INFLUENȚA TEMPERATURII DE SINTEZĂ PIROSOL ASUPRA CARACTERISTICILOR PULBERILOR DE HIDROXIAPATITĂ
THE INFLUENCE OF THE PYROSOL SYNTHESIS TEMPERATURE ON THE HYDROXYAPATITE POWDERS' CHARACTERISTICS

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In order to obtain phosphate biomaterials, non-conventional wet-chemical methods are generally used. Therefore in this work the spray-pyrolysis method was chosen. For this purpose, calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and triethyl phosphate ($C_6H_{15}O_4P$) were used as raw materials. By optimizing the spray-pyrolysis synthesis parameters, hydroxyapatite (HAp) nanopowders were prepared at different pyrolysis temperatures ranged between 600 and 1000°C.

The thermal behavior of the precursors was investigated by thermal analysis methods (TG- DTG). The HAp nanopowders were characterized from phase composition, chemical and morphological point of view by X-ray diffraction, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM).

Duo to these techniques, information regarding the effect of the synthesis temperature on the main characteristics of the HAp powders were provided.

În vederea obținerii de biomateriale fosfatice în general sunt utilizate metode neconvenționale, pe cale umedă. Astfel, în lucrarea de față a fost utilizată metoda de sinteză de tip pirosol. Ca materii prime utilizate s-au folosit azotat de calciu tetrahidrat ($Ca(NO_3)_2 \cdot 4H_2O$) şi trietil fosfat ($C_6H_{15}O_4P$). Optimizând parametrii de sinteză pirosol au fost obținute nanopulberi de hidroxiapatită (HAp), la diferite temperaturi de piroliză, cuprinse între 600 şi 1000°C.

Amestecul precursor a fost caracterizat prin tehnici de analiză derivatografică (TG- DTG). Nanopulberile de HAp au fost caracterizate din punct de vedere chimico-compozițional şi morfologic prin difracție de raze X (DRX), microscopie electronică de baleaj (SEM) cuplată cu analiză de difracție de raze X dispersivă (EDX) şi microscopie electronică de transmisie (TEM). Aceste tehnici au permis obținerea de informații privind influența temperaturii de sinteză asupra caracteristicilor pulberilor de hidroxiapatită obținute.

Keywords: *spray-pirolysis, thermal analysis, X-ray methods, SEM, TEM*

1. Introduction

The hydroxyapatite is a material that is chemically similar to the mineral part of the hard tissues and has the osteoconductive property, thus allowing the bone to grow inside the implant, leading to bone integration.

There are many synthesis methods for the hydroxyapatite, but choosing one depends on the structure – composition – properties correlation, according to the specific applications. The main application domain for the hydroxyapatite is represented by medicine, where it's mainly used because of its biocompatibility, as covering layers for metallic implants (such as orthopedic prosthesis) or bone substitutes synthesis [1].

The hydroxyapatite synthesis techniques are multiple: solid phase reactions, co-precipitation reactions, sol – gel processes, combustion, hydro thermal reactions, biomimetic preparation, pirolysis of an aerosol [1-5]. The pirolysis of aerosol synthesis methods has been initially used for obtaining zirconia based nanopowders [6 - 8]. In order to obtain powders with desired morphology and dimensions, a series of experimental parameters which are influencing the pyrosol synthesis method process must be optimized. Among these, the most important are: the ultrasound vibration frequency of the piezoelectric ceramics, the gas flow which engages the formed aerosol and the temperature of the pirolysis kiln [6, 7, 9-11].

In the present paper the objective was to obtain phosphatic biomaterials, of apatite type, using the method of the pirolysis of an aerosol, involving as raw materials tetra hydrate calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and tri ethyl phosphate ($C_6H_{15}O_4P$). Hydroxyapatite (HAp) nanopowders were obtained, at different pirolysis temperatures, ranging from 600 to 1000°C, keeping the other experimental parameters constant. The obtained powders were characterized both chemical – mineralogical and microstructure using different analyzing techniques such as: derivatographic analysis (TG- DTG), X rays diffraction (DRX), scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). All these

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techniques have allowed us to obtain information about the influence of the synthesis temperature on the characteristics of the obtained hydroxyapatite powders. Later, these powders will be processed and tested in what it concerns the ceramic properties and biocompatibility, for possible usage in the medical domain.

2. Experimental

The pirolysis of an aerosol installation is formed by three main components that correspond to the main stages of the pirolysis process. For producing aerosols, the mixture of raw materials solutions is introduced in a container with piezoelectric ceramics that are producing ultrasound fascicles by vibration. The wavelength of the ultrasound vibrations is depending, mainly, on the vibration frequency of the ultrasound ceramics (f) and on the solutions characteristics. The frequency of the ultrasound fascicle at which the aerosol is formed ranges, usually, between 100 KHz and 10 MHz. The average diameter of the aerosol drops, as indicated in the literature [5], is a proportional function with a factor which depends on the vibration frequency of the ultrasound ceramics, meaning $f^{2/3}$.

The installation used is presented in Figure 1 [9].

The formed aerosol is engaged by a carrier gas, having a fixed flow (D), in a high temperature pirolysis kiln. During this stage, important specific physical and chemical transformations are taking place. In the kiln, the temperature causes different processes, such as: solvent evaporation, soluble species precipitation. The precipitation takes place homogenous and in the volume of the solvent particles, and as a result dense, sphere shaped grains will form. The pirolysis temperature (T) represents a very important parameter in the architecture and the properties of the obtained powders. The kiln is of cylinder type and, at the powder exit, has a molybdenum wire to electrostatically collect the obtained particles. The applied tension on this wire is about 10KV.

The most important experimental parameters which are influencing the synthesis process of the pirolysis of an aerosol method are: the concentration of the raw materials solutions, the ultrasound frequency of the piezoelectric ceramics (f), the gas flow (D) that carries the formed aerosol and leads it in the kiln, the pirolysis kiln temperature (T).

The precursor mixtures of the oxide components necessary to obtain apatite powders were aqueous solutions of tetra hydrate calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$), concentration 0.1M şi and tri phosphate ($C_6H_{15}O_4P$), concentration 0.1M, dosed at a molar ratio Ca/P=1.67 [5].

The apatite powders were obtained using the pyrosol method at temperature of 600, 700, 800 and, respectively, 1000°C from the aqueous solutions mentioned above, with maintain constant of ultrasound frequency of the piezoelectric ceramics (f), the gas flow (D) [8-10].

The powders were characterized as chemical – mineralogical and microstructure, using different analysis techniques such as:

- thermal analysis (TG- DTG), using a derivatographic apparatus type DTG-TA- 50H SHIMATZU, in the rage 20-1000°C, at a heating speed of 10°C /min, in air;
- X rays diffraction analysis (XRD), using a SHIMATZU XRD 6000 diffractometer, with rationd CuK_α (λ = 1,5406Å), scanning speed of 2°/min., in the range 20 - 60 degrees;
- scanning electron microscopy analysis (SEM) with energy-dispersive X-ray spectroscopy (EDX) using a Quanta Inspect F type microscope and transmitting electron microscopy (TEM) using a TecnaiTM G2 F30 S-TWIN type microscope equipped with STEM/HAADF detector.

These techniques have allowed obtaining information about the influence of the synthesis temperature on the characteristics of the obtained hydroxyapatite powders.

3. Results and discussions

3.1. Complex thermal analysis

Figure 2 shows the derivatographic analysis (TG- DTG) for the powders obtained at the pirolysis kiln temperature of 800°C. One can

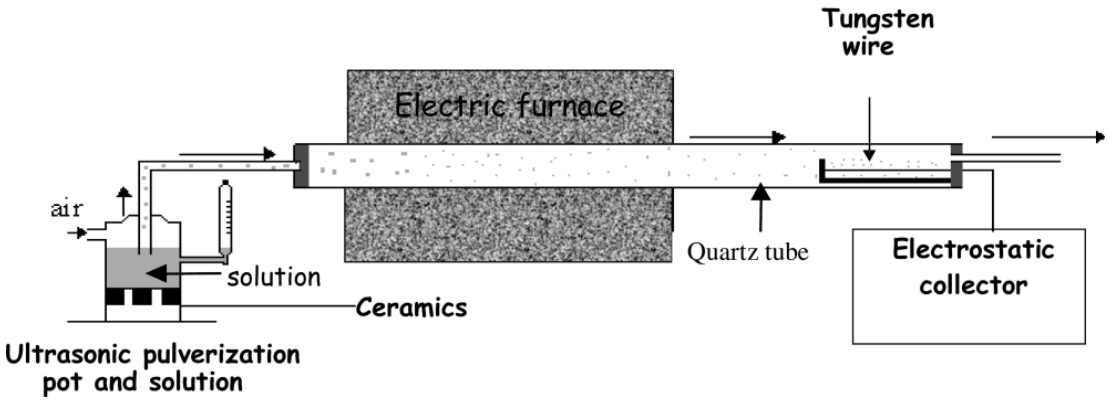


Fig. 1- Spray-pyrolysis equipment / *Instalația de pirosol* [9].

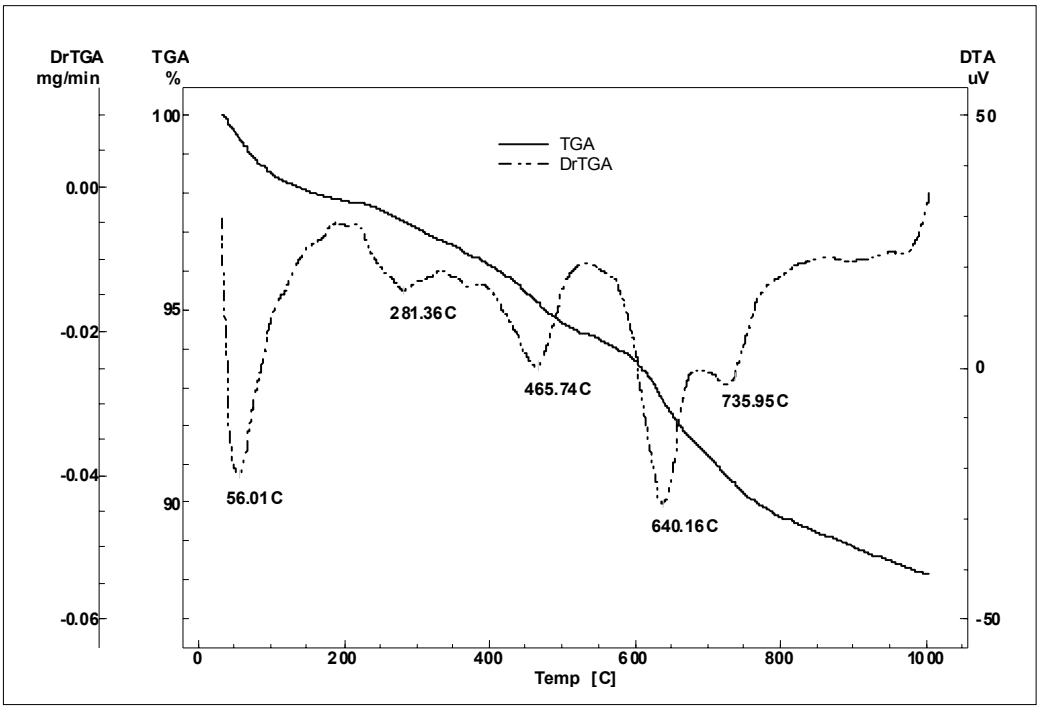


Fig. 2 - Thermal analysis of the powder synthesized at 800°C / *Analiza termică a pulberii sintetizate la 800°C.*

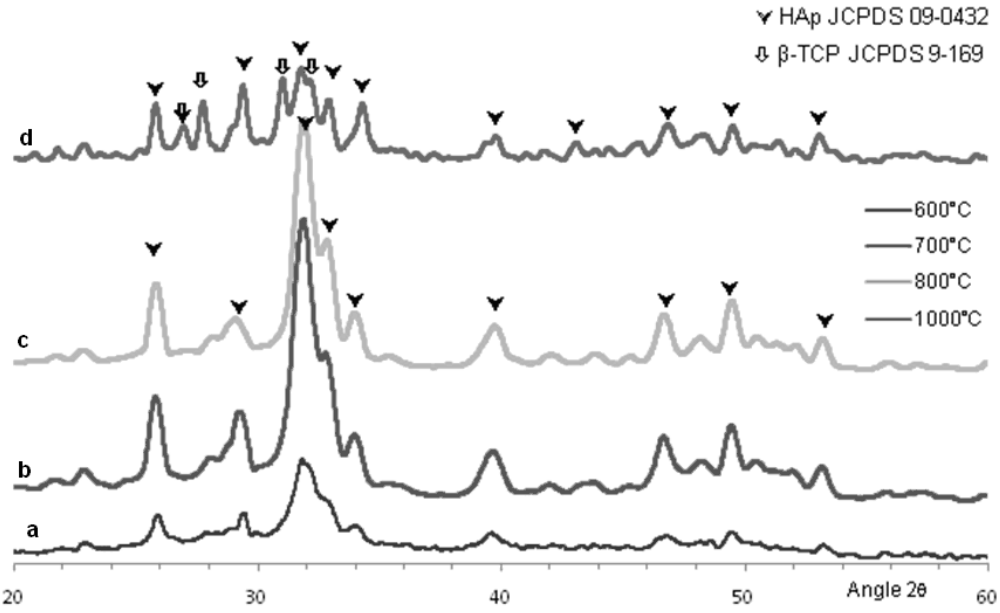


Fig. 3 - X rays diffraction patterns for powders synthesized at kiln temperatures of 600 (a), 700 (b), 800(c) and respectively 1000°C (d). / *Spectrele de difracție de raze X pentru pulberile sintetizate la 600(a) , 700(b), 800(c) şi respectiv 1000°C(d).*

see the total mass loss in the analyzed temperature range is 11.79%. This mass loss can be assigned to water loss of moisture, the dehydroxylation reactions, the decarbonization processes of the $CaCO_3$, formed accidentally during the synthesis process, in the presence of the atmospheric CO_2, and the decomposition of the calcium nitrate which is re-precipitated in a very small quantity.

3.2. X rays diffraction

Figure 3 shows the X rays diffraction patterns for the powders synthesized by pirolysis of an aerosol at kiln temperatures of 600, 700, 800 and respectively 1000°C. One may see the partial crystalline type of the obtained powders. In the same time, one can see that as the pirolysis temperature increases, the crystallinity degree increases (from 600 to 800°C), the X rays diffraction interferences becoming more sharp and formed in the case of the powders that are obtained in synthesis conditions over 800°C. The diffraction patters are showing the presence of hexagonal hydroxyapatite (HAp; JCPDS 09-0432)

until 800°C, while at 1000°C one can identify a mixture of hydroxyapatite and tri calcium phosphate (βTCP; JCPDS 9-169).

The average crystallite dimensions for HAp calculated using the Debye – Scherrer relation were: 9.69 Å for temperature of 600°C; 10.14 Å for temperature of 700°C; 10.81 Å for temperature of 800°C; 15.74 Å for temperature of 1000°C. One can see that the crystallite dimension increases as the synthesis temperature rises.

3.3. Scanning electron microscopy

Information about the morphological and textural characteristics of the synthetized powders using the pirolysis of an aerosol was obtained using the scanning electron microscopy analysis of the powders obtained at temperatures of the pirolysis kiln of 800°C (Fig. 4), at which, according to the X rays diffraction analysis, the hydroxyapatite with the highest crystallization degree was formed as single phase.

The SEM images shown in Figure 4a are emphasizing sphere shaped particles, homogenous, with submicron dimensions. Also, one can see that the particles have a harsh and porous surface due to a faster solvent evaporation process, which supposes a precipitation phenomenon of the solute at the surface of the particle (Figures 4b-e). The fast evaporation (the short time in which the aerosol drop crosses the cylinder shaped kiln) leads to a concentration gradient in the volume of the aerosol drop before the precipitation reaction.

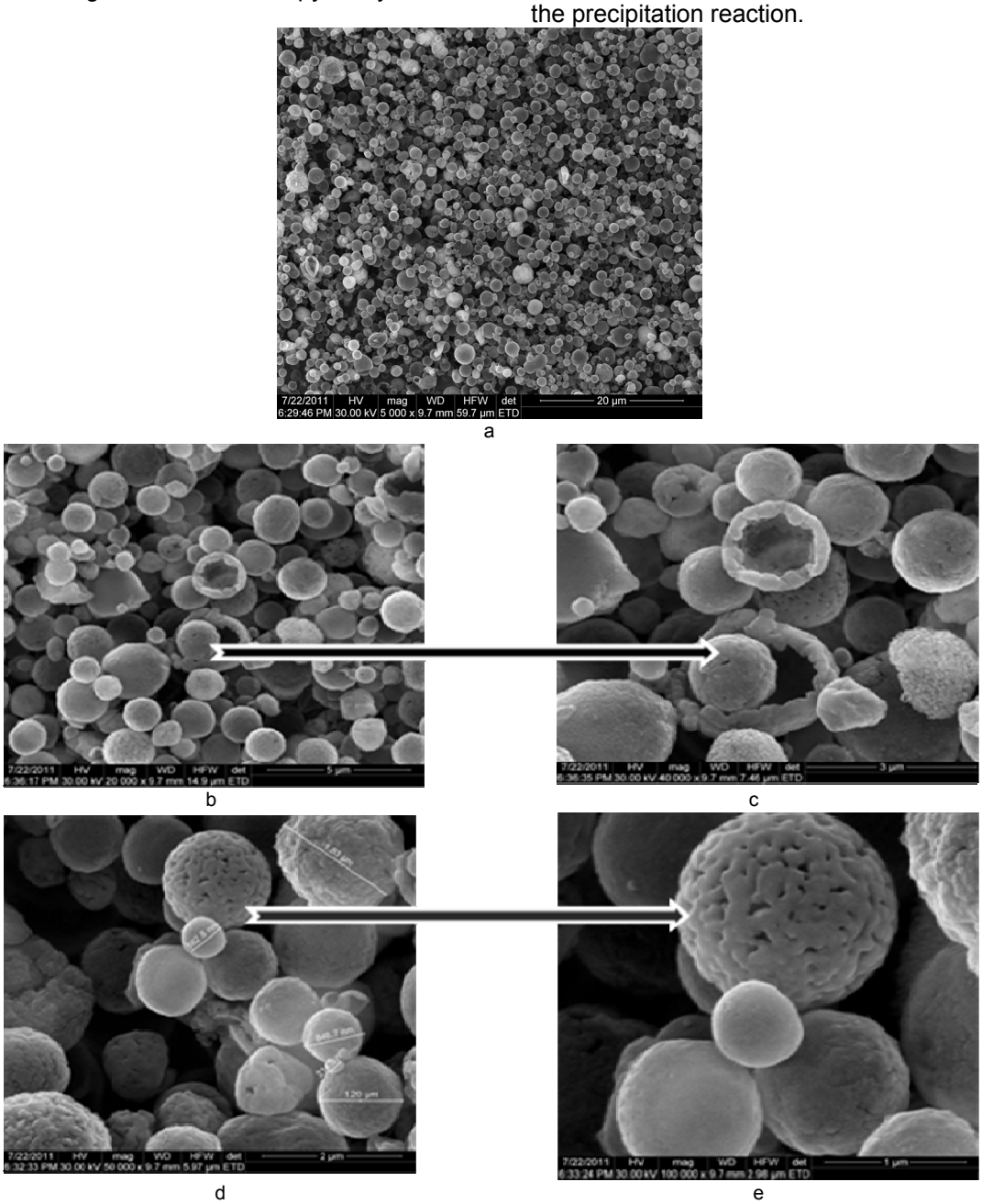


Fig. 4 - SEM images of the powder synthetized at a pirolysis kiln temperature of 800°C:
Imagini SEM pentru pulberea sintetizată la 800°C:
a - x5000, b – x20000, c – x40000, d - x50000, e - x100000.

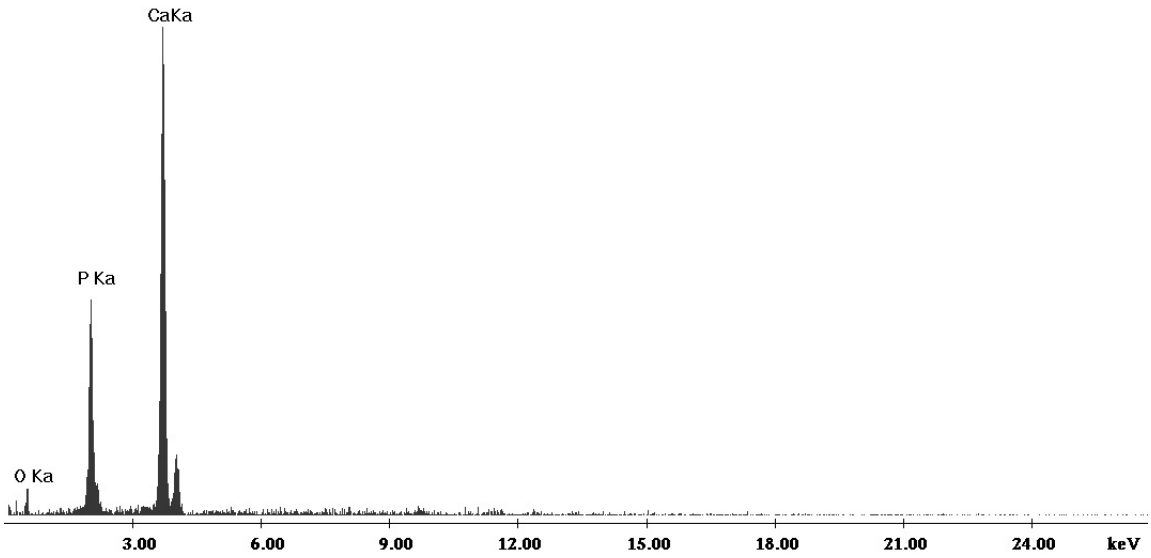


Fig. 5 - EDX spectra for the powder synthetized at pirolysis kiln temperature of 800°C. / *Spectrul EDX pentru pulberea sintetizată la 800°C.*

Figures 4c-e shows also spherical particles that are composed of nanometric particles of ellipse shape, deformed and show cavities that are filled with other particles sphere shaped, smaller, but dense. The particles dimension varies and fits in the nanometer scale.

Figure 5 shows the quantitative spectra of the powder synthetized at the pirolysis kiln temperature of 800°C. One can see the presence of Ca and P ions, as main elements, and the Ca/P ratio is approximately 1.67.

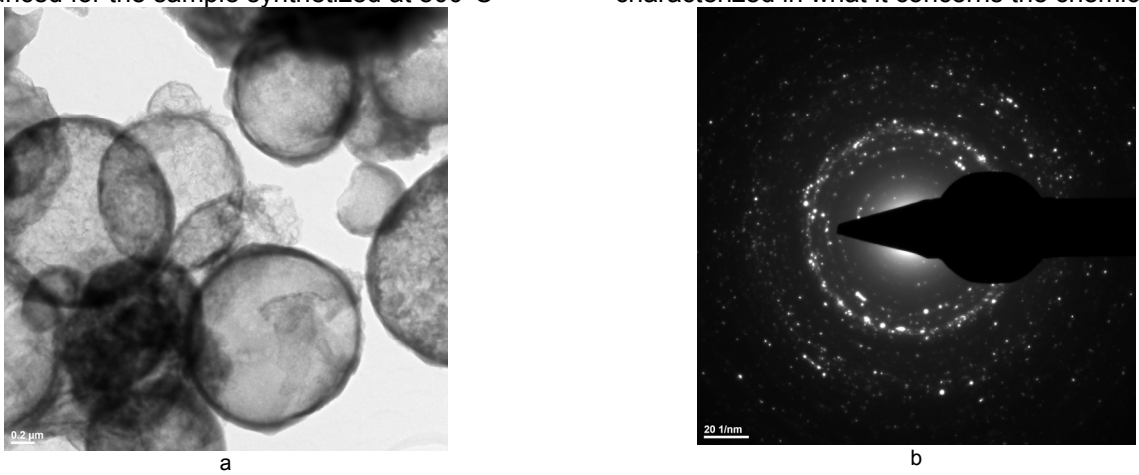
3.4. Transmission electron microscopy

On the powders that were synthetized at 600, 700 and 800°C transmission electron microscopy and electron diffraction on selected area analysis were performed – Figures 6-8. One can see that the particles size increases while the synthesis temperature increases, as well as the crystallinity degree (the diffraction circles are more pronounced for the sample synthetized at 800°C than for that of 600°C and 700°C – by comparing figure 8b with figure 6b and with figure 7b). This data are correlated with the X rays diffraction patterns shown in figure 3.

4. Conclusions

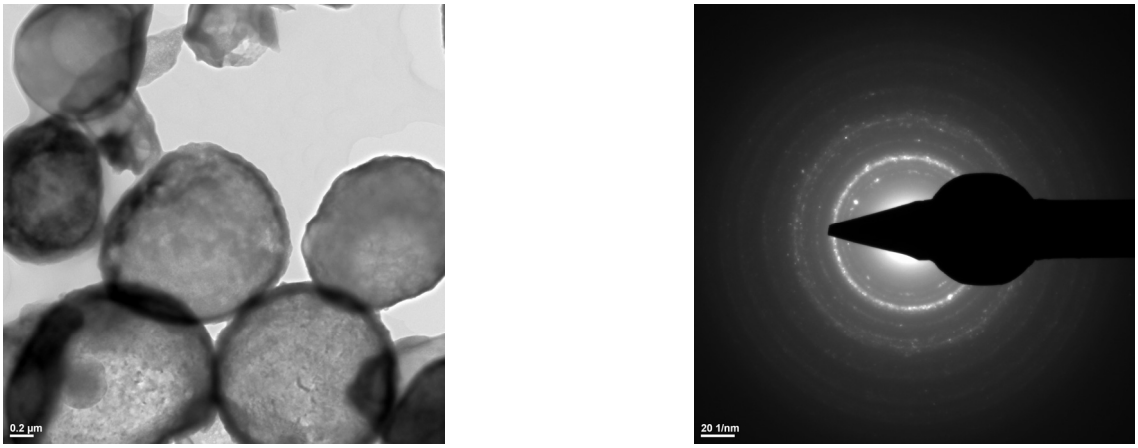
In the present paper it was performed the synthesis of nanopowders using the pirolysis of an aerosol method, involving as raw materials aqueous solutions of tetra hydrate calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and tri ethyl phosphate ($C_6H_{15}O_4P$). The optimization of the experimental parameters has lead to the obtaining of apatite type powders at various temperatures of the pirolysis kiln: 600, 700, 800°C. For the synthesis that takes place at a pirolysis kiln temperature of 1000°C a mixture of hydroxyapatite and tri calcium phosphate is obtained.

The synthetized phosphatic powders were characterized in what it concerns the chemical and



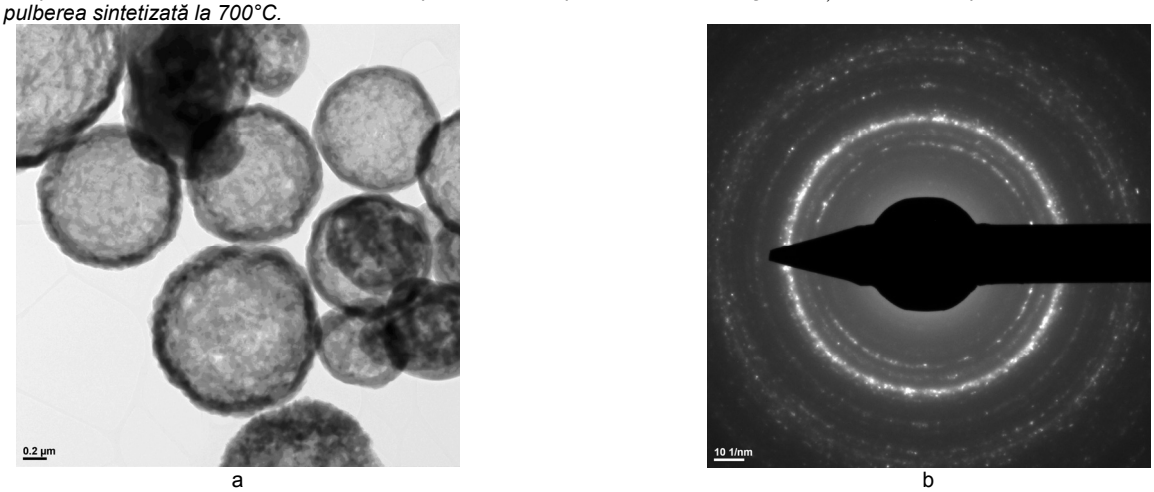
a b

Fig. 6 - Transmission electron microscopy – a, and electron diffraction on selected area - b for the powders synthetized at the pirolysis kiln temperature of 600°C. / *Analiza de microscopie electronică prin transmisie – a, şi difracție de electroni pe arie selectată – b pentru pulberea sintetizată la 600°C.*



a b

Fig. 7 - Transmission electron microscopy - a, and electron diffraction on selected area - b for the powders synthetized at the pirolysis kiln temperature of 700°C. / *Analiza de microscopie electronică prin transmisie – a, şi difracție de electroni pe arie selectată – b pentru pulberea sintetizată la 700°C.*



a b

Fig. 8 **-** Transmission electron microscopy – a, and electron diffraction on selected area - b for the powders synthetized at the pirolysis kiln temperature of 800°C. / *Analiza de microscopie electronică prin transmisie – a, şi difracție de electroni pe arie selectată – b pentru pulberea sintetizată la 800°C.*

mineralogical composition, as well as for the microstructure, using various analysis techniques. These techniques allowed obtaining information about the influence of the synthesis temperature on the characteristics of the obtained hydroxyapatite powders. The synthetized powders have particle dimensions that vary with the temperature at which the synthesis takes place in the pirolysis kiln, but are ranging in the nanometer scale. Thereby, the particle dimension increases as the synthesis temperature is increasing, as well as the crystallinity degree of the obtained powders. The result of the synthesis is powders of spherical shape, with a harsh and porous surface, due to the rapid evaporation of the solvent. In the same time are obtained also deformed particles with cavities filled with sphere shaped particles, smaller, but dense. All these properties lead to a high specific surface area that improves the biocompatibility of the phosphatic powders.

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