-chemical and technological properties of alloys from platinic materials. From 2002- until now she has been Full Professor at University Valahia of Targoviste, Romania, Faculty of Material Science, Mecatronics and Robotics, supervisor of doctoral studies – Fundamental field: Engineering sciences; Field: Materials Engineering, from 2006.

Professor Zorica Bacinschi has taught many courses at the University Valahia of Targoviste, i.e. Smart materials, Shape memory alloys, Composite materials, Emergent materials, Nanotechnologies. Scientific activity includes: Handbooks, courses, guidelines – 10 (3 author), Patents – 4 (co authors), Articles 100, Academy reviews – 1 (co author), Profile Society Reviews – 7 (co author), University gazettes – 19 (authors), International conferences in the country – 4 (co author), International conferences abroad 9 (author), 7 (co author), Foreign specialized reviews – 1 (author), 5 (co author).

National Scientific Events – 15 (author), 1 (co author), 9 research projects (majority as responsible of project).

Representative Awards selected :Attestation CNRS – Vitry – Centre d'Etudes de Chimie Metallurgique, iulie 2002 ; Excellence Award for outstanding and new materials in Microtechnologies, November, 2003; Standardisation. Standard Promotion, Report of The Twenty –Eight International Training Programme in Standardisation and Quality Systems for Developing Countries, New Delhi, 11 October to 8 December 1995, India (Bureau of Indian Standards);

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