CONCENTRATION INFLUENCE IN THE HYDROTHERMAL SYNTHESIS OF HYDROXYAPATITE AT 160 ℃

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Abstract

The work presented here is the hydrothermal synthesis of hydroxyapatite (HA) at 160℃ for 8h, starting from solutions of four different concentrations. The purpose of the study was to investigate the influence of the concentration on the morphology of the synthetic powder obtained. The identification of the synthesized compounds was performed by X-ray Diffraction, while the size and shape of the crystals was studied by means of Scanning Electron Microscopy. Results have showed that with raising the solution concentration, a secondary phase of $CaHPO_4$ appears and grows in direct relationship to solution concentration, while the hydroxyapatite morphology does not seem to have been influenced by concentration changes. Phase pure hydroxyapatite was obtained only for an initial solution concentration of 0.02 M, the smallest used in this study.

Introduction

Hydroxyapatite (HA), having the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, is a natural mineral present in the human hard tissues in large amounts. Given this reason, synthetic HA has been intensively investigated and used as a replacement material for damaged natural tissues, either alone or in combination with other substances, in the form of powders, cements, solid pieces, layers deposited onto metallic substrates, etc.

In a tight relationship to its uses, the properties of the synthetic HA are highly influenced by its morphological characteristics (such as size and shape of crystals) [1], so the method by which it was obtained has to be carefully chosen because each of the methods presents advantages as well as disadvantages. The hydrothermal technique is a facile and low-energy consuming method, which allows a good control over the properties of the desired material, such as crystallinity, morphology, size of particles, etc [2].

In the present study, hydrothermal technology has been used in a study meant to lead to pure-phase HA by running experiments at 160°C for 8h. Four different concentrations of the starting solutions have been used, in order to investigate the relationship between the concentration and the morphology of the final product.

Experimental

Analytical grade $Ca(NO_3)_2.4H_2O$ (Sigma-Aldrich) was used as Ca precursor and the P precursor used was $(NH_4)_2HPO_4$ (Merck). Solutions of the 2 precursors were prepared with the following concentrations:

Sample name	Ca solution concentration (mol/L)	P solution concentration (mol/L)
1-S	0.02	0.02
2-S	0.05	0.05
3-S	0.1	0.1
4-S	0.2	0.2

After mixing the solutions with preservation of the Ca:P ions ratio of 10:6 under continuous stirring at room temperature, the solutions were transferred to Teflon liners and heated at 160°C for 8h. The initial pH was in the range 6.1-6.4 and the final pH was 4.3-4.9.
After cooling naturally to room temperature, the precipitates were extracted and washed with double-distilled water until pH returned to neutral. Then the powders were dried in the oven at 50°C for 6h.
The physico-chemical characterization of the powder samples was performed using a PANalytical X'Pert Pro MPD Diffractometer equipped with a Cu anode and PixCEL detector, powder samples supported on zero background silicone holders, working parameters: 45 kV, 30 mA and an Inspect S Scanning Electron Microscope (FEI Company), where the powder samples were supported on carbon tape.

Results and discussion
The X-ray diffraction results are presented in Figure 1. For the smallest concentration, of 0.02M, the sample consists in pure crystalline HA. With rising concentration, a secondary phase appears, of $CaHPO_4$, whose amount is growing with concentration. The peaks which are not nominated with a or b in Figure 1 belong to either $CaHPO_4$ or its mixture with HA (many small peaks belonging to these two compounds have identical position reflexions).

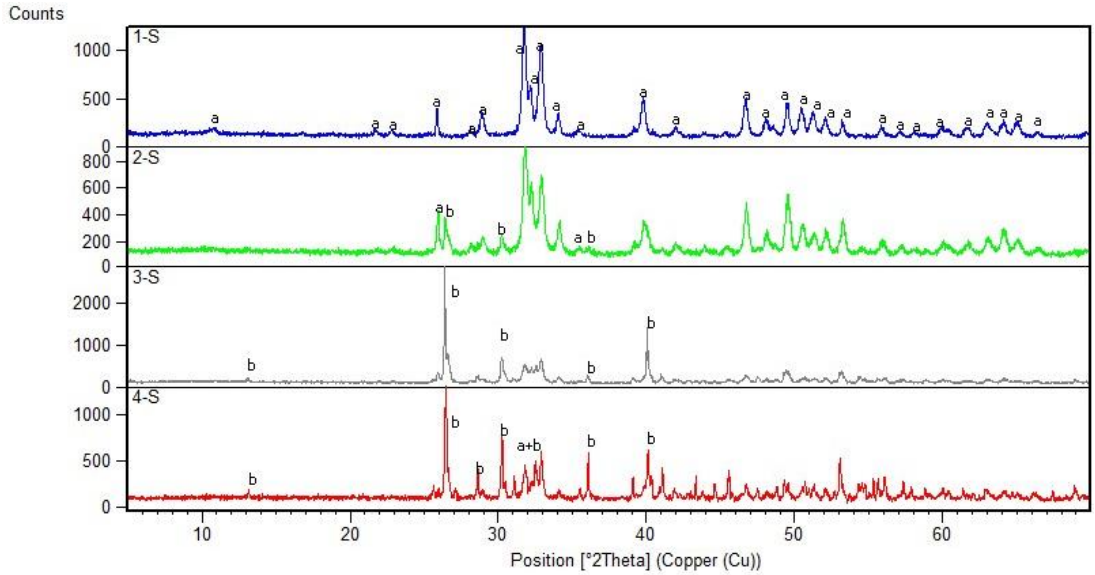

Figure 1. X-ray diffraction patterns of the four samples, where a=HA, b=$CaHPO_4$

Scanning electron microscopy images are presented in Figure 2. The morphology of sample 1-S is of submicronic acicular crystals, agglomerated in the shape of clews, typical for HA. When concentration increased (sample 2-S), the agglomerated formation of needles became less fluffy, because the HA crystals are combined with particles of $CaHPO_4$. For samples 3-S and 4-S the $CaHPO_4$ crystals present a dramatic growth, while HA preserves its acicular

morphology and submicronic size. At the same time, the amount of HA is higher in the sample 3-S compared to the sample 4-S.

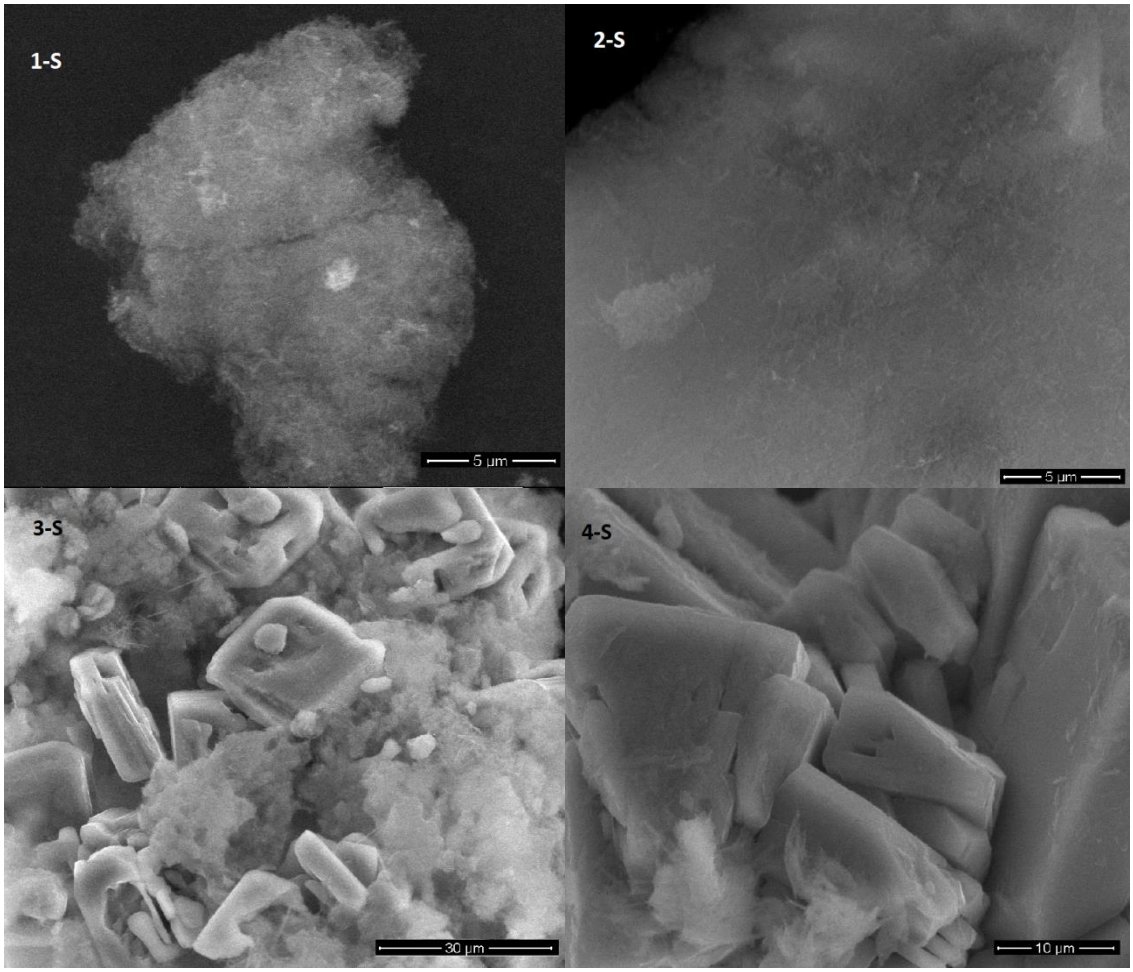

Figure 2 Scanning electron microscopy images

The chemical reactions implicated in the process are presumed to be:

$Ca(NO_3)_2 \rightarrow Ca^{2+} + 2(NO_3)^-$ (1)

$(NH_4)_2HPO_4 \rightarrow 2\ (NH_4)^+ + HPO_4^{2-}$ (2)

$Ca^{2+} + HPO_4^{2-} \rightarrow CaHPO_4$ (3)

$6CaHPO_4 + 4Ca^{2+} + 8HO^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H_2O$ (4)

First, the precursors are dissociated in their own solution, and then, when the two solutions are mixed, the ions interact according to eq (3) to form dicalcium phosphate (dihydrate or anhydrous). With rising temperature, the hydrolysis of $CaHPO_4$ starts and HA crystallizes, but the transformation is incomplete, probably due to either insufficient time or insufficient temperature.

The reactions sequence described by equations (1-4) is supported by the low pH values recorded at the end of the hydrothermal treatment, values located in the generally known pH region where dicalcium phosphate forms and HA is soluble. $CaHPO_4$ is recognized as an intermediate in the synthesis of HA [3, 4] during low pH. Due to the existence of the both phases in the final product (experimental results), we assume the reaction given by eq (4) is not complete in our case. Nevertheless, HO^- ions existence and number, vital for the formation of HA, is conditioned by the low pH, lowering the chances of formation of the

desired phase. HA morphology does not seem to have been influenced by the changes in the precursors concentration.

Conclusions

The hydrothermal synthesis at 160°C for 8h starting from pH values of 6.1-6.4 has led to the formation of a mixture of hydroxyapatite and dicalcium phosphate, the latter in direct proportional relationship to the concentrations of precursors solutions. Only when the starting concentration was as low as 0.02 (lowest in the present study), pure-phase HA was synthesized. The morphology or crystal size of hydroxyapatite was not influenced by the concentration changes. Time period allocated to the hydrothermal treatment needs to be increased and pH must be raised to alkaline domain, in order to obtain pure phase HA at higher concentrations.

References

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