Preparation of CaCO3/MgO from Bangkalan's dolomite for raw biomaterial

S P Sholicha1, W Setyarsih1, G J Sabrina1, and L Rohmawati1

1Departement of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya, Kampus Unesa Ketintang, Surabaya 60231, Indonesia

E-mail: worosetyarsih@unesa.ac.id

Abstract. Dolomite is a double salt consisting of calcium carbonate (CaCO3) and magnesium carbonate (MgO) and is one of the two forms of limestone. This dolomite can be found in the Bangkalan area, which only used as the landfill and making light stone. Existence the great potential for dolomite as a biomaterial then in this research was carried by making CaCO3/MgO from dolomite using a simple calcination method at 600°C, 700°C and 800°C for one hour. The results of the calcination then carried out of XRD characterization. From the results of XRD found that the CaCO3/MgO phase was formed optimally at a temperature of 700°C.

1. Introduction
Bangkalan district which is located on the island of Madura, East Java, has the potential high rock minerals in the form of Jaddih mountainous, which are carbonate bases limestone, which consists of limestone, calcite mineral and dolomite limestone. The limestone hill is a mining location carried out by local residents, which is usually used as bricks, soil fillings, plant fertilizer [1] and animal feed [2] even sold to other areas. The existence of massive exploitation by local residents, then the government transferred the function of the mining site into a tourism area. But currently, there is still illegal mining of the limestone, especially dolomite minerals. The result of dolomite mining is sold to consumers at relatively cheap prices because ordinary people do not yet know the use of dolomite material as an advanced raw material. Advanced materials bases on dolomite are known as raw materials for biomaterials and ceramics. Dolomite as a biomaterial including functioning as antibacterial substances [3,4] that have not been studied optimally. Dolomite contains 94.5 % Ca and 5.5 % Mg [5]. Yamamoto et al report that calcination of dolomite with carbon coatings at a temperature of 400°C to 800°C produced optimum CaCO3/MgO content at temperature 700°C [3]. Furthermore, in the research of the same carried out calcination of dolomite without coating carbon at a temperature of 600°C to 800°C, the optimum CaCO3/MgO content was produced at a temperature of 800°C [6]. CaCO3/MgO showed good antibacterial activity in Staphylococcus aureus and Escherichia coli [6]. This is because CaCO3/MgO is a porous material that has adsorption ability that can damage the surface of bacterial growth to hamper [3]. Based on the above research, then the synthesis of CaCO3/MgO from natural limestone for raw biomaterial preparations with calcination temperatures of 600°C to 800 °C for one hour. Then the performer of XRD characterization to determine the phases contained in dolomite and the results of
the decomposition process [7]. The results of this research expected that CaCO₃/MgO content from dolomite formed optimally and can be used as raw biomaterial preparation.

2. Materials and Methode

2.1. Materials

The material used in this research was dolomite powder, which was taken from Jaddih hill limestone, Bangkalan District, Madura, East Java. To the resulted in the fine powder used mortal and pestle tools, and the sieves of 200 mesh. The calcination process uses a type furnace is L5/11/B170.

2.2. Preparation of CaCO₃/MgO

Preparation of CaCO₃/MgO was carried out by refining dolomite limestone using mortal and pestle until obtained dolomite powder. After that, the powder was sieved using a 200 mesh sieve and obtained homogeneous dolomite powder. The weighed using digital balance the brand of OHAUS PA224 amounted of 5 grams. Then the dolomite powder was calcined at a temperature of 600°C, 700°C and 800°C for one hour.

3. Instrumentation

The result of calcination from dolomite powder was characterized using XRD type of Philips X’Pert MPD (Multi Purpose Diffractometer) system, with radiation of anode Cu 40 kV, 30 mA, wavelength CuKα 1.54056Å and Bragg-Brentano optical light. The powder tested as big as 0.1 gram. Information generated from X-ray diffraction patterns in the form of a peak position (2θ), distance between fields (d) which shows the phase Miller index, diffraction (I). Each formula has a different crystal structure both on a single phase and several phases. The results of the characterization of XRD are then carried out using software match, so that obtained each percentage of CaCO₃ and MgO.

4. Result and Discussions

In phase identification and analysis of the size crystal from a simple tested needed some data from X-ray diffraction. Among them are, peak position (2θ), the distance between fields (d) and diffraction intensity (I). The result of this research match for CaCO₃/MgO powder at the calcination of 600°C (Figure 1). The result of this search match shows four phases that appear in software match, among other of CaCO3 (pdf card 96-900-0969), MgO (pdf card 96-100-0054), Dolomit (96-900-1419) and CaO lime (pdf card 96-900-6699). Each phase has a different percentage, which shows the optimum level that appears in the calcined dolomite powder, which is indicated by the number of peaks that appear. In Figure 1 shows the peak that appears on dolomite powder for the Magnesium Oxide Periclase phase was identified at the diffraction angle 2θ = 36.86°, 42.8°, 62.19°, 74.43°, and 78.56°. Calcite is the CaCO₃ phase detected at the diffraction angle 2θ = 22.94°, 29.18°, 30.90°, 36.04°, 39.40°, 43.19°, 46.91°, 46.99°, 48.25°, 56.52°, 57.19°, 57.51°, 60.47°, 60.63°, 60.74°, 62.95°, 64.40°, 64.73°, 72.70°, 78.56°, 81.33°, 83.66° and 84.74°. Referring to Rahman et al, the calcite phase was formed at 2θ = 29.8° [8]. Dolomite is the CaMg((CO₃)₂) with the intensity formed at 2θ = 16.93°, 31.50°, 34.41°, 36.04°, 37.56°, 41.85°, 45.39°, 46.18°, 49.88°, 51.96°, 52.43°, 60.36°, 60.97°, 63.48°, 64.10°, 65.73°, 67.17°, 78.42°, 78.56°, 83.53°, 84.60° and 84.84°. Lime is the CaO phase with the intensity formed at 2θ = 31.99°, 37.15°, 53.61°, and 63.77°.
Figure 1. Match analysis results for CaCO$_3$/MgO powder at the calcination 600°C

The highest peaks are dominated by the MgO and CaCO$_3$ with the percentages showed in Table 1.

### Table 1. Percentage of MgO and CaCO$_3$ phase at the calcination 600 °C

| Phase                  | Percentage (%) |
|------------------------|----------------|
| MgO Periclase          | 36.2           |
| Calcite (CaCO$_3$)     | 51.2           |
| Dolomite (CaMg(CO$_3$)$_2$) | 5.3   |
| Lime (CaO)             | 7.3            |

In Table 1, shows the percentage of each phase identified by the software Match. Calcite has the highest percentage compared to the other three phases. This proves that calcite is the most dominant mineral in dolomite from the Jaddih hill. However, in the results of the calcination process, there are various impurities detected such as Table 2.

### Table 2. Impurity at the calcination 600°C

| 2theta [°] | I/I0       |
|------------|------------|
| 17.80      | 279.48     |
| 28.41      | 125.37     |
| 29.22      | 1000.00    |
| 33.85      | 371.34     |
| 35.80      | 147.67     |
| 39.27      | 185.81     |
| 42.72      | 820.36     |
| 47.31      | 282.78     |
| 50.68      | 136.62     |
| 53.80      | 104.59     |
| 62.08      | 486.58     |

The appearance of dolomite and CaO phases for CaO for CaCO$_3$/MgO powder at the calcination 600°C in Table 2, because of the impurities are still bound to the main phase of CaCO$_3$/MgO, so that
Calcination is required at high temperatures of 700°C and 800°C. The following results of match analysis for CaCO$_3$/MgO powder at the calcination 700°C (Figure 2) and 800°C (Figure 3).

Figure 2 shows the phase formed in the calcination of 700°C identified by the software Match. The phase formed is three phases namely the Magnesium Oxide Periclase (MgO) phase, Calcite (CaCO$_3$) phase and Lime (CaO) phase. The CaCO$_3$ phase obtained is the dominant phase shown in Table 3. Magnesium Oxide Periclase (MgO) is formed at diffraction angle $2\Theta = 36.95^\circ$, $42.92^\circ$, $62.32^\circ$, $74.66^\circ$, and $78.66^\circ$. Calcite (CaCO$_3$) is formed at diffraction angle $2\Theta = 23.03^\circ$, $29.41^\circ$, $31.38^\circ$, $36.00^\circ$, $39.37^\circ$, $43.26^\circ$, $47.05^\circ$, $47.53^\circ$, $48.50^\circ$, $56.52^\circ$, $57.43^\circ$, $60.62^\circ$, $60.96^\circ$, $61.29^\circ$, $62.97^\circ$, $64.69^\circ$, $65.57^\circ$, $69.13^\circ$, $70.21^\circ$, $72.87^\circ$, $81.53^\circ$, $83.72^\circ$ and $84.73^\circ$. Lime (CaO) is formed at diffraction angle $2\Theta = 32.25^\circ$, $37.46^\circ$, $53.94^\circ$ and $64.23^\circ$.

| Table 3. Percentage of MgO and CaCO$_3$ phase at the calcination 700 ° C |
|-------------------------|-----------------------------|
| Phase                  | Percentage (%)              |
| Periclase (MgO)        | 36.2                        |
| Calcite (CaCO$_3$)     | 51.2                        |
| Calcium oxide lime (CaO)| 5.3                         |

At the calcination 700°C, in addition to the MgO, CaCO$_3$ and CaO phases is also impurities detected in the software Match and shown in Table 4.

| Table 4. Impurity at the calcination 700°C |
|-------------------------------------------|
| 2theta [°] | I/I0          |
| 18.00      | 204.33        |
| 28.70      | 145.26        |
| 34.07      | 362.93        |
| 43.04      | 668.66        |
| 50.79      | 155.90        |
| 62.37      | 468.99        |
Figure 3. Match analysis results for CaCO$_3$/MgO powder at the calcination 800°C

Figure 3 shows the phase formed at the calcination 800°C namely the Magnesium Oxide Periclase (MgO) phase, Calcite (CaCO$_3$) phase and Lime (CaO) phase. The percentage of the phase formed is shown in Table 5. Magnesium Oxide Periclase is formed at the diffraction angle $2\Theta = 36.88^\circ$, 42.96°, 62.35°, 74.66°, and 78.62°. Calcite is formed at the diffraction angle $2\Theta = 23.02^\circ$, 29.40°, 31.37, 36.04°, 39.42°, 43.11°, 47.13°, 47.48°, 48.50°, 56.54°, 57.39°, 57.99°, 60.65°, 60.93°, 61.27°, 63.00°, 64.59°, 65.46°, 78.36°, 81.48°, 83.92° and 86.24°. Lime is formed at the diffraction angle $2\Theta = 32.20^\circ$, 37.36°, 53.86°, 64.16°, 67.37°, 79.57°, and 88.56°. There is an impurity shown in table 6.

**Table 5. Percentage of MgO and CaCO$_3$ phase at the calcination 800 °C**

| Phase                | Percentage (%) |
|----------------------|----------------|
| Periclase (MgO)      | 40.3           |
| Calcite (CaCO3)      | 39.0           |
| Calcium oxide lime (CaO) | 20.7         |

**Table 6. Impurity at the calcination 800°C**

| 2theta [°] | I/I0       |
|------------|------------|
| 17.99      | 189.40     |
| 32.24      | 306.14     |
| 34.02      | 233.69     |
| 43.19      | 300.70     |
| 50.63      | 102.65     |

Based on the three XRD test results obtained the largest CaCO$_3$/MgO concentration on calcination 700°C with MgO of 42.3% and CaCO$_3$ of 54.9%. By increasing the temperature of calcination, the presence of CaO element has increased, such as the calcination temperature of 800°C, which is 20.7%. The presence of impurities in the form of CaO in the powder of CaCO$_3$/MgO then it is possible to reduce its potential as an antibacterial activity.

**5. Conclusion**

In this research, calcination was done at dolomite with a temperature of 600°C to 800°C. After XRD characterization, we can know the largest concentration of CaCO$_3$ and MgO with calcination of
700°C. The largest concentration of CaCO$_3$ and MgO composites was calcined at 700°C with MgO concentration of 42.3% and CaCO$_3$ of 54.9%.

**Acknowledgment**

Thanks to the Direktorat Riset Pengabdian Masyarakat Direktorat Jendral Penguatan Riset dan Pengembangan Kementerian Riset, Teknologi, dan Pendidikan Tinggi in the fiscal year 2017 trough UNESA Rector’s decision number 522/UN38/HK/LT/2017 and fiscal year 2018 number 252/UN38/HK/LT/2018. This research has been supported by the Department of Physics Universitas Negeri Surabaya. The research process was conducted at the Materials Physics Laboratory of Universitas Negeri Surabaya, Laboratory of Materials and Metallurgy and Chemical Engineering Laboratory of Institut Teknologi Sepuluh Nopember.

**References**

[1] Andriani R 2009 Analisa kadar kalsium oksida (CaO) dan magnesium Oksida (MgO) pada pupuk dolomit dan kiserit secara metode titrasi kompleksometri (Medan: Universitas Sumatra Utara).

[2] Yustanti E and Manaf A 2006 Dasar-dasar Teknik Kimia 1-9.

[3] Yamamoto O, Ohira T, Mohan D J, Fukuda M, Ozkal B, Sawai J and Nakagawa Z 2008 Tanso 232 77-81.

[4] Jannah Z, Mubarok H, Syamsiyah F, Putri A A H and Rohmawati L 2018 IOP Conf. Series: Mater. Sci. Eng. 367 012005.

[5] Munawaroh F, Muharrami L K, Triwikantoro and Arifin Z 2017 Identifikasi dan analisis komposisi kimia batu kapur di Kabupaten Bangkalan sebagai bahan dasar sintesis kalsium karbonat presipitas SNFP ID 20242.

[6] Yamamoto O, Ohira T, Alfarez K and Fukuda M 2010 Mater. Sci. Eng. 173 208-212.

[7] Royani A, Sulistiyono E and Sufiandi D 2016 J. Sains Materi Indonesia 18 41-46.

[8] Rahman M A, Halfar J and Shinjo R 2013 J. Sci: Adv. Mater. Phys. Chem. 3 120-125.