Magnesium Doped Hydroxyapatite through Mechanochemical Synthesis

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Abstract
The mechanochemical synthesis method was employed to synthesis hydroxyapatite (HA) and magnesium (Mg) doped hydroxyapatite (HA) powders. The effects of Mg\(^{2+}\) into the synthesized HA powder properties were investigated. Characterization of the synthesized HA and Mg doped HA at various concentrations (1% - 9% MgHA) were accomplished through X-ray diffraction (XRD) analysis. The nano size powder of HA and Mg-doped HA were successfully synthesized through the present method and the influenced of Mg\(^{2+}\) in the HA was also indicated by the different peaks intensity and the crystal sizes obtained.

Keywords:Magnesium, Mechanochemical, Hydroxyapatite, X-ray Diffraction, Fourier Transform Infrared.

Introduction
Hydroxyapatite (HA) has been applied as materials for orthopaedic implant due to the chemical similarity to that of human hard tissue [1, 2]. HA has a limited ability in the development of new bone tissue stimulation and exhibits less degradation ability. Generally, biological apatite in bone mineral is characterized by nonstoichiometric chemical formula consist of small amount of cations or anions which works in biological performance [3]. Magnesium ion (Mg\(^{2+}\)) is one of the main substitutes for calcium in biological apatites where it is the fourth most abundant cation in the human body (0.44–1.23 wt %) and bone contains 0.72 wt % of Mg\(^{2+}\) [4]. Thus, Mg\(^{2+}\) is necessitates in all stages of skeletal metabolism and facilitates in the growth of osteoblast and osteoclastic activities by inhibiting the fragility of bone [5, 6]. There were several synthesis techniques that have been reported in synthesis Mg-doped HA such as precipitation [4], and sol-gel [7]. Mechanochemical method is a simple method in powder synthesis especially in a dry condition [8, 9]. This study reports the HA and Mg doped HA powders synthesized through dry mechanochemical method and the effect of Mg\(^{2+}\) to the synthesized powder properties of HA.

Experimental Method
The mixed precursors of Ca(OH)\(_2\), (NH\(_4\))\(_2\)HP\(_4\) and Mg(OH)\(_2\), with molar ratio of 1.67 (Ca+Mg)/P were milled in planetary ball mill (Retsch) by using zirconia vials (50 ml) and balls as milling medium. The powder-to-ball mass ratio was fixed at 1/5. The rotation speed and milling time were set at 370 rpm and 15 h respectively based on our previous method [2, 9]. The interval pause was set for 15 minutes after every 45 minutes of milling. The reaction equation for Mg doped HA from the three precursors is described in Eq. 1:
(10-X)Ca(OH)$_2$+XMg(OH)$_2$ + 6(NH$_4$)$_2$HPO$_4$ → Ca$_{10-x}$Mg$_x$(PO$_4$)$_6$(OH)$_2$ + 12NH$_4$OH + (6-X)H$_2$O \hspace{1cm} (1)

Where X = 0, 0.1, 0.3, 0.5, 0.7, 0.9 is denoted as Mg$^{2+}$ molar concentration. The phase analysis of the synthesized powders was carried out by using X-ray diffraction (XRD, Shimadzu) with Copper Kα radiation ($\lambda$ = 1.5406 Å) produced at 40 kV and 40 mA with diffraction angles of 2θ = 25 – 55 in 2θ and with a step size of 0.02° 2θ s$^{-1}$.

**Results and Discussion**

All the synthesized powders of Mg-free HA and Mg-doped HA in various concentrations exhibited the apatite phase that belong to HA (PDF No. 74-566 for Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) as shown in Figure 1. The peak at 32.1° (1 1 2) is clearly visible in 1% MgHA compared to Mg-free HA. However, this peak decreased in 3% - 9% MgHA which manifested by the peak broadening which was also observed in other peaks of HA at different degrees (2θ) with increasing Mg$^{2+}$ concentration. This happened due to the substitution of Mg$^{2+}$ in various concentrations into the HA leading to the decrease of the HA peaks intensity with the increase of Mg$^{2+}$. Table 1 shows that increasing Mg$^{2+}$ has led to the decrease of crystal size from 25.9 nm in Mg-free HA to 9.3 nm in 9% MgHA. The hexagonal lattice parameters of a and b, were also reduced with Mg$^{2+}$ doping from 1% to 9% MgHA. In contrast, there was no any significant change observed in lattice parameter along the c-axis. larger than HA with increasing Mg$^{2+}$ concentration.

**Summary**

Hydroxyapatite (HA) and magnesium (Mg) doped HA nano powders were successfully synthesized through dry mechanochemical method as it has been confirmed by XRD analysis. Mg$^{2+}$ doping reduced the intensity of the peaks as well as the crystal size and lattice parameters. The formation of calcium deficient HA showed that Mg$^{2+}$ was substituted into HA structure.

![Figure 1: XRD pattern of the synthesized Mg-free HA and Mg-doped HA powders.](image)

**Table 1:** Crystal size, lattice parameters of the synthesized Mg-free HA and Mg-doped HA powders.

<table>
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<th>X (%)</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
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<td>0.9</td>
<td>22.5</td>
<td>9.017</td>
<td>6.4070</td>
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**References**