Morphology Modification of Barium Hexaferrite to Nanorod Particle Using Chitosan and Starch as Template

Syahwin\textsuperscript{1}, Nasruddin MN\textsuperscript{1}, Muhammad Zarlis\textsuperscript{1}, Bambang Sunendar\textsuperscript{2}

\textsuperscript{1}University of North Sumatera, Jln. Bioteknologi - USU, Medan, 20155, Indonesia
\textsuperscript{2}Bandung Institute of Technology, Jln. Ganesha No.10 - Bandung 40132, Indonesia

Abstract. Barium hexaferrite is known as a permanent magnet that has hexagonal or granules morphologies. Magnetic field of barium hexaferrite can be increased by changing its morphology. A rod-shaped barium hexaferrite is expected to result in higher magnetic field compared to granules even though the volumes of both are the same. This study aims to synthesize a rod-shaped barium hexaferrite and to evaluate its magnetic properties. Barium hexaferrite was synthesized using sol-gel method by mixing barium nitrate and iron (III) nitrate nonahydrate with molar ratio of 1:12. Chitosan 1\% was added as dispersant and starch 0.5\% (w/v) was used as template with variation in volume (5\%, 10\% and 15\% (v/v)). The solution was dried at 100°C for 48 hours and resulting xerogel was then calcined at 1000°C for 2 hours to obtain barium hexaferrite powder. X-Ray D result demonstrated the presence of barium hexaferrite with small fraction of hematite and pure barium hexaferrite. Scanning electron microscopy images showed different concentrations of starch generated different size and morphologies of resulting barium hexaferrite. A rod shaped barium hexaferrite was formed for all samples that prepared using starch template, however hexagonal shape was still found in all samples. The size of resulting barium hexaferrite is decrease by increasing the concentration of starch. The particle size of barium hexaferrite measured was 125 nm thickness with 500 nm length for 5\% starch, 109 nm thickness and 406 nm length for 10\% starch and 62.5 nm thickness and 406 nm length for 15\% starch. Barium hexaferrite synthesized without using starch and chitosan produced hexagonal morphology with the thickness of 240-574 nm and length of 574-957 nm. Vibrating Sample Magnetometer showed hysteresis curve as the percentage variation of starch was used, higher amount of starch used tends to increase the values of saturation and remanence. An very significant increase in coercivity value amounted to 457.1\% occurred in the use of 10\% starch. It can be concluded that starch can be used as rod-shaped template in sol-gel method to produce barium hexaferrite. By using chitosan and starch in the process of synthesis of barium hexaferrite using sol-gel method can increase the value of the magnetization and the coercivity barium hexaferrite.

1. Introduction

Barium hexaferrite (BaFe\textsubscript{12}O\textsubscript{19}) is one of high-coercive magnetic material that is among the most commonly used and it is still promising because of its superior properties such a slow production costs, high Curie temperature, high coercivity, chemical stability and corrosion resistance as reported by Burak Kaynar M. et al., Dursun Set al., Samira Mandizadeh et al., Mahgooba A and Hudeish A. Y.,
Jun Young Kwak et al[1-5]. Barium hexaferrite is one of the M-type hexagonal ferrite that belong to magnetoplumbite group. The molecular structure of M-type ferrite is made up of one R and one S block with an overlap of hexagonally and cubically packed layers by Chauhan et al [6]. Hexagonal ferrites, also called ashexaferrites, are magnetic materials that are important and useful for various industrial applications such as magnetic recording, data storage devices, microwave devices, and permanent magnets. The most famous type of hexaferrite are the M-type, Y-type, Z-type, W-type, X-type and N-type as reported by Pullar R.C. [7]. Barium hexaferrites is also known as an organic-based magnet because it constitutes its morphology oxygen tends to form hexagonal. Organic molecule-based magnet has all the traits commonly associated with metal-based (or atom based) magnets, for example, hysteresis and remanence, saturation magnetization and coercivity it as reported by Joel S. Miller[8]. Some work reported that the most common morphologies of barium hexaferrite were hexagonal shapes [9-17]. Based on the morphology of the barium ferrite, a magnetic field can be increased by forming the rod-shaped[18].This study aims to modify the morphology of the barium hexaferrite to a nanorod shape. In this study barium hexaferrite was prepared using wet-chemical Sol-Gel method. The sol–gel method can realize molecular level mixing and that the dispersant can improve the activity of the reactants, which helps to form the single-phase spinel barium ferrite [19], by using the sol-gel method it is easy to add the dispersant and nanorod template. In this research we used chitosan 1% as a dispersant and 0.5% starch with different volume ratio as a template to obtain a rod-shaped morphology which will increase the value of magnetization.

Chitosan is a biosourced polysaccharide obtained by alkaline deacetylation of chitin [20,21]. Chitosan acts as a structural dispersant as it contain amino and hydroxyl functional group that are the able to bind the metal ions. Chitosan is a good dispersant for iron oxide [22].

Starch is an insoluble glucan composed of two polymers of glucose, amyllopectin and amyllose[23]. The amyllopectin has branched structure while amyllose has linear structure. The amyllose content in the starch is expected to be able to act as nanorod template.

2. Materials and Method
Barium nitrate (Ba (NO₃)₂, 99.9%, Merck), Iron(III) Nitrate nanohydrate (Fe (NO₃)₃·9H₂O, 99.9, Merck) were used as a precursor with a molar ratio of 1:12 according to the stoichiometric ratio. Acetate acid (CH₃COOH, 99.8%, Merck) was used as solvent chitosan, low molecular weight chitosan, starch commercial products, Demineralized water (DM water) as the solvent. Before hand prepared solution of 1% chitosan (a ratio of 1g chitosan was dissolved in 100 ml of 2% acetate acid) here after starch solution 0.5% was prepared by dissolving 0.5 g of starch in 100ml DM water at a temperature of 70°C.

Precursor solution was made by inserting the Ba(NO₃)₂ into DM water while stirring using a magnetic stirrer for 10 minutes then Fe(NO₃)₃·9H₂O was added into the precursor solution and stirred constantly for 10 minutes. To the precursor solution was added a solution of chitosan 1% of 10% v/v solution was continuously stirred for 15 minutes then added a 0.5% starch solution: 5% v/v, 10% v/v and 15% v/v of the solution keep stirring for 30 minutes, then the solution was stirred using homogenizer at 1000 rpm rotational speed in order to form a homogeneous solution. After the solution was dried in an oven with a temperature of 100°C for 48 hours, resulting xerogel was taken and crushed using a mortar to obtain a powder. Powder was then calcined in a furnace at a temperature of 1000°C with holding time for 2 hours to obtain a compound BaFe₁₂O₁₉. The powder was tested contentcrystal using a X-Ray Diffraction (XRD) Philips Analytical type: PW1710 basedthen photographed morphology using a Scanning Electron Microscope (SEM) JEOL-JSM-6510 LV and last tested properties of magnetic using a Vibration Sample Magnetometer (VSM) Oxford type: VSM 1.2H while the flow chart of the experiment can be seen in Figure 1.
3. Results and Discussion

3.1. XRD-analysis.

The XRD diffraction pattern shows that barium hexaferrite is successfully formed as can be seen in Figure 2, as also indicated by reflection peaks at: 32.60°; 34.46°; 35.37°; 37.29°; 40.62° (2θ). The sample prepared using 5% (v/v) starch still contains hematite while in the one using 10% (v/v) starch no hematite has been found indicating it is a pure BaFe$_{12}$O$_{19}$. 

**Figure 1.** The flow chart of barium hexaferrite powders synthesis.
3.2. SEM-analysis
The SEM microgram images of barium hexaferrite morphologies can be seen in Figure 3. The addition of starch would cause the formed morphology tends to decompose due to the dispersant, and the obtained rod-shaped morphology is caused by the template while the size of its morphology is likely to first get the thick size and then dwindling to reach a size of 62.5nm, the amount of the morphology of rod-shaped is still less than the morphology of hexagonal shape, and it is likely due to the lower amount of amylase than amylopectin. The chemical structure is linear amylase it binds morphological precursor that has been separated by 1% Chitosan solution. Thus Starch can be used as a template to obtain nanorod morphology.

![Figure 2. Diffraction pattern of barium hexaferrite.](image)

![Figure 3. The shape and size BaFe$_{12}$O$_{19}$ morphology of various samples. (a) BaFe$_{12}$O$_{19}$ (unused chitosan and starch); (b) BaFe$_{12}$O$_{19}$(starch 5%v/v); (c) BaFe$_{12}$O$_{19}$(starch 5%v/v); (d) BaFe$_{12}$O$_{19}$(starch 15%v/v).](image)
Table 1. SizeMorphology of BaFe$_{12}$O$_{19}$.

| No | Starch Template (v/v) | Morphology            | Thick (nm)  | Length (nm) |
|----|-----------------------|-----------------------|-------------|-------------|
| a  | 0 %                   | Hexagonal & Granular  | 240 – 574   | 574 - 957   |
| b  | 5 %                   | Hexagonal & Rod       | 125 – 775   | 500 – 625   |
| c  | 10 %                  | Hexagonal & Rod       | 109 – 312,5 | 406 – 531,5 |
| d  | 15 %                  | Hexagonal & Rod       | 62.5 – 140.6| 406 – 1250  |

From Table 1 shows the result obtained by adding starch rod-shaped morphology are getting smaller.

3.3. VSM-analysis.
Results of characterization using Vibration Sample Magnetometer (VSM) can be seen in Table 2 and Figure 4.

Table 2. Magnetization of BaFe$_{12}$O$_{19}$

| No | Starch Template (v/v) | Saturation $M_s$ (emu/g) | Remanence $M_r$ (emu/g) | Coercivity $H_c$ (tesla) |
|----|-----------------------|--------------------------|-------------------------|-------------------------|
| A  | 0 %                   | 58.6                     | 33                      | 0.07                    |
| B  | 5 %                   | 54                       | 31.6                    | 0.21                    |
| C  | 10 %                  | 59.8                     | 36.4                    | 0.32                    |
| D  | 15 %                  | 62.2                     | 37.5                    | 0.28                    |

Figure 4. Hysteresis curve of BaFe$_{12}$O$_{19}$ at different used starch

Based on Table 2, and Figure 4 an increasingly high percentage of starch is used which tends to increase the value of saturation, remanence and coercivity of barium hexaferrite but the optimal value of coercivity is obtained on the use of 10% (v/v) starch, to demonstrate that the use of starch would enhance the magnetic properties of barium hexaferrite. Magnetization values obtained in
this study is still lower than the theoretical value of about 72 emu/gas reported by the Haneda K. And Kojima[24], this is likely due to the morphology of the formed stem, in addition the value of the magnetization is also influenced by many factors, such as the chemical composition, particle size, degree of crystallinity, magnetic anisotropy, and so on. Nevertheless, the novelty introduced through the use of an organic template derived from natural polymer starch has improved the value of the magnetization of barium hexaferrite.

4. Conclusion

Materials which have been synthesized in this study are barium hexaferrite as was verified or confirmed by the experimental inspection employing the X-Ray Diffraction technique. Barium hexaferrite morphology can be modified into a nanorod shape through the wet chemical process using sol-gel method by adding a 1% solution of chitosan as a dispersant and 0.5% starch solution as a template. Magnetization values barium hexaferrite obtained increased after use starch as a template that is characterized by the formation of nanorod morphology. This results also obtained a significant increase in coercivity value amounted to 457.1% the use of starch 10% (v/v) in the precursor solution. For further research it is expected to increase the amount of amylose which is used in a manner that reduces the amount amylopectin exist in starch that can multiply the number of nanorod morphology formed it is expected to further increase the value of the magnetization of barium hexaferrite.

References

[1] Kaynar M B, Özcan S, Shah S I 2015 Synthesis and magnetic properties of nanocrystalline \( \text{BaFe}_{12}\text{O}_{19} \) Ceramic International. (http://dx.doi.org/10.1016/j.ceramint.2015.05078)
[2] Dursun S, Topkaya R, Akdogan N, Akloy S 2012 Comparison of the structural and magnetic properties of submicron barium hexaferrite powders prepared by molten salt and solid state calcination routes Ceram Int 38 3801–6.
[3] Mandizadeh S, Soofivand F, Salavati-Niasari M 2015 Sol–gel auto combustion synthesis of \( \text{BaFe}_{12}\text{O}_{19} \) nanoceramics by using carbohydrate sugars as a novel reducing agent Advanced Powder Technology xxxx
[4] Mahgooba A and Hudeish A Y 2012 Thermal annealing effect on the structural and magnetic properties of barium hexaferrite powders American Academic & Scholarly Research Journal 4 5.
[5] Kwak J Y, Lee C S, Kim D and Kim Y I 2012 Characteristics of Barium Hexaferrite Nanoparticles Prepared by Temperature-Controlled Chemical Coprecipitation. Journal of the Korean Chemical Society 2012, 56 5.
[6] Chauhan C C, Jotania K B, Jotania K R 2013 Structural Properties Of Cobalt-Substituted Barium Hexaferrite Nanoparticles Prepared By A Thermal Treatment Method Nanosystems: Physics, Chemistry, Mathematics 4 3 363–36.
[7] Pullar R C 2012 Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite Ceramics 57 1 191
[8] Miller J S 2014 Organics and molecule-based magnets Review Materials Today 17 5
[9] Jie L, Wu Z H, Xun L Y, Li L Y, Bing M Y 2012 The structural and magnetic properties of barium ferrite powders prepared by the sol gel method Chin. Phys. B 21 1 017501.
[10] Tan G, Chen X 2013 Structure and multiferroic properties of barium hexaferrite ceramics. Journal of Magnetism and Magnetic Materials 327 87–90.
[11] Zhao L, Lv X, Wei Y, Ma C, Zhao L 2013 Hydrothermal synthesis of pure \( \text{BaFe}_{12}\text{O}_{19} \) hexaferrite nanoplatelets under high alkaline system Journal of Magnetism and Magnetic Materials 332 44–47.
[12] An G H, Hwang T Y, Kim J, Kim J B, Kang N, Jeon K W, Kang M, Cho Y H 2014 Novel Method For Low Temperature Sintering Of Barium Hexaferrite Withmagnetic Easy-Axis Alignment. Journal of the European Ceramic Society 34 1227–1233.
[13] Ahmed N M A, Helmy S I 2013 Innovative methodology for the synthesis of ba-m hexaferrite BaFe₁₂O₁₉ nanoparticles Materials Research Bulletin 48 3394–3398.

[14] Chen D, Liu Y, Li Y, Zhong W, Zhang H 2012 Low-temperature sintering of m-type barium ferrite with BaCu(B₂O₅) additive Journal of Magnetism and Magnetic Materials 324 449–452

[15] Khorrami S A, Isllampour R., Bakhtiari H., Naeini Q S M 2013 The Effect Of Molar Ratio on Structural and Magnetic Properties of BaFe₁₂O₁₉ nanoparticles prepared by sol-gel auto-combustion method Int. J. Nano Dimens. 3 3 191-197.

[16] Mosleh Z, Kamelin P, Ranjbar M, Salamati H 2014 Effect of annealing temperature on structural and magnetic properties of BaFe₁₂O₁₉ hexaferrite nanoparticles Ceramics International 40 7279–7284.

[17] Xu X, Park J, Hong Y K, Lane A M 2015 Synthesis and characterization of hollow mesoporous BaFe₁₂O₁₉ spheres Journal of Solid State Chemistry 222 84–89.

[18] Mohapatra J, Mitra A, Tyagi H, Bahadur D, Aslam M 2015 Iron oxide nanorods as high-performance magnetic resonance imaging contrast agents The Royal Society of Chemistry.

[19] Jie L, Wu Z H, Xun L Y, Li L Y and Bing M Y 2012 The structural and magnetic properties of barium ferrite powders prepared by the sol gel method Chin. Phys. B 21 1 017501

[20] Elsabee M Z and Abdou E S 2013 Chitosan based edible films and coatings: A Review. Mater Sci Eng. C 33 1819–41.

[21] Baouche N M, Elchingier P H, de Baynast H, Pierre G, Delattre C, Michaud P 2014 Chitosan as an adhesive European Polymer Journal 60 198–213

[22] Tsai Z.-T 2010 In situ preparation of high relaxivity iron oxide nanoparticles by coating with chitosan: A potential MRI contrast agent useful for cell tracking J. Magn. Magn. Mater., 322 208–213.

[23] Corre D L, JBras J and Dufresne A 2010 Starch Nanoparticles: A Review Biomacromolecules 11 1139–1153.

[24] Haneda K and Kojima J H 1973 Appl. Phys 44, 3760