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This volume contains the papers presented at , 6th International Conference on Electrical, Electronic and Computing , (Ic)ETLAN 2019 in conjunction of ETRAN 63rd National Conference on Electrical, Electronic and Computing Engineering held on June 3-6, 2019 in Veliko Gradište.

There were 247 submissions. Each submission was reviewed by at least 1, and on the average 2, reviewers. The committee decided to accept papers as follows. Invited papers are included and presented as papers in Sessions.

During the Conferences were held three Special Sessions:

- **Special Session dedicated to academician Rajko Tomović**

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- **Special Session: New Materials**

Moderators:

Corresponding member SASA Velimir Radmilović: **Decoupling of Electrical and Thermal Properties in Nanostructured Materials;**

Prof. Vladimir Srdić: **Ultrafast Spin Dynamics in Multiferroic Oxides;**

Prof. Petar Uskoković: **Synthesis and Supercapacitive performances of Electrospun Carbon Nanofibers Decorated with Spinel $\text{Co}_{1.5}\text{Mn}_{1.5}\text{O}_4$ Nanocrystals**

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August 27, 2019

Belgrade

Boris Loncar

Synthesis and Characterization of Hydroxyapatite and Fluorapatite Powders

Željko Radovanović, Abdulmoneim Mohamed Kazuz, Predrag Vulić, Lidija Radovanović, Đorđe Veljović, Rada Petrović, Đorđe Janačković

Abstract— The biomaterial powders of hydroxyapatite (HAp) and fluorapatite (FAP) were synthesized by a hydrothermal method. Powders were analyzed by energy-dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FESEM), and X-ray powder diffraction analysis (XRPD). EDS analysis shows the presence of non-stoichiometries FAp and HAp with molar ratio Ca/P < 1.67. FESEM analysis of both powders indicates the presence of agglomerates of micrometric dimensions, while primary nanoparticles are rod-like. The Rietveld refinement of XRPD data showed that the single phase powders of FAp and HAp were synthesized. The results showed that obtained nanomaterials can be potentially applied in dentistry.

Index Terms—Biomaterial; Hydroxyapatite; Fluoroapatite; Nanoparticles; Rietveld refinement.

I. INTRODUCTION

A new trend in the treatment of teeth is the application of material that would fill the cavity after removal of damaged dental tissue and also remineralize the surrounding tissue. The appropriate material could be a hydroxyapatite (HAp) as well as fluorapatite (FAP). Synthetic HAp, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, is similar to the inorganic part of bones and the dentine of teeth. It is biocompatible, bioactive, nontoxic, and osteoconductive [1, 2]. Replacement of the OH^- groups in HAp with F^- gives FAp, an implant material with better hardness, greater stability, less solubility and better antimicrobial effect than HAp [1].

Taheri *et al.* [3] synthesized the FAp by hydrothermal method at different pH values and temperatures. They found that the pH value of hydrothermal solution is more significant

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factor than temperature in terms of shape and dimension of the synthesized FAp. Ge *et al.* [4] obtained FAp after heat treatment at 600 °C in a water vapor environment for 3 h started from the as-deposited amorphous fluoridated calcium phosphate. They revealed that FAp had significantly better antibacterial activity than HAp. Stanić *et al.* [5] synthesized FAp powders by neutralization method. They found that the antimicrobial activity of the samples increases with the increase of concentration of F^- and decrease of pH value of saline solution. Zhao *et al.* [6] have shown that by the solution combustion method is possible to obtain single phase FAp and HAp starting from inexpensive raw materials and applying relatively simple preparation process and low-cost experimental installation.

The aim of this study was to synthesize the pure nanosized powders of FAp and HAp and investigate the properties of these materials. For this purpose, modified hydrothermal synthesis was applied.

II. MATERIALS AND METHOD

FAp and HAp powders were synthesized by a previously described modified hydrothermal method [7–10]. Pure HAp was synthesized from stoichiometric quantities of the chemicals: $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (VWR Prolabo, 99.8%), NH_4OH (Zorka Pharma, p. a.) and $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Roth, $\geq 98\%$). In the synthesis of FAp, beside aforementioned chemicals, NaF (Riedel de Haen, 99%), were also used. Synthesis was performed with a constant molar ratio $\text{Ca/P} = 1.67$. After dissolution of the chemicals in 2 L of distilled water, the dish with the solution was inserted into an autoclave, previously filled with the 1.5 L of distilled water. The solution was heated at 160 °C for 3 h. After slow cooling, the obtained suspension was filtered, and the residue was washed with distilled water and dried at 105 °C for 4 h.

Energy-dispersive X-ray spectroscopy (EDS) of the powders was performed on a Jeol JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK).

The morphologies of the powders were observed by Tescan Mira 3 XMU field emission scanning electron microscopy (FESEM). Before analysis, the powders were coated with Au using a Polaron SC502 sputter coater. The particle size distribution was determined and presented using Mira software and Microsoft Excel programme, respectively.

The X-ray powder diffraction (XRPD) measurements were performed on a Rigaku SmartLab diffractometer using $\text{Cu K}\alpha$ radiation, at 40 KV and 30 MA, in Bragg–Brentano geometry.

Diffraction data were collected in the range $5^\circ < 2\theta < 120^\circ$ (scan speed: 1° min^{-1} , step width: $0.01^\circ 2\theta$) at room temperature.

III. MAIN RESULTS

The atomic % of O, Ca, P and F were determined from the results of EDS analysis (Table I). This analysis shows the presence of non-stoichiometric HAp and FAp with molar ratio $\text{Ca/P} < 1.67$, which means that in both cases Ca-deficient apatite is synthesized.

TABLE I
EDS RESULTS FOR FAp AND HAp POWDERS.

Atomic %	Powder	
	HAp	FAp
O	72.71±0.23	66.16±1.06
F	–	5.00±0.58
P	11.53±0.05	11.58±0.27
Ca	15.75±0.20	17.26±0.69
Ca/P	1.37	1.49

The FESEM micrographs of the hydrothermally obtained HAp and FAp powders are shown in Fig. 1. Both powders consist of rod-like nanosized particles with average particle size of $87 \pm 17 \text{ nm}$ for HAp and $87 \pm 20 \text{ nm}$ for FAp. Also, the particle size distribution (Fig. 2.) are very similar and more than 60 % of particles are in the range of 70–90 nm for both powders. The particles form the agglomerates of micrometric dimensions. In the case of HAp, the agglomeration is more pronounced.

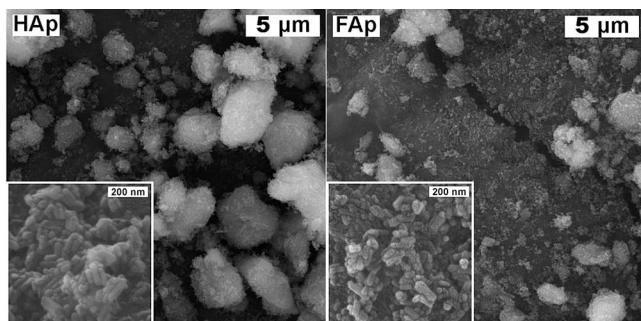


Fig. 1. FESEM micrographs of the HAp and FAp powders.

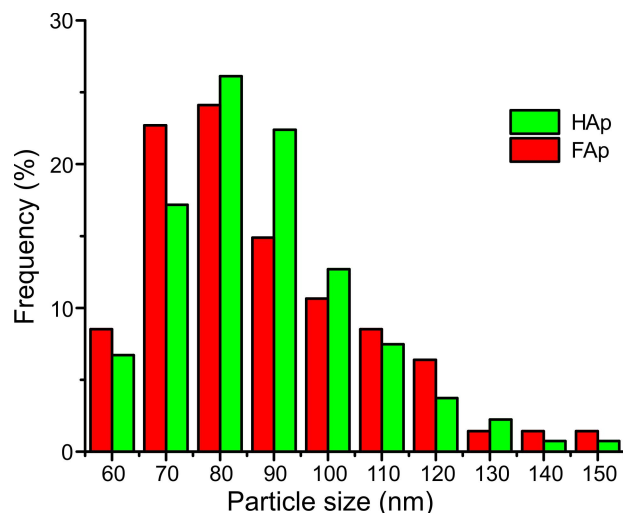


Fig. 2. Particle size distribution of the HAp and FAp powders.

TABLE II
CRYSTALLOGRAPHIC AND RIETVELD REFINEMENT PARAMETERS OF HAp AND FAp.

Phase	HAp	FAp
Crystal system	hexagonal	hexagonal
Space group	$P6_3/c$	$P6_3/c$
a [Å]	9.4205(1)	9.3760(1)
c [Å]	6.88151(9)	6.88276(9)
V [Å ³]	528.9(1)	524.0(1)
Crystallite size [Å]	346(1)	330(1)
	$[-0.356, 0.935, 0]$	$[0.356, -0.935, 0]$
Crystallite size [Å]	346(1)	330(1)
	$[0.935, 0.356, 0]$	$[0.935, -0.356, 0]$
Crystallite size [Å]	886(9) [0, 0, 1]	983(1) [0, 0, 1]
Strain [%]	0.096(2)	0.105(1)
R_{wp} [%]	4.87	4.92
R_p [%]	3.76	3.82
R_c [%]	3.92	3.92
χ^2	1.5414	1.5744
S	1.2451	1.2548
Maximum shift/e.s.d.	0.081	0.022

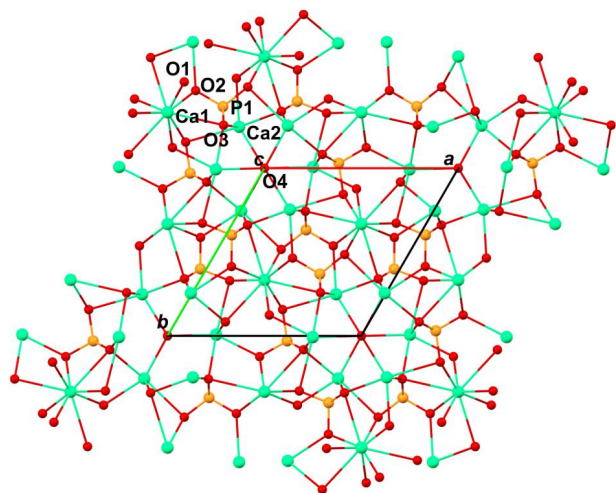
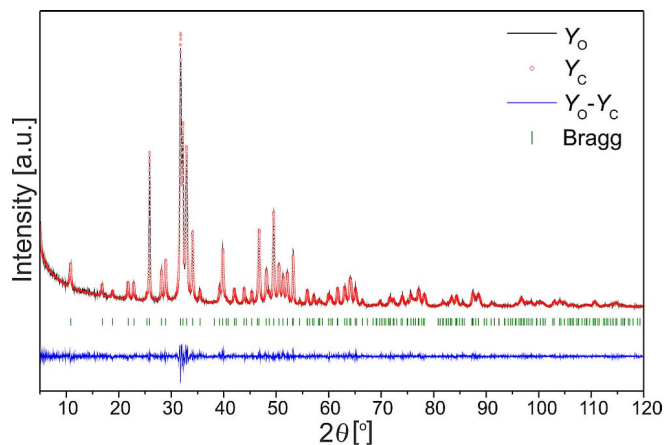


Fig. 3. Rietveld refinement (up) and crystal packing diagram in *ab* plane (down) of HAp.

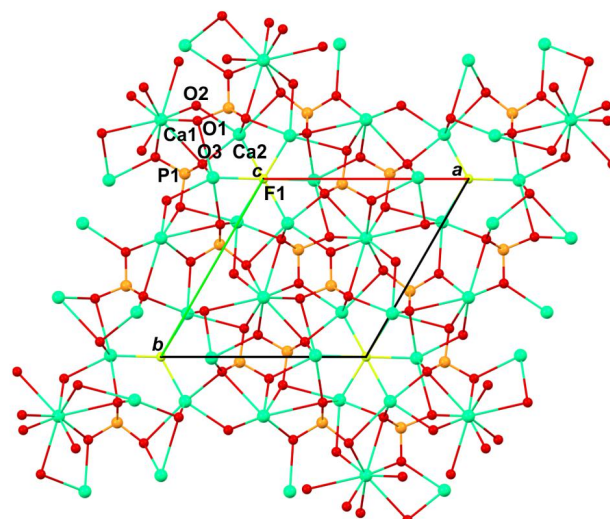
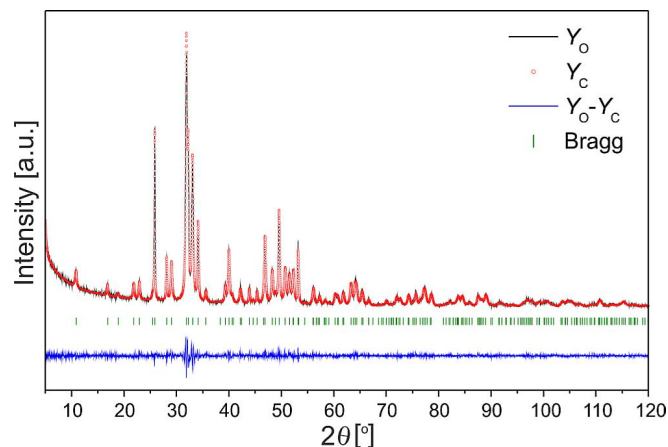


Fig. 4. Rietveld refinement (up) and crystal packing diagram in *ab* plane (down) of FAp.

XRPD patterns of HAp and FAp (Figs. 3 and 4, respectively) are very similar, but the peaks in the XRPD pattern of FAp are mildly shifting to higher values of 2θ angles indicating that unit cell of FAp is smaller.

The structures of HAp and FAp are presented in Figs. 3 and 4, respectively. The both structures crystallize in the hexagonal space group $P6_3/c$, with two formula units $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ per unit cell, for HAp and with two formula units $\text{Ca}_5(\text{PO}_4)_3\text{F}$ for FAp. The lattice parameters for both structures are presented in Table II, from which it can be seen that unit cell of FAp is slightly smaller because of the substitution of OH^- group with F atom. Also, the crystallites of HAp and FAp are more elongated along the *c* axis (Table II) which is in accordance with rod-like morphology of particles observed by FESEM.

Rietveld refinement showed that there is no deficiency of Ca atoms in the structures of HAp and FAp, so the ratio $\text{Ca}/\text{P} < 1.67$ obtained by EDS analysis can be attributed to the errors of this method.

TABLE III
SELECTED BOND LENGTHS (Å) FOR HAP AND FAP

HAp	FAp
Ca1–O1 2.401	Ca1–O1 2.392
Ca1–O2 2.452	Ca1–O2 2.449
Ca1–O3 2.836	Ca1–O3 2.820
Ca2–O1 2.703	Ca2–O1 2.689
Ca2–O2 2.365	Ca2–O2 2.367
Ca2–O3 2.329	Ca2–O3 2.338
Ca2–O4 2.396	Ca2–F1 2.312
P1–O2 1.536	P1–O1 1.537
P1–O1 1.535	P1–O2 1.542
P1–O3 1.537	P1–O3 1.542

The selected bond lengths for HAp and FAp are listed in Table III. The Ca2–F1 bond length in FAp is shorter than Ca2–O4 (O4 is from the OH^- group) bond length in HAp, which can possibly be the reason for smaller unit cell of FAp.

IV. CONCLUSION

The pure, rod-like nanoparticles of HAp and FAp, suitable for application in teeth treatment, have been prepared by simple hydrothermal synthesis. Due to the presence of very small particles, using these materials in filling the tooth's canal is more preferable in comparison with similar materials but with microsized particles.

The future investigations will be oriented towards the synthesis of nanosized Ca-deficient HAp and FAp powders that could be doped further with different metal ions (Mg^{2+} , Si^{4+} , Na^+ , Cu^{2+} , etc.). Also, the composite materials will be prepared by mixing of the appropriate ratio of HAp and FAp and their potential use as dental material will be examined.

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REFERENCES

- [1] S. V. Dorozhkin, "Calcium orthophosphates Occurrence, properties, biomineralization, pathological calcification and biomimetic applications," *Biomater*, vol. 1, no. 2, pp. 121–164, 2011.
- [2] L. L. Hench, "Bioceramics," *J. Am. Ceram. Soc.*, vol. 81, pp. 1705–1728, 1998.
- [3] M. M. Taheri, M. R. Shirdar, A. Keyvanfar, A. Shafaghath, "Evaluating hydrothermal synthesis of fluorapatite nanorods: pH and temperature," *J Exp Nanosci.*, vol. 12, no. 1, pp. 83–93, 2017.
- [4] X. Ge, Y. Leng, C. Bao, S. L. Xu, R. Wang, F. Ren, "Antibacterial coatings of fluoridated hydroxyapatite for percutaneous implants," *J Biomed Mater Res A*, vol. 95, pp. 588–599, 2010.
- [5] V. Stanić, S. Dimitrijević, D. G. Antonović, B. M. Jokić, S. P. Zec, S. T. Tanasković, S. Raičević, "Synthesis of fluorine substituted hydroxyapatite nanopowders and application of the central composite design for determination of its antimicrobial effects," *Appl Surf Sci.*, vol. 290, pp. 346–352, 2014.
- [6] J. Zhao, X. Dong, M. Bian, J. Zhao, Y. Zhang, Y. Sun, J.H. Chen, X.H., Wang, "Solution combustion method for synthesis of nanostructured hydroxyapatite, fluorapatite and chlorapatite," *Appl Surf Sci.*, vol. 314, pp. 1026–1033, 2014.
- [7] Đ. Janačković, I. Petrović-Prelević, Lj. Kostić-Gvozdenović, R. Petrović, V. Jokanović, D. Uskoković, "Influence of synthesis parameters on the particle sizes of nanostructured calciumhydroxyapatite," *Key Eng. Mater*, vol. 203, pp. 192–195, 2001.
- [8] Đ. Veljović, E. Palcevskis, A. Dindune, S. Putić, I. Balać, R. Petrović, Đ. Janačković, "Microwave sintering improves the mechanical properties of biphasic calcium phosphates from hydroxyapatite microspheres produced from hydrothermal processing," *J Mater Sci.*, vol. 45, pp. 3175–3183, 2010.
- [9] B. Jokić, D. Radmilović, D. Drmanić, S. Drmanić, R. Petrović, Đ. Janačković, "Synthesis and characterization of monetite and hydroxyapatite whiskers obtained by a hydrothermal method," *Ceram Int.*, vol. 37, pp. 167–173, 2011.
- [10] Ž. Radovanović, B. Jokić, Đ. Veljović, S. Dimitrijević, V. Kojić, R. Petrović, Đ. Janačković, "Antimicrobial Activity and Biocompatibility of Ag^+ and Cu^{2+} doped biphasic Hydroxyapatite/ α -Tricalcium phosphate Obtained from Hydrothermally Synthesized Ag^+ and Cu^{2+} doped Hydroxyapatite," *Appl Surf Sci.*, vol. 307, pp. 513–519, 2014.