



# Characterization of calcium phosphate apatite with variable Ca/P ratios sintered at low temperature

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## Abstract

The characterization of calcium phosphate apatite with variable Ca/P ratios synthesized by the hydrolysis method and sintered at 1073 K has been investigated. When the precipitate powders are sintered at 1073 K for 4 h, the major phase observed is hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HA), and the minor phases are rhenanite ( $\text{NaCaPO}_4$ ) and  $\beta$ -tricalcium phosphate ( $\beta$ -TCP,  $\beta\text{-Ca}_3(\text{PO}_4)_2$ ). The shrinkage increased from 5.15 to 21.00%, and the grain size of the pellets also increased from 31 to 348 nm along with the ratios of Ca/P. The TEM microstructure identified with SAED and EDS analyses show that an amorphous phase of  $\text{NaCaPO}_4$  is present at the grain boundaries of HA, which promotes the sintering of calcium phosphate, but reduces the mechanical properties.

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## 1. Introduction

Solid implants consisting of synthetic materials called bio-substitute (or bone substitute) implants are used to reconstruct bone and support it mechanically, in order to minimize complications [1]. Hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , hereafter HA] powders were obtained using wet synthesis, and the particles ranged from the submicronic to the nanometric range, with a large surface area which provided enhanced densification and better bioactivity than that with coarser crystallites [2–4]. The dehydration reaction of HA, causing loss of the OH functional group, occurred when

sintering was performed at an elevated temperature. This reaction also caused some HA decomposition into  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP),  $\beta$ -tricalcium phosphate ( $\beta$ -TCP), and tetracalcium phosphate (TTCP) [5].

Sintering behavior and mechanical properties of magnesia (MgO)-doped HA/ $\beta$ -TCP ceramics have been investigated by Ryu et al. [6]; they indicated that a high density without phase transformations of  $\beta$ -TCP was obtained when samples were heated to 1573 K. Compared to conventional plasma-sprayed HA coating, the HA yttria-stabilized zirconia/Ti–6Al–4V composite coating has superior mechanical properties [7]. The calcium–phosphate-based biomaterials were used as bone substitutes, and it was found that different forms such as granules, cements blocks and composites, or coatings on orthopedic and dental implants have medical and dental applications [8]. HA deposition onto titanium with a new coincident process provides biological responses for a well-adhered layer [9]. Carayon and

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Lacout [10] investigated the Ca/P atomic ratio of the amorphous phase in plasma-sprayed hydroxyapatite coatings, and pointed out that during the plasma spraying process, the thermal decomposition of HA products generated tricalcium phosphate (TCP), tetracalcium phosphate (TTCP), calcium oxide (CaO), oxyhydroxyapatite ( $O_x$ HA) and a molten phase. The 3D printing of bone substitute implants used  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) and a material similar to the 45S5 Henschglass<sup>®</sup> as raw materials and sintering was performed at 1323 K. XRD analysis of this experiment revealed that the phase of  $\beta$ -TCP disappeared while two other phases occurred:  $CaNaPO_4$  and  $CaSiO_3$  [1]. Moreover, Raynaud et al. [11] studied the calcination and sintering of calcium-deficient HA ( $Ca$ -def HA,  $Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$ ,  $0 \leq x \leq 1$ ) and reported that the particle coalescence occurred without densification when temperatures were lower than 973 K.

On the other hand, the effect of the Ca/P ratio on the properties of calcium phosphate apatite or HA have been investigated by several researchers [11–18]. Ślósarczyk et al. [12] pointed out that when using the wet process, with calcium oxide (CaO) and phosphoric acid ( $H_3PO_4$ ) as initial materials, the Ca/P molar ratio of the initial precipitates was determined by the Ca/P molar ratio of reactants and the pH of the reaction environment. When the precipitates sintered at 1523 K, monophasic, biphasic, or triphasic ceramics consisting of HA,  $\beta$ -TCP,  $\alpha$ -TCP and CaO were obtained. Moreover, Raynaud et al. [13] used diammonium phosphate  $(NH_4)_2HPO_4$  and calcium nitrate as the initial materials for synthesizing the single phase of calcium phosphate apatite ( $Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$ ) with variable Ca/P atomic ratios ranging from 1.5 to 1.667 ( $0 \leq x \leq 1$ ) prepared using the wet method. When outside this compositional range, the powders were biphasic mixtures composed of calcium phosphate apatite and  $CaHPO_4$  (Ca/P < 1.5) or  $Ca(OH)_2$  (Ca/P > 1.667).

Amorphous calcium phosphate was precipitated at 293 K from highly supersaturated solutions with compositions of Ca/P ratios between 1.5 and 2.0 at pH=11, as also reported by Kim et al. [14], who demonstrated that a higher Ca/P ratio of the starting solution resulted in faster crystallization of HA. The effect of Ca/P ratios (1.57, 1.67 and 1.87) on the densification behavior of nanocrystalline HA prepared by a chemical precipitation route was investigated by Ramesh et al. [15]. The use of  $Ca(NO_3)_2$  and  $NH_4H_2PO_4$  as the initial materials for the synthesis of nanocrystalline HA powders via a precipitation method with the acid of ultrasonic irradiation was studied by Cao et al. [16], who demonstrated that the crystallinity of HA nanopowders was influenced by the precipitation temperature, Ca/P ratio, concentration of  $Ca^{2+}$  and ultrasonic power. The aqueous based sol-gel route has been employed to synthesize HA powders with nanorod-like morphology and controlled size. It has been found that variation in the molar concentration in the initial sol and the pH of the reaction environment can be used to control the Ca/P ratio of the crystallite size and surface morphology of the final product HA powders [17]. The use of  $Ca(NO_3)_2 \cdot 4H_2O$  and  $(NH_4)_2HPO_4$  as the initial materials, and employing a homogeneous hydrothermal precipitation process with acetamide to synthesize the Ca-def HA whiskers with different Ca/P ratios was reported by Zhang et al.

[18]. They found that the whiskers had high crystallinity for a Ca/P ratio greater than 1.54, with a mean length of 79–113  $\mu m$  and an aspect ratio of 85–103. Moreover, the Ca/P ratios of whiskers greater than 1.54 are morphologically stable at temperatures below 1473 K, with minor TCP appearance after heat-treatment at 1073 K.

Although many studies on sintered HA and its relative properties have been conducted, the low temperature sintering and characterization of calcium phosphate apatite powders with variable Ca/P ratios synthesized by the hydrolysis method have not been studied in detail. In the present study, in order to understand the characterization of calcium phosphate apatite powders with various Ca/P ratios and sintering at low temperature, the pellets were sintered at 1073 K for 4 h and studied in detail using X-ray diffraction (XRD), density and linear shrinkage measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy-dispersive spectrometry (EDS). This investigation seeks to: (1) study the crystalline phases of freeze-dried calcium phosphate apatite powders with variable Ca/P ratios; (2) investigate the effect of variable Ca/P ratios on the phase development of calcium phosphate apatite powders after sintering at 1073 K for 4 h; (3) study the effect of variable Ca/P ratios on the variation of density and linear shrinkage for calcium phosphate apatite powders sintered at 1073 K for 4 h; and (4) observe the microstructure of sintered calcium phosphate apatite pellet samples.

## 2. Experimental procedure

### 2.1. Sample preparation

The initial materials were calcium hydrogen phosphate dehydrate ( $CaHPO_4 \cdot 2H_2O$ , DCPD; purity  $\geq 98.0\%$ , supplied by Riedel-de Haën, Germany) and  $CaCO_3$  (purity  $\geq 98.5\%$ , supplied by Riedel-de Haën, Germany), which were mixed with Ca/P ratios between 1.0 and 1.80 (greater than that of 1.67 for HA), poured into a 2.5 M NaOH solution (pH=13.6, purity  $\geq 90.0\%$ , supplied by Showa, Japan) in a volume of 500 mL, and finally mixed in a high-speed agitator at 348 K for 1 h. The reaction was terminated after hydrolysis by cooling in ice water. The HA aggregates were filtered and then rinsed in deionized water five times. The synthetic products were dried at 333 K and then ground for use.

The synthesized HA powders were used as produced, without an additive or binder. Each sample used 0.25 g of HA powder that was uniaxially cold-pressed at 23 MPa to form a 10 mm  $\varnothing$  pellet.

All uniaxially cold-pressed pellets were sintered in air at 1073 K for 4 h with a heating rate of 2 K/min from 298 to 1073 K and held for 4 h. After sintering, the samples were cooled to room temperature in a furnace at a rate of 5 K/min.

### 2.2. Sample characterization

For phase determination and line broadening, XRD analyses were conducted on dried powders and sintered samples by using an X-ray diffractometer (Model D-Max/IIIIV, Tokyo,

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