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The pH Level Influence on Hydroxyapatite Phase Composition Synthesized with Hydrothermal Method

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Abstract. This paper reports the pH level influence on hydroxyapatite phase composition synthesized with hydrothermal method in $Ca(OH)_2$-H_3PO_4, $Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH, $Ca(OH)_2$-$NH_4H_2PO_4$.The obtained samples were studied with X-Ray diffraction, Fourier Transform Infrared (FTIR) and Raman spectroscopy. The one phase $Ca_5H_2O_{13}P_3$ high crystallinity hydroxyapatite was synthesized with hydrothermal method at pH equal to 11. The crystallinity degree was calculated from the X-Ray diffraction pattern and became 0.96. The increasing pH level from 7 to 11 provides obtaining one phase hydroxyapatite at pH level 11 instead the two phase $Ca_{9.04}(PO_4)_6(OH)_{1.68}$, $CaHPO_4$ at pH level 9 and $CaPO_3(OH)$, $Ca(OH)_2$ at pH level 7.

1. Introduction

Biomaterials attract increasing interest owing to their applicability in a field of medicine [1]. The hydroxyapatite materials due to specific properties [2] find application as a biomedical material [3]. The hydroxyapatite properties, like crystallinity degree, crystal dispersity, porosity and stoichiometry make hydroxyapatite [4] widely used as scaffold for tissue engineering [4], fillers for healing defect in bones [5] and drug delivery systems [6].

Ceramic materials are a class of biomaterials used in biomedical devices. Ceramics based materials are widely used as implant materials due to their ability to be fabricated into a variety of shapes, along with their variable porosity, bioactive properties in the body and high compressive strength [7]. The calcium phosphates and hydroxyapatite have close chemical composition to human bone minerals [8]. Ceramic materials based on calcium phosphate and hydroxyapatite demonstrate high biocompatibility, perfect osteoconduction and bioactivity [9]. Also HAp finds application as biocompatible cover for implants made of metal materials [10]. The hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is the most thermodynamically stable in its crystalline state. HAp could be integrated with bones without any local toxicity and inflammation of body response [11].

The synthesis methods and synthesis parameters provide the phase composition, morphological and dispersity control of the obtained materials. The two ways of hydroxyapatite fabrication exist extracting from nature sources and synthetic by different methods dry, wet and high temperature methods [9]. The HAp could be synthesized by the various methods including solid-state method [12], mechanochemical [13], chemical precipitation [14], hydrolysis [15], sol-gel [16], hydrothermal [17], emulsion [18], sonochemical [19], combustion [20], pyrolysis [21], synthesis from biogenic sources [22] and combined methods [23] methods. Any method provides its own special phase composition, dispersion and morphology of the hydroxyapatite. The hydroxyapatite properties depend on the synthesis parameters.

The aim of the presented paper is to estimate the initial precursor influence in precursor systems $Ca(OH)_2$-H_3PO_4, $Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH and $Ca(OH)_2$-$NH_4H_2PO_4$ on the hydroxyapatite phase composition, dispersion and crystallinity degree. Also, the pH level influence during synthesis process described at [24, 25] on the hydroxyapatite samples properties.

This paper discuss the first time using of chemical precipitation and hydrothermal synthesis method to obtain the calcium phosphate and hydroxyapatite powders. The synthesized hydroxyapatite powder will be used as an initial material in granulation process to produce hydroxyapatite spherical granules for 3D printing of the ceramic implants.

2. Materials and Methods

2.1. Hydrothermal synthesis of hydroxyapatite sampleshe

Calcium nitrate tetrahydrate ($Ca(NO_3)_2$•$4H_2O$, AR Grade), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, AR Grade) ammonium hydroxide (NH_4OH, AR Grade), calcium hydroxide ($Ca(OH)_2$, AR Grade), phosphoric acid (H_3PO_4 AR Grade) produced by Reachem Co. (Russia) were used as initial precursors for obtaining HAp samples. The HAp samples were synthesized in three systems: $Ca(OH)_2$-H_3PO_4, $Ca(OH)_2$-$NH_4H_2PO_4$ and $Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH. In $Ca(OH)_2$-H_3PO_4 system calcium hydroxide was added to the phosphoric acid. The Ca/P element ratio was calculated equal to 1.67. Calcium hydroxide was added to diammonium hydrogen phosphate in system $Ca(OH)_2$-$NH_4H_2PO_4$. In $Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH system the diammonium hydrogen phosphate solution was added to the calcium nitrate solution and ammonium hydroxide was used to increase pH level. The obtained suspensions were treated in stainless steel autoclave at 250 °C with 150 bar during 24 hours. The obtained suspensions were washed with distilled water till pH level became equal to 7 by decantation method.

The next step was samples washing suspensions with decantation method until pH level became equal to 7 using the distilled water. The vacuum filtration system separated the HAp samples from the dispersant liquid. The HAp samples dried at 90 °C during 12 hours in the drying chamber SNOL HS-80-01. The obtained samples are presented in table 1.

Table 1. The obtained samples of hydroxyapatites.

Sample	Synthesis condition	
	System	pH
HAp 1.1	$Ca(OH)_2$-H_3PO_4	7
HAp 1.2	$Ca(OH)_2$-$NH_4H_2PO_4$	7
HAp 1.3	$Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH	7
HAp 1.4	$Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH	9
HAp 1.5	$Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH	11

2.2. Analytical methods to study hydroxyapatite samples

Phase composition and crystallinity degree were characterized with X-Ray diffractometer Scientific Instruments Difray 401 (Russia) with Cr Kα emission (wave length of 2.2909 Å) using PDF-2004 and

COD (Crystallography Open Database). The diffraction patterns were detected in the range from 14 to 140° 2θ with the interval 58 degrees and equilibrium time 300 second. The crystallinity degree (X_c) was calculated with the equation (1). The $V_{112/300}$ meant the minimum intensity between two intensity peaks reflected from the crystallography planes (112) and (300) consequently. The I_{300} meant the maximum intensity for the peak reflected from crystallography plane (300).

$$X_c = 1 - \frac{V_{112/300}}{I_{300}}$$

Also, the Fourier Transform Infrared spectroscopy (FTIR spectroscopy) Thermo Scientific Nicolet 380 (USA) and Raman spectroscopy Thermo Scientific DXR Microscope (USA) with OMNIC operation system were used to determine hydroxyapatite samples phase composition. The specters determination was carried out via book [26].

3. Results and discussion

The Figure 1 demonstrates XRD patterns of the hydroxyapatite samples obtained via hydrothermal method. The HAp 1.1 sample is one phase $Ca_3(PO_4)_2$ [00-009-0169]. In the sample HAp 1.2 $CaHPO_4$ [00-001-0653] and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ [01-72-1243] phases were detected. Also, the HAp 1.3 sample consists from two phases $Ca(OH)_2$ [00-050-0008] and $CaPO_3(OH)$ [00-009-0080]. The HAp 1.4 sample has two phase composition with $CaHPO_4$ [00-003-0423] and hydroxyapatite phase $Ca_{9.04}(PO_4)_6(OH)_{1.68}$ [01-086-1203]. The sample HAp 1.5 is one phase sample hydroxyapatite $Ca_5H_2O_{13}P_3$ [96-900-2215].

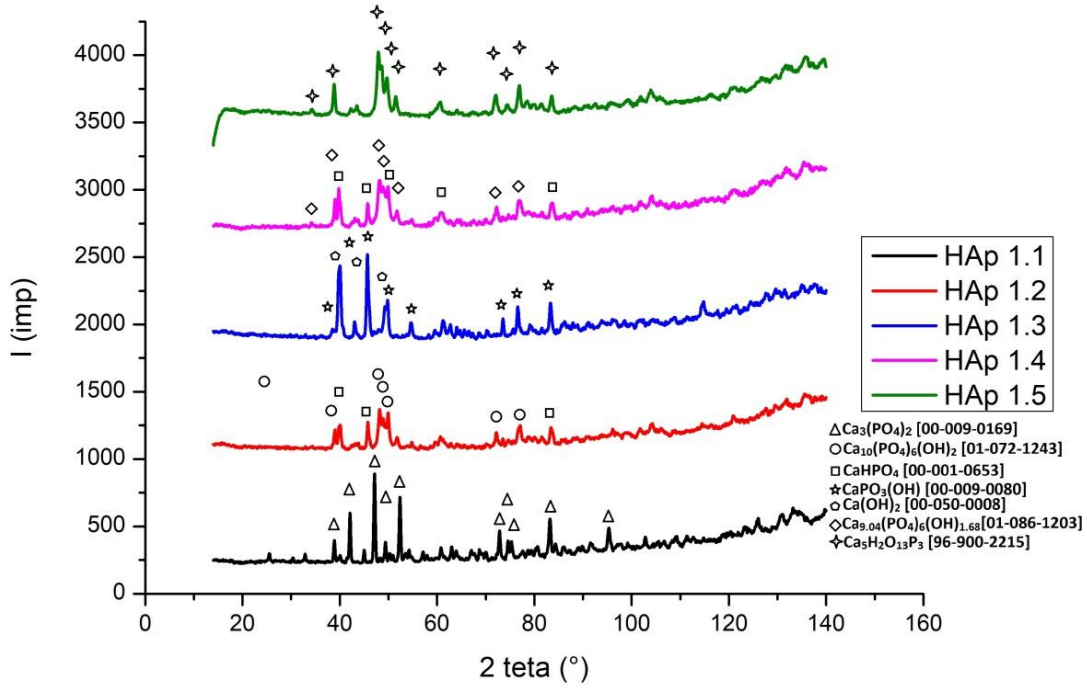

Figure 1. XRD Patterns of the hydroxyapatite samples.

The phase composition of the HAp samples was presented in table 2.

Table 2. HAp samples phase composition.

Sample	Phase composition
HAp 1.1	$Ca_3(PO_4)_2$ [00-009-0169]
HAp 1.2	$CaHPO_4$ [00-001-0653], $Ca_{10}(PO_4)_6(OH)_2$ [01-72-1243]
HAp 1.3	$Ca(OH)_2$ [00-050-0008], $CaPO_3(OH)$ [00-009-0080]
HAp 1.4	$CaHPO_4$ [00-003-0423], $Ca_{9.04}(PO_4)_6(OH)_{1.68}$ [01-086-1203]
HAp 1.5	$Ca_5H_2O_{13}P_3$ [96-900-2215]

The hydroxyapatite crystallinity degree can be analyzed only for the HAp 1.5 sample due to HAp 1.1 and HAp 1.3 haven't hydroxyapatite phase. The HAp 1.2 and HAp 1.4 consists more than one phase. The presence of the second phase makes crystallinity degree analysis impossible due to intensity peaks of the second phase are overlaying on diffraction patterns. The hydroxyapatite samples crystallinity degree was calculated for the sample HAp 1.5 using figure 2. The figure 2 presents the HAp 1.5 remaster XRD pattern without background.

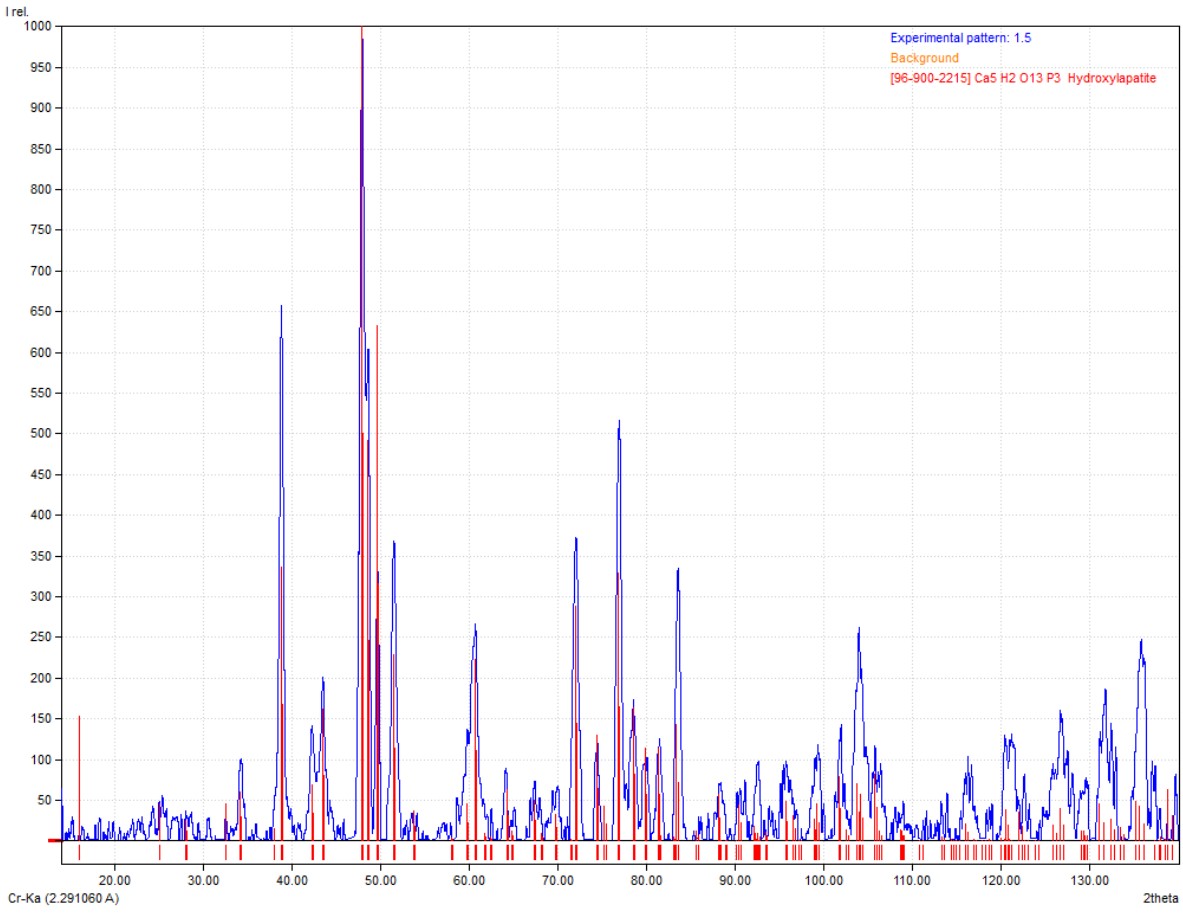

Figure 2. Hydroxyapatite HAp 1.5 XRD pattern without background.

The crystallinity degree calculated via equation (1) was equal to 0.96. This fact provides the ability to use high crystallinity hydroxyapatite as a material for the biomedical application.

The results of FTIR and Raman spectroscopy are presented in figure 3.

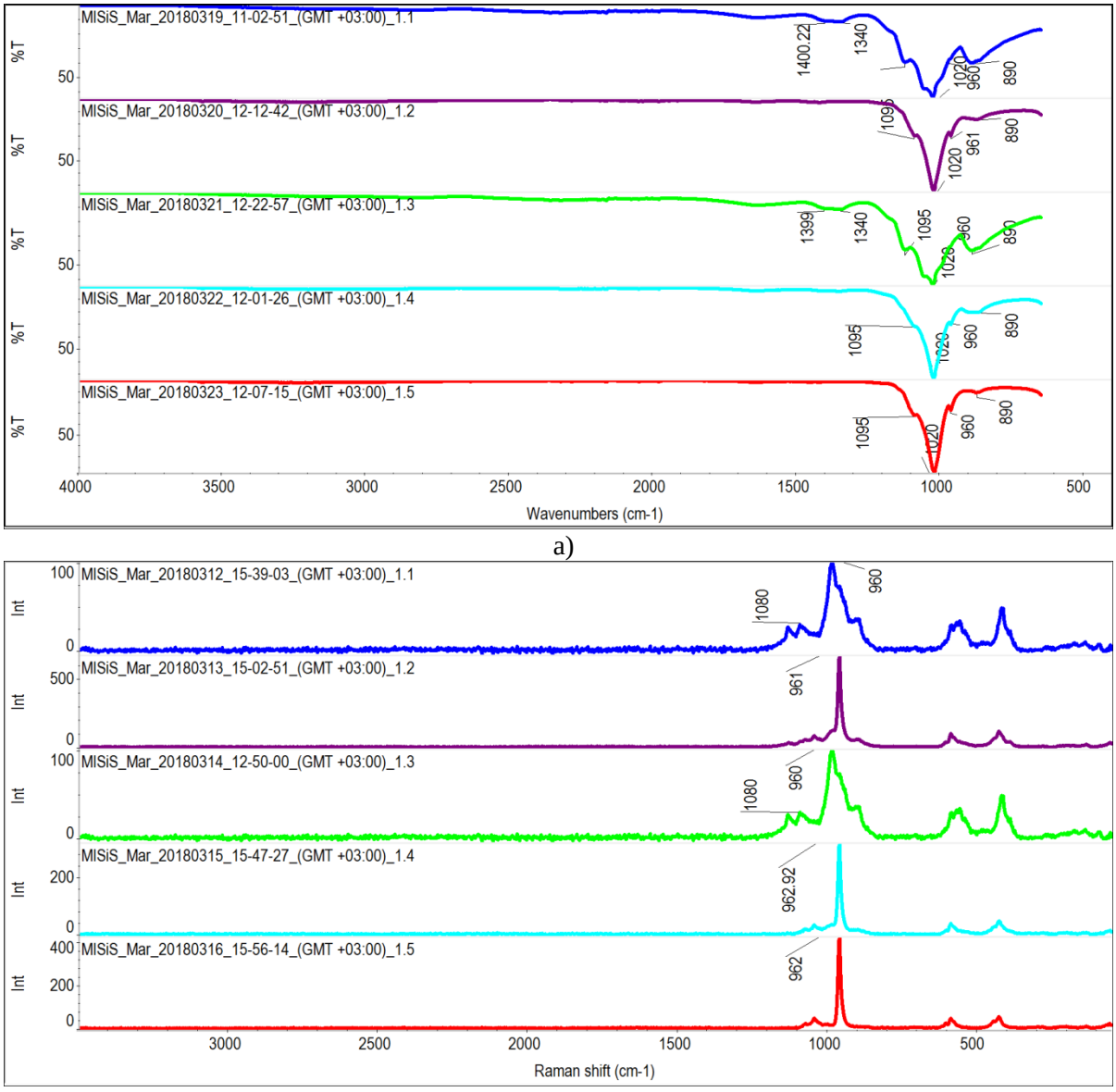

Figure 3. FTIR a) and Raman b) spectroscopy results.

The FTIR specters of the HAp obtained samples demonstrate peaks on 890, 960 1020 and 1095 cm^{-1} reciprocal wavelength. Peak at 890 cm^{-1} refer to vibrations of OH^-. Peak at reciprocal wavelength 960 cm^{-1} leads to valence oscillations of phosphate groups (PO_4^{3-}). Peaks at 1020 and 1095 cm^{-1} lead to phosphate group deformation oscillations.

Raman specters show the oscillation mode at 960 cm^{-1} determined as phosphate group.

The HAp 1.1 FTIR specter has additional three peaks which could be described as out-of-plane oscillations of carbonate groups (CO_3^{2-}) and peaks at 1340 and 1400 cm^{-1} described as carbonate group oscillations. The same results are on the FTIR specter of the HAp 1.3 sample.

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

The presented X-RAY diffraction FTIR and Raman spectroscopy data show the good perspectives of the $Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH precursor system using to obtain the one phase high crystallinity hydroxyapatite powder. Also, the combined chemical precipitation and hydrothermal synthesis method makes possible the hydroxyapatite synthesis. The chemical precipitation at pH level

11 with following hydrothermal synthesis method in stainless steel at 250 °C and 150 bar provide the one phase hydroxyapatite powder with high (0.96) crystallinity degree.

4. Conclusion

The high crystallinity one phase hydroxyapatite $Ca_5H_2O_{13}P_3$ was synthesized used hydrothermal method. The hydroxyapatite samples synthesized using three systems $Ca(OH)_2$-H_3PO_4, $Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH, $Ca(OH)_2$-$NH_4H_2PO_4$, shows the perspective of using $Ca(NO_3)_2$-$(NH_4)_2HPO_4$-NH_4OH to obtain one phase high crystallinity hydroxyapatite. The crystallinity was determined at for sample HAp 1.5 was equal to 0.96.

Acknowledgements

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