

The Hydrothermal Synthesis Duration Influence on Calcium Phosphate and Hydroxyapatite Phase Composition

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Abstract. This paper reports the hydrothermal synthesis process duration influence on phase composition, crystallinity degree, morphology and dispersity of the hydroxyapatite powder. The calcium phosphate and hydroxyapatite were synthesized in precursor system $\text{Ca}(\text{NO}_3)_2\text{-(NH}_4)_2\text{HPO}_4\text{-NH}_4\text{OH}$. The obtained powders were characterized with X – Ray diffraction, Fourier Transform spectroscopy (FTIR) and Raman spectroscopy. The results demonstrate: the increasing of the synthesis time duration has no influence on the phase composition. However, the synthesis duration time growth from 12 to 48 hours make possible increase the crystallinity degree from 0.68 to 0.98.

1. Introduction

Nowadays biocompatible materials are attracting growing interest due to own unusual properties and applicability in a field of medicine for tissue engineering, fillers for healing defect in bones and drug delivery systems [1]. Calcium phosphates are the wide class of the ceramic materials. The hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_3(\text{OH})_2$) is one the most thermodynamically stable phase of calcium phosphate phases. Human bone material composition could be divided in three material groups: bone tissue as a calcium phosphate/hydroxyapatite 65 – 70 %, water 5 – 8 % and other percentage is the organic components mainly collagen [2]. Collagen provides elastic resistance properties and acts as a matrix for the mineral crystal formation and crystal growth. The native calcium phosphate usually calcium deficient and carbon surplus HAp with the Ca/P element proportion less than 1.67 [3]. For a long time synthetic hydroxyapatite (HAp) has been interest due to high biocompatibility properties [4], affinity to biopolymers [5] and osteogenic possibility [6]. Also, hydroxyapatites are perspective material as a drug delivery system [7].

The morphology, size (dispersity), phase composition, crystallinity degree, surface area and porosity have an important influence on hydroxyapatite mechanical and biomedical properties. The changes in synthesis parameters make possible control of the mechanical and biomedical properties of the hydroxyapatite samples [8].



The solid state [9], mechanochemical [10], chemical precipitation [11], hydrolysis [12], sol-gel [13], hydrothermal [14], emulsion [15], sonochemical [16], combustion [17], pyrolysis methods [18], synthesis from biogenic sources [19], mixed methods [20] are used to synthesize hydroxyapatite with variable properties.

The mission of presented paper was to analyze the phase composition, crystallinity degree, dispersity and morphological properties of the hydroxyapatite samples synthesized with the hydrothermal technique described at papers [21,22] with variable duration of the hydrothermal treatment process.

The hydrothermal treatment duration influence on the phase composition and crystallinity degree of the calcium phosphate and hydroxyapatite powder was first time discussing in the presented paper. The calcium phosphate based powders were synthesized first time via combined chemical precipitation method with followed hydrothermal synthesis method.

2. Materials and Methods

2.1. Hydrothermal synthesis of hydroxyapatite samples

The calcium phosphate and hydroxyapatite samples were synthesized in the precursor system $\text{Ca}(\text{NO}_3)_2 \cdot (\text{NH}_4)_2\text{HPO}_4 \cdot \text{NH}_4\text{OH}$. The calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) analytical grade reagent (AR Grade) made by Rechem Co. (Russia), diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ (AR Grade) made by Rechem Co. (Russia) and ammonium hydroxide (NH_4OH) (AR Grade) made by Rechem Co. (Russia) were used as an initial precursors for the hydroxyapatite synthesis.

The 10 weight % diammonium hydrogen phosphate water solution was added to the 10 weight % calcium nitrate water solution. The ratio Ca/P was calculated as 1.67. The addition of the 10 weight % water solution ammonium hydroxide increased the pH level, controlled with the pH-meter Mettler Toledo MP230, up to 11. Chemicals precursors were constantly mixed with the rotation mechanical mixer Heidolph RZR 2051 at 500 rpm for 2 hours. The chemical reaction provided with the chemical reaction (1).



The obtained suspension was treated with hydrothermal synthesis method. The hydrothermal synthesis was carried out in stainless steel autoclave fettled with polytetrafluorethylene (PTFE) at 250 – 270 °C and 150 – 200 atm. for 12, 24, 36 and 48 hours consequently. The hydroxyapatite samples obtained with the hydrothermal synthesis presented in table 1.

Table 1. The hydroxyapatite samples obtained with hydrothermal method.

Sample	Synthesis condition		
	Precursor system	pH	Treatment duration, h
HAp 2.1	$\text{Ca}(\text{NO}_3)_2 - (\text{NH}_4)_2\text{HPO}_4 - \text{NH}_4\text{OH}$	11	12
HAp 2.2	$\text{Ca}(\text{NO}_3)_2 - (\text{NH}_4)_2\text{HPO}_4 - \text{NH}_4\text{OH}$	11	24
HAp 2.3	$\text{Ca}(\text{NO}_3)_2 - (\text{NH}_4)_2\text{HPO}_4 - \text{NH}_4\text{OH}$	11	36
HAp 2.4	$\text{Ca}(\text{NO}_3)_2 - (\text{NH}_4)_2\text{HPO}_4 - \text{NH}_4\text{OH}$	11	48

The next step was washing the hydroxyapatite samples in distilled water until pH level goes down to 7. After that, samples were dried out in vacuum dryer Binder ED 23 at 90 °C for 12 hours.

2.2. Analytical methods to study hydroxyapatite samples

The X-Ray diffraction method Scientific Instruments Difrey 401 (Russia) using Cr $K\alpha$ emission with wave length 2.2909 Å was used to make a diffraction pattern. The diffraction patterns were detected in angles 14 – 140 ° 2θ with interval 58 ° and time of equilibrium 300 second. The PDF-2004 and COD (Crystallography Open Database) were used to determine the diffraction patterns. The equation (2) was used to analyze crystallinity degree (X_c) of the obtained HAp samples. $V_{112/300}$ described the minimum

intensity between two reflections from crystal plane (112) and (300) and I_{300} was the intensity reflection for plane (300).

$$X_c = 1 - \frac{V_{112/300}}{I_{300}} \quad (2)$$

The Fourier Transform Infrared spectroscopy (FTIR spectroscopy) Thermo Scientific Nicolet 380 (USA) and Raman Spectroscopy Thermo Scientific SXR microscope (USA) with the OMNIC operation system and database were used to analyze the phase composition of the hydroxyapatite samples. The IR and Raman specters were determined with book [23].

3. Results and discussion

The X-Ray diffraction patterns presented in the figure 1 show the phase composition of hydroxyapatite synthesized with hydrothermal method. All samples have one phase composition: HAp 2.1 - $\text{Ca}_{9.04}(\text{PO}_4)_3(\text{OH})$ [01-068-1203], HAp 2.2 - $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [01-089-4405], HAp 2.3 - $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [96-900-2216] and HAp 2.4 - $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [96-900-2216].

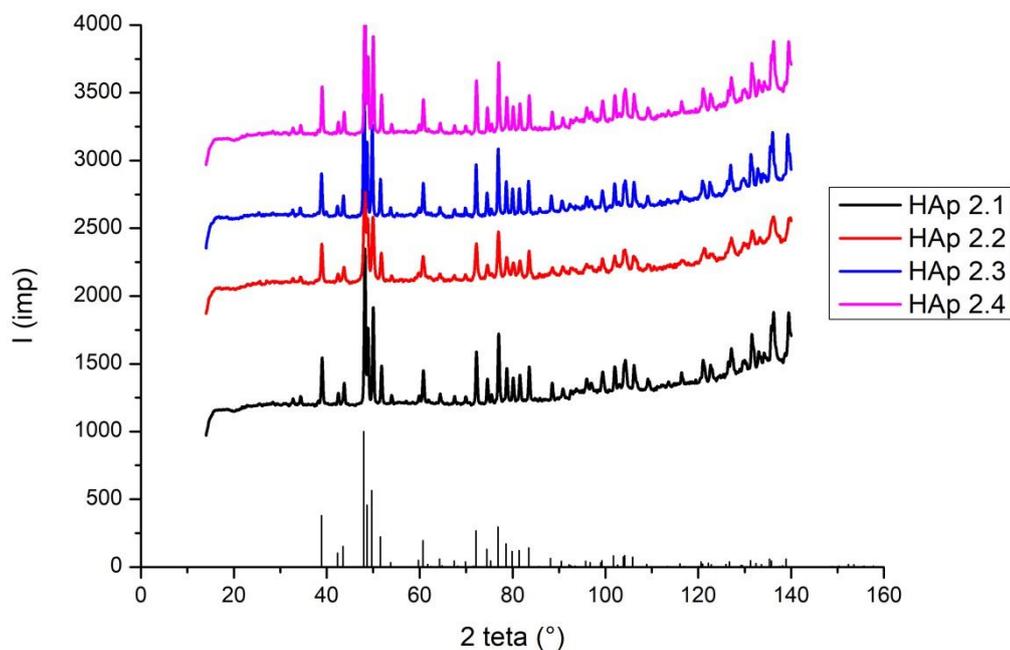


Figure 1. Hydroxyapatite XRD patterns.

The crystallinity degree was calculated with equation 2. The remastered (without background) X-Ray patterns are presented in the figure 2.

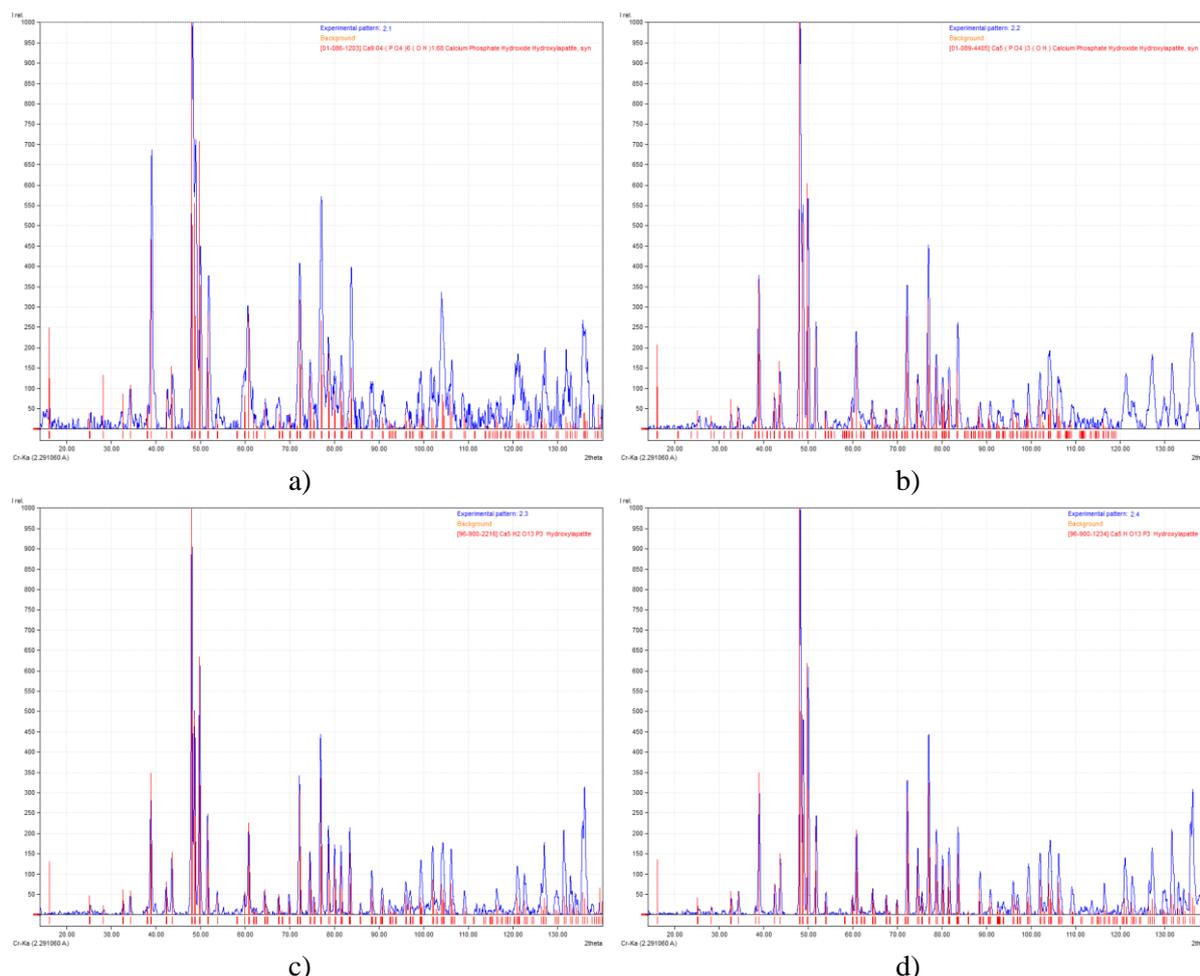


Figure 2. Remastered X-Ray patterns of HAp samples a) HAp 2.1, b) HAp 2.2, c) HAp 2.3, d) HAp 2.4.

The phase composition and crystallinity degree of HAp samples are presented in table 2. The crystallinity degree increases from 0.68 up to 0.98 with the duration hydrothermal synthesis growth from 12 up to 48 hours. The crystallinity degree makes a sharp spike (from 0.68 to 0.98) when time duration increases from 12 to 24 hours. The hydrothermal treatment duration rise from 24 to 48 hours hasn't effect on the crystallinity degree of the hydroxyapatite samples. The difference in crystallinity could be described as a measurement error.

Table 2. The phase composition and crystallinity degree of HAp samples.

Sample	Treatment duration, h	Phase composition	Crystallinity degree
HAp 2.1	12	$\text{Ca}_{9.04}(\text{PO}_4)_3(\text{OH})$ [01-068-1203]	0.68
HAp 2.2	24	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [01-089-4405]	0.95
HAp 2.3	26	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [96-900-2216]	0.96
HAp 2.4	48	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [96-900-2216]	0.98

Figure 3 shows FTIR and Raman spectroscopy results.

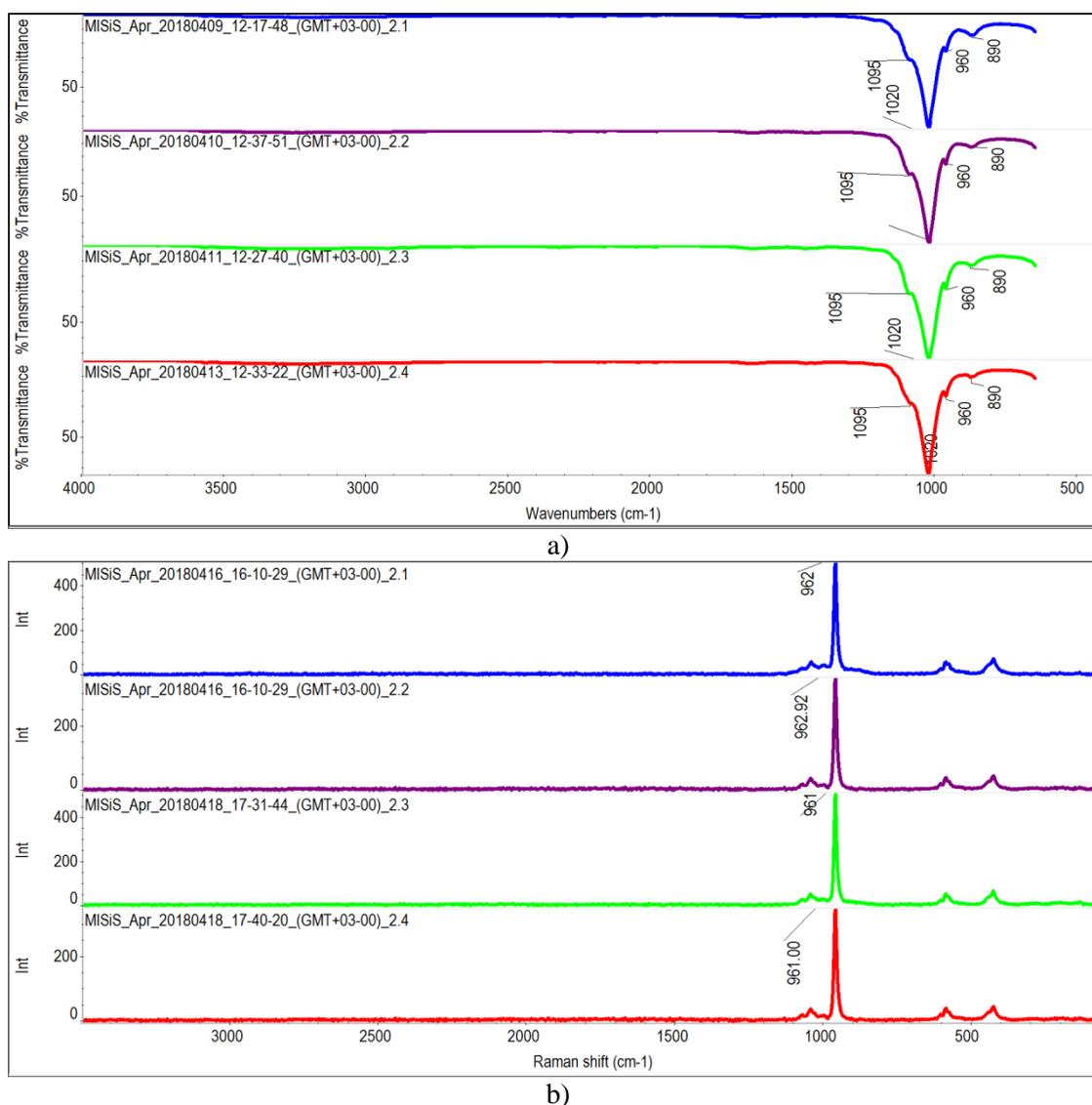


Figure 3. FTIR a) and Raman b) spectroscopy data.

For all samples FTIR specters have 4 lines at 890, 960, 1020 and 1095 cm^{-1} . Peak of intensity at 890 cm^{-1} corresponds for vibrations of the OH hydroxide group. Line at 960 cm^{-1} responses for valence vibrations phosphate group (PO_4^{3-}), and lines at 1020 and 1095 cm^{-1} refer to phosphate group deformation vibrations.

Line at 960 cm^{-1} at Raman specter corresponds to fundamental vibrations of phosphate groups PO_4^{3-} and it was the most intensive line on all the specters.

The FTIR and Raman data support the results of X-Ray diffraction analysis.

The presented X-Ray diffraction, FTIR and Raman spectroscopy datas show the good perspectives of the combined chemical precipitation with the followed hydrothermal synthesis method to produce hydroxyapatite powders. The obtained data demonstrate the chemical precipitation in a precursor system $\text{Ca}(\text{NO}_3)_2\text{-(NH}_4)_2\text{HPO}_4\text{-NH}_4\text{OH}$ at pH level 11 with followed hydrothermal treatment at 250 $^\circ\text{C}$ and 150 bar provide synthesis of the one phase hydroxyapatite powder.

The crystallinity degree analysis demonstrates the increasing of the crystallinity degree from the 0.68 up to 0.95 with the growth of the hydrothermal treatment duration from 12 to 24 hours. The follow increasing of the hydrothermal treatment duration from 24 to 48 hours has insignificant effect on the

crystallinity degree (X_c (HAp 2.2) = 0.95, X_c (HAp 2.3) = 0.96 and X_c (HAp 2.4) = 0.98). The difference between crystallinity degree can be described as the measurement error.

4. Conclusion

The hydroxyapatite synthesized with hydrothermal method at different time duration (12, 24, 36 and 48 hours) at 250 – 270 °C and 150 – 200 atm using precursor system $\text{Ca}(\text{NO}_3)_2\text{-(NH}_4)_2\text{HPO}_4\text{-NH}_4\text{OH}$ shows one phase composition. Primary, all samples consist of the $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ phase for all obtained HAp samples. The FTIR and Raman results support the X-Ray analysis data. The crystallinity degree sharply increases from 0.68 to 0.95 with the growth of the time duration of hydrothermal synthesis from 12 to 24 hours. The time duration of the hydrothermal treatment process increases from 24 to 48 hours slightly rises the crystallinity degree of the HAp samples up to 0.98.

Acknowledgements

The authors acknowledge the financial support of the Ministry of Education and Science of the Russian Federation (Project no. RFMEFI57517X0168).

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