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# Ceramic materials on the basis of hydroxyapatite and tricalcium phosphate

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**Abstract**

Studies on mono-, bi-, or triphase ceramic materials consisting of hydroxyapatite (HAp), β tricalcium phosphate (β-TCP), α tricalcium phosphate (α-TCP) and CaO are reported. The synthesis of powder precursors were carried out at Ca/P molar ratios below, equal or over 1.67 and at pH of reaction environment equal 5, 6 or 11. The microstructure, phase composition and density of the uniaxially or isostatically compacted samples after sintering at 1250°C were analysed using SEM, QXRD, FTIR, EDS and porosymetric techniques. Elastic properties of the investigated materials were determined by the ultrasonic method. The relationship between the precipitation conditions and the properties of final calcium phosphate ceramics was confirmed. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

*Keywords:* Hydroxyapatite (HAp); Tricalcium phosphate (TCP); Ultrasonic method; Elastic properties

## 1. Introduction

Previous studies on calcium phosphate ceramics cover the production, biological evaluation as well as their clinical applications [1–6]. Non-destructive ultrasonic measurements allowed the material constants as well as degree of their anisotropy and uniformity to be determined [7,8].

The aim of the present work was to find the effect of the synthesis conditions on microstructure, phase composition and the elastic properties of calcium phosphate ceramics.

## 2. Experimental details

Eight precipitates of calcium phosphates with various Ca/P molar ratios were prepared by slow addition of $H_3PO_4$ solution to a suspension $Ca(OH)_2$. Four precipitates were produced at Ca/P ratio below, three above, and one at strictly stoichiometric ratio corresponding to hydroxyapatite—$Ca_{10}(PO_4)_6(OH)_2$. The pH of reaction environment (pH = 5, 6 or 11) was controlled by use of ammonium aqueous solution (1:1). This was another variable parameter determining the conditions of synthesis.

The precipitates were aged for 48 h at room temperature, filtered, dried at 90°C and ground in a rotating-vibrating mill. The powders were calcined at 800°C for 3 h, mixed with 5% solution of polyvinyl alcohol and uniaxially compacted under 125 MPa to form the rectangular shape samples 70×3.5 mm. The second group of the compacts was obtained by initial uniaxially pressing under 78 MPa followed by isostatic repressing under 350 MPa.

Sintering was performed in air at 1250°C with 2 h soaking time. The rate of temperature increase was $100°C\,h^{-1}$ while the cooling was carried out in the furnace. The samples prepared from the commercial hydroxyapatite powder produced by Merck were simultaneously sintered as reference.

## 3. Methods

The Ca/P molar ratio of the precipitates was measured by chemical wet method, i.e., by $KMnO_4$ titration for Ca and phosphomolybdate technique for phosphate. The grain size distribution of calcined powders was determined using an X-ray grain size analyser, Sedigraph 5100. The green compact densities was

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measured from the weight and size of the samples while the bulk density of the sintered samples was measured by helium pycnometer, ACCU-PYC 1330. X-ray diffraction (Philips) and FTIR spectrometry (Digilab FTS-60 V) were used to determine the phase composition of the sinters. The fracture surfaces were investigated by SEM (Jeol-5400). The carbon concentration in the samples containing CaO was estimated by EDS (Link AN 10 000).

Non-destructive ultrasonic investigations measuring in the velocity of the longitudinal wave propagation, were carried out using a material tester MT-541 (Unipan, Poland) with ultrasonic transducers having a frequency $f = 0.5$ MHz. The material constants: Young's modulus, $E$, and modulus of rigidity, $G$, were determined. The propagation velocity of the longitudinal ($f = 10$ MHz) and transverse ($f = 2$ MHz) waves within the samples were measured (the apparatus UZP-1, Inco,Poland). The condition of a three dimensional body is fulfilled at the indicated frequencies [7].

## 4. Results and discussion

The precipitates produced in consecutive synthesis, depending on the ratio of initial reagents and pH of reaction environment show variable Ca/P molar ratio in the range of 1.50 ± 0.01 to 1.76 ± 0,01 (Table 1).

The calcined powders from 1 to 8 reveal similar grain size distribution, with the average grain size 7–9 µm. Different pressing ability of the individual powders and the method of their compaction influence the green body densities (48–58% of theoretical density for uniaxially pressed and 58–65% for isostatically repressed samples). After sintering, relative densities of the sinters increase to 99.4% and 99.8% for the uniaxially and istostatically compacted samples, respectively. The relative densities of the investigated materials are presented in Fig. 1.

Table 1
Ca/P molar ratio of the starting powders

| Powder number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | M |
|---|---|---|---|---|---|---|---|---|---|
| Ca/P molar ratio | 1.50 | 1.51 | 1.62 | 1.63 | 1.66 | 1.67 | 1.70 | 1.76 | 1.64 |

M, commercial hydroxyapatite powder.

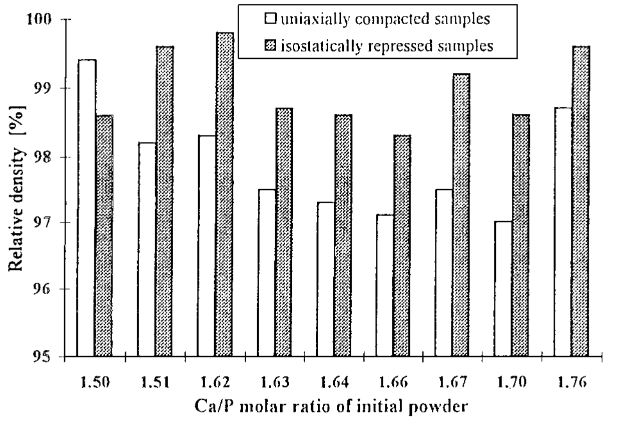

Fig. 1. Relative densities of the investigated materials after sintering at 1250°C.

Table 2
Phase composition of calcium phosphate materials after sintering at 1250°C.

| Sample number | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | SM |
|---|---|---|---|---|---|---|---|---|---|
| Hydroxy-apatite (wt %) | 0 | ~5 | ~60 | ~90 | ~95 | 100 | ~99 | ~98 | ~98 |
| TCP(wy%) | ~100<br>(β+α) | ~95<br>(β+α) | ~40<br>(β+α) | ~10<br>(β) | ~5<br>(β) | 0 | 0 | 0 | ~2<br>(β) |
| CaO(wt%) | 0 | 0 | 0 | 0 | 0 | 0 | ≥1 | ≥2 | 0 |

SX, material on the basis of the powder $X$, where $X = 1, 2, 3, 4, 5, 6, 7, 8,$ M.

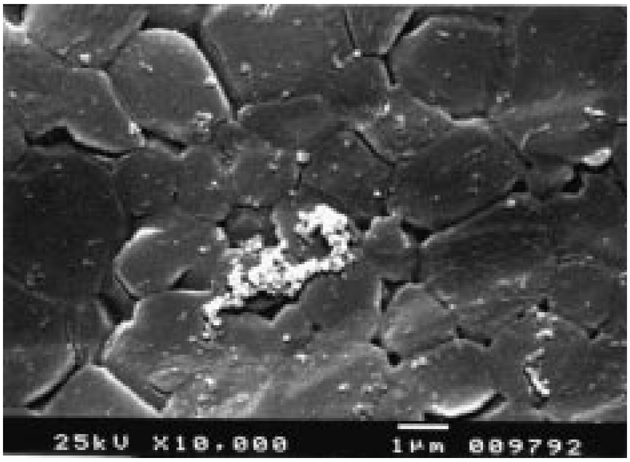

Fig. 2. SEM micrograph of material S-7 with the agregates of fine $CaCO_3$ crystals obtained from the precipitate with a Ca/P molar ratio = 1.70.

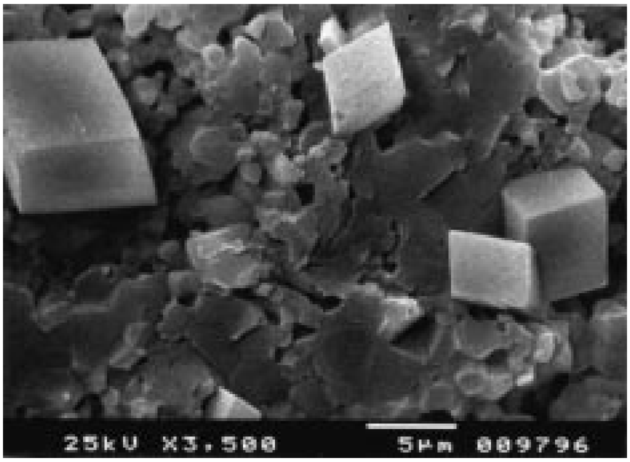

Fig. 3. SEM micrograph of material S-8 with well-shaped $CaCO_3$ crystals obtained from the precipitate with a Ca/P molar ratio = 1.76.

The QXRD and FTIR studies show a significant variability of phase composition (Table 2). A monophase hydroxyapatite ceramic was produced only from the precipitate with a Ca/P molar ratio = 1.67 (material S-6). The sinters obtained both from the commercial hydroxyapatite powder and from the precursor with a Ca/P molar ratio = 1.66 show after sintering the presence of 2 and 5 wt.%, β tricalcium phosphate, $\beta Ca_3(PO_4)_2$ (β-TCP), respectively (materials SM and S-5). As expected, the materials produced from the precipitates with Ca/P molar ratios of 1.70 and 1.76, apart from hydroxyapatite as a predominant phase, had CaO contents up to 2 wt.% [9]. Free calcium oxide constitutes a very undesirable impurity of the hydroxyapatite ceramics and in general it excludes the possibility to use such material in biological applications. CaO occuring on the fracture surfaces transforms in air to $Ca(OH)_2$ and subsequently to $CaCO_3$, as confirmed by SEM observations and EDS studies (Figs. 2 and 3).

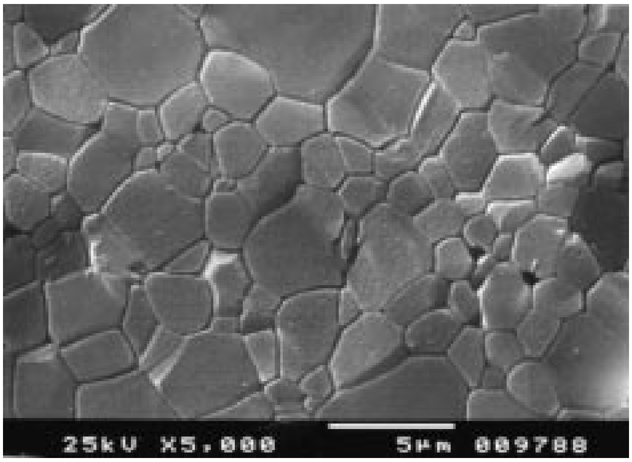

Fig. 4. SEM micrograph of monophase, hydroxyapatite material S-6 obtained from the precipitate with a Ca/P molar ratio = 1.67.

The microstructure of particular sinters differ strongly. Apart from the highly densified, non-porous samples produced at Ca/P ratios ≥ 1.63 (Fig. 4) the other three materials, obtained from the powders precursors with Ca/P molar ratios ≤ 1.62, contain pores of irregular shape. The differentiation in microstructure and density of the bodies reflects in the ultrasonic measurements: for samples uniaxially and isostatically compacted from the powder precursors with Ca/P molar ratios in the range of 1.62 ≤ Ca/P ≤ 1.70, the velocity of longitudinal ultrasonic wave was about 6.4 $km\,s^{-1}$ and 6.6 $km\,s^{-1}$, respectively (Fig. 5).

An anisotropy of longitudinal wave velocity was found and estimated as 6.6% for the uniaxially pressed samples and 4.1% for those isostatically repressed; this anisotropy is defined as: $A = 100\ (V_L - V_G)V_L$ (%), where $V_L$ and $V_G$ are wave velocities along the sample length and thickness, respectively. Isostatic compaction generally improves the degree of anisotropy and the uniformity of the investigated materials, which results in

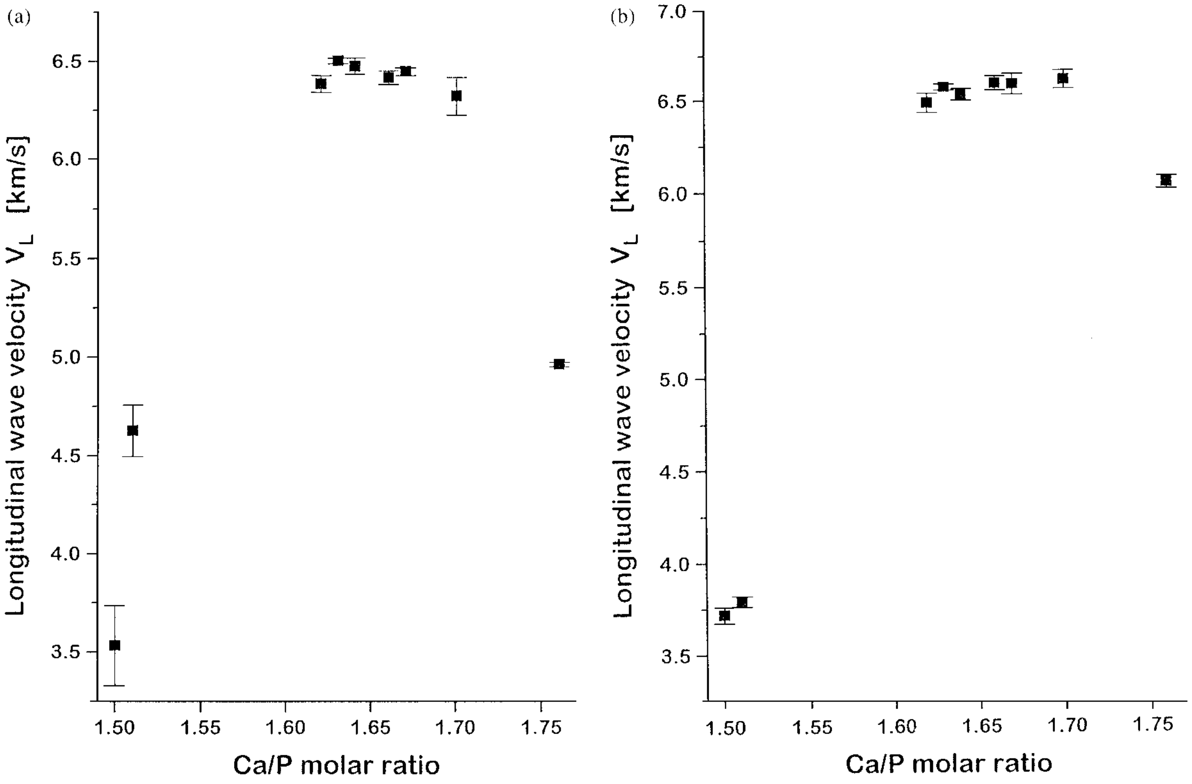

Fig. 5. Longitudinal ultrasonic ware velocity $V_L$: (a) uniaxially compacted samples; (b) isostatically repressed samples.

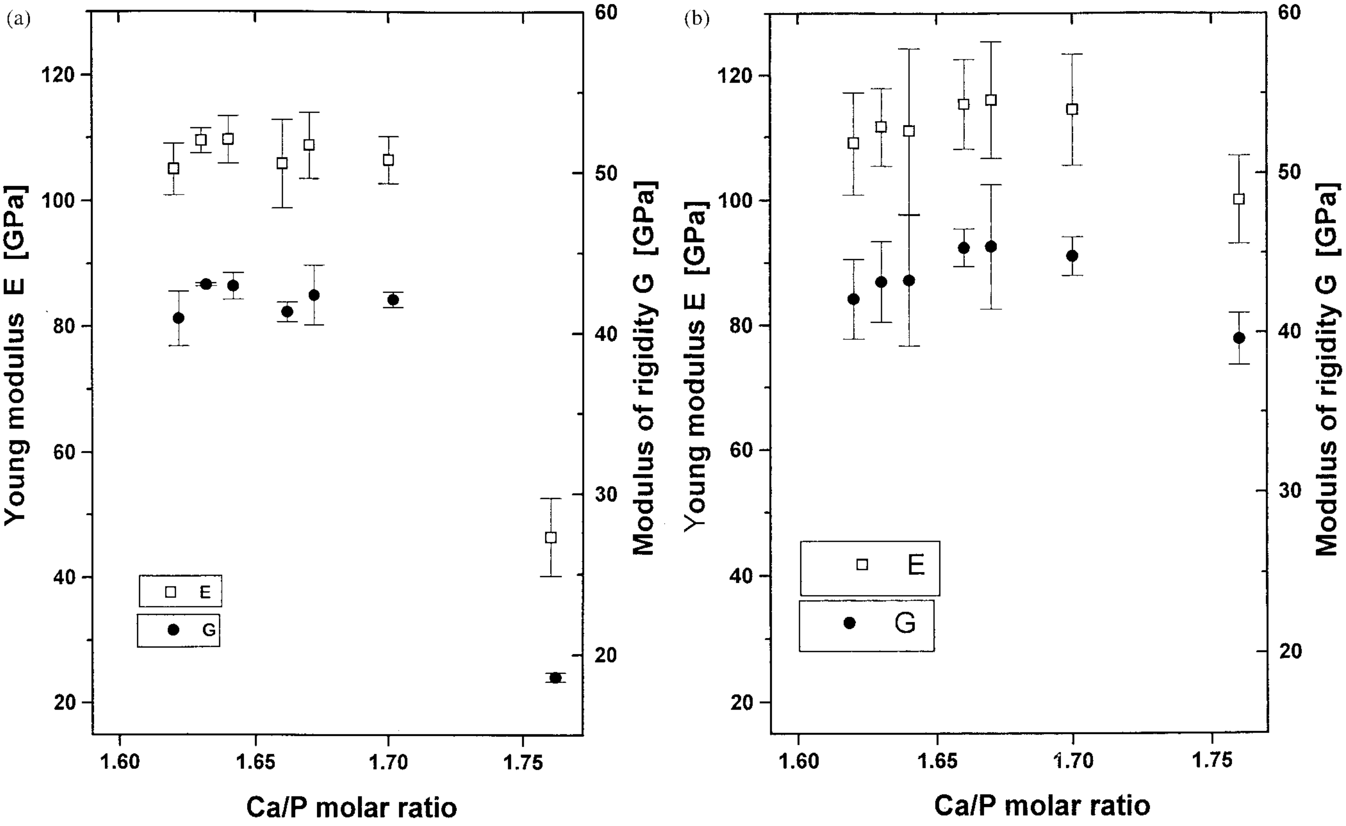

Fig. 6. Material constants: $E$, Young modulus; G, modulus of rigidity: (a) uniaxially compacted samples; (b) isostatically repressed samples.

the higher velocity of both longitudinal and transverse waves and in the higher bulk density. The material constants calculated for particular samples are given in Fig. 6.

The samples S-1 and S-2 produced both by uniaxial and isostatic pressing as well as pressed uniaxially samples S-8, after sintering at 1250°C effectively decrease the ultrasonic wave propagation velocity. The same samples reveal highly complex, non-uniform microstructure under SEM investigations.

The monophase hydroxyapatite materials after sintering at 1250°C with a soaking time of 2 h exhibit Young's modulus values of 109–116 GPa while their modulus of rigidity is 42–45 GPa.

## 5. Conclusions

Pressing ability depends on the powder preparation conditions. Compacts made of the starting powders with Ca/P molar ratio in the range of 1.50–1.76 show green body densities up to 58% of theoretical density for uniaxially pressed samples and up to 65% for those isostatically repressed.

The sinters, after firing at 1250°C are mono-, bi-, or triphase ceramics and consist of hydroxyapatite (HAp), β tricalcium phosphate (β-TCP), α tricalcium phosphate (α-TCP) and CaO. CaO occuring on the fracture surfaces transforms in air to $CaCO_3$ which forms well-shaped crystals.

The monophase HAp material was obtained only from the precipitate characterised by a Ca/P molar ratio = 1.67.

Ultrasonic wave propagation proved to be an efficient and non-destructive method of characterisation for the calcium phosphate ceramics from the point of view of their uniformity and anisotropy. The correlation between microstructure and the ultrasonic wave velocity in the case of calcium phosphate materials was confirmed. The isostatically repressed samples produced from the starting powders with Ca/P molar ratios in the range of 1.62–1.70, after sintering at 1250°C, gave dense sinters, with less than 4% anisotropy: the velocity of longitudinal ultrasonic wave for these materials is about 6.6 km $s^{-1}$.

The monophase dense HAp ceramics are characterised by having Young's moduli in the range of 109–116 GPa and moduli of rigidity 42–45 GPa.

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