Journal of Physical Chemistry and Functional Materials

Home Page of Journal: https://dergipark.org.tr/jphcfum

Investigation of structural properties of Pr-doped hydroxyapatites synthesized via an ultrasonic-assisted wet chemical method

Tankut Ates [a,*], Niyazi Bulut [b], Omer Kaygili [b], Serhat Keser [c]

[a] *Department of Engineering Basic Sciences, Faculty of Engineering and Natural Sciences, Malatya Turgut Özal University, Battalgazi, Malatya, Türkiye*

[b] *Department of Physics, Faculty of Science, Firat University, 23119 Elazig, Türkiye*

[c] *Department of Chemical Technology, EOSB Higher Vocational School, Firat University, 23119, Elazig, Türkiye*

** Corresponding author: E-mail: tankut.ates@ozal.edu.tr*

ABSTRACT

In this study, the effects of the duration of ultrasonication for Pr-doped hydroxyapatite (HA) were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) analyses. Pr-containing HA samples at a constant amount (atomic percent of 0.25) were prepared by the ultrasonic-assisted wet chemical route using different ultrasonication times of 0, 30, 60, 90, and 120 min.The formation of the HA phase was confirmed by the FT-IR and XRD data for each sample. The morphology was significantly affected by the duration of ultrasonication. Compared to the untreated sample, remarkable decreases in both the crystallite size and the crystallinity were observed with the duration of ultrasonication.

ARTICLE INFO

Keywords:
Bioceramics,
X-ray techniques
Hydroxyapatite

Received: 2023-04-24
Accepted: 2023-06-14
ISSN: 2651-3080
DOI: 10.54565/jphcfum.1287104

1. INTRODUCTION

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), which is a non-toxic biomaterial similar to the hard tissues of teeth and bones, is one of the most known and most used bioceramic materials due to its high biocompatibility and osteoconductivity [1,2]. As reported, there have been lots of ways to synthesize the HA, such as wet chemical method, sonication, microwave, sol-gel, emulsion, precipitation, combustion, hydrothermal and a combination of the as-mentioned techniques, which can affect some properties (mechanical properties, solubility, and so on) of the HA [3-6].

Doping is an advantageous way to control and change the properties of the HA. Pr is a rare earth element and can be used as a dopant for the HA at its low levels [7]. In the present work, the HA samples containing a low amount of Pr were prepared by the combination of the sonication and wet chemical routes. The effects of the sonication period on the structural properties of the HA were investigated.

2. MATERIALS AND METHOD

All the samples doped with Pr at a constant amount were prepared by a wet chemical route followed by ultrasonication at different periods. In the synthesis, calcium nitrate tetrahydrate (Sigma-Aldrich), praseodymium (III) nitrate hexahydrate (Alfa Aesar), and diammonium hydrogen phosphate (Sigma-Aldrich) were used. Distilled water was used to dissolve each compound. For all the samples, 100 mL of the solution of 49.875 mmol calcium nitrate tetrahydrate and 0.125 mmol praseodymium (III) nitrate hexahydrate was prepared in a flask. In another flask, 100 mL of 30.0 mmol of diammonium hydrogen phosphate solution was prepared, poured drop wisely into the first solution, and the pH was adjusted to 10.0 by adding an ammonia solution. This solution was mixed in a magnetic stirrer for 120 min. at

room temperature. This final mixture was ultrasonicated for the different times of 0, 30, 60, 90, and 120 min. in the stainless steel ultrasonic bath filled with the DW. The samples will now be referred to as UP0, UP30, UP60, UP90, and UP120, respectively, according to their ultrasonication periods. Each mixture was put in an oven at 120 °C for 19 h to dry, and this dried powder was heated in an electrical furnace at 900 °C for 90 min.

To collect the XRD data for each sample, a Rigaku Rad B-DMAX II X-ray diffractometer was used. Fourier transform infrared (FT-IR) spectroscopy analysis was performed by using a PerkinElmer Spectrum One spectrophotometer using the well-known KBr method. The morphology for each sample was investigated by a scanning electron microscope (SEM, FEI Quanta 450 FEG) and an energy dispersive X-ray (EDX) analyzer of the Amatek Octane plus.

3. RESULTS AND DISCUSSIONS

3.1. XRD ANALYSİS

The XRD patterns illustrated in Fig. 1 confirm the formation of main phase of the HA (JCPDS No: 09-0432) together with the minor one of beta-tricalcium phosphate (β-TCP, (JCPDS No: 09-0169) for each sample, and there it is observed a polycrystalline structure with high crystallinity.

The crystallite size (t), crystallinity percent (X_C%), lattice parameters (a and c) and unit cell volume (V) were estimated from the following relations, respectively [8,9]:

$$t = \frac{0.9\lambda}{B_{1/2}\cos\theta} \quad (1)$$

$$X_C\% = \left(1 - \frac{V_{112/300}}{I_{300}}\right) \times 100 \quad (2)$$

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (3)$$

$$V = 0.866a^2c \quad (4)$$

where λ is the X-ray wavelength, β is the full width at the half maximum, d is the interplanar spacing, $V_{112/300}$ is the intensity of the hollow between (112) and (300) peaks, and I_{300} is the intensity of (300) peak. The as-estimated values of the parameters mentioned above are given in Table 1. The ultrasonication period affected the lattice parameters, unit cell volume and phase distribution for all the samples having the same composition. All the ultrasonicated samples had larger crystallite size and crystallinity than that was not subjected to ultrasonic mixing.

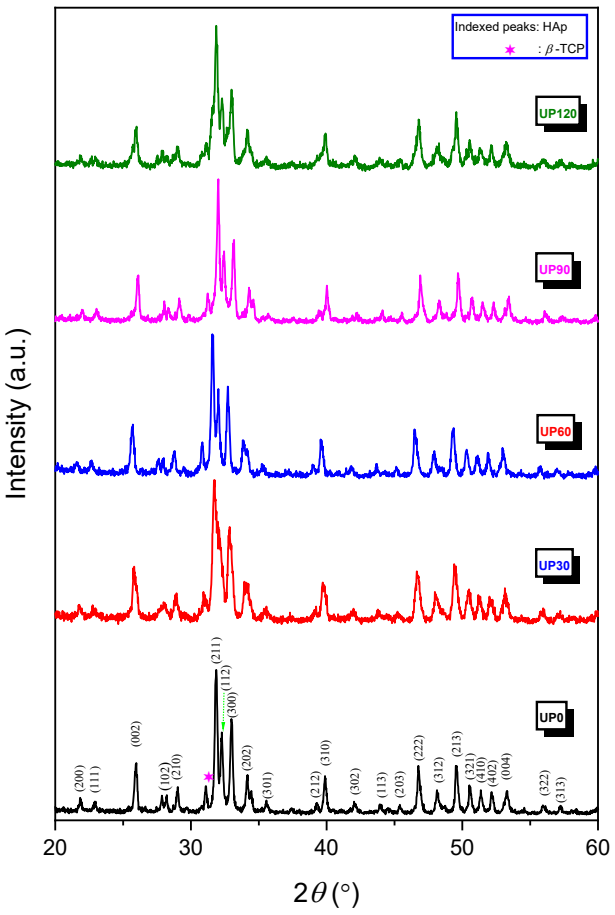

Fig. 1 XRD patterns of the as-synthesized HA samples

Table 1. XRD analysis results for all the samples

	UP0	UP30	UP60	UP90	UP120
a (nm)	0.9395	0.9434	0.9473	0.9351	0.9401
c (nm)	0.6859	0.6896	0.6932	0.6828	0.6854
c/*a*	0.7301	0.7310	0.7318	0.7302	0.7291
V $(nm)^3$	0.5243	0.5315	0.5387	0.5170	0.5248
HAp phase (%)	98.66	97.71	97.64	98.29	99.23
β-TCP phase (%)	1.34	2.29	2.36	1.71	0.77
t (nm)	34.3	22.9	28.3	30.2	23.3
X_C%	88.24	75.11	83.33	78.60	67.83

3.2. FT-IR RESULTS

Fig. 2 shows the FT-IR spectrum for each HA sample. Two functional groups including the phosphate and hydroxyl were detected in these spectra. While the bands of 474, 561, 599, 962, 1027, and 1088 cm^{-1} are associated with the phosphate group the ones at 630, and 3573 cm^{-1} are assigned to the hydroxyl group [10,11]. Both functional groups and their band positions verify the formation of the HA structure for all the as-produced samples.

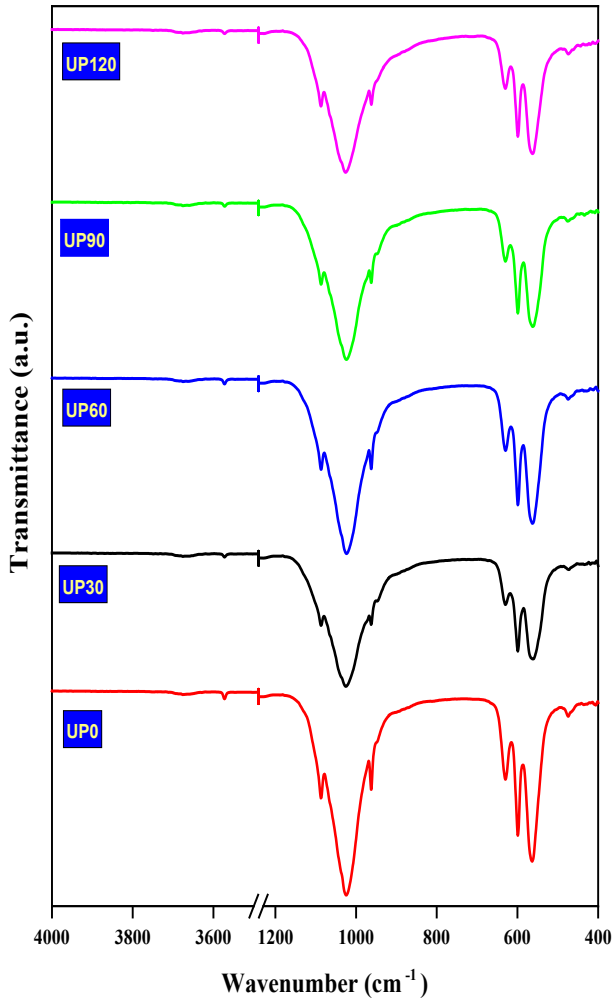

Fig. 2 FTIR results

3.3. SEM OBSERVATIONS

Fig. 3 includes the SEM images, EDX spectra and calculated values of the Ca/P and (Ca+Pr)/P stoichiometric ratios for all the as-prepared samples. A significant change in the morphology of the agglomerated structures was seen for each sample. No contaminant is present in the samples, according to the EDX findings. The above-mentioned molar ratios are different from each other. This may be related to the field, where the EDX analysis was taken, and/or the effects of the ultrasonic treatment period, which may be caused the inhomogeneity for the samples.

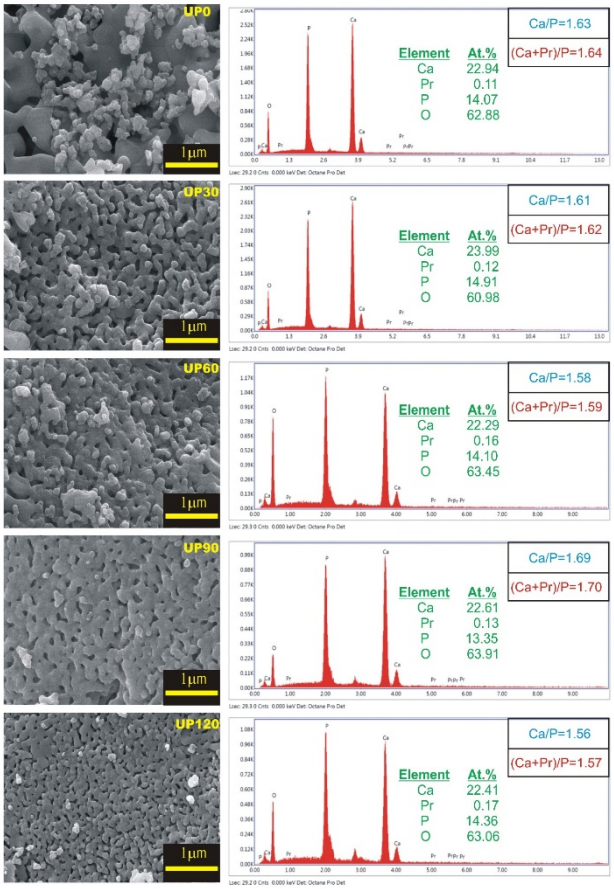

Fig. 3 SEM observations with the EDX analysis results

4. CONCLUSIONS

In the present study, the effects of the ultrasonication time on the structural properties of the HA samples with the same chemical composition prepared by ultrasonic-assisted wet chemical method for various periods of the sonication such as 0, 30, 60, 90, and 120 min. were investigated. The functional groups belonging to the HA structure was not affected by the duration of ultrasonication. Some changes in the morphology, lattice parameters, unit cell volume, and phase distribution were observed. The time for the ultrasonication caused a decrease in the crystallite size and crystallinity compared to the un-treated sample.

Competing interests

The authors declare that they have no competing interests.

Acknowledgments

This work was supported by the Management Unit of Scientific Research Projects of Firat University (FUBAP) (Project Numbers: FF.23.12 and FF.23.13).

REFERENCES

[1] J. P. Monte, A. Fontes, B. S. Santos, G. A. L. Pereira and G. Pereira. Recent advances in hydroxyapatite/polymer/silver nanoparticles scaffolds with antimicrobial activity for bone regeneration. Materials Letters. 2023;338:134027. doi:https://doi.org/10.1016/j.matlet.2023.134027.

[2] H. G. Ateş, O. Kaygili, N. Bulut, F. Osmanlıoğlu, S. Keser, B. Tatar, B. K. Mahmood, T. Ates, F. Ercan, I. Ercan, B. Ates and İ. Özcan. Investigation of the structural, thermal, magnetic and cell viability properties of Ce/Sr co-doped hydroxyapatites. Journal of Molecular Structure. 2023;1283:135318. doi:https://doi.org/10.1016/j.molstruc.2023.135318.

[3] P. Rouhani, N. Taghavinia and S. Rouhani. Rapid growth of hydroxyapatite nanoparticles using ultrasonic irradiation. Ultrasonics Sonochemistry. 2010;17(5):853–856. doi:https://doi.org/10.1016/j.ultsonch.2010.01.010.

[4] O. Kaygili and S. Keser. Sol–gel synthesis and characterization of Sr/Mg, Mg/Zn and Sr/Zn co-doped hydroxyapatites. Materials Letters. 2015;141:161–164. doi:https://doi.org/10.1016/j.matlet.2014.11.078.

[5] N. A. S. Mohd Pu'ad, R. H. Abdul Haq, H. Mohd Noh, H. Z. Abdullah, M. I. Idris and T. C. Lee. Synthesis method of hydroxyapatite: A review. Materials Today: Proceedings. 2020;29(1):233–239. doi:https://doi.org/10.1016/j.matpr.2020.05.536.

[6] T. Baskaran, N. F. Mohammad, S. S. Md Saleh, N. F. Mohd Nasir and F. D. Mohd Daud. Synthesis Methods of Doped Hydroxyapatite: A Brief Review. Journal of Physics: Conference Series. 2021;2071:012008. doi:https://doi.org/10.1088/1742-6596/2071/1/012008.

[7] L. Ibrahimzade, O. Kaygili, S. Dundar, T. Ates, S. V. Dorozhkin, N. Bulut, S. Koytepe, F. Ercan, C. Gürses and A. H. Hssain. Theoretical and experimental characterization of Pr/Ce co-doped hydroxyapatites. Journal of Molecular Structure. 2021;1240:130557. doi:https://doi.org/10.1016/j.molstruc.2021.130557.

[8] B. D. Cullity. Elements of X-ray Diffraction, Addison, Wesley Mass: 1978. p. 127–131.

[9] E. Landi, A. Tampieri, G. Celotti and S. Sprio. Densification behaviour and mechanisms of synthetic hydroxyapatites. Journal of the European Ceramic Society. 2000;20(14-15):2377–2387. doi:https://doi.org/10.1016/s0955-2219(00)00154-0.

[10] S. Kumar Balu, P. Bargavi, S. Chitra, S. Kannan, R. Ramadoss and S. Andra. Morphological evaluation of HAp nanostructures and its shape-dependent protein adsorption study. Materials Letters. 2023;331:133491. doi:https://doi.org/10.1016/j.matlet.2022.133491.

[11] T. Ates, S. Keser, N. Bulut and O. Kaygili. The effects of duration of ultrasonication on the morphology and structural properties of Ni-doped hydroxyapatite structure. Journal of Physical Chemistry and Functional Materials. 2022;5(2):22–25. doi:https://doi.org/10.54565/jphcfum.1193117.