SINTEZA ŞI CARACTERIZAREA HIDROXIAPATITEI OBȚINUTĂ PRIN METODA SOL-GEL
SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE OBTAINED BY SOL – GEL METHOD

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Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and triethyl phosphate ($C_6H_{15}O_4P$) were used as raw materials in order to prepare at room temperature by the sol-gel method a phospahate-based nanopowder, as precursor for hydroxyapatite (HAp).

The thermal behavior of the precursors was investigated by thermal analysis methods (DTA/TG).The precursor powder was uniaxially pressed as cylindrical specimens, which were thermally treated at temperatures range between 850 and 1300°C for 2 hours. The as-prepared ceramics were investigated 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).

Besides, the HAp-based ceramics were characterized from the point of view of the mechanical behavior by determining the compressive mechanical proprieties.

Prin metoda sol-gel a fost sintetizată, la temperatura camerei, o nanopulbere fosfatică ca precursor pentru obținerea de hidroxiapatită (HAp), folosind ca materii prime azotatul de calciu tetrahidrat ($Ca(NO_3)_2{\cdot}4H_2O$) şi trietil fosfat ($C_6H_{15}O_4P$). Pulberea a fost presată uniaxial sub formă de epruvete cilindrice care au fost tratate termic în vederea sinterizării la diferite temperaturi cuprinse între 850 şi 1300°C, palier 2 ore.

Amestecul precursor a fost caracterizat prin tehnici de analiză derivatografică (DTA/TG).

Materialele ceramice obținute au fost caracterizate din punct de vedere chimico-mineralogic prin difracția de raze X (XRD) şi analiză de spectroscopie de difracție de raze X dispersivă (EDX), iar din punct de vedere microstructural prin tehnici de microscopie electronică de baleiaj (SEM) şi microscopie electronică de transmisie (TEM). De asemenea, materialele ceramice au fost caracterizate din punct de vedere mecanic prin determinarea rezistenței mecanice la compresiune, iar valorile obținute indică o bună comportare a acestora.

Keywords: *sol-gel method, thermal analysis, X-ray methods, SEM, TEM*

1. Introduction

The biomaterials are synthetic materials that have as objective living tissue restoration or function replacement and which come continuously or intermittently in contact with the physiological fluids. The biomaterials must be biocompatible (to not produce harmful effects on the living tissues: toxic, allergic, carcinogenic), biochemically stable (to not suffer degradation processes in time, when in contact with the physiological environment) and to have mechanical properties that are similar to those of the replaced tissue, in order to assume in optimal conditions its mechanical function. To this category belong also the phosphatic materials, such as hydroxyapatite (HAp), whose chemical composition is $Ca_{10}(PO_4)_6(OH)_2$ [1, 2]. This is one of the calcium phosphates which are mostly used in the orthopedic and dental implantology. The dense hydroxyapatite is compatible with the bone and in time shows no biodegradation after implantation.

Between the bone and HAp a strong chemical bond is developed. The hydroxyapatite allows a very rapid bone growth inside its micro and macro pores [3, 4].

The hydroxyapatite may be obtained using various synthesis methods [2-9]. Choosing one depends on the desired composition, the properties that must be met and the specific medical applications.

In the present paper the sol–gel method was chosen. The starting point was aqueous solutions that bring the desired chemical species, from which a sol was obtained. The sol gelled as a result of polycondensation processes, and the resulting gel was dried in air leading to the formation of a xerogel that was later thermally treated for sintering. The purpose was to obtain phosphatic biomaterials, of apatite type, starting from the following raw materials: tetra hydrate calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$) and tri ethyl phosphate ($C_6H_{15}O_4P$). The synthetized powder was calcined

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at 650°C, for 2 hours and then it was pressed in cylinder shaped samples (10x10) which were thermally treated in the temperature range 850 - 1300°C. Both the synthetized powder and the sintered masses were characterized in what it concerns the chemical and morphological point of view, as well its microstructure. The sintered ceramic materials were analyzed for compression strength. In the following research work, their biocompatibility will be tested, for possible medical applications.

2. Experimental

The sol–gel synthesis method was employed in order to obtain phosphatic nanopowders of apatite type. The used raw materials were the tetra hydrate calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and tri ethyl phosphate ($C_6H_{15}O_4P$), and the reaction parameters were as follows:

- the molar ratio Ca/P = 1.67;
- the synthesis took place at room temperature.

The stages of the sol – gel synthesis were the following:

1) dissolution of the water soluble salts and the hydrolysis of the tri ethyl phosphate;
2) mixing the homogenizing the aqueous solutions;
3) the solution's pH adjustment at about 12, by gradually addition of ammonium hydroxide;
4) sol and gel formation by polycondensation processes;
5) gel maturation, for 48 hours;
6) gel drying at 100°C for 48 hours.

The obtained powder by gel drying was calcined at 650°C, for 2 hours. The powder was subsequently shaped by uniaxial pressing in cylindrical samples, with 10 mm diameter and 10 mm height. The samples were thermally treated for sintering at various temperatures ranging from 850 and 1300°C for 2 hours. The obtained ceramic materials were characterized in what it concerns the chemical and mineralogical composition using the thermoanalytic technique (DTA/TG), X rays diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX). Its microstructure was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The sintered ceramic materials were analyzed for compression strength, using a mechanical tests equipment with double piston type MATEST.

The X rays diffraction patterns (XRD) were obtained by using a SHIMATZU XRD 6000 diffractometer, with radiation CuK_α (λ = 1,5406Å), scanning speed of 2°/min., in the range 20 - 60 degrees.

The thermal analysis (DTA/TG) was performed using a DTG-TA- 50H SHIMATZU derivatograph, in the range 20-1000°C, at a heating speed of 10°C /min, in air.

The scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDX) was performed with a Quanta Inspect F type microscope and the transmitting electron microscopy (TEM) with a TecnaiTM G2 F30 S-TWIN type microscope, equipped with a STEM/HAADF detector.

3. Results and discussions

The derivatographic analysis of the dried gel – Figure 1, shows a total mass loss of 68.65%

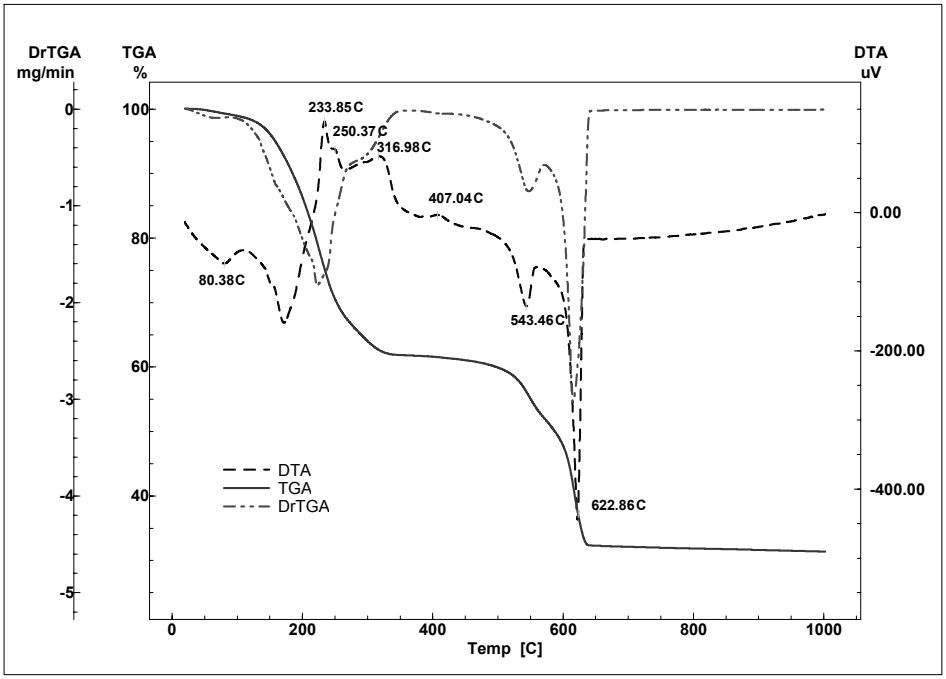

Fig. 1. - Derivatographic analysis of the dried gel powder / *Analiza derivatografică pe pulberea de gel uscată*.

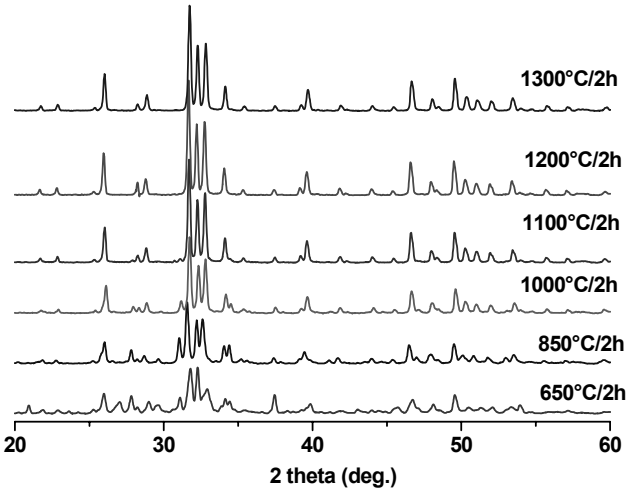

Fig. 2 - X rays diffraction patters for the powder synthetized and thermally treated at various temperatures / *Spectre de difracție de raze X pentru pulberea sintetizată şi tratată termic la diferite temperature.*

which accompanies the following thermal processes:

- endothermic processes with peaks at: 80°C, assigned to the residual dehydration; 544°C and 623°C corresponding to HPO_4^{2-} decomposition at $P_2O_7^{4-}$ and water in according literature data [7, 11]; over 650°C the $P_2O_7^{4-}$ reactions with OH^- and formed PO_4^{3-};
- exothermic processes with peaks at about 234°C, 250°C and 317°C and 408°C, assigned to the combustion of the residual organic substances.

The presented data emphasizes that, in order to finalize all the gas generating processes, so that the powder may be shaped, the dried gel powder may be thermally treated at 650°C for 2 hours, considered enough by the referencing authors.

The X rays diffraction patters of the powder thermally treated at 650°C for 2 hours, as well as for the masses which were treated at temperatures of 850, 1000, 1100, 1200 and 1300°C, for 2 hours, are presented in Figure 2. These patters emphasizes that at any temperature the powder is synthetized, the only identifiable phase is the hexagonal hydroxyapatite (HAp - JCPDS 09-0432). Also, as the temperature is rising, the crystallinity degree increases proportionally – the X rays diffraction interferences are more sharp and better defined for the powder thermally treated at 1300°C, compared with the diffractions performed on powders which were subject of thermal treatment at lower temperatures.

The scanning electron microscopy analysis (SEM) has given information about the morphological and texture characteristics of the synthetized powder and about the microstructure of the sintered masses.

Figure 3 shows the SEM images for the powder obtained using the sol – gel method and calcined at 650°C for 2 hours. One can see the

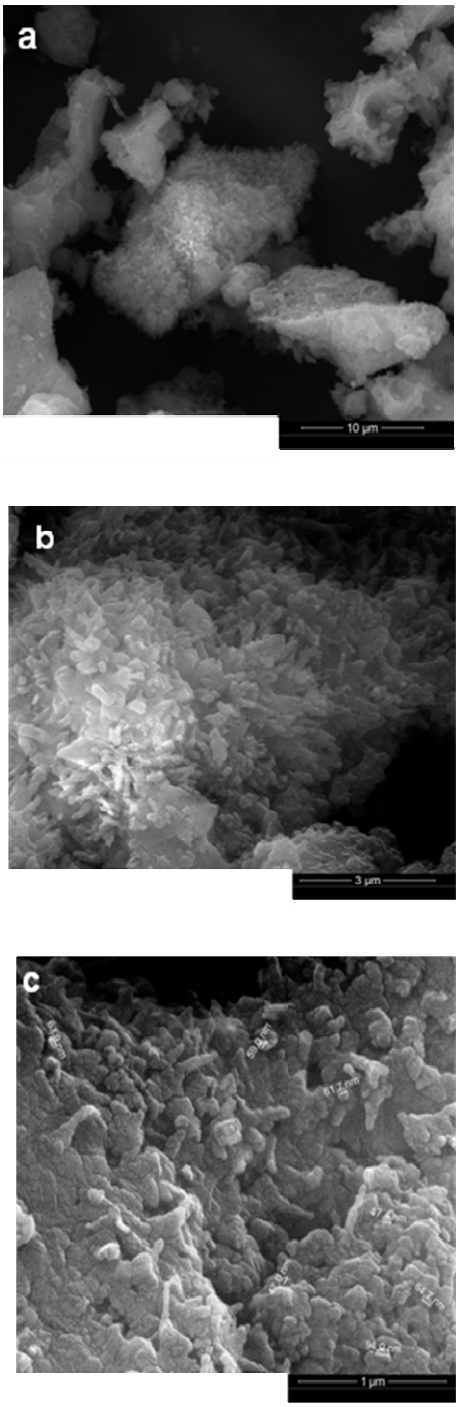

Fig. 3 - SEM images of the powder calcined at 650°C/2h: / *Imagini SEM pentru pulberea calcinată la 650°C/2h.:* a - x8000; b - x30000; c - x100000.

presence of clusters composed of spherical nanometric particles (Fig. 3c), shaped as worms (Fig. 3 b,c). The latest are forming polyhedral aggregates (Fig. 3a).

Moreover, the TEM analysis for the powder calcined at 650°C for 2 hours – Figure 4, emphasizes clusters of hydroxyapatite crystals of polyhedral geometry, hexagonal, well outlined, having the average dimension of 100nm (Fig. 4a). The high resolution TEM analysis (HRTEM) -

Figure 4b, highlights the existence of the hydroxyapatite crystallographic planes, having crystallite dimensions of about 6 nm and its polycrystalline character is reflected by the selected area electron diffraction (SAED) - Figure 4c.

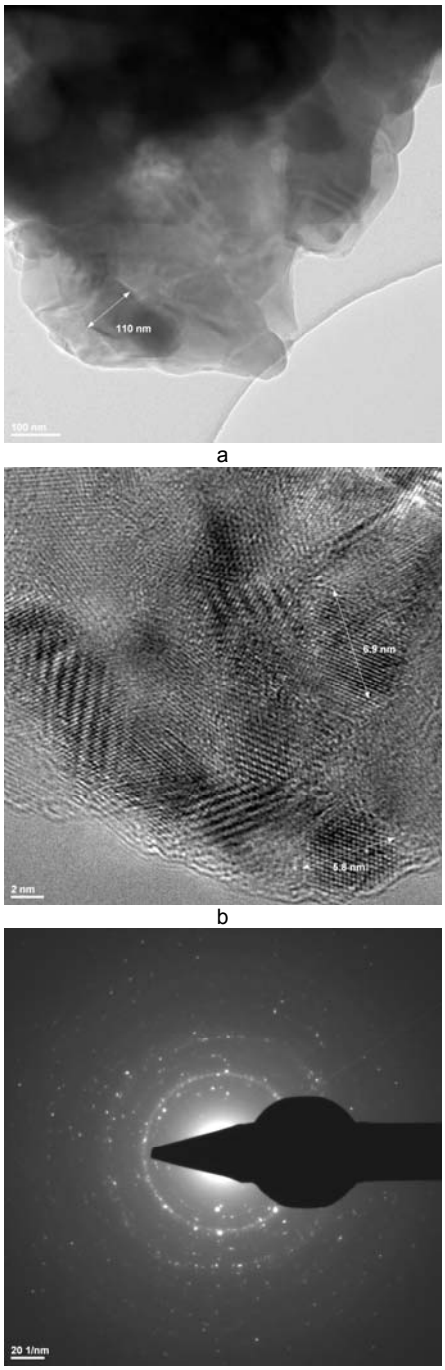

Fig. 4 - Analysis of transmitting electron microscopy – a (TEM), high resolution – b (HRTEM) and selected area electron diffraction – c (SAED) for the powder calcined at 650°C/2h. / *Analiza de microscopie electronică prin transmisie - a (TEM), înaltă rezoluție – b (HRTEM) şi difracție de electroni pe arie selectată – c (SAED) pentru pulberea calcinată la 650°C/2h.*

The information about the microstructure of the samples sintered at various temperatures –

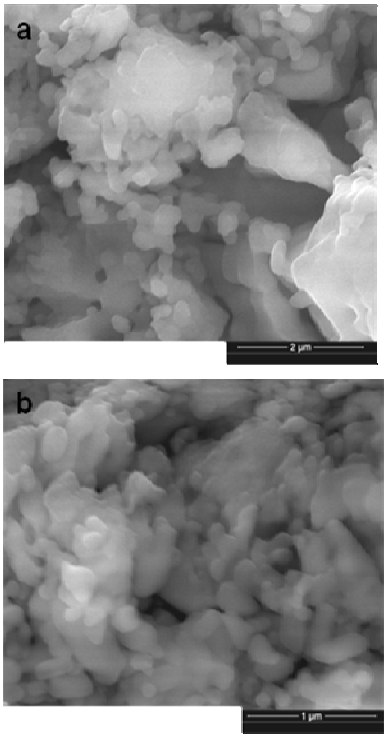

Fig. 5 - SEM image of the mass sintered at 850°C/2h: *Imagini SEM ale masei sinterizate la 850°C/2h:* a - x50000; b – x100000.

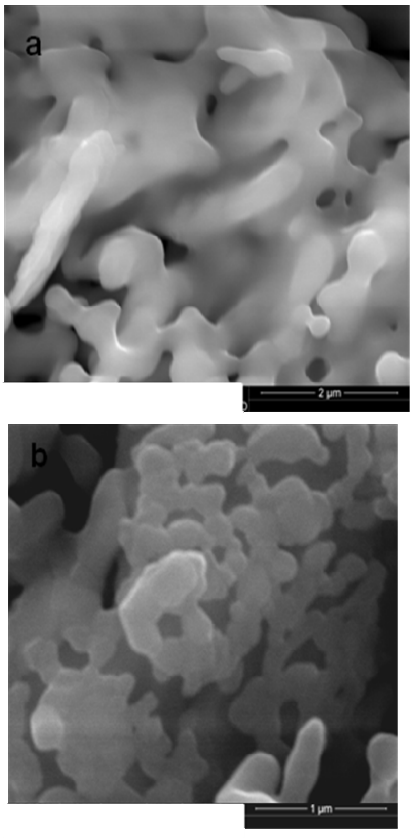

Fig. 6- SEM image of the mass sintered at 1000°C/2h: *Imagini SEM ale masei sinterizate la 1000°C/2h:* a - x50000, b – x100000.

850, 1000, 1100, 1200 and 1300°C for 2 hours, are obtained using scanning electron microscopy, shown in Figures 5 – 9. One can see that, while the sintering temperature is increasing, the grains are rounding and the microstructure is denser, the crystals dimension is higher and the porosity decreases.

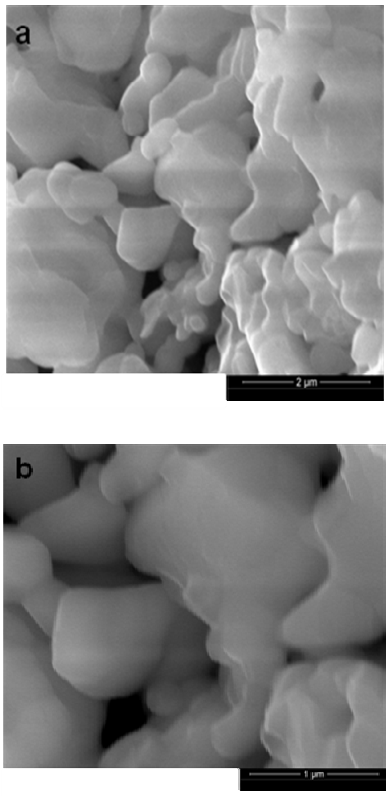

Fig. 7 - SEM image of the mass sintered at 1100°C/2h: *Imagini SEM ale masei sinterizate la 1100°C/2h:* a - x50000, b – x100000.

Also, the EDX spectra show a Ca/P molar ration of about 1.67 for all sintered masses, as results for example from Figure 10.

The values of the compression strength for the sintered cylindrical samples are shown in Table 1. One can see that they are increasing proportionally with the sintering temperatures, varying from 11 MPa until 78 MPa. Thereby, the values of the compression strength are correlated with the microstructure date mentioned above.

Table 1

Compression strength (Rc) variation as a function of the sintering temperature / *Variația rezistenței la compresiune (Rc) funcție de temperature de sinterizare.*

Sintering temperature *Temperatura de sinterizare* (°C)	850	1000	1100	1200	1300
Rc (MPa)	11	23	35	61	78

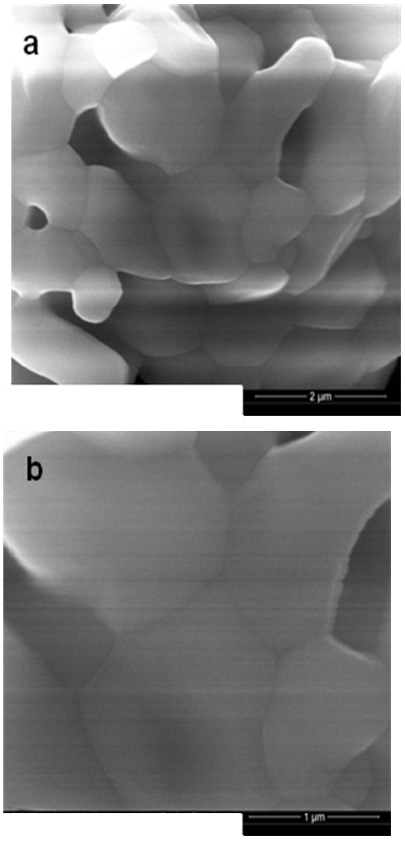

Fig. 8 - SEM image of the mass sintered at 1200°C/2h: *Imagini SEM ale masei sinterizate la 1200°C/2h:* a - x50000, b – x100000.

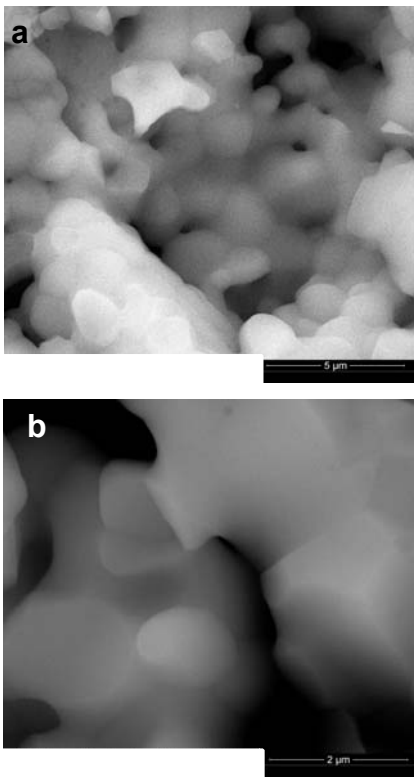

Fig. 9 - SEM image of the mass sintered at 1300°C/2h: *Imagini SEM ale masei sinterizate la 1300°C/2h:* a – x20000, b - x50000.

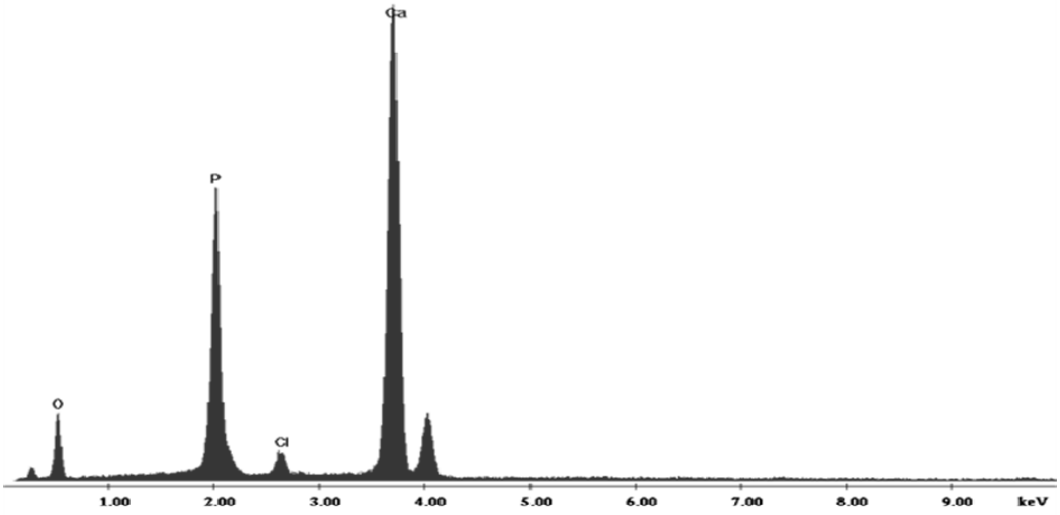

Fig. 10 - EDX spectra for the mass sintered at 1200°C/2h. / *Spectrul EDX pentru masa sinterizată la 1200°C/2h.*

4. Conclusions

Following the research work performed within the present paper, one can conclude the following:

- by using the sol – gel method, an apatite powder was synthetized, with spherical shape, nanometric dimension, with clusters as worms and polyhedral aggregates;
- by X rays diffraction, high resolution transmitting microscopy and selected area electron diffraction, the hydroxyapatite presence as single phase, polycrystalline in the synthetized powder was demonstrated;
- shaping this powder and the thermal treatment for sintering at temperatures ranging from 850 to 1300°C has led to compression strength of maximum 78 MPa, which may be explained by the microstructure densification and the growth of the crystals while the sintering temperature increases; also, the only phase formed in all masses was polycrystalline hydroxyapatite, having a Ca/P molar ration of 1.67.

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