Synthesis of Magnesium-Hydroxyapatite Crystal via microwave irradiation

F N Hariowibowo¹, Nurlely¹, Y W Sari²

¹ Department of Physics, University of Indonesia, 16424, Depok, Indonesia
² Department of Physics, Bogor Agricultural University, 16680, Bogor, Indonesia

Email: nurlely@sci.ui.ac.id

Abstract. Magnesium-Hydroxyapatite (MgHA) is synthesized by substituting magnesium (Mg) into hydroxyapatite (HA). The study’s aim was to synthesize MgHA nano-powder via microwave irradiation and determine the effects of the microwave irradiation’s power and irradiation time variation on the synthesis of the MgHA crystal. The synthesis of MgHA was done by titrating solutions of diammonium hydrogen phosphate and magnesium hydroxide into a solution of calcium hydroxide. The microwave irradiation was done with variations of irradiation power and time. The phase composition, functional groups, morphology, particle size, and the element composition of the MgHA powder was evaluated using the following characterization method; XRD, FTIR, and SEM-EDX. The XRD patterns show that lattice parameters a and c, crystallinity index, and crystallite size of MgHA decreases as the irradiation time increases. The FTIR results show that a stretching mode is caused by the bonding of Mg²⁺ and the hydroxyl group. The SEM and EDX results shows that the substitution of Mg²⁺ causes the particles to agglomerate and the Ca/P value of MgHA was determined to be lesser than 1.67, showing that some Ca²⁺ was released from the apatite. The results show that higher irradiation power and longer irradiation time is more effective in MgHA synthesis.

Keywords: Magnesium, Hydroxyapatite, Biomaterial, Microwave Irradiation

1. Introduction

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) or HA is one of the main mineral components found in bone tissue and teeth which makes it commonly used as a material for bone tissue and teeth substitution or treatment [1,2]. In the bone tissue, HA is formed by the interaction of calcium phosphate (Ca₃(PO₄)₂) and calcium hydroxide (Ca(OH)₂) [3]. The crystal structure of HA is hexagonal, with the lattice parameters of a = b = 0.95 nm and c = 0.68 nm [4,5].

Magnesium is known to be an essential element in bone tissue and teeth. During the early phases of osteogenesis, magnesium plays a role by stimulating osteoblast proliferation [2,6]. Magnesium-hydroxyapatite (MgHA) could be synthesized via microwave irradiation [7]. Substituting magnesium ion into the calcium ion in HA would cause the crystal’s bioactivity and solubility to increase, it would also reduce the crystallinity of the apatite, and reduce the crystal size, due to the radius of Magnesium being smaller than calcium ion (~0.28 Å difference in radius according to the Pauling scale) [2,7,8,9].

In microwave irradiation, heat is generated internally instead of coming from an external source, heating the material via energy conversion, rather than energy transfer [10]. Due to this process, the material is heated faster (rapid heating), the synthesizing time is shorter, the energy is transformed effectively, and the material volume is heated thoroughly [11].
2. Materials and methods

2.1. Sample Preparation
Magnesium-Hydroxyapatite (MgHA) powders were synthesized by using diammonium hydrogen phosphate, magnesium hydroxide, calcium hydroxide as sources of phosphate, magnesium, and calcium. MgHA solution was prepared via precipitation method, 0.6 M aqueous phosphate solution and 0.2 M aqueous magnesium solution was dropped into 1 M aqueous calcium solution with a constant debit with constant stirring. The solution is irradiated in microwave with variations of irradiation power (450 and 720 W) and irradiation time (2, 4, 6, 8, and 10 minutes). The irradiated solution is filtered using filtration paper (Whatman Grade 5, Fisher Scientific, USA). The filtered sample was dried in the oven until the mass is constant, then grounded into fine powder for further characterization and analysis.

2.2. Sample Characterization
The MgHA powders were analyzed using several characterizations. X-ray diffractometer (XRD, Panalitycal X’Pert Pro MPD) was used for the crystal phase analysis. The examination took the 2θ range of 20°–60° with a step of 0.4°/s. The crystallite size was determined using the Scherrer formula [12]. The crystallite size of MgHA powders was determined involving (002) plane. The functional group of MgHA was analyzed using Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 37). The analysis was applied in the range of 400–4000 cm⁻¹ (mid IR-spectrum) with resolution of 4 cm⁻¹. Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) were used to analyze the morphology and element composition of MgHA powders.

3. Results and discussion

3.1. Mass efficiency and X-ray diffraction
Comparing both irradiation powers used in the process, higher irradiation power (720 W), in general, produced a higher mass product compared to the lower irradiation power (450 W). By comparing the irradiation time, it is determined that sample mass increases as the irradiation time increases. Higher irradiation power and irradiation time increase the heat in the microwave and causes the atoms to accelerate. The acceleration of the atoms caused collisions between the atoms, causing the atoms to bond with each other [13]. The time needed for the synthesis is shortened, causing a higher mass to be produced at a higher irradiation power and higher irradiation time.

![Figure 1](image-url)  
**Figure 1.** Mass obtained for MgHA synthesized via microwave irradiation with variations of irradiation power and time.
Figure 2. XRD patterns of MgHA with irradiation power of (a) 450 Watt (b) 720 Watt

Table 1. Lattice parameters and calculated mass of MgHA samples irradiated at 450 Watt.

| Irradiation Time (minutes) | Mass (gr) | Lattice Parameter a (Å) | Lattice Parameter c (Å) | Crystallite Size (nm) | Crystalinity Index |
|----------------------------|-----------|-------------------------|-------------------------|----------------------|-------------------|
| 2                          | 9.61      | 9.3361                  | 6.8602                  | 28.2845              | 0.5764            |
| 4                          | 9.03      | 9.3385                  | 6.8565                  | 23.6475              | 0.3367            |
| 6                          | 9.27      | 9.3287                  | 6.8451                  | 20.8771              | 0.2317            |
| 8                          | 9.03      | 9.3276                  | 6.8450                  | 20.2369              | 0.2110            |
| 10                         | 9.52      | 9.3255                  | 6.8440                  | 20.0231              | 0.2045            |

Table 2. Lattice parameters and calculated mass of MgHA samples irradiated at 720 Watt.

| Irradiation Time (minutes) | Mass (gr) | Lattice Parameter a (Å) | Lattice Parameter c (Å) | Crystallite Size (nm) | Crystalinity Index |
|----------------------------|-----------|-------------------------|-------------------------|----------------------|-------------------|
| 2                          | 9.46      | 9.3180                  | 6.8443                  | 27.8430              | 0.5497            |
| 4                          | 9.45      | 9.2967                  | 6.8436                  | 22.8548              | 0.3040            |
| 6                          | 9         | 9.2893                  | 6.8434                  | 20.2621              | 0.2118            |
| 8                          | 10.5      | 9.2739                  | 6.8426                  | 19.8162              | 0.1981            |
| 10                         | 10.51     | 9.2493                  | 6.8391                  | 19.2157              | 0.1806            |

The XRD patterns show that the irradiated samples that use 450 W have a larger average of lattice parameters compared to the samples that are irradiated in 720 W. Comparing the lattice parameters of the samples with to the lattice parameters of standard HA (JCPDS no. 09-0432), it is determined that reduction happens in both lattice parameters a and c. One of the factors that could cause the reduction on both lattice parameters a and c is the substitution of Mg$^{2+}$ in the Ca(I) site [14]. Mg$^{2+}$ is a known inhibitor to the growth of HA, where Mg$^{2+}$ inhibits the phase transformation of amorphous calcium phosphate to HA and inhibits the growth of HA especially in the c-axis [15]. Mg$^{2+}$ also has a smaller radius than Ca$^{2+}$, hence, by substituting Mg$^{2+}$ in HA, the lattice parameter, crystallite size, and crystallinity index would be reduced [2].

Higher irradiation power and irradiation time increase microwave temperature, resulting in accelerated atomic motion and solvent viscosity reduction, this would cause a decrease in the diffusion barrier. Triggered by these factors, atoms would fill the lattice easier [13,16]. The crystallite size and
crystallite index were calculated on the (002) peak, determining that as the irradiation power and irradiation time increases, the value of the crystallite size and crystallinity index are reduced.

The sample that has the smallest lattice parameters, size and crystallinity index among the other samples are determined to be produced at the maximum irradiation power (720 W) and maximum irradiation time (10 minutes). The reduction of the lattice parameters, crystallite size, and crystallinity index as the irradiation power and irradiation increases indicates more Mg$^{2+}$ substitution in higher irradiation power and irradiation time.

3.2. Fourier transform-IR

The FTIR spectra of the irradiated sample of 720 W; 10 minutes shows a peak at 3690 cm$^{-1}$, this peak indicates the presence of Mg$^{2+}$ in the apatite structure. When magnesium and hydroxyl groups combine, a stretching mode is caused, hence resulting on this peak [6,17]. The peak was not found in the sample that was irradiated for 2 minutes with the same power, which means that longer irradiation time is more effective in forming MgHA. The 873 cm$^{-1}$ band indicates a formation between C-O, which is the adsorbed surface carbonate ions [18]. The peak at 1384 cm$^{-1}$ shows the presence of carbonation, which could happen between Mg$^{2+}$ and CO$_2$ or Ca$^{2+}$ and CO$_2$[19].

**Table 3.** Bands assigned to MgHA at irradiation powers 720 W and irradiation time of 2 and 10 minutes.

| Functional Group                  | 720 Watt                  |
|-----------------------------------|---------------------------|
|                                   | 2 minutes | 10 minutes |
| $v_3$ $PO_4^{3-}$ (stretch)       | 1032      | 1032       |
| $v_4$ $PO_4^{3-}$ (bend)          | 563       | 563        |
| $CO_3^{2-}$ (surface)             | 873       | 873        |
| H$_2$O (stretch)                  | 3421      | 3423       |
| H$_2$O (bend)                     | 1642      | 1641       |
| CO$_2$ (bend)                     | 2361      | -          |
| Mg(HCO$_3$) or Ca(HCO$_3$) (bend) | 1384      | 1384       |

**Figure 3.** FTIR patterns of MgHA powders with irradiation power 720 Watt.

Amorphous calcium phosphate and crystalline HA exhibits different splitting degrees on their respective phosphate ion antisymmetric bending mode. The degree of infrared splitting and percentage crystallinity has a straight line correlation, thus, the crystallinity of the sample could be determined by
examining the splitting of the phosphate ion antisymmetric bending mode from the FTIR spectra [20]. The determined SF values are shown in Table 4:

**Table 4.** Splitting Factor values for MgHA at irradiation power of 720 W.

| Irradiation Time | SF  |
|------------------|-----|
| 2 minutes        | 2.32|
| 10 minutes       | 2.19|

Smaller SF value is shown to be determined at the longer irradiation time. This correlates to the lower crystallinity value of the sample that was irradiated at a longer irradiation time as shown in Table 2, which could be caused by more Mg$^{2+}$ substitution in the apatite, where Mg$^{2+}$ has a smaller radius than Ca$^{2+}$, and Mg$^{2+}$ inhibits the growth of HA, which leads to the reduction of the lattice parameter, crystallite size, and crystallinity [15].

3.3. **SEM & EDX**

The MgHA samples of 720 W; 10 minutes are analysed using SEM-EDX. The morphology of the sample (720 W, 10 minutes) is shown in Figure 4b. Based on the image, the mean particle size is determined using Fiji ImageJ software, resulting in a range of particle sizes, between 72-97 nm, and an average particle size of 90 nm. The SEM image shows particle agglomeration, which is caused by the small size of MgHA crystallites and the amorphous phase of MgHA. The more Mg$^{2+}$ substituted into HA, the more the particle agglomerates [11].

The EDX shows that the Ca/P ratio of MgHA is 1.12, and the Mg/P ratio is 0.42 (Mg$^{2+}$ ~ 5.8wt%). The literature Ca/P ratio of HA is known to be 1.67. The decrease of the Ca/P ratio indicates that some of the Ca$^{2+}$ in HA has been substituted by Mg$^{2+}$.

![SEM image of MgHA with irradiation power and time of 720 W and 10 minutes](image)

![EDX result of MgHA](image)

**Figure 4.** SEM image of MgHA with irradiation power and time of 720 W and 10 minutes (a) EDX result of MgHA (b)
4. Conclusions
Magnesium-Hydroxyapatite (MgHA) powders could be synthesized via microwave irradiation. The X-ray diffraction results show that increasing the irradiation power and time reduces lattice parameters, crystallite size, and crystallinity index, this is caused by the substitution of Mg$^{2+}$, where Mg$^{2+}$ has a smaller radius than Ca$^{2+}$, and that Mg$^{2+}$ inhibits the growth and the phase transformation of amorphous calcium phosphate into HA. The FTIR result shows that the presence of Mg$^{2+}$ is detected in the highest irradiation power with the longest irradiation time, indicating more Mg$^{2+}$ substitution in the sample. MgHA has a smaller Ca/P ratio (1.12) compared to HA (1.67), meaning that some of the Ca$^{2+}$ have been substituted by Mg$^{2+}$. The SEM results shows that the presence of Mg$^{2+}$ in HA caused the particles to agglomerate, due to the small size of the crystallite and the amorphous phase of MgHA. MgHA powders synthesized via microwave irradiation produces 72-97 nm rod particles.

References
[1] Szcześ A, Hołysz, L, & Chibowski, E.(2017). Advances in Colloid and Interface Science, 249, 321–330.
[2] Laurencin D, Almora-Barrios. (2011). Biomaterials. 32, 1826-1837.
[3] Martini. (2012). Fundamental of Anatomy and Physiology. Pearson Education.
[4] Feng, X. (2009). Current Chemical Biology, 3(2), 189–196.
[5] Vallet-regi, M. and Gonzalez-Calbet, J. (2004). Progress in Solid State Chemistry, 32(1-2), pp.1-31.
[6] Farzadi A, F Bakhshi. (2014). Ceramic International. 40, 6021-6029.
[7] Shepherd, J H, Shepherd, D V, & Best, S M (2012). Journal of Materials Science: Materials in Medicine, 23(10), 2335–2347.
[8] Chen Y, & Miao, X. (2005). Biomaterials, 26(11), 1205–1210.
[9] Onder S, F Kok. (2013). Materials Science and Engineering: C. 33, 4337-4342.
[10] Agrawal, D. (1998). Current Opinion in Solid State and Materials Science, 3(5), pp.480-485.
[11] Hasson, M N, Mahmoud, M M, El-Fattah, A. A., & Kandil, S. (2016). Ceramics International, 42(3), 3725–3744.
[12] Monshi, A, Foroughi, M R (2012). World Journal of Nano Science and Engineering. 2, 154–160.
[13] Hayes B L. (2002). Microwave Synthesis–Chemistry at the Speed of Light, CEM Publishing, Mathews, NC.
[14] Bigi, A., Falini, G., Foresti, E., Gazzano, N., Ripamonti, A., & Roveri. N. (1996). International Tables for X-ray,87-92.
[15] Kanzaki N, Onuma K, Treboux G, Tsutsumi S, Ito A, J. Phys. Chem. B 104 (17) (2000) 4189–4194.
[16] Landi E, Tampieri A. (2000). Journal of the European Ceramic Society. 20, 2377–2387
[17] Wang, Z, G Wu, Y Hu, Y Ding, K Hu, W Fan. Polym. Degrad. Stab. 77 (3) (2002) 427–434.
[18] Elliot J C, Holcomb D W. (1985). Calcif. Tissue Int. 37, 372–375
[19] Matthaioucos, V., Oulego, P., Frontistis, Z., Collado, S., & Hela, D. (2019). Chemical Engineering Journal, 360(November 2018), 728-739.
[20] Termine J D, Posner A S. (1966). Science, New Series, Vol. 153, No. 3743 (1966), 1523-1525
[21] Ren, F., Leng, Y., Xin, R., & Ge, X. (2010). Acta Biomaterialia, 6(7), 2787–2796.

Acknowledgement
This work is supported by Hibah PITTA 2018 funded by DRPM Universitas Indonesia No.5000/UN2.R3.1/HKP.05.00/2018