

Characterization of Hydroxyapatite Materials by FTIR Spectroscopy

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Abstract

The structure of synthetic hydroxyapatite powders obtained by chemical precipitation route have been studied with Fourier transform infrared (FTIR) spectroscopy. Various alternative techniques as diffuse reflectance (DRIFT) and attenuated total reflectance (ATR) have been supplementary used for identify different bands attributions in FTIR spectra of hydroxyapatite. The quality of the structural and compositional detail which can be revealed by these techniques, makes FTIR spectroscopy a very attractive technique for the analysis of biomaterials. Materials can be easily analysed by FTIR without need to reduce the particle size or dilute with KBr.

Keywords: hydroxyapatite, PAS FTIR, ATR, DRIFT

Introduction

Apatite is one of few inorganic materials that are classed as bioactive, since it supports bone ingrowth and osseointegration when used in orthopaedic, dental and maxillofacial applications. [11].

Hydroxyapatite (HAp) is a suitable material for medical applications, for repair or replacement of bone tissues since it resembles mineral component of bone and teeth, because is a primary constituent of human hard tissues [1]. The structure of artificially prepared HAp is the same as that of the HAp of the natural bone. Due to its good compatibility with human organism and strong binding to bone, it can be used for artificial tooth roots, filler of bone defects, etc. [2, 3]. Hydroxyapatite (HAp) is biovitroceramics with broad clinical applications because of the similarity with the bone tissue. It belongs to the monoclinic crystal system with unit cell dimensions $a = 9.4214(8) \text{ \AA}$, $b = 2a$, $c = 6.8814(7) \text{ \AA}$, and $c = 120$ and space group P21/b.

Sintering time, temperature and the atmosphere are important parameters to control the level and type of carbonate substitution. FTIR spectra at room temperature of the reaction mixture heated to various temperatures were used to determine the extent of the reaction [13]. Besides this method, many others could be used for structure elucidation of this biomaterial: UV-Vis spectroscopy, XRD, EDXRF, AFM, SEM, TEM [13].

In the present paper we have investigated a number of three HAp samples at different temperatures of calcinations, in order to monitor in situ the changes in the OH band positions during heating. The studies have been achieved only by FTIR (and second derivative spectra), in

order to complete our previous published results and to conclude about the final and certain preparation conditions of HAp.

Materials and methods

Chemical reagents used in this work: calcium nitrate with four water molecules [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] and ammonium phosphate dibasic [$(\text{NH}_4)_2\text{HPO}_4$] was dissolved in deionized water separately. The dropwise addition of calcium nitrate [$\text{Ca}(\text{NO}_3)_2$] aqueous solution to vigorously stirred ammonium phosphate dibasic [$(\text{NH}_4)_2\text{HPO}_4$] solution at room temperature for about 1h result a milky and somewhat gelatinous precipitate which was then stirred for 1h. The mixture is sintering at 100°C for 24h. It was then washed and filtered in a filter glass [2].

After filtration the compact, sticky filter cake was dried at 80°C in laboratory oven. Dried powders was crushed by using mortar and pestle and calcined in alumina crucible at different temperatures: 800 , 1000°C , and 1200°C for 1h [3].

In the figure 1 the wet-chemical process to obtain HAp powder are presented.

Three hydroxyapatite synthetic samples have been obtained by varying the calcination temperature.

Table 1. Conditions of obtaining of some HAp samples

Method	Sample	Calcination temperature ($^\circ\text{C}$)	Concentration (M)
Reflux after mixing	HA1	800	0.1:0.06
Reflux after mixing	HA2	1000	0.1:0.06
Reflux after mixing	HA3	1200	0.1:0.06

Fourier Transform IR Spectroscopy (FT-IR) standard spectra were collected by using a Perkin Elmer Spectrum GX spectrometer with a potassium bromide beam splitter and deuterated triglycine sulfate (DTGS) detector were used for all readings. The ATR accessory used a 3-reflection diamond crystal plate, providing a 3-fold increase in sample response compared to the standard single-reflection crystal plate (Pike Technologies). A range of 400–4000 scans were accumulated for each spectrum at a spectral resolution of 4 cm^{-1} and 32 scans. It was possible to use the drift accessory with the powdered pure substance, thereby allowing for a better and easier analysis. DRIFT spectra were recorded as Kubelka-Munk transformed spectra against a KBr background. KBr sample were run versus a blank KBr pellet in the reference beam to cancel KBr impurity bands, mainly H_2O bands. KBr pellets were prepared by mixing (not grinding) the pre ground HA-SRM (0.8mg and 4.0mg; particle cluster size $\leq 5\mu\text{m}$ composed of crystal sizes of $0.1\mu\text{m}$ to $0.5\mu\text{m}$) with 400mg of IR quality KBr (about $20\mu\text{m}$ to $40\mu\text{m}$ particle sizes). Grinding the sample and KBr together was avoided to reduce additional moisture adsorption from the ground and smaller KBr particles.

Attenuated Total Reflection Infrared Spectroscopy. The mid-infrared spectra were recorded in the range between 650 and 4000 cm^{-1} in a nine reflection configuration using a diamond-ZnSe ATR crystal. About 2-3 mg of tomato samples was placed on the surface of the ATR crystal (diameter, 0.5 mm^2). Three spectra for each sample were accumulated from 32 scans with a spectral resolution of 4 cm^{-1} . For further analyses, averaged spectra were used.

Second derivative spectra of absorbance spectra for the ν_3 and $\nu_4\text{ PO}_4$ bands were obtained in the ranges 1120cm^{-1} to 1000cm^{-1} and 670cm^{-1} to 530cm^{-1} with a Perkin-Elmer Model 621 spectrometer purged with dry CO_2 - free air.

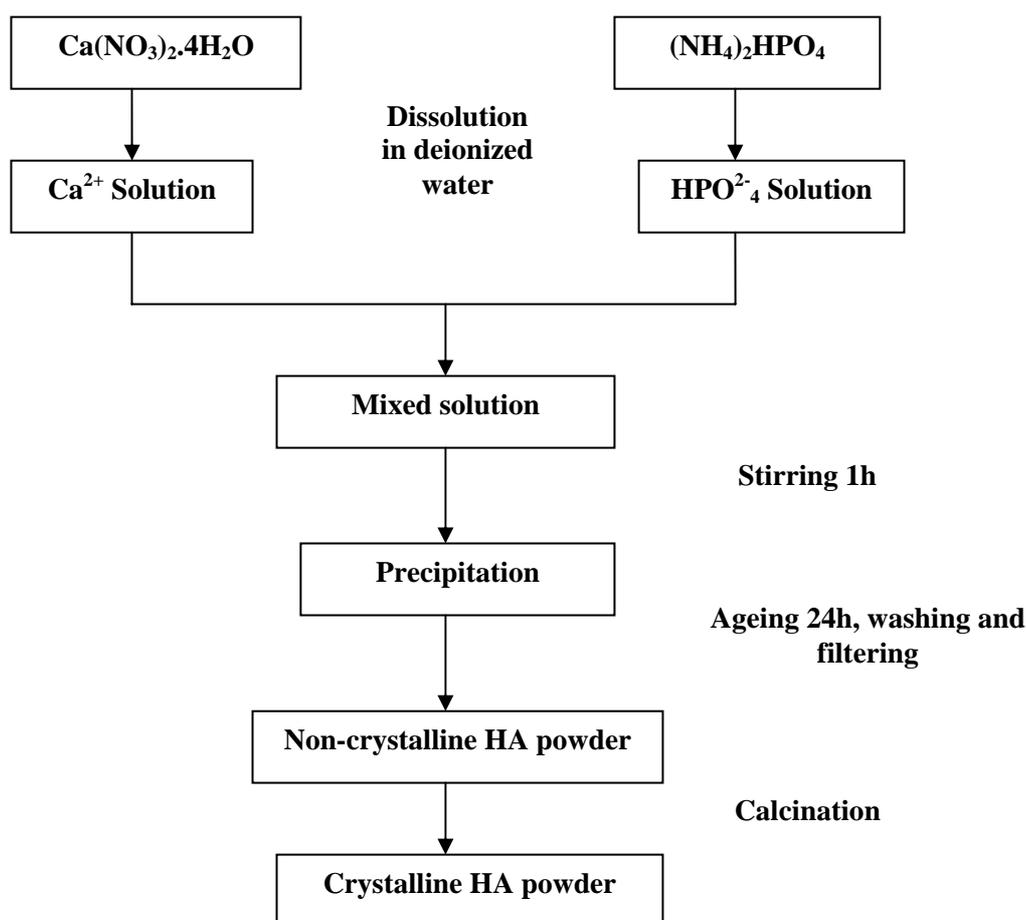


Fig. 1. Modified chemical precipitation route for HA powder preparation [3]

Results and discussion

FTIR spectra displayed a weak peak at 3670 cm^{-1} (assigned to the OH stretching vibrations of the surface P-OH groups), a sharp band at 3572 cm^{-1} (assigned to the stretching vibration of the lattice OH ions) and three bands at 2142 , 2077 and 1989 cm^{-1} (assignable to the overtone and combination bands of PO_4^{3-} ions). The spectra show ill-defined and low intensity absorption bands of P-O due to PO_4^{3-} groups in the $1080\text{--}1020\text{ cm}^{-1}$ region, which are characteristic of the HAp, as well as of the OH-O bands of adsorbed water. Also, for O-H vibrational mode is characteristic a well distinguished peak around $600\text{--}610\text{ cm}^{-1}$. For selected spectra the ratios of integrated intensities as well as integrated areas of the bands corresponding to CO_3^{2-} groups in the range of $1380\text{--}1580\text{ cm}^{-1}$ and those due to PO_4^{3-} at $900\text{--}1300\text{ cm}^{-1}$ were calculated. [6].

By analyzing the spectra, could be concluded that by increasing the sinterization temperature and annealing time is 800°C and 1 hour, respectively, because after this temperature and time, a decreasing process of OH content is observed. Also, clear FTIR bands could be observed attributable to the main chemical groups present in the HAp structure, as a proof for the purity and preparation success (Fig. 1).

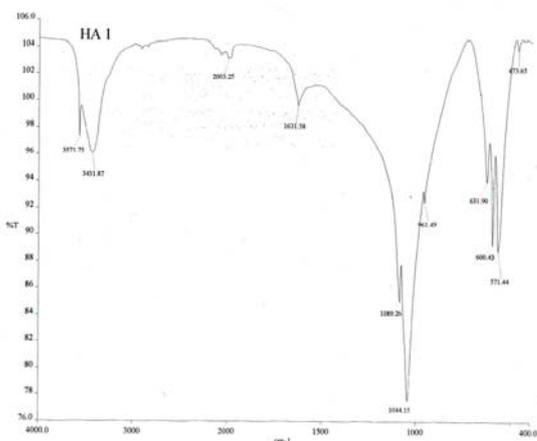


Fig. 2. FTIR analysis of the HA1 powders

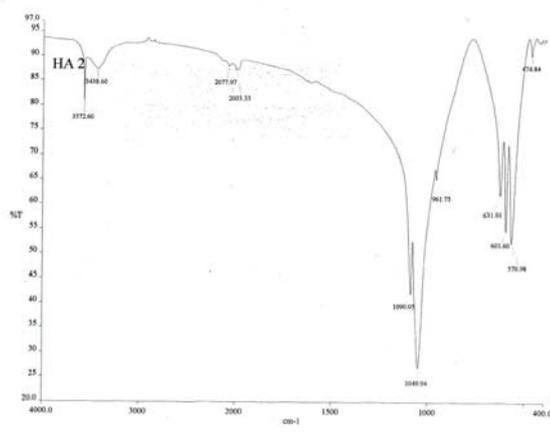


Fig. 3. FTIR analysis of the HA2 powders

In Fig. 2 and 3 are presented FTIR analysis of HA samples sintered at 800°C respectively 1000°C.

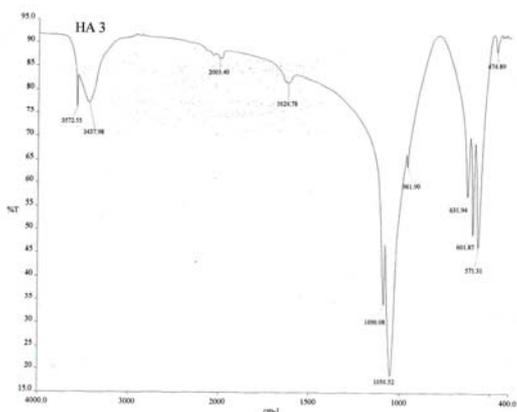


Fig. 4. FTIR analysis of the HA3 powders

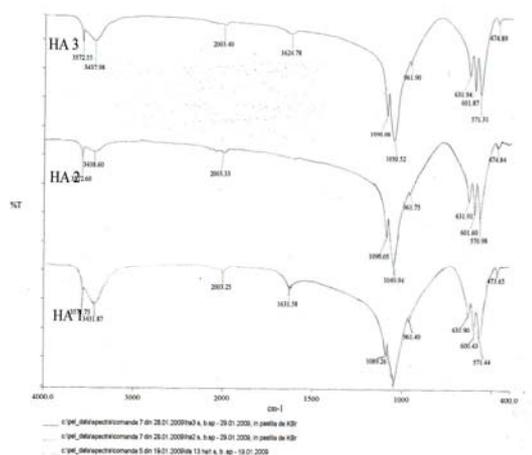


Fig. 5. FTIR analysis of the HA powders after annealing for 1 h at different temperatures.

IR Second Derivative Spectra

High quality absorbance spectra without interference fringes and with low noise are required to obtain meaningful second derivative spectra. IR second derivative spectra allow to:

- (1) reduce interference fringes, wedge-shaped KBr pellets;
- (2) remove the introduction of possible fringes in the background spectrum;
- (3) increase the signal/noise ratio.

KBr has no bands or impurity bands in the investigated regions. The second derivative wavenumber positions for the ν_3 and ν_4 PO_4 bands were determined with a standard uncertainty of 0.1cm^{-1} [4].

In Fig. 3, five second derivative ν_4 PO_4 bands were detected; the absorbance band and second derivative band at 633cm^{-1} derive from the OH^- librational mode [5,6].

The FTIR analysis showed a wide O–H band that transformed into a narrow peak after annealing at high temperature (Fig. 4). The data is consistent with the presence of 6–7 wt.% of adsorbed water in the starting powders [7].

Conclusions

All the conditions of the wet synthesis used in the present work make it possible to obtain pure hydroxyapatite, corresponding to a Ca/P=1.67 ratio and a correct stoichiometry. The usefulness of integrated FTIR studies in evaluation of hydroxyapatite powders has been confirmed.

The chosen method was the wet precipitation because the wet-chemical precipitation route is the most talented route owing to its ease in experimental operations, low working temperature, high percentages of pure products and inexpensive equipment requirement.

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Caracterizarea hidroxiapatitei prin spectroscopie FTIR

Rezumat

Structura pulberii de hidroxiapatita sintetica obtinute prin precipitare chimice au fost studiate cu infrarosu cu transformata Fourier (FTIR) spectroscopie. Diverse tehnici alternative ca reflexie difuze (în derivă) și reflexie atenuate total (ATR) au fost predilect folosite pentru a identifica benzile de atribuții diferite în spectrele FTIR de hidroxiapatită. Calitatea de detaliu structurale și de compoziție care pot fi dezvaluite de aceste tehnici, face PAS-spectroscopie FTIR o tehnica foarte atractiv pentru analiza de biomateriale.