

## Crystal and Phase Evolution of Sol-Gel Derived Hydroxyapatite Synthesis with Various Ca/P Ratios

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### 1- Introduction

Hydroxyapatite (HAp) due to biocompatibility and chemical and biological affinity with bone tissue is used for orthopedic implants, dental implants, oral and maxillofacial surgery and as a coating film on metal or alloy implants. Hydroxyapatite has been used as hard tissue in the form of coatings or bone substitutes. Porous HAp ceramic is used as a cancellous bone graft substitute material in non-load bearing situations. However, dense HAp ceramic is used in load bearing situations such as artificial joints. Despite all of these advantages, the application of HAp has been restricted by its low toughness and low flexural strength. The mineral component of bone and teeth consists primarily of non-stoichiometric and highly substituted hydroxyapatite in poorly crystalline or nearly amorphous forms. The impurity components that are at significant levels include sodium, potassium, magnesium, and strontium substituting for calcium, carbonate for phosphate and chloride and fluoride for hydroxyl ions. Methods that have been used for synthesis of nano or micro HAp powder include chemical precipitation followed by spray drying, hydrothermal treatment, sol-gel, microemulsion techniques, precipitation from complex solutions followed by microwave heating, wet chemical methods incorporating a freeze drying step, mechanochemical synthesis and electrodeposition. Sol-gel approaches have attracted much attention recently because of the well-known inherent advantages of these methods such as homogeneous molecular mixing, low processing temperatures, ability to generate nanosized particles and nanocrystalline powders, bulk amorphous monolithic solids and ability to generate thin films of glass, glass-ceramic and ceramic coatings. In this study, the sol-gel method was applied for synthesis of hydroxyapatite powder with different Ca/P ratios.

### 2- Experimental procedure

A stable gel of hydroxyapatite with different Ca/P ratios was prepared according to Fig. 1. In this study, hydroxyapatite powders were synthesized with three different ratios of Ca/P=1.6 (H1.6), Ca/P=1.5 (H1.5) and Ca/P=1.67 (H1.67) using sol-gel method and utilizing P<sub>2</sub>O<sub>5</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O as starting materials. Calcination of the gel is achieved after 3h

at 600°C. The compacted sample is sintered for 3h at 1100°C. The phase analysis and cross-sectional microstructural observations of the calcined gel, sintered samples and also samples tested for biocompatibility were carried out by X-ray diffraction (JEOL YDX 8030, Japan- CuK<sub>α</sub> anode) and scanning electron microscope (VEGA3 TESCAN, Czech), respectively. Biocompatibility evaluation of the sintered sample was carried out by immersing the samples in SBF solution for 21 days

### 3- Results and discussion

Fig. 1 demonstrates the role of the molar ratio of Ca/P in the phase composition and degree of crystallization of the obtained HAp. By increasing the Ca/P ratio, the width of the diffraction peaks are reduced suggesting an increase in the degree of crystallization. It can also be seen that additional peaks related to the crystalline phases of tricalcium phosphate (β-TCP) appear in the H1.6 sample.

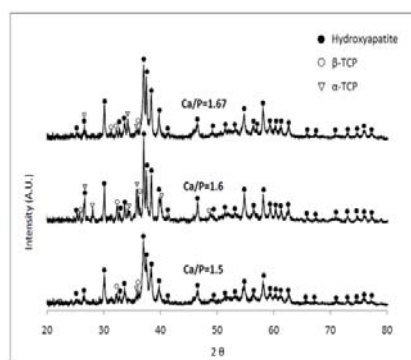
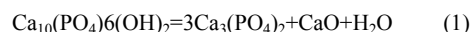


Fig. 1 X-ray diffraction patterns for HAp gel with different molar ratios of Ca/P

The intensity of the HAp peaks is reduced after sintering of the compacted sample; it can be concluded that the HAp has decomposed into β-TCP and CaO during sintering. The additional crystalline phases of β-TCP and CaO can also be seen in the H1.5 sample (Fig. 2). The reaction is proposed as follows:



The peak intensity of β-TCP phase for all three ratios of Ca/P is increased after sintering (Fig. 2). By increasing the Ca/P ratio to 1.6, the grain size of the sintered samples is increased which will yield a coarser morphology.

Results of the biocompatibility evaluation of the synthesized hydroxyapatite show that by increasing the Ca/P ratio, the volume and rate of apatite formation on the surface of the sintered samples also increases. Fig. 3 shows the morphology of the H1.6 sintered sample after the biocompatibility test. The results show that by immersing and keeping the sintered samples in a simulated solution for 21 days, biological apatite layers formed on the surface of the

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HAp sample by replacing the phosphate ions with carbonate ions (white spherical areas in Fig. 3a). This results in a faster response and better compatibility of the biomaterial in contact with body tissue. The pores in the material (Fig. 3b) suggest the dissolution of hydroxyapatite in parts of the surface and the cluster areas indicate the deposition of apatite.

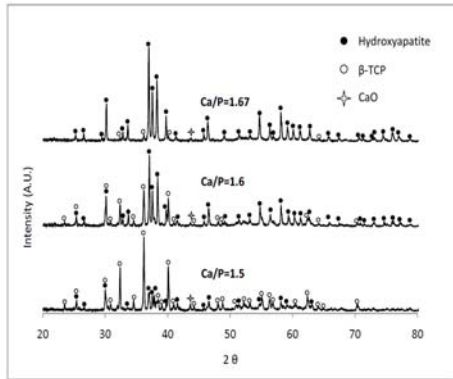


Fig. 2 X-ray diffraction patterns for sintered samples with different molar ratios of Ca/P

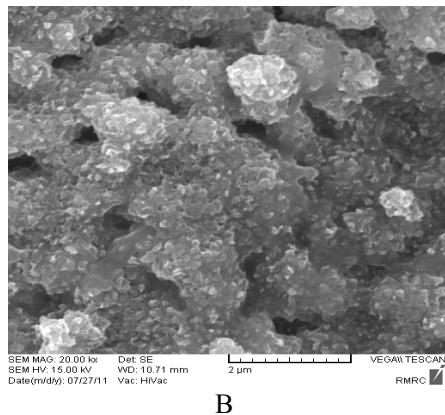
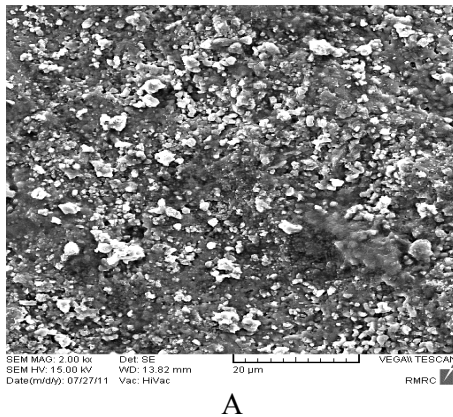


Fig. 3 SEM images of the H1.6 sample sintered at 700 °C and tested in SBF solution for 21 days at (a) low magnification; (b) high magnification

#### 4- Conclusions

The results show the highest intensity of XRD peaks for hydroxyapatite and β-TCP, a dual-phase

bioceramic with high ossification ability, belonging to the synthesized powder with Ca/P=1.6. Microstructural studies (SEM) at high and low magnification show a uniform distribution of hydroxyapatite nanoparticles (10-400 nm) and a cluster of nano-particles, respectively. The intensity of β-TCP phase peaks is increased for all three ratios of Ca/P after sintering. By increasing the Ca/P ratio to 1.6, the grain size of the sintered samples is increased and a coarser morphology is achieved. Results of the biocompatibility evaluation show that by increasing the ratio of Ca/P, an increase in the volume and rate of apatite formation on the surface of the sintered samples is observed.