Synthesis of Precipitated Calcium Carbonate (PCC) as a Raw Paramagnetic Material Based on Ferrite-Calcite (Fe-CaCO3) and Its Potential Application

N Nurhayati1, E H Sujiono1, V Zharvan1, M Saleh1, A T Awiseng1 and M F Nursetya1

1Physics Department, Universitas Negeri Makassar, Makassar, Indonesia

*Email : nurhayati@unm.ac.id

Abstract. Precipitated calcium carbonate (PCC) has been conducted by solid-liquid-gas route process. The PCC powder was prepared from limestone from lime powder contain dolomite as raw material and 0.5 M of glucose solution. The PCC powder then characterized using XRD to identify the phase and FTIR to identify the functional group. Further analysis shows that the PCC have one major phase CaCO3 with peak characteristic at 2θ = 29.3° also the FTIR spectra shows the presence of CaCO3 at 871.70 cm⁻¹ and 1397.23 cm⁻¹.

1. Introduction

Precipitated calcium carbonate (PCC) widely used material in industrial world. They use a filler, adhesive, sealant, and reinforcement, and make it one the most high current demand in industry [1]. The PCC material chemically formulated as (CaCO₃) synthesized from carbonate/metacarbonate rock[2].

Some kind carbonate/metacarbonate rock syntesized into PCC is calcitic containing mineral (CaCO₃) embedded in limestone and dolomite[3]. Dolomitic rock is a carbonate rock tainted with impurity mixed dolomite mineral CaMg(CO₃)₂. On dolomitic rock there is calcium and calcite mineral which are able to produce PCC in industrial scale[4,5].

Calcium ferrite compounds exhibit soft ferromagnetism which has wide application in biomed, absorbing material. Therefore, it can be used for radar-absorbing materials in the calcium ferrite/graphite nano-composites which use (CaCO₃) as raw material of Calcium ferrite[6].

Based on the phase diagram of CaO-Fe₂O₃ system, it is known that there are three main phases of calcium ferrite compounds and those are 2CaO·Fe₂O₃ (Ca₂Fe₂O₅), CaO·Fe₂O₃ (CaFe₂O₄), and CaO₂·Fe₂O₃ (CaFe₂O₅). It is possible that the reaction between CaO and Fe₂O₃ results in other unstable calcium ferrite phases, such as CaFe₁₂O₁₉[7].

In previous study, some researchers succesfully conducted material CaFeO using mixture of CaCO₃ and Fe₂O₃ using some method [8,9,10]. The main objective of this reasearch is to synthesized PCC using dolomite. However, in dolomitic metacarbonate rock, contain some impurities mainly Mg and some SiO₂. Magnesium (Mg) can also influence the strength or morphology of the PCC[11].

Based on the previuos research by Jimoh, a green method to use for extracting Ca from Mg using glucose resulted until 87 % PCC yield. In this research we want to make more dolomite widely applicable in some field by modifying parameters for calcium ferrite paramagnetic material application[12].
In this paper, the PCC material was synthesized from dolomite limestone using carbonation route as a main process. The PCC then characterized to obtain its crystal structure and chemical bond.

2. Experimental Method
The materials that used in this research are natural lime powder contain dolomite, glucose, (D+glucose anhydrous (merch)), and Carbondioxide gas. The lime powder is crushed then filtered using 100 mesh filter. The filtered result of the powder then calcined in 900°C for 4 hours. Further, 40 g of the this powder then dissolved in 400 ml of 0.5M glucose solution and filtered to get soluble calcium glucose.

In carbonation process, the soluble calcium glucose is bubbled in carbonation chamber until pH 6.5 is obtained. Furthermore, the solution then centrifuge and washed to get clean precipitated. The sample then characterized by x-ray diffraction (Rigaku X’Pert, 2θ = 20° - 70°, λCuKα = 1.5406Å) method. The crystal size of the PCC powder can be obtained by using Debye-Scherrer equation [16]:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

with D is crystal size (nm), β is full width at half maximum (FWHM) parameter, θ is the Bragg diffraction angle (°) and λ is the wavelength. The functional groups of PCC were determined by fourier transform infrared (FTIR) method.

3. Results and Discussion
Figure 1 shows the x-ray diffraction of raw lime powder. It can be seen from the result of phase analysis using Match! software that the lime powder contains of three main phases: Ca(OH)₂, CaCO₃ and CaMg(CO₃)₂. Based on this data, the calcite phase (CaCO₃) is already exist on the that powder and has a metastable phase [15] but two major phases also exist as an additional phase: the calcium hydroxide and dolomite. Figure 2 shows the x-ray diffraction pattern of the raw lime powder after carbonation process. It can be confirmed from the result that only calcite as a major without any impurity. The calcite phase has a trigonal crystal structure (a=b=4.9915Å and c=17.0880Å) with characteristic value at 2θ = 29.36° and hkl value corresponding to (104) that same with others[17,18,19]. Further, by using Debye-Scherrer equation the crystal size of the PCC can be estimated is 23 nm.

Result analysis of FTIR can be seen in fig.3. In this characterization, PCC chemically was analyzed for the identification of substances formulated as CaCO₃. The measurement of the molecular bond vibration compounds, excited by radiation of a suitable frequency, when given the conditions for energy absorption by the molecules. This peak on the graph analyzed and matched based on functional group table and previous study[14]. Characteristic of calcite absorption peak are 871.70 cm⁻¹ and 1397.23 cm⁻¹.
Figure 1. The x-ray diffraction pattern of lime powder as a raw material (●=CaCO₃, ■=CaMg(CO₃)₂ and ♦=Ca(OH)₂).

Figure 2. The x-ray diffraction pattern of lime powder after carbonation process (●=CaCO₃).
The extraction process of Ca from CaMg(CO$_3$)$_2$ is done by heated CaMg(CO$_3$)$_2$ at 900°C for 4 hours. This heating process change the phase CaMg(CO$_3$)$_2$ into CaO,MgO and CO$_2$. The calcination process in dolomite occurs in two stages, first breakdown of MgCO$_3$ to MgO, followed by the decomposition of CaCO$_3$ into CaO and finally the total decomposition. The dolomite calcination reaction is as follows:

\[ \text{CaCO}_3 \cdot \text{MgCO}_3 + \text{Heat}1 \Rightarrow \text{CaCO}_3 \cdot \text{MgO} + \text{CO}_2 \]

\[ \text{CaCO}_3 \cdot \text{MgO} + \text{Heat} 2 \Rightarrow \text{CaO} \cdot \text{MgO} + \text{CO}_2 \]

The decomposition reaction of magnesium carbonate occurs earlier than that of calcium carbonate, because the energy required for the decomposition process of magnesium carbonate is lower. The reaction range of magnesium carbonate occurs at temperatures of 510°C - 750°C and calcium carbonate has a temperature of 800°C - 900°C[13]. Calcium Glucose solution filtered in Whatman filter paper then bubbled into carbonation chamber. The measured intial pH was 12.3 then bubbled by CO$_2$ gas with flowrate 1l/m. After a few second the solution then began turn into white orange colour that indicated CO$_2$ gas starting react with calcium glucose solution. The pH value was an important indicator in the carbonation test. The decrease of pH indicates that OH$^-$ ions are consumed and each Ca$^{2+}$ ion is carbonated due to adding CO$_2$ gas.

4. Conclusion

The PCC from lime powder has been succesfully synthesized by using carbonation route process. The raw material has three major phase: Ca(OH)$_2$, CaCO$_3$ and CaMg(CO$_3$)$_2$. After carbonation process, the calcite phase was obtained without any impurity phase. Further analysis show that the calcite phase has a trigonal crystal structure with peak characteristic at 2θ = 29.36° with hkl value corresponding to (104). Using Debye-Scherrer equation, the crystal size of the synthesized PCC is estimated near 23 nm.
From FTIR spectra, the synthesized PCC has a characteristic wavenumber at 871.70 cm\(^{-1}\) and 1397.23 cm\(^{-1}\).

**Acknowledgment**

This research was funded by Universitas Negeri Makassar under research scheme PNBP 2020, science laboratory of Universitas Hasanuddin, laboratory of oxide physics and laboratory of microstructure department of physics Universitas Negeri Makassar.

**References**

[1] Jimoh O.A., Ariffin, K.S., Hussin H.B., Temitope A.E., 2017a, Synthesis of precipitated calcium carbonate: a review. Carbonates Evaporites DOI 10.1007/s13146-017-0341-x.

[2] Gomez-Villalba LS, Lo’pez-Arce P, Alvarez de Buergo M, Fort R (2012) Atomic defects and their relationship to aragonite-calcite transformation in portlandite nanocrystal carbonation. Cryst Growth Des 12(10):4844–4852

[3] Apodaca L., E., dan Corathers L., A., (2017) Minerals Yearbook: LIME [ADVANCE RELEASE]. U.S. Department of the Interior U.S. Geological Survey.

[4] Jimoh, O.A., Ariffin, K.S., Hussin, H.B., Abdulkareem, T., 2017b. Compositional appraisal and quality implication of Emiworo metacarbonate deposit in Central Nigeria. J. Geol. Soc. India 89, 413e418.

[5] Somarathna, Y.R., Mantilaka, M.M.M.G.P.G., Karunaratne, D.G.G.P., Rajapakse, R.M.G., Pitawala, H.M.T.G.A., Wijayantha, K.G.U., 2016. Synthesis of high purity calcium carbonate micro- and nano-structures on polyethylene glycol templates using dolomite. Cryst. Res. Technol. 51, 207e214.s.

[6] Holmquist S., 1960, Two New Complex Calcium Ferrite Phases, Nature Vol 185., 10.1038/185604a0.

[7] Baqiya M., Asih R., Mastuki M., Triwikanotoro T. (2019) Ferrite-Based Nanoparticles Synthesized from Natural Iron Sand as the Fe\(^{3+}\) Ion Source. Intechopen.88027.

[8] Baqiya M., Asih R., Mastuki M., Triwikanotoro T. (2019) Ferrite-Based Nanoparticles Synthesized from Natural Iron Sand as the Fe\(^{3+}\) Ion Source. Intechopen.88027

[9] Amorim B.,, Morales M.,, a ,, Bohn F.,, Carriço A.,, de Medeiros S.,, N., Dantas A.,, 2016, Synthesis of stoichiometric Ca\(_2\)Fe\(_2\)O\(_5\) nanoparticles by high-energy ball milling and thermal annealing. Physica B.

[10] Madesa T., Dewi S., H., Adi W., A., 2016, Sintesis Dan Karakerisasi Komposit Smart Magnetic Berbasis Brownmillerite Ca\(_2\)Fe\(_2\)O\(_5\)/NiFe\(_2\)O\(_4\), Jurnal Forum Nuklir (JFN) Volume 10, Nomor 2.

[11] Jimoh, O.A., Ariffin, K.S., Hussin, H.B., Abdulkareem, T., 2017b. Compositional appraisal and quality implication of Emiworo metacarbonate deposit in Central Nigeria. J. Geol. Soc. India 89, 413e418.

[12] Jimoh O.A., Okoye P.U., Otojoju T.A., Ariffin K.S., 2018, Aragonite precipitated calcium carbonate from magnesite rich carbonate rock for polyethersulfone hollow fibre membrane application. Journal of Cleaner Production 195 (2018) 79e92.

[13] Sulistiyoeno E., Firdiyono F., Natasha N. C., Sufiandi D., (2015) Pengaruh Ukuran Butiran Terhadap Struktur Kristal Pada Proses Kalsinasi Parsial Dolomit, Majalah Metalurgi 3: 125-132.

[14] Fan, M., Dai, D., Huang, B. (2012). Fourier Transform Infrared Spectroscopy for Natural Fibres, in: Salih, S. (Ed.), Fourier Transform - Materials Analysis. InTech.

[15] Boulos R. A., Zhang F., Tjandra E. S., Martin A., D., Spagnoli D., & Raston C., L., 2014, Spinning up the polymorphs of calcium carbonate, Scientific Reports volume 4, Article number: 3616.

[16] Sujiyono, E. H., Zharvan, V., Dahlan, M. Y., Said, A. C. M., Agus, J and Samnur, S. Materials Today: Proceedings 13 (2019) 258-263.
[17] Munawaroh, F., Muharrami, L. K., Triwikantoro, T. and Arifin Z. ICBSA 2018, KnE Engineering pp. 98-104.
[18] Thriveni, T., Ahn, JW., Ramakrishna, C., Ahn, YJ and Han, C. Journal Korean Phys Soc 2016 68 131.
[19] Kirboga, S. and Oner, M. Chem Eng Trans 2003 32:2119-24 doi:10.3303/CET1332354.