

Synthesis and Characterization of Borohydroxyapatite for Bone Cement Application

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Abstract: *Hydroxyapatite the one of the most used as biomaterial because of it has excellent osteoconductive, bioactive properties and non-toxic. The HA bone cement is a substance or component used to healing or repairing broken bones. Boron is the element that plays the role of the bone metabolism and calcium balance. So, this we study a synthesizing boron substitution into hydroxyapatite structure bone cement by the wet chemical method, is called BHA. 10 and 20 mol.% of Boron was substituted into HA structure. There was poor crystallinity when boron was added into the HA structure. Substitution of boron in HA structure had the effect of unit cell volume of HA because the atomic radius of boron smaller than phosphorus. Also, the boron substitution are occurred at PO_3^{4-} in HA structure.*

Keywords: Hydroxyapatite, Hydroxyapatite substitution, Boron hydroxyapatite, Boron.

I. BACKGROUND/ OBJECTIVES AND GOALS

Bioceramics are based on calcium phosphate compounds. Hydroxyapatite (HA) the most of bioceramics which widely used as excellent osteoconductive and bioactive properties that result in no rejection from the human body. One of the most of their medical application is bone cement which is a substance or component used to heal or repair broken bone for reduced the time and minimally invasive surgery (Ginebra, 2009). There are two types of materials that using as bone cement such as Polymethyl methacrylate (PMMA) (Arora, 2013) (Magnan et al., 2013) and calcium phosphate bone cement (Ambard & Mueninghoff, 2006) (Xu et al., 2017). However, PMMA has high temperature during setting (Sun, Kwok, & Nguyen, 2006), these is cause to damage a surrounding tissue, therefore, calcium phosphate have using as bone cement but it have poor the mechanical

properties than PMMA.

The substitution is one of the most to improvement the HA properties (Nabiyouni, Ren, & Bhaduri, 2015) (Ratnayake, Mucalo, & Dias, 2017). So, in this study, has focus on the development of HA bone cement by substitution Boron into HA structure via wet chemical process, is called "Borohydroxyapatite: BHA" because boron very importance to increase the bone metabolism process and prevent the osteoporosis (Larsson & Fazzalari, 2014)

II. METHODS

A. Synthesis and characterization

The synthesis atmosphere had a controlled temperature of 30°C for synthesis of the pure HA, as well as HA substituted with boron (BHA) with 10 and 20 mol.% of B^{3+} ion by the aqueous precipitation method. In addition, all final products maintained the experimental ratio of Ca/P or Ca/(P+B) of 1.67.

HA was prepared by dissolving $Ca(OH)_2$ in DI-water to 0.5 M, (solution 1) was stirred for overnight, followed by dissolving H_3PO_4 in DI-water to 0.3 M (solution 2) was stirred for 2 hrs at room temperature. Solution 2 was added to solution 1 and the pH was maintained at 11 using ammonia solution (NH_3 solution) during the reaction. After mixing, the precipitate was aged at room temperature overnight. The HA precipitate was dried at 100°C for 24 hrs (Jamarun, Elfina, Arief, Djamaan, & Mufitra, 2016). BHA synthesis is similar to the precipitation process of HA. A solution of B^{3+} was added to the HA precipitate and stirred at 30°C overnight and dried at 100°C for 24 hrs

The crystalline structure of HA and BHA were also characterized by X-ray Diffraction (XRD) using Philips:

X'pert diffractometer, the powders were analyzed with Cu-K α radiation ($\lambda = 1.5406$ nm) produced at 40 kV. The XRD results were compared to XRD pattern standard number 74-0565 (Joint Committee Powder Diffraction Standard: JCPDS). The lattice parameters of hydroxyapatite *a*- and *c*-axis (Å) for hexagonal structure were calculated from peak (0 0 2) and (2 2 2), respectively by using equation 2.1 using equation 1 (Cullity, 1978)

$$\frac{1}{d^2} = \frac{4}{3} \cdot \left(\frac{h^2+h \cdot k+k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

Where *d* is distance (Å) between adjacent planes in the set of Miller indices (*h k l*).

The hexagonal unit cell values are calculated using equation (2) (David, 2005);

$$V = a^2 \cdot c \cdot \sin 60^\circ \quad (2)$$

The percentage of crystallinity (X_c) for all samples were determined using the equation 3;

$$X_c = \frac{I_{300} - V_{112/300}}{I_{300}} \cdot 100 \quad (3)$$

where I_{300} is intensity of (3 0 0) diffraction peak and $V_{112/300}$ is the intensity of the trough between (112) and (300) reflections, which completely disappears in noncrystalline samples. (Landi et al, 2000).

B. Functional group

To study the functional group of contained materials, the middle infrared spectroscopy (FT-IR) that the spectra was recorded in rang using 4000 – 400 cm⁻¹ in Attenuated total reflectance (ATR) mode.

III. RESULTS

A. Phase analysis

HA, 10BHA and 20BHA were synthesized by a wet chemical process and the phase composition was determined by X-ray diffraction (XRD). Data was identified with reference to Joint Committee on Powder Diffraction Standards (JCPDS) files. The samples were

found to be comparable to calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) JCPDS file no. 74-0565. The XRD pattern of HA samples had an XRD pattern similar to that of synthetic HA in accordance with JCPDS No. 74-0565, as following in fig. 1. Also, the XRD patterns of 10BHA and 20BHA have the same trend with HA that an XRD pattern similar to that of synthetic HA in accordance with JCPDS No. 74-0565, as showed in fig. 2. However, all XRD patterns were found the low crystallinity degree was due to its just dried at 100°C for overnight only.

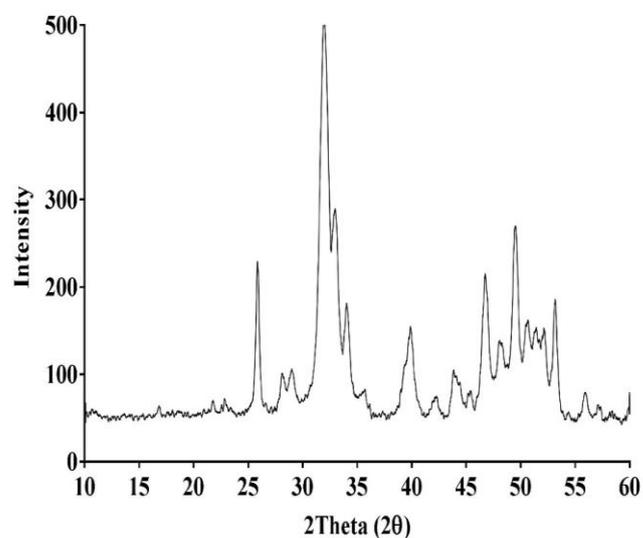


Fig. 1: XRD pattern of HA

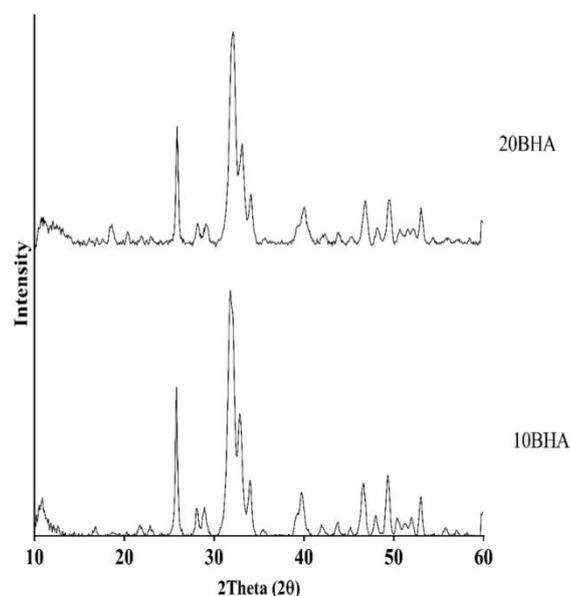


Fig. 2: XRD patterns of 10BHA and 20BHA

Table 1 shows that both of unit cell volume and % crystallinity of HA are decreased with the addition of B^{3+} in the HA structure, due to the ionic radius of the B^{3+} (90 pm) being smaller in size than P^{3+} (110pm)(Cox, 1951).

Table 1: Crystallinity (% X_c), unit cell volume and lattice parameter (a and c) of HA and 10BHA and 20BHA

Samples	Unit cell volume	%Crystalline
HA	527.22	60.91
10BHA	526.48	56.57
20BHA	519.26	55.42

B. Function group analysis

The IR spectra of the HA samples as showed in fig. 3. It was found that the peak at 2864 cm^{-1} to 3697 cm^{-1} and at 1642 cm^{-1} assigned to OH^- group and peak at 1423 cm^{-1} is assigned to CO stretching of CO_3^{2-} and at 970 cm^{-1} to 1030 cm^{-1} and at 450 cm^{-1} –610 cm^{-1} of the peak assigned to P-O bend PO_4^{3-}

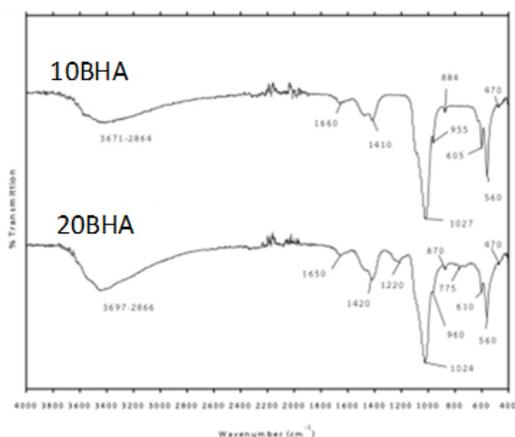


Fig. 3: The IR spectra of HA synthesis via wet chemical method

From the IR result found that HA was synthesis by wet chemical method at the room temperature without control atmosphere, it can be contaminated by CO_3 (Anwar, Asghar, Kanwal, Kazmi, & Sadiqa, 2016), so called carbonated apatite as following the chemical formular as $Ca_{10}(PO_4)_{6-x}(CO_3)_x(OH)_2$

While Fig.4 showed the IR spectra of 10BHA and 20BHA. Both of 10BHA and 20BHA can be presence of

the peak of BO_3 . The peak at 775 and 1220 cm^{-1} presented the signal of BO_3 (Ternane et al., 2002).

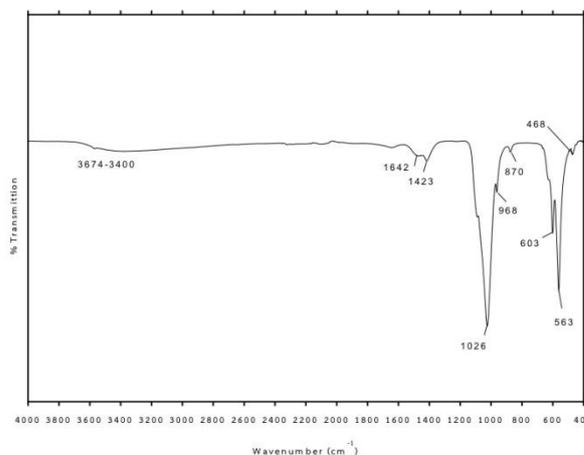


Fig. 4: IR spectra of 10BHA and 20BHA were synthesis by wet chemical method

From the IR results found that HA was synthesis by wet chemical method at the room temperature without control atmosphere, it can be contaminated by CO_3 (A. Anwar et al. 2016) so the chemical formula as $Ca_{10}(PO_4)_{6-x-y}(CO_3)_x(BO_3)_y(OH)_2$.

IV. CONCLUSION

It can be synthesized hydroxyapatite and boro hydroxyapatite via the co-precipitate method. However, the atmosphere has affect to the carbonated contamination of HA structure. The crystalline of HA decreased when B^{3+} increased.

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REFERENCES

[1] Ambard, A. J., & Mueninghoff, L. (2006). Calcium phosphate cement: Review of mechanical and biological properties. Journal of Prosthodontics. <https://doi.org/10.1111/j.1532-849X.2006.00129.x>.
 [2] Anwar, A., Asghar, M. N., Kanwal, Q., Kazmi, M., & Sadiqa, A. (2016). Low temperature synthesis and characterization of

- carbonated hydroxyapatite nanocrystals. *Journal of Molecular Structure*. <https://doi.org/10.1016/j.molstruc.2016.03.061>.
- [3] Arora, M. (2013). Polymethylmethacrylate bone cements and additives: A review of the literature. *World Journal of Orthopedics*. <https://doi.org/10.5312/wjo.v4.i2.67>.
- [4] Cox, E. G. (1951). Structural inorganic chemistry. *Nature*. <https://doi.org/10.1038/168756a0>.
- [5] Cullity, B. D. (1978). Elements of X-ray diffraction, 2nd edition. Addison-Wesley Publishing Co. Reading MA. <https://doi.org/10.1119/1.1934486>.
- [6] Ginebra, M. P. (2009). Cements as bone repair materials. In *Bone Repair Biomaterials*. <https://doi.org/10.1533/9781845696610.2.271>.
- [7] Jamarun, N., Elfina, S., Arief, S., Djamaan, A., & Mufitra. (2016). Hydroxyapatite material: Synthesis by using precipitation method from limestone. *Der Pharma Chemica*.
- [8] Larsson, S., & Fazzalari, N. L. (2014). Anti-osteoporosis therapy and fracture healing. *Archives of Orthopaedic and Trauma Surgery*. <https://doi.org/10.1007/s00402-012-1558-8>.
- [9] Magnan, B., Bondi, M., Maluta, T., Samaila, E., Schirru, L., & Dall'Oca, C. (2013). Acrylic bone cement: Current concept review. *Musculoskeletal Surgery*. <https://doi.org/10.1007/s12306-013-0293-9>.
- [10] Nabiyouni, M., Ren, Y., & Bhaduri, S. B. (2015). Magnesium substitution in the structure of orthopedic nanoparticles: A comparison between amorphous magnesium phosphates, calcium magnesium phosphates, and hydroxyapatites. *Materials Science and Engineering C*, 52. <https://doi.org/10.1016/j.msec.2015.03.032>.
- [11] Ratnayake, J. T. B., Mucalo, M., & Dias, G. J. (2017). Substituted hydroxyapatites for bone regeneration: A review of current trends. *Journal of Biomedical Materials Research - Part B Applied Biomaterials*. <https://doi.org/10.1002/jbm.b.33651>.
- [12] Sun, Y., Kwok, Y. C., & Nguyen, N. T. (2006). Low-pressure, high-temperature thermal bonding of polymeric microfluidic devices and their applications for electrophoretic separation. *Journal of Micromechanics and Microengineering*. <https://doi.org/10.1088/0960-1317/16/8/033>.
- [13] Ternane, R., Cohen-Adad, M. T., Panczer, G., Goutaudier, C., Kbir-Arighuib, N., Trabelsi-Ayedi, M., ... Massiot, D. (2002). Introduction of boron in hydroxyapatite: Synthesis and structural characterization. *Journal of Alloys and Compounds*. [https://doi.org/10.1016/S0925-8388\(01\)01558-4](https://doi.org/10.1016/S0925-8388(01)01558-4).
- [14] Xu, H. H. K., Wang, P., Wang, L., Bao, C., Chen, Q., Weir, M. D., ... Reynolds, M. A. (2017). Calcium phosphate cements for bone engineering and their biological properties. *Bone Research*. <https://doi.org/10.1038/boneres.2017.56>