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Synthesis and ultrasonic characterization of hydroxyapatite ceramic powders

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Calcium phosphate compounds have been studied for biomedical applications due to chemical and structural similarity to the mineral phase of bone and tooth. The composition, physico-chemical properties, crystal size and morphology of synthetic apatite are extremely sensitive to preparative conditions and sometimes it resulted into non-stoichiometric calcium deficient hydroxyapatite (HAp) powders. The present paper refers to calcinations of hydroxyapatite ceramics at 600, 800 and 1000^0C. The effect of heat treatment was previously investigated by X-ray diffraction (XRD). The ultrasonic characterisation of hydroxyapatite powders were performed using the ultrasonic air-coupling technique. Modulated ultrasonic signals of 450 kHz central frequency have been transmitted through the hydroxyapatite ceramics specimens. Correlation between signals allowed some conclusions concerning density, attenuation and preparation temperature influence on these specimens. These comparisons and correlation of methods, allow a better characterization of such important materials.

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1. Introduction

Acoustic properties of porous materials represented an important research objective during the last decades. From the pioneering works of Biot [1, 2] which are dedicated mainly to porous materials saturated with fluids of comparable densities, many other specialists were involved in such researches, with two main directions: audible frequency-range with obvious technical and architectural applications and high frequency range, have various applications among which the biomedical ones. From the first category, the study [3] has applications in sea-bed characterization.

A new macroscopic theory of acoustic wave propagation through porous media, valid at high frequencies, is presented in [4], which explains the occurrence of a slow compressional wave. The theory is experimentally verified for an artificial rock saturated with water [5]. A plane-wave analysis derives expressions for the slowness, attenuation, and energy velocity vectors, and quality factor for homogeneous viscoelastic waves. The slow wave is proven to have an anomalous polarization behavior [6]. The method of acoustical holography is used in [7] to measure the reflection coefficient of a porous layer at oblique incidence.

Ultrasonic attenuation measurements are used in [8] to determine the viscous characteristic length of an air-filled material. A model based on the systems theory is used in [9] to estimate propagation characteristics of sound in porous media. Nonlinear dynamic equations introduced by Biot to model porous media are revised and a mathematical model of the physical nonlinearity is established in [10]. Expressions for the viscosity correction function, density, compressibility, and propagation constant, are obtained in [11] for a rigid frame porous medium whose pores are prismatic with fixed cross-sectional shape having variable pore size distribution.

Surface waves above porous layers between 1.8 and 6 mm of plastic foams, saturated by air, at ultrasonic frequencies are investigated in [12]. Acoustical characterization of absorbing porous materials through transmission measurements in a free field is presented in [13]. A theory of compressional and shear wave propagation in consolidated porous rocks is developed in [14] by extending ideas already introduced in connection with unconsolidated marine sediments. For thin bead layers saturated by air, a pole of the reflection coefficient related to a trapped mode inside the layer and a surface wave in air is predicted in [15]. Acoustic wave propagation in porous medium, which is assumed in [16] to have a rigid frame, so that the propagation takes place in the air which fills the material. In [17] is presented the application of a simple model for the prediction of the acoustic properties of porous granular media with some assumed pore geometry and pore size distribution close to log-normal. One of the first biomedical studies of the bone as a porous medium is presented in [18] with the objective of proving if scattering alone may cause such a high attenuation as that observed in calcaneus. A water-saturated porous cylinder is tested in a shock tube. Agreement was found between the experimental data and the two-dimensional modeling of the shock tube which was based on Biot's theory in [19]. A temporal model of

the direct and inverse scattering problem for the propagation of transient ultrasonic waves in a homogeneous isotropic slab of porous material having a rigid frame is investigated in [20]. The porous medium is modeled via Biot's theory and the scattering by a single pore is characterized from the definition of a scattering matrix. A general set of time-domain equations describing linear sound propagation in a rigid-frame gas-saturated porous medium is derived in [21].

2. Experimental

2.1 Powder preparation

The Hap ceramic powder was prepared (Ca/P molar ratio: 1, 67) using Ca $(NO_3)_2 \cdot 4H_2O$ and P_2O_5 by a simple sol-gel approach. A designed amount of phosphoric pentoxide (P_2O_5, Merck) was dissolved in absolute ethanol to form a 0.5 mol/l solution. A designed amount of calcium nitrate tetrahydrate was also dissolved in absolute ethanol to form a 1.67 mol/l solution [22-23]. The mixture was stirred constantly for 24 h by a mechanical stirrer, allowing the reaction to complete at ambient temperature. A transparent gel was obtained. The gel was dried at 80^0C for 24h in an electrical air oven. The dried gels were individually heated at a rate of 5^0C/min up to 600^0C (HAp-600), 800^0C (HAp-800) and 1000^0C (HAp-1000). The sintered powders were ball milled at 100 rpm to get fine powders.

2.2. Powder characterization

The samples were characterized for phase content by X-ray diffraction (XRD) with a Bruker D8-Advance X-ray diffractometer in the scanning range $2\theta = 20 - 70$ using $CuK_{\alpha 1}$ incident radiation. An estimation of crystallite sizes was done from the width of the diffraction lines using the Scherrer formula.

The experimental layout consists of two air-coupled ultrasonic transducers mounted coaxially and face to face (Fig. 1-4). The distance between the two transducers has been selected such that diffraction of ultrasonic waves around the samples is minimised, yet allowing all signals to be determined in the same time interval, so 60 mm have been selected (Fig. 2).

The samples have been slightly pressed between two hard paper diaphragms mounted in two teflon discs which are kept parallel by two screws (Fig. *3* and Fig. *4*). Expecting a high attenuation of the ultrasonic signals in air, a relatively low frequency burst signal has been selected.

Fig. 1. General view of the experimental setup

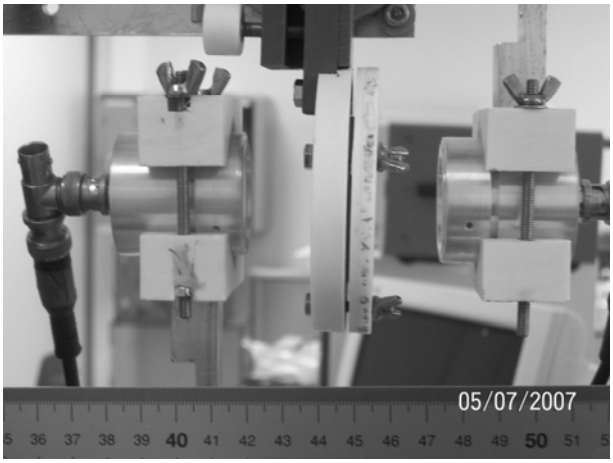

Fig. 2. Side-view of the specimen inserted between the two air-coupled transducers.

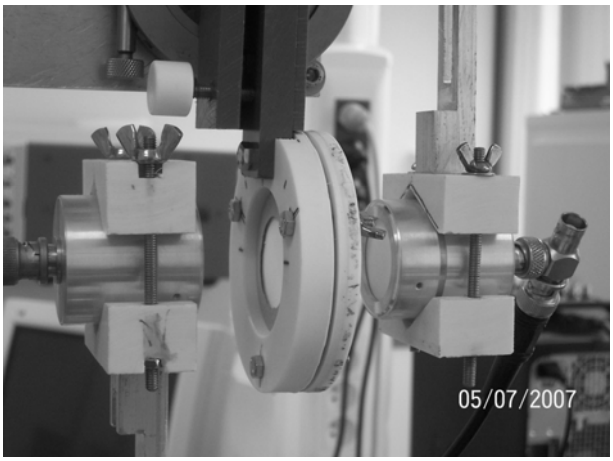

Fig. 3. View of the transmission side of the propagation path

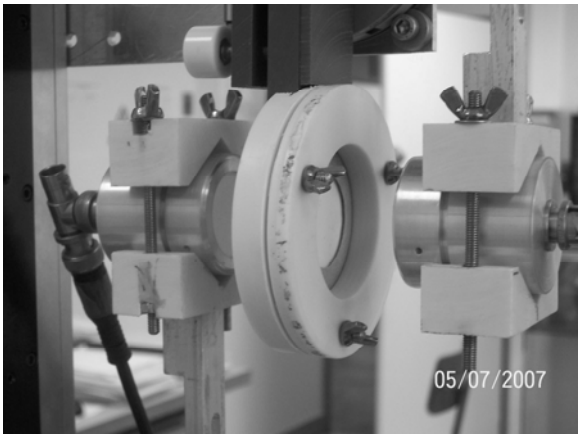

Fig. 4. View of the incident and reflection side of the propagation path

3. Results and discussions

The micro-structure of the ceramic powders prepared by sol-gel synthesis is strongly affected by the sintering temperature [24-27]. In Figure 5 one can observe also that the HAp peaks become narrower as the sintering temperature increases from 600 to 1000 ^{o}C, that suggest an increase of the crystallite size, and/or of the lattice ordering. The determination of the average crystallite size by XRD method is based on the Scherrer equation:

$$D_{crystallite} = K\lambda/B\cos\theta$$

where $D_{crystallite}$ is the averaged length of coherence domains (that is of perfectly ordered crystalline domains) taken in the direction normal to the lattice plane that corresponds to the diffraction line taken into account, B is the line broadening due to the small crystallite size, λ is the wavelength of X-rays, θ is the Bragg angle, and K a constant related to crystallite shape (0.9) and to the definition of B (integral breadth or full width at half maximum).The analysis was performed on the basis the full width at half maximum of the (222) reflection of HAp ($2\theta \approx 46.7^{o}$). A corundum reference sample (NIST SRM 1976) was used in order to correct for the instrumental line width.

Besides hydroxylapatite, a very small amount of CaO was identified in the powder treated at 800 ^{o}C [23], that increases after heat treatment at 1000^{o}C. The concentration of CaO at 800^{o}C is around 0.4 wt % as obtained by Rietveld quantitative phase analysis. With the increase of the calcination temperature HAp would have started losing hydroxyl groups forming various phosphates. This is in agreement with those reported earlier by Kutty [28] and Skinner et al [29]. The proposed reaction is [22]:

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow[H_2O]{} 3Ca_3(PO_4)_2 + CaO + H_2O$$

The relative intensities of HA were well fitted so that the unit cell structure is very close to the ideal one. The following results were obtained: D≈32 (±0.6) nm at 600 ^{o}C, D=114 (±4) nm at 800 ^{o}C and D= 300 (±15) nm at 1000^{o}C. The concentration of CaO is around 0.4 wt %, and increases to 1.8 wt % at 1000^{o}C.

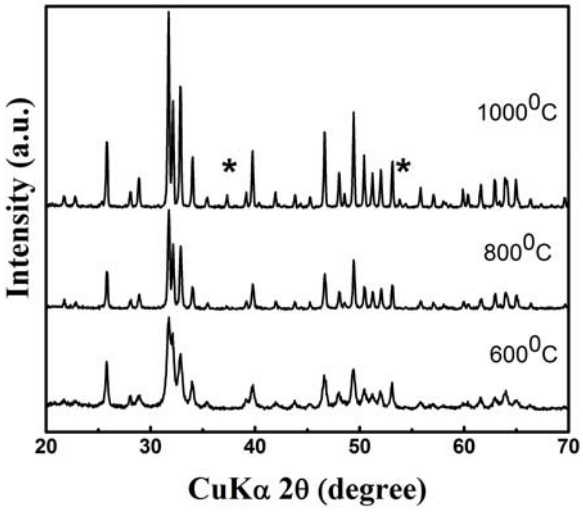

Fig. 5. The X-ray diffraction patterns of the powder after heat treatment at 600^{0}C, 800^{0}C and 1000^{0}C (= CaO).*

Expecting a high attenuation of the ultrasonic signals in air, a relatively low frequency burst signal has been selected [30]. The reference signal sent as a burst, is received as indicated in figure 6. It is a relatively long burst because it was intended to keep a narrow frequency bandwidth, around 450 kHz (Fig 7).

The hydroxyapathite samples which were tested were 40 mm in diameter, thickness 4, 3.2 and 2.7 mm respectively. Their sintering temperatures are indicated in Table 1.

Table 1. Sample properties

Sample	Sintering temperature (ºC)	Mass density (g/cm^3)	C_{11} (GPa)
HAp-600	600	0.4795	2.3
HAp-800	800	0.5505	1.8
HAp-1000	1000	0.6472	1.5

The received signals at the same scale and same time origin are presented in Fig 8.

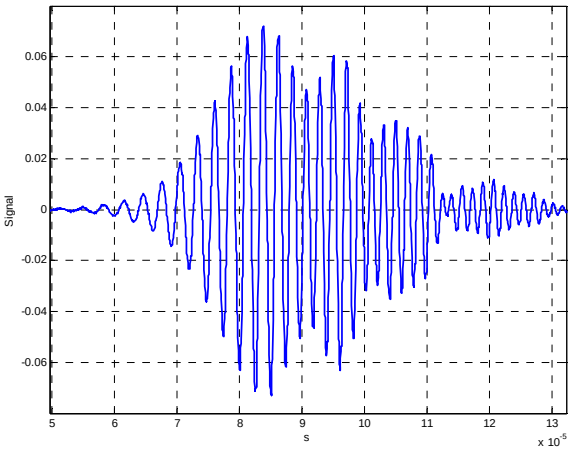

Fig. 6. Reference signal in direct propagation

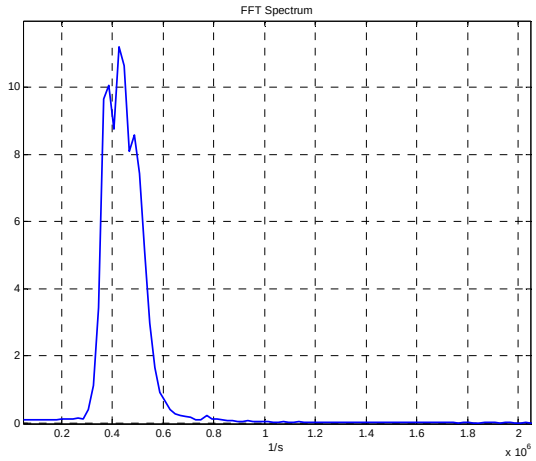

Fig. 7. Frequency spectrum of the incident signal

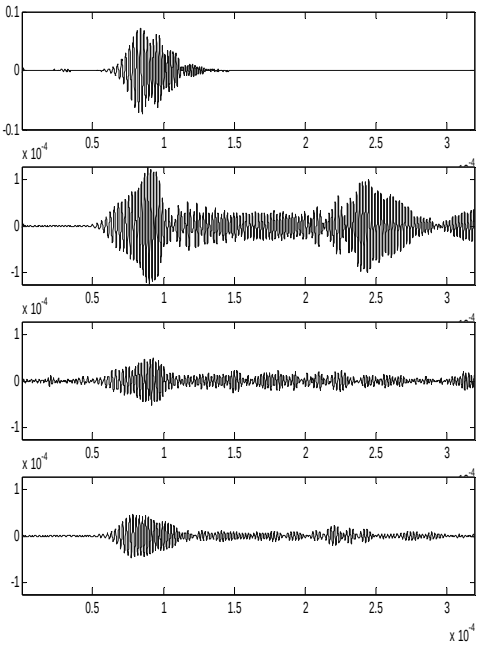

Fig. 8. Time history of the reference signal (a) and of the three samples (b, c, d). (Abscissa in s).

Using these time signals and samples data, the following velocities in the three samples have been determined: c_1=2200 m/s, c_2=1800 m/s, c_1=1500 m/s, respectively. These values correspond to the elastic coefficients of the equivalent homogeneous material indicated in the last row of Table 1.

The maximum levels of signals after transmission, relative to the maximum incident amplitude are 1.5e-3 (a), 6.25e-4 (b) and 5.75e-4 (c) respectively.

The long trailing signals bear information about internal reflections in the samples, which are influenced by the porosity. The first sample (HAp-600) has a peculiar behavior in the transmitted signal. After a trail lasting more than 0.12 ms, a large amplitude signal appears with opposite gradient compared to the first transmitted burst. It can be attributed to the specular reflection of the transmitted signal back and forth between the sample and the receiver transducer, but this phenomenon is not repeated for the next two samples.

4. Conclusions

The sol-gel method provides a simple route for synthesis of hydroxyapatite nanopowder. The crystalline degree and morphology of the obtained nanopowder depend on the sintering temperature.

The experimental measurements of ultrasonic bursts transmitted through three sintered discs of hydroxyapatite are presented. The time history of the signals allowed estimation of one elastic constant and signal attenuation as function of preparation conditions. More detailed experiments are however required to predict with some degree of confidence, the porosity of the material and this is the object of ongoing researches.

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