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Journal of Non-Crystalline Solids 351 (2005) 2945–2950
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

The modulus formalism used in the dielectric analysis of hydroxyapatite and calcium phosphate with titanium formed by dry ball milling

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Available online 25 July 2005

Abstract

The bioceramic hydroxiapatite ($Ca_{10}(PO_4)_6(OH)_2$ – HAP) is the main mineral constituent of teeth and bones with excellent biocompatibility with hard and muscle tissues. These materials exhibit several problems of handling and fabrication, which can be overcome by mixing them with a suitable binder. The dry milling process of fabrication of HAP presents the advantage that melting is not necessary and the powder obtained is nanocrystalline. The HAP has been obtained from three different experimental procedures (HAPA: $Ca(H_2PO_4)_2 + Ca(OH)_2$; HAPB: $Ca(H_2PO_4)_2 + CaCO_3$ and HAPC: $CaHPO_4 + CaCO_3$). In the reactions HAPA and HAPB the hydroxiapatite phase was obtained after 5, 10 and 15 h of milling and after 15 h in the reaction HAPC. In order to improve the mechanical properties of HAP, calcium phosphate ceramics with titanium (CaP–Ti) has been prepared by dry ball milling ($Ca(H_2PO_4)_2 + TiO_2$). The calcium titanium phosphate phase, $CaTi_4P_6O_{24}$, was obtained. The dielectric study in function of frequency, at constant temperature of the ceramics, was made using the *Modulus* formalism ($M^* = 1/\varepsilon^*$) and a distribution of relaxation times was observed. The values of the dielectric constant of the ceramics measured at room temperature are between 5.04 (CaP–Ti_5H) and 13.70 (HAPA_10H). The structure of the samples was studied by X-ray diffraction.

PACS: 81.05.Je; 81.05.Mh; 81.20.Ev; 81.07.Bc

1. Introduction

Hydroxyapatite, (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is widely used in reconstructive orthopaedic and dental surgery of bone gaps and as surface coatings [1,2]. The human bone is formed basically by an organic phase and other mineral phase. In the organic phase, the fibres of collagen serve as a matrix for the precipitation of HAP, determining the structure of the crystals. The collagen gives to the bone its elastic resistance. The mineral phase is formed by HAP. The space group of HAP (which is a non-ferroelectric material) has been determined by X-ray diffraction methods to be $P6_3/m$, the same as flourapatite, but theoretical considerations suggests the space group of HAP to be $P6_3$ [3].

The synthesis of HAP and ceramic system with titanium (CaP–Ti) was developed because titanium oxide (TiO_2) is a strengthening agent thoroughly used, due to his superb force and fracture toughness [4]. Titanium alloys have already been used with some success in several bioimplant applications. However, they can suffer certain disadvantages, such as poor osteoinductive properties and low corrosive-wear resistance. Attempts to

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doi:10.1016/j.jnoncrysol.2005.04.082

overcome the first of these drawbacks have involved coating the metal with hydroxyapatite (HAP). Since TiO_2 coatings are also known to be effective as chemical barriers against the in vivo release of metal ions from the implants, a double layer of HAP–TiO_2 coating on titanium alloys with HAP as the top layer and a dense TiO_2 film as the inner layer should possess a very good combination of bioactivity, chemical stability and mechanical integrity [5]. In this work we report the application of mechanical alloying technique to produce HAP and ceramic with titanium starting from elementary powders. The advantage of this procedure remains on the fact that melting is not necessary and the powders formed are nanocrystalline [6–8]. It can also be easily shaped (injected, compacted, etc.) into any geometry. Recently Silva et al. [9,10] studied the dielectrics properties of the HAP deposited in alumina formed thick films obtained by the screen-printed method. These properties are important in view of possible applications of these films in the fabrication of biological sensors and the dielectric properties of HAP are of interest because electromagnetic fields have been shown to accelerate healing in bone fractures [11].

In this work the structural properties of the ceramics prepared by ball milling are discussed and related with the dielectric properties.

2. Experimental procedure

The mechanical alloying has been used successfully to produce nanocrystalline powders of hydroxyapatite (HAP) using three different experimental procedures:

$$3Ca(H_2PO_4)_2 + 7Ca(OH)_2 \xrightarrow{\text{IMPACTS}} Ca_{10}(PO_4)_6(OH)_2 + 12H_2O \quad (1)$$

(HAPA)

$$3Ca(H_2PO_4)_2 + 7CaCO_3 \xrightarrow{\text{IMPACTS}} Ca_{10}(PO_4)_6(OH)_2 + 5H_2O + 7CO_2 \quad (2)$$

(HAPB)

$$6CaHPO_4 + 4CaCO_3 \xrightarrow{\text{IMPACTS}} Ca_{10}(PO_4)_6(OH)_2 + 2H_2O + 4CO_2 \quad (3)$$

(HAPC)

Commercial oxides: $Ca(H_2PO_4)_2$ (Aldrich, 85%); $Ca(OH)_2$ (Vetec, 97% with 3% of $CaCO_3$); $CaHPO_4$ (Aldrich, 99%) and $CaCO_3$ (Aldrich, 99%) were used in the HAP preparation.

To produce nanocrystalline powder of calcium phosphate with titanium (CaP–Ti) it was used $Ca(H_2PO_4)_2$ (Aldrich, 85%) and TiO_2 (BDH, 98%).

$$Ca(H_2PO_4)_2 + TiO_2 \xrightarrow{\text{IMPACTS}} CaP\text{–}Ti + H_2O \quad (4)$$

(CaP–Ti)

For all the reactions the material was ground on a Fritsch Pulverisette 6 planetary mill with the stechiometric proportionality between the oxides given in reactions (1)–(4). Milling was performed in sealed stainless steel vials balls in air. The ratio between powders to the ball mass used in all the reactions was near 1/6. To avoid excessive heat the milling was performed in 60 min milling steps with 10 min pauses. Mechanical alloying was performed during 5, 10 and 15 h for all the reactions.

The X-ray diffraction (XRD) patterns data were obtained at room temperature using powder samples in an X'Pert MPD Philips diffractometer (with K_α radiation, $\lambda = 1.54056$ Å) at 40 KV and 30 mA. Intensity data were collected by the step counting method (step 0.05°, and a time per step of 4 s) in the range 2θ (20 60°).

For the electrical measurements, the samples were prepared as discs of 5×10^{-3} m diameter and about 10^{-3} m of thickness, with gold electrodes on the opposite sides of the samples. The modulus function $M = j\omega C_c Z = M' + jM''$ and the complex permittivity $\varepsilon^* = M^{*-1} = Y/(j\omega C_c) = \varepsilon' - j\varepsilon''$ measurements were carried out at room temperature, in the frequency range of 100 Hz–100 kHz using a *SR850 DSP Lock-In Amplifier*, in the typical lock-in configuration, measuring the 'in-phase' (V_f) and the 'quadrature' (V_q) components of the output signal [12].

3. Results and discussion

Figs. 1–4 present the XRD powder pattern of reactions (1)–(4) (HAPA, HAPB, HAPC and CaP–Ti) with

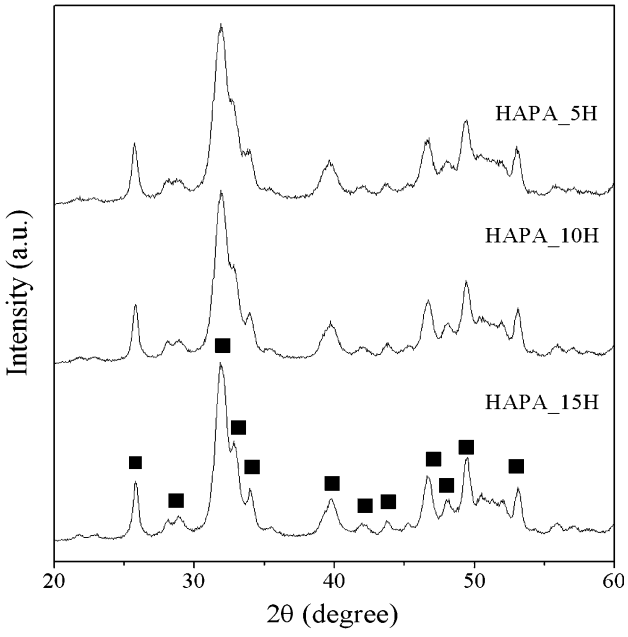

Fig. 1. XRD patterns of reaction HAPA milled for 15 h. HAP (■).