Synthesis and Characterization of Magnesium Doped Biphasic Calcium Phosphate

A R Toibah*, I Sopyan*, M Mel**

*Department of Manufacturing and Materials Engineering, Faculty of Engineering, International Islamic Universiti Malaysia, P.O. Box 10, 50728 Kuala Lumpur, Malaysia, **Department of Biotechnology Engineering, Faculty of Engineering, International Islamic Universiti Malaysia, PO Box 10, 50728 Kuala Lumpur, Malaysia

SUMMARY

The incorporation of magnesium ions into the calcium phosphate structure is of great interest for the development of artificial bone implants. This paper investigates the preparation of magnesium-doped biphasic calcium phosphate (Mg-BCP) via sol gel method at various concentrations of added Mg. The effect of calcinations temperature (ranging from 500°C to 900°C) and concentrations of Mg incorporated into BCP has been studied by the aid of XRD, TGA and infrared spectroscopy (IR) in transmittance mode analysis. The study indicated that the powder was pure BCP and Mg-BCP with 100% purity and high crystallinity. The results also indicated that β-tricalcium phosphate (β-TCP) phase can be observed when the powder was calcined at 800°C and above.

INTRODUCTION

Biphasic calcium phosphate (BCP) [1] is a mixture of non-resorbable hydroxyapatite (HA) and the resorbable tricalcium phosphate (TCP) is an interesting material for bone implant as it shows biocompatibility and bioactivity to tissue bone [2]. Doping of magnesium ions[3] into BCP will bring biological improvement. Magnesium ion was found to cause the acceleration of nucleation kinetics of bone minerals[4]. Magnesium depletion adversely affects all stages of skeletal metabolism, leading to decrease in osteoblastic activities and bone fragility. Moreover, the incorporation of Mg ions into the TCP phase will produce more stable phase composition after heat treatment is that which compose HA and Mg-TCP. In order to obtain BCP materials, the thermal analysis on Mg-doped BCP has been studied. Here we produced Mg-doped biphasic calcium phosphate (Mg-BCP) at different Mg concentration through a sol-gel method. The calcinations temperature was varied from 500 to 900ºC.

MATERIALS AND METHODS

Mg doped BCP powders were prepared by sol-gel method using Ca $(NO_3)_2.4H_2O$ and $(NH_4)_2HPO_4$ as the precursors for calcium and phosphorus respectively. Mg $(NO_3)_2.6H_2O$ was used as the source of the dopant. In order to produce Mg-doped BCP powders, ammonium solution was heated at 60ºC, and EDTA was added while stirring until it dissolved. Into this, aqueous solution of Ca $(NO_3)_2.4H_2O$ and Mg $(NO_3)_2.6H_2O$ were poured, and then $(NH_4)_2HPO_4$ and urea were subsequently added. The mixture was then refluxed while stirring until a white gel of Mg doped BCP mixture were obtained. The obtained gel was then dried under ambient air and subsequently subjected to heat treatment.

Powders were characterized by X-ray diffraction (XRD) to determine the phases present in the powder. For IR data, the powders were directly placed onto the ATR holder of the FT-IR spectrometer in order to follow the chemical evolution from the gel to the BCP and to determine the presence of anions partially substituting PO_4^{3-} and/ or OH- groups. In order to study the weight loss of the Mg-doped BCP powders, thermogravimetric analysis was performed by using Perkin Elmer apparatus (Pyris Diamond TG/DTA) with 2°C/min heating rate.

RESULTS AND DISCUSSION

The XRD patterns for the synthesized powders at different concentrations of Mg calcined at 900°C are illustrated in Fig. 1. Calcinations of the powders at this temperature have indicated the formation of β-TCP phase together with HA phase. The presence of Mg ions has stabilized the β-TCP structure[5]. Thus, when the concentration of Mg was increased, the β-TCP peak also increased. The increased in β-TCP peak can be correlated with the incorporation of Mg into the β-TCP phase. Moreover, due to the existence of Mg, the diffraction peaks shifted to larger angles in the pattern, compared with pure BCP. Though, when the Mg concentration was increased up to 10% and above, the solubility limit of the Mg in the β-TCP phase was decreased and Mg started to segregate as free MgO. Thus, at higher concentration of Mg (10% Mg-BCP and 15% Mg-BCP), MgO phase at 2θ~ 43° was observed.

XRD patterns for selected sample pure BCP calcined at different temperature condition are presented in Fig. 1. The transformation of amorphous phase with broaden peak to crystalline phase occurred in between 500 to 600ºC. This result also showed that β-TCP peak was started to be observed clearly at 800°C.

This study showed the presence of hydroxyl (OH) stretch mode bands at ~3570 cm^{-1} (Fig. 2). The band at ~627 cm^{-1} is derived for librational modes of OH groups in BCP. Phosphate bands are observed at 563 cm^{-1}, 599 cm^{-1}, 961 cm^{-1}, 1024 cm^{-1} and 1085 cm^{-1}. The spectra also showed that the intensity of peak resolution of OH and PO_4 bands are viewed less intensity with the increased in Mg concentration. FT-IR spectra for the pure BCP calcined at different temperatures are presented in Fig. 2. The spectra show that C-O band at 1300-1600 cm-1 was decreased in its intensity of peak resolution as the calcinations temperature was increased. Besides, the decreased in carbonate band has increased the OH and PO_4 bands. Moreover, the spectrum revealed the presence of

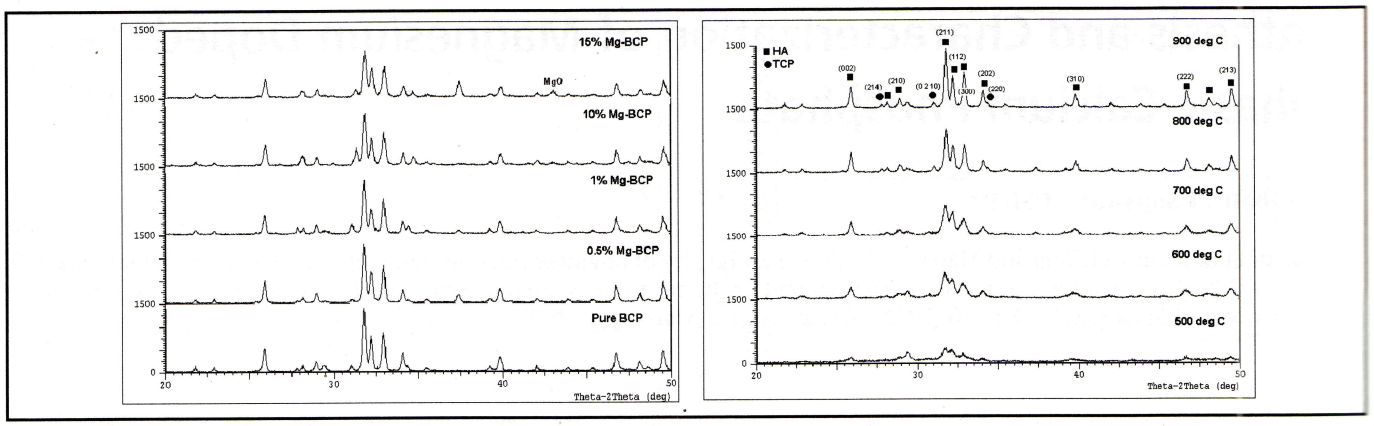

Fig. 1: XRD patterns of pure BCP and Mg-doped BCP (left) and pure BCP at different calcinations temperature (right).

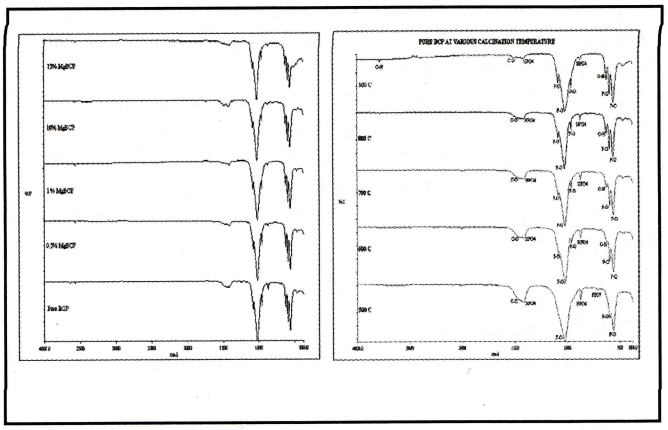

Fig. 2: FT-IR spectra of pure BCP and Mg-doped BCP (left) and FT-IR spectra of pure BCP at different calcinations temperature.

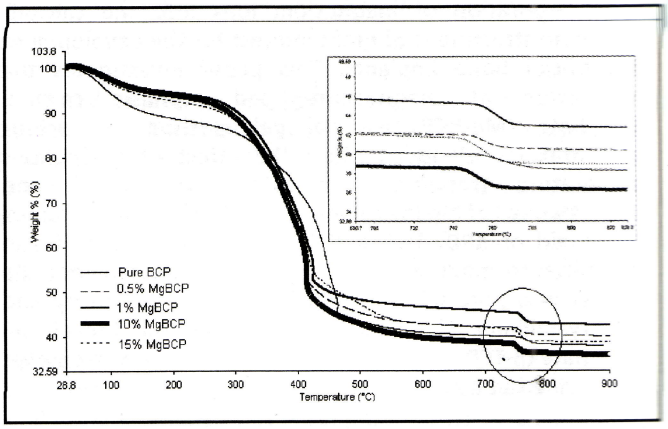

Fig. 3: TGA plots for pure BCP and Mg-doped BCP.

hydrogen phosphate groups (HPO_4^{-2}) and pyrophosphate ($P_2O_7^{-4}$) bands are evident at 500°C for the peak at 875 cm^{-1} and 715 cm^{-1}, respectively. However, these bands tend to decrease as the calcinations temperature was increased.

The TGA plots report the weight loss for the synthesized powders with different concentrations of Mg are illustrated in Fig. 3. The first drop occurs at temperature ~30 to ~250ºC was due to evaporation of water. The plots revealed that the calcinations have changed the amorphous phase of the dried gel to crystalline phase of BCP within the temperature range between 250-500°C in which all samples have showed a similar weight loss of about ~50%. The decomposition of HPO_4^{-2} and $P_2O_7^{-4}$ bands to biphasic mixtures is apparent by the observed similar weight losses of about ~2% for all samples within the temperature range ~740 to ~800°C. This result was in good agreement with FT-IR results as it shows the decreasing in intensity resolution of HPO_4^{-2} and $P_2O_7^{-4}$ bands as the calcinations temperature was increased. From the TGA analysis, it also shows that the decomposition temperature of HPO_4^{-2} and $P_2O_7^{-4}$ bands to biphasic mixtures occur at lower temperature for 10% Mg-BCP. This confirmed the formation of β-TCP phase is higher at this Mg concentration as Mg act as sintering additive. This result was supported by XRD result as it shows highest intensity of β-TCP phase at 10% Mg-BCP compared to other samples.

CONCLUSION

Mg–doped BCP powders were successfully prepared via a novel, relatively simple sol-gel procedure using Ca $(NO_3)_2.4H_2O$ and $(NH_4)_2HPO_4$ as the precursors and Mg $(NO_3)_2.6H_2O$ as the source of the dopant. All the powders exhibited highly crystalline BCP characteristic after calcinations at 900ºC. In addition, as the concentration of Mg doped into BCP increased, the TCP peak will increased in intensity as Mg was incorporated into the TCP phase of BCP rather than HA phase.

ACKNOWLEDGEMENT

The authors would like to thank Ministry of Science, Technology, and Innovation (MOSTI) Malaysia for the partial support provided through the e-Science Research Grant No. 03-01-08-SF0020.

REFERENCES

1. Kivrak N, Tas AC. Synthesis of Calcium Hydroxyapatite-tricalcium Phosphate (HA-TCP) Composite Bioceramic Powders and Their Sintering behavior. J. Am. Ceram. Soc. 1998; 81(9): 2245-52.
2. Manjubala I, Sampath Kumar TS. Preparation of Biphasic Calcium Phosphate Doped with Magnesium Fluoride for Osteoporotic Applications. J. Mater. Sci. Lett. 2001; 20: 1225-7.
3. *LeGeros RZ, LeGeros JP. An Introduction to Bioceramics: Dense* Hydroxyapatite, Singapore. 1993.
4. Landi E, Sprio S, Sandri M, *et al.* Biomimetic Mg- and Mg, CO3-substituted hydroxyapatites: synthesis characterization and in vitro behaviour. J. Euro. Ceram. Soc. 2006; 26: 2593-601.
5. Kannan S, Lemos IAF, Rocha JHG, *et al.* Synthesis and characterization of magnesium substituted biphasic mixtures of controlled hydroxyapatite/ ,-tricalcium phosphate ratios. J. Solid State Chem. 2005; 178: 3190-96.