

# Synthesis of Biomaterial Hydroxyapatite from Limestone by Using Two-Step Conversion

S. Arif<sup>a\*</sup>, G. N. Hermana<sup>a</sup>, Z. Khalida<sup>a</sup>, Moch. Wisnu Arif S<sup>a</sup>, Ika Puspita<sup>b</sup>

<sup>a</sup>Mechanical Engineering Department, State Polytechnic of Malang PSDKU Kediri, Kediri, East Java, Indonesia

<sup>b</sup>Engineering Physics Department, Sepuluh Nopember Institut of Technology, Surabaya, East Java, Indonesia

## ABSTRACT

Hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] is natural ceramic material which is often used for artificial bone reconstruction. Hydroxyapatite consists calcium orthophosphate which the calcium element can be obtained from calcium hydroxide (Ca(OH)<sub>2</sub>), then the orthophosphate groups can be obtained from phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) In this research, hydroxyapatite was synthesized from mineral of Calcite (CaCO<sub>3</sub>) which obtained from the Campurdarat, Tulungagung. The hydroxyapatite synthesis steps are encompassed by the preparation of precursors and the synthesis process by using wet chemical manipulation or routes with 0, 0.6, and 0.8 M H<sub>3</sub>PO<sub>4</sub> concentrations. The XRF characterization shows that the percentage of calcium from the raw material is around 99%. This study successfully obtains the compound of Ca(OH)<sub>2</sub> as a source of hydroxyapatite. The concentration of H<sub>3</sub>PO<sub>4</sub> in hydroxyapatite synthesis process influences the synthesis results. For the concentration of H<sub>3</sub>PO<sub>4</sub> 0.6 M is still found the compound of Ca(OH)<sub>2</sub> due to not sufficient concentration for generating stoichiometric reaction to form the hydroxyapatite crystal phase. The difference result is shown H<sub>3</sub>PO<sub>4</sub> with concentration 0.8 M which the total synthesis product is hydroxyapatite.

**Keywords:** Hydroxyapatite, Calcite, Synthesis, Biomaterial.

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## 1. Introduction

Hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] is natural ceramic material which is often used in bone tissue reconstruction (Rodríguez-Lorenzo, 2001). Hydroxyapatite is an ideal artificial substitution or replacement for bone which fulfills the material properties such as osteogenic, biocompatible and non-toxic (Kurashina, 2002; Szcześ, 2017). Hydroxyapatite consists calcium orthophosphate which the calcium element can be obtained from calcium hydroxide (Ca(OH)<sub>2</sub>), then the orthophosphate groups can be obtained from phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) (Hsu, 2009). Naturally, (Ca(OH)<sub>2</sub> is obtained in the bones, shells and skins of anthropods and limestone in CaCO<sub>3</sub> phase.

Patel et.al. successfully synthesized the Hydroxyapatite by using calcium from egg shells by using wet chemical routes (Patel et al., 2019). Londoño-Restrepo, dkk has synthesized hydroxyapatite by calcining cow bone waste (Londoño-Restrepo et al., 2019). Klinkaewnaronga and Utara synthesized the nano particle of hydroxyapatite from limestone compounds by using ultrasonic waves (Klinkaewnarong and Utara, 2018). In this study, the source of hydroxyapatite was synthesized from local natural ingredients as an alternative from the dependence of imported bone filler materials for biomedical field. The local natural material is Calcite (CaCO<sub>3</sub>) mineral from Campurdarat, Tulungagung. Calcite becomes the main mineral in high

calcium limestone (Nancollas and Reddy, 1971). Therefore, calcite mineral can be used as a main source of calcium for the production of hydroxyapatite. In addition, the investigations were carried out on the phase transition from calcium precursor to calcium phosphate hydroxyapatite phase at different precursor concentration ratios.

## 2. Experimental Method

The hydroxyapatite biomaterial is synthesized in two stages. The first stage is the preparation of Ca(OH)<sub>2</sub> precursor from Mineral Calcite as a source of calcium for hydroxyapatite. Then in the second stage, the hydroxyapatite synthesis process is carried out by using the precipitation method or wet chemical route (Abidi and Murtaza, 2014).

The precursor is generated from manual milling and calcination of the calcite mineral. The calcination process was carried out at a temperature of 900 oC for 5 hours (Klinkaewnarong and Utara, 2018). Ca(OH)<sub>2</sub> was dissolved by using DI water until the concentration of Ca(OH)<sub>2</sub> becomes 1M. While the concentration of phosphates are H<sub>3</sub>PO<sub>4</sub> 0.6 M and 0.8 M. whereas for controlling pH in range 9-10, the ammonia is dripped on the solution. Furthermore, filtering and washing with aquadest is carried out. After filtering, the samples were dried at 100 oC for 24 hours. The final result is the characterization of synthesized hydroxyapatite by using XRD to analyze the crystal structure.

\* Corresponding author. Phone : +0-000-000-0000 ; fax: +0-000-000-0000.  
E-mail address: [author@institute.xxx](mailto:author@institute.xxx) .

### 3. Results and Discussions

To determine the percentage of calcium in calcite, an XRF result is shown in Table 1.

| Compound | Conc.Unit (%) |
|----------|---------------|
| S        | 0.013         |
| Ca       | 99            |
| Fe       | 0.17          |
| Co       | 0.094         |
| Cu       | 0.045         |
| Sr       | 0.038         |
| Er       | 0.1           |
| Lu       | 0.19          |

The XRF data shows the dominant element in calcite is calcium with the percentage is around 99%. The calcite mineral is calcined for removing or decreasing CO<sub>2</sub> and converting the CaCO<sub>3</sub> compound into crystalline Calcium Oxide (CaO) with the following reaction:



The XRD wave of material with calcite calcination is compared to the CaO model (AMCSD 0008276) which is shown in Figure 1.

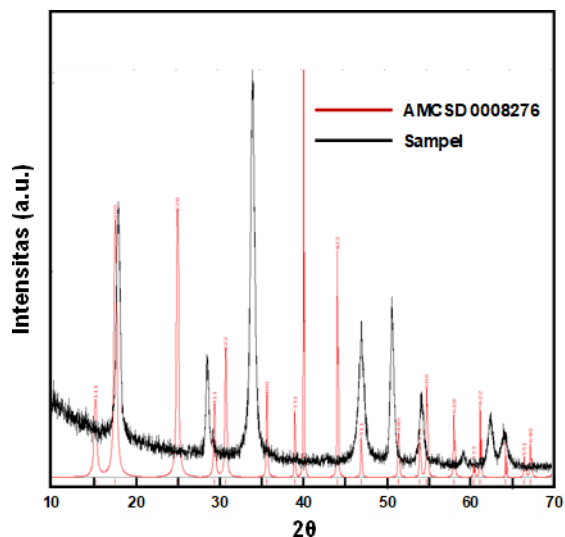


Figure 1. The diffraction pattern (XRD) of samples and AMCSD 0008276 model.

The fitting result between samples and AMCSD model 0008276 does not show the suitability of material formed with the CaO compound. This indicates that the peak in the sample is not the CaO crystalline phase.

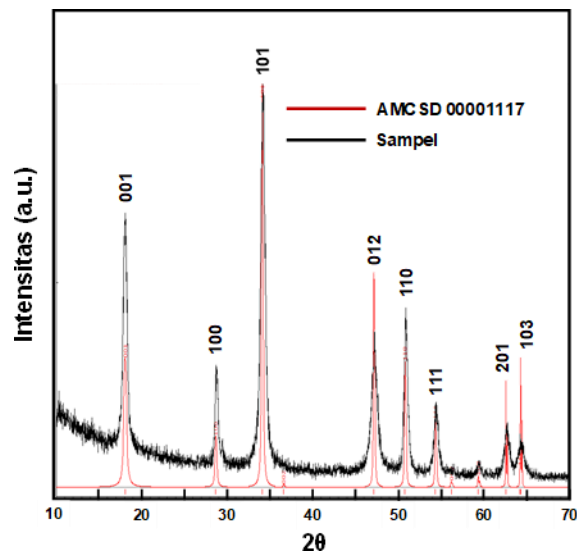


Figure 2. The diffraction pattern (XRD) of the sample and AMCSD 00001117 model

However, the calcite material has diffraction peaks which correspond to AMCSD 00001117 as shown in Figure 2. Based on the fitting results, the sample is more likely as crystalline calcium hydroxide Ca(OH)<sub>2</sub> phase. Thus, the callization process has succeeded in forming hydroxyapatite Ca(OH)<sub>2</sub>.

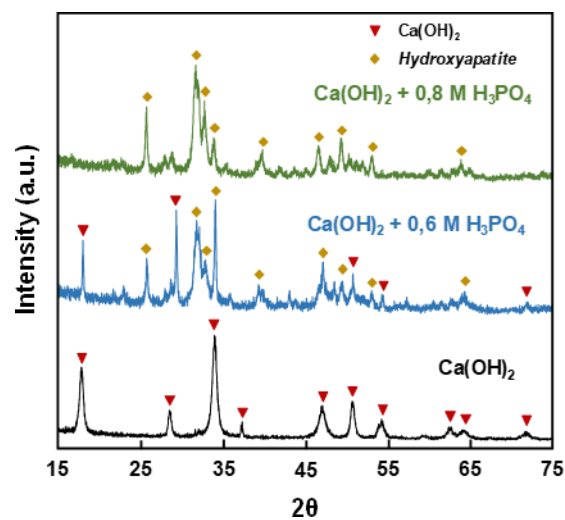


Figure 3. The XRD patterns of the synthetic products with concentration H<sub>3</sub>PO<sub>4</sub> 0.6 M and 0.8 M

The formation of the Ca(OH)<sub>2</sub> phase is started by formation of the CaO which is influenced by the calcination temperature. At temperatures of 700 – 900 oC, Calcite mineral loses around 34% of its constituent mass and CO<sub>2</sub> compounds are drastically reduced (Klinkaewnarong and Utara, 2018). Thus, the calcination process with temperature range 700 – 900 oC leads the crystal phase of the CaCO<sub>3</sub> compound to be whole CaO crystal. The changes of CaO phase to be crystalline Ca(OH)<sub>2</sub> due to the oxidation process after calcination. The samples which

contains CaO compounds are more easily oxidized and very reactive to interact with H<sub>2</sub>O in free air environment.

Figure 3 shows the hydroxyapatite peaks which suitable to JCPDS no. 09-0432 with space group P6<sub>3</sub>/m hexagonal crystal system. The hydroxyapatite sample with concentration of H<sub>3</sub>PO<sub>4</sub> 0.8 M produced good crystal structure. This is indicated by the absence of Ca(OH)<sub>2</sub> crystalline phase. Meanwhile, the hydroxyapatite sample with a concentration of H<sub>3</sub>PO<sub>4</sub> 0.6 M still leaves the precursor Ca(OH)<sub>2</sub> phase. This occurs due to the concentration ratio between Ca(OH)<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> is not sufficient for generating stoichiometric reaction to form the hydroxyapatite crystal phase. The formation of the hydroxyapatite phase depends on the availability of ions on PO<sub>4</sub><sup>3-</sup>, Ca<sup>2+</sup> and OH<sup>-</sup> in solution (Giardina and Fanovich, 2010).

#### 4. Conclusions

The hydroxyapatite biomaterial from calcite mineral which obtained from the Campurdarat, Tulungagung was successfully synthesized by using the precipitation method or wet chemical route. The XRF characterization result shows the percentage of calcium from the raw material around 99%. In this study also succeeded in obtaining calcium as Ca(OH)<sub>2</sub> solution as main source for producing hydroxyapatite. The concentration of H<sub>3</sub>PO<sub>4</sub> in hydroxyapatite synthesis process influences the results of its synthesis. For the concentration H<sub>3</sub>PO<sub>4</sub> 0.6 M, Ca(OH)<sub>2</sub> compounds were still found. Unlike the case with the concentration of H<sub>3</sub>PO<sub>4</sub> 0.8 M which the result of the whole synthesized is hydroxyapatite.

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