Journal of Magnetism and Its Applications, 2 (1) 2022, 9-13

http://www.jourmag.org/index.php/jma

Journal of Magnetism and Its Applications

Received August 17th 2022; received in revised August 22nd 2022; accepted August 25th 2022

Research articles

Fabrication and Characterization of Cobalt Ferrite ($CoFe_2O_4$) using Sonochemical Method for Promising Hyperthermia Sensor

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Article info

Keywords:
Cobalt ferrite
Sonochemical method
Hyperthermia sensor
Sintering temperature
Nanosphere

Abstract

This research aimed to identify the effect of the sintering temperature on the morphology and magnetic properties of $CoFe_2O_4$ using sonochemical methods. The prepared $CoFe_2O_4$ was characterized by X-ray diffraction (XRD) for phase identification, scanning electron microscope (SEM) for morphology, and magnetic properties using a vibrating sample magnetometer (VSM). Phase identification analysis showed that single phase $CoFe_2O_4$ with crystallite size of unsintered and sintered at 500, 600, and 700 °C were 24, 18, 21, and 27 nm, respectively. In the morphological analysis, the sample showed a nanosphere and an agglomerated form. The sample with the largest grain size was 34.11 nm sintered at 700 °C. Saturation magnetization, remanent magnetization, and coercivity field had more substantial values of 75.24 emu/g, 39.39 emu/g, and 0.198 T, respectively.

1. Introduction

In recent years, nanoparticles have become a thought-provoking subject since the material in the nanodimension carries particles with more exceptional chemical or physical properties than material with more sizeable dimensions, such as the 1-100-nm particles. In addition, their natures can be altered through controlling the material dimension, adjusting the chemical composition, modifying the surface, and particle interaction of the particles. The cobalt ferrite ($CoFe_2O_4$) nanoparticle is one of the potential materials [1]. It has the potential for superparamagnetic characteristics [2], high coercivity [3], electrical resistivity, and high saturation magnetization [4]. Therefore, cobalt ferrite can be applied in the biomedical field as a drug administrator, magnetic resonance imaging (MRI), hyperthermia for cancer treatment, and an excellent material for high-density magnetic storage [5].

One of the most effective and efficient nanoparticle synthesis methods is a sonochemical method [6]. The principle of the sonochemical process is the use of a high-frequency ultrasound wave radiated to the liquid medium. If a solution is radiated using an ultrasonic wave, collisions among high-pressure particles compose the solution. In addition to its practicality and fast reaction rate, the sonochemical method can also properly increase the reaction results, accelerate the reaction rate, break down the massive crystal aggregate into smaller pieces (up to nanosize), and facilitate the catalytic process [7].

Cobalt ferrite can also applicate to medical applications because of its magnetic properties. Hyperthermia is one the modality cancer treatments with elevated temperature between 41 °C and 45 °C and treatment time of at least 30 minutes, has been paid considerable attention due to its clinical efficacy, such as minimizing clinical side effects and can selectively destroy a localized or deep seated cancer tumor by heating with magnetic field [8]. Well-dispersed cobalt nanoparticles in hyperthermia application give effective and controlled heat generation [9].

To date, studies on effective synthesis methods to obtain single-phase $CoFe_2O_4$ resulted in the best magnetic properties seem sparse. This research describes how the magnetic properties change from hard magnetic to soft magnetic material as the sintering conditions vary and also study the sintering temperature in term of physical and magnetic properties. The sintering temperature should be modified in the synthesis process using the sonochemical method. Adjustment of the temperature in the magnetic nanoparticle synthesis using the sonochemical method affects the size and morphology. Therefore, temperature adjustment becomes one of the determinant factors in concluding the size and magnetic feature in nanoparticle synthesis using the sonochemical method. This study investigates four variations in the sintering temperature used in the synthesis of cobalt ferrite through the sonochemical process.

2. Materials and Methods

2.1 Material Preparation

This study was experimental research that aimed to obtain descriptive data on the phase characteristic, magnetic characteristic, and morphology of cobalt ferrite powder prepared using the sonochemical method. It sought to identify the effects of sintering temperatures in the phase, morphology, and magnetic feature of $CoFe_2O_4$. The raw material for cobalt ferrite is cobalt nitrate hexahydrate ($Co(NO_3)\cdot 6H_2O$) with 99% purity, iron (III) nitrate nonahydrate ($Fe(NO_3)\cdot 9H_2O$) with 99% purity that were bought from Merck and deionized water as the solvent.

2.2 Sonochemical Synthesis

Cobalt nitrate hexahydrate and iron (III) nitrate nonahydrate were mixed in the deionized water with a 1:10 ratio (material: solvent). In addition, this study also used a magnetic stirrer for the blending process with 200 rpm. The ultrasonic process was carried out for five minutes, followed by dropwise NaOH (1:1) with the solvent and another ultrasonic method for 30 minutes. In the next stage, it was placed in a centrifuge for 10 minutes at 4000 rpm until the solution agglomerated. Then, it was washed using distilled water until it reached pH 7. After that, the sample was dried and crushed to transform it into powder. After that, the samples were sintered at temperature of 500, 600, and 700 °C, and one sample was unsintered with a holding time of one hour.

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DOI: 10.53533/JMA.v2i1.20

2.3 Characterizations

The samples were tested using X-ray diffraction (XRD) PAN Analytical Cu-Kα (λ = 1.54 Å) to identify the formulated phase and the crystallite size. Meanwhile, the scanning electron microscopy (SEM) of Phenom was used to decide the grain size and morphology, and the vibrating sample magnetometer (VSM) of Oxford 1.2H at room temperature was used to determine the magnetic properties of the samples.

3. Results and Discussion

3.1 Phase Identification of Cobalt Ferrite

The results of the cobalt ferrite XRD test results with different sintering temperatures using the sonochemical method are illustrated in Figure 1. The figure shows that the sintered and unsintered samples have peaks and form a single phase. From the highest peak in the 311 indexes, the sintering temperature of 700 °C produces the highest peak. Consequently, the sample with 700 °C sintering temperature also has the highest degree of crystallinity. The high degree of crystallinity is affected by the swift and simultaneous nucleation and crystal growth process due to the high degree of oversaturation when the temperature was increased during the synthesis process [10, 11]. The crystallite size of the cobalt ferrite nanoparticles was determined using the Scherrer formula [12] as shown in Equation (1).

$$d = \frac{K.\lambda}{\beta \cos\theta} \quad (1)$$

Description:
d : crystallite size diameter (nm)
K : constant (0.9)
λ : wavelength (1.5406 Å)
β : FWHM (rad)

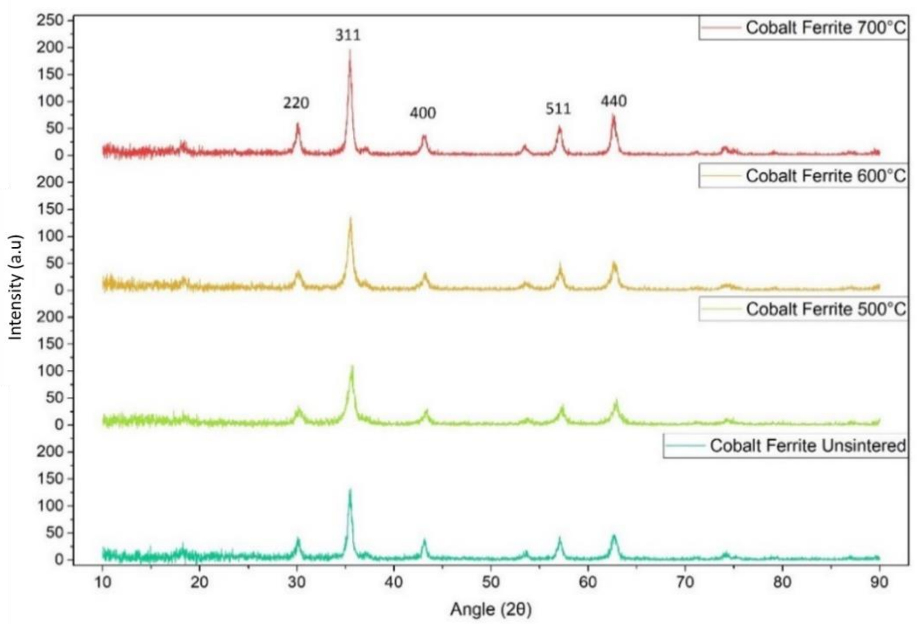

Fig. 1. X-ray diffraction patterns of cobalt ferrite at different sintering conditions

The results of the analysis on the XRD data at 311 peak using the sintering temperature of 500, 600, 700 °C, and the unsintered sample are illustrated in Figure 1. The results of the Scherer analysis show that the crystallite sizes of the sintering temperature of 500, 600, and 700 °C are 18, 21, and 27 nm, respectively. The increasing size of the crystallite due to the higher sintering temperature that causes the agglomeration of non-uniform particle increases [13]. Meanwhile, the unsintered sample has a crystallite size of 24 nm. Table 1 shows that a higher sintering temperature produces a greater crystallite size caused by increasing heat treatment that simultaneously accelerates the crystallite formulation but generates a larger grain size [14]. In addition, the cobalt ferrite synthesis using sonochemical processes has peaks and creates a single phase.

Table 1. Results of the XRD analysis on cobalt ferrite at the peak [311]

No	Sintering Temperature	Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Crystallite size (nm)
1	500° C	35.62	85.95	0.47	2.52055	18
2	600° C	35.50	115.63	0.39	2.52833	21
3	700° C	35.47	166.87	0.31	2.53030	27
4	Unsintered	35.48	103.91	0.35	2.52977	24

3.2 Morphology of Cobalt Ferrite

Figure 2 illustrates the morphology of the SEM test results in all samples. The SEM test aims to analyze and compare the morphology of the cobalt ferrite with different treatments. This test used a 100,000 times of magnification. The morphology of the unsintered sample, samples with sintering temperatures of 500, 600, and 700 °C, are presented in Figures 2a-2d, respectively. In the material characterization stage, to analyze the morphology, the average distribution of the crystallite size was also examined. The grain size can be measured on the surface using SEM.

According to the illustration in Figure 2, the grain size is 33.87 nm, while samples that have been sintered with 500 °C and 600 °C generate the smallest grain size of 31.85. Additionally, the sample that has been sintered with a temperature of 700 °C has an enormous grain size of 34.11 nm. The data illustrated in Figure 2 also shows that the unsintered sample and the samples sintered with a temperature of 500, 600, and 700 °C temperature have no significant difference, while all samples have a homogeneous form. Also, the results of SEM synthesis on cobalt ferrite using a sonochemical shows no agglomeration, even with various sintering temperatures. It means that the particles of cobalt ferrite particles will adjust, connect, and form a single phase in a new lattice structure [4, 15].

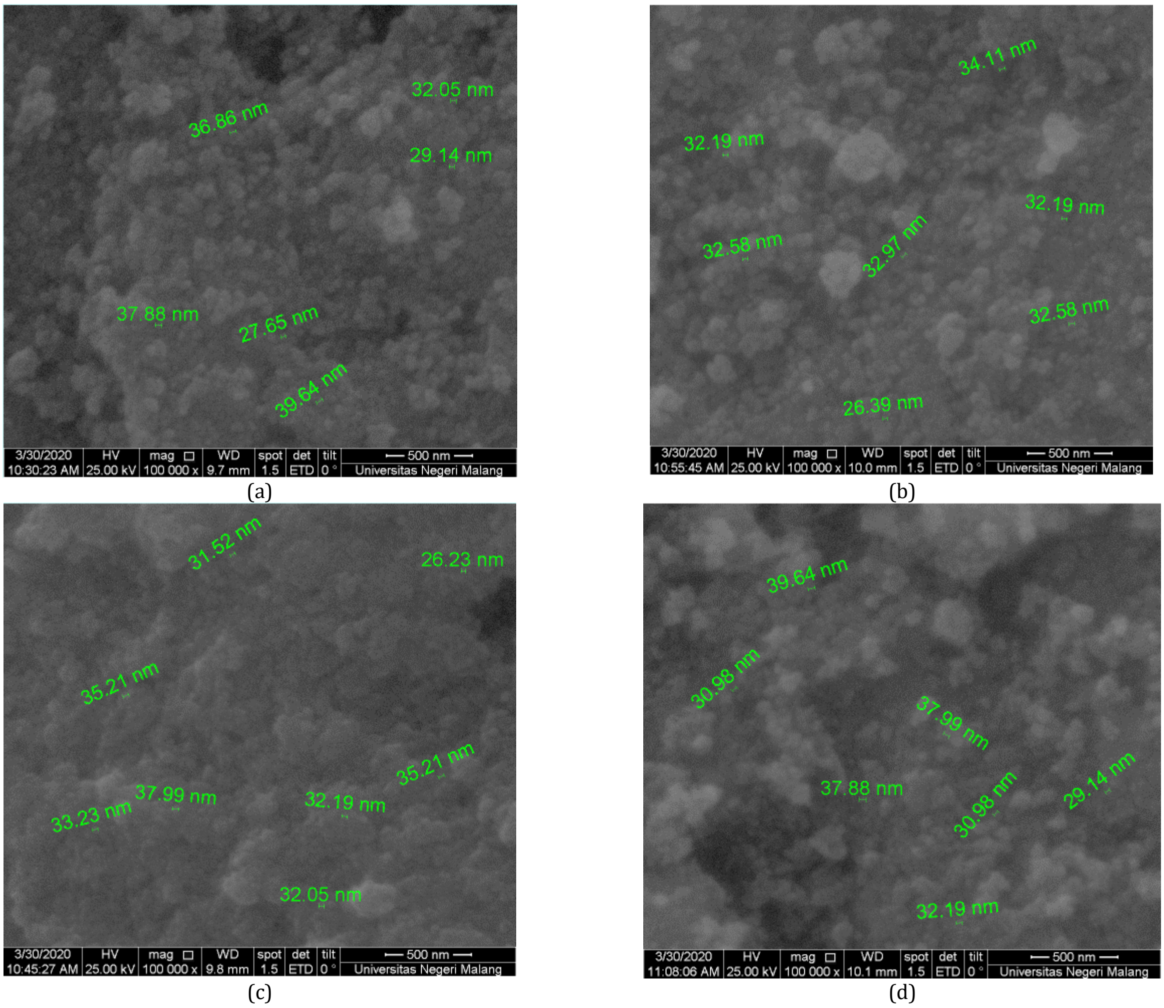

Fig. 2. Morphology of cobalt ferrite under different sintering conditions (a) unsintered, (b) 500 °C, (c) 600 °C, and (d) 700 °C

3.3 Magnetic Properties of Cobalt Ferrite

The graphic of the results of the VSM test presented in Figure 3 show the results of the VSM test on the unsintered sample and the samples sintered at temperatures of 500, 600, and 700° C temperature. The data indicate a transformation in the samples' magnetic features of the samples. The magnetization saturation (*Ms*), magnetization remanent (*Mr*), and coercivity field (*Hc*) of the four samples show that they have impressive alteration with changing magnetic nature after treatment.

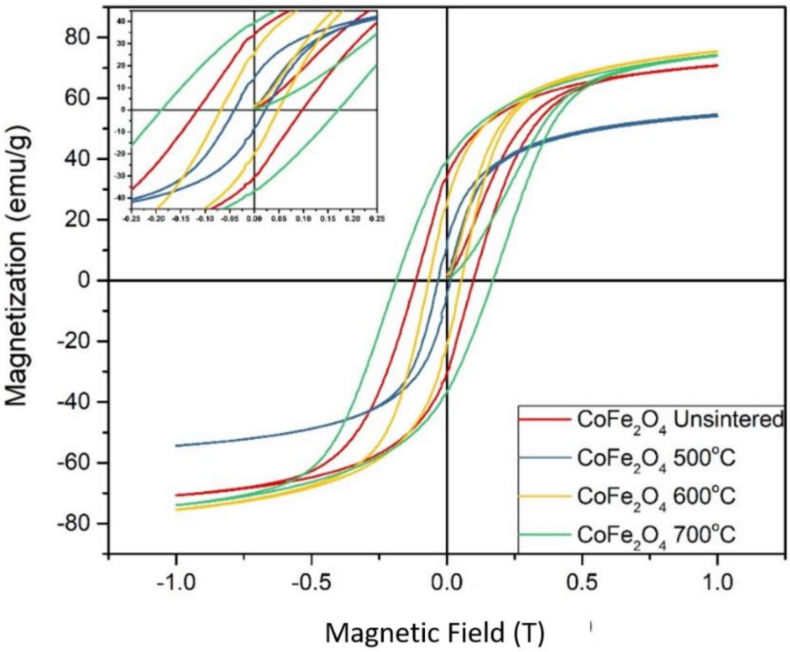

Fig. 3. Hysteresis curves of cobalt ferrite at different sintering condition

The results of cobalt ferrite synthesis with the sonochemical method with different sintering temperature variations indicate that the increase of the temperature causes acceleration on the crystallite and particle size, along with higher and more robust magnetic properties. According to Figure 3, the unsintered sample is classified as a hard magnet with high saturation, with a broad curve and a high magnetic saturation value, and a high magnetic coercivity value. Additionally, the sample that has been sintered at 500 °C temperature encounters a decrease in its *Ms*, *Mr*, and *Mc*, as shown by the narrow curve. Thus, this sample has soft magnetic characteristics. In addition, the hysteresis loop of the sample with a sintering temperature of 600 °C is similar to the sample sintered with a temperature of 500 °C. Therefore, that sample also has a soft magnetic characteristic. However, different from the sample with 500° C sintering temperature, the sample with 600 °C sintering temperature becomes a soft magnet with high saturation, represented with the insignificantly different curve shape and coercivity value, but with high magnetic saturation value. After the sintering temperature is accelerated to 700 °C, the sample becomes a hard magnet with high saturation and high coercivity, as shown from a wider curve in Figure 3 and higher coercivity. However, compared to unsintered samples that have the hard magnet characteristic, the sample with a sintering temperature of 700 °C has a more significant coercivity value. Therefore, the sample with sintering temperature has a more excellent hard magnet characteristic than the unsintered sample with a lower coercivity value. Similarly to the features of the hard magnet material, a greater coercivity value/(BH) max represents a harder magnetic characteristic [6, 10, 16].

Table 2. Magnetic characteristic analysis of cobalt ferrite samples

No.	Sintering Temperature	Crystallite Size (nm)	*Ms* (emu/g)	*Mr* (emu/g)	*R* (Mr/Ms)	*Hc* (T)
1	Unsintered	24	70.73	33.83	0.48	0.127
2	500 °C	18	54.12	13.95	0.26	0.021
3	600 °C	21	75.76	25.95	0.34	0.038
4	700 °C	27	75.24	39.39	0.52	0.198

Each sample demonstrates an uncommon magnetic characteristic transformation. The unsintered sample shows hard magnet characteristics with very high saturation, represented by its high saturation and coercivity values. However, the sintered cobalt ferrite with a sintering temperature of 700 °C has a harder magnetic feature, as shown in Table 2. The sample with 700 °C sintering temperature has a higher coercivity value of 0.198 T, compared to the unsintered sample with a coercivity value of 0.127 T. Therefore, the cobalt ferrite synthesis with a sonochemical method does not require any other sintering process at a lower temperature than 700 °C because a lower temperature produces cobalt ferrite with soft magnetic material. It is caused by the proper heat treatment of cobalt ferrite creates a minimal and very magnetic single domain [17, 18]. With increasing temperatures at sintering conditions, the anisotropy field of $CoFe_2O_4$ decreases markedly, so the average reversal field of the hard and soft phases may be occur. The decrease in coercivity caused by thermal activation of particle moments over the anisotropy barriers [19].

The transition change was caused by the critical diameter of $CoFe_2O_4$ that was 40 nm and therefore, after passing the critical diameter, the coercivity was reduced [20, 21]. With the decrease in *Hc*, there was an increase of *Ms* from 54.12 emu/g to 75.76 emu/g following the Brown equation as shown in Equation (2) [22, 23].

$$Hc = \frac{2K1}{\mu 0Ms} \tag{2}$$

The increase in sintering temperature from 500 °C to 700 °C changed the *Hc* value from 0.021 T to 0.198 T and the curve was inclined. The sonochemical sample was thought to have a paramagnetic curve because the NaOH titration did not entirely disappeared in the sample. The remanence ratio is a function of the particle size and is somewhat similar to the coercivity. The random distribution of noninteracting uniaxial particles resulted in a Mr/Ms value of 0.5 [24]. All samples had a close remanence ratio and of to 0.5, thus, if $R < 0.5$, there was a static magneto interaction between the granules [23]. The low coercivity and proximity to superparamagnetic behaviour make this material suitable for hyperthermia sensor application. In this case, $CoFe_2O_4$ sintered at 500 °C is the best sample**.**

4. Conclusions

Based on the phase identification through XRD testing, the synthesis of cobalt ferrite using the sonochemical method on the unsintered and sintered samples with sintering temperatures of 500, 600, and 700 °C results in a single phase in a single lattice. From this process, the identified crystallite size of the sintered samples at 500, 600, and 700 °C are 18, 21, and 27 nm, respectively. Therefore, a higher sintering temperature produces a larger crystallite size. The morphology identification carried out by SEM test shows that all samples are homogeneous, and the cobalt ferrite synthesis with the sonochemical method and different sintering temperatures results in no agglomeration. In addition, the increase in the sintering temperature brings a greater bulk size on the 500, 600, and 700 °C temperatures of 32.95, 31.85, and 34.11 nm, respectively. Meanwhile, the recorded bulk size of the unsintered sample is 33.87 nm. It is caused by the particle rearrangement and bonds with each other, formulating a single phase in a new lattice structure that causes a more substantial bulk size. The magnetic characteristic of the cobalt ferrite was identified using the VSM test. The results show that cobalt ferrite synthesis using the sonochemical method on the unsintered sample and the sintered samples with sintering temperatures of 500, 600, d 700° C result in contrasting characteristic magnetic changes. The unsintered sample that initially has a hard magnet with high saturation characteristics becomes a soft magnet at a sintering temperature of 500 °C. Then, it transforms into a soft magnet with high saturation at a sintering temperature of 600 °C. After the temperature is increased to 700 °C, the sample turns back into a hard magnet with high saturation and high coercivity. The ferromagnetic behaviour was confirmed by a hysteresis curve which was comparable to the condition by sintered and unsintered process. Therefore, the prepared $CoFe_2O_4$ has been proven to be a potential candidate for hyperthermia sensor application.

Acknowledgment

The authors appreciate Universitas Negeri Malang for funding this research through *Hibah Internal* UM 2022 for PP.

References

[1] R. A. Bohara, N. D. Throat, N. A. Mulla, and S. H. Pawar, "Surface-Modified Cobalt Ferrite Nanoparticles for Rapid Capture, Detection, and Removal of Pathogens: a Potential Material for Water Purification," *Appl. Biochem. Biotechnol.*, vol. 182, no. 2, pp. 598–608, Jun. 2017, doi: 10.1007/s12010-016-2347-6.

[2] T. Tatarchuk, M. Liaskovska, V. Kotsyubynsky, and M. Bououdina, "Green synthesis of cobalt ferrite nanoparticles using *Cydonia oblonga* extract: structural and mössbauer studies," *Mol. Cryst. Liq. Cryst.*, vol. 672, no. 1, pp. 54–66, Sep. 2018, doi: 10.1080/15421406.2018.1542107.

[3] E. A. Brocchi, D. W. Macedo, G. Solórzono, and F. J. Moura, "Characterisation of synthesised nickel and cobalt nanoscale oxides," *Mater. Charact.*, vol. 63, pp. 70–76, Jan. 2012, doi: 10.1016/j.matchar.2011.11.002.

[4] J. Parhizkar and M. H. Habibi, "Investigation and Comparison of Cobalt ferrite composite nanoparticles with individual Iron oxide and Cobalt oxide nanoparticles in azo dyes removal," *J. Water Environ. Nanotechnol.*, vol. 4, no. 1, Jan. 2019, doi: 10.22090/jwent.2019.01.002.

[5] M. Lenglet *et al.*, "Initial stages of cobalt oxidation by FTIR spectroscopy," *J. Phys. IV*, vol. 03, no. C9, pp. C9-477-C9-483, Dec. 1993, doi: 10.1051/jp4:1993951.

[6] P. Puspitasari, L. S. Budi, "Physical and Magnetic Properties Comparison of Cobalt Ferrite Nanopowder Using Sol-gel and Sonochemical Methods," *Int. J. Eng.*, vol. 33, no. 6, Jun. 2020, doi: 10.5829/ije.2020.33.05b.20.

[7] K.-Y. A. Lin, J.-Y. Lin, and P.-Y. Li, "Valorization of aluminum waste as a heterogeneous catalyst for activation of oxone for sulfate radical-based advanced oxidation process," *Sep. Purif. Technol.*, vol. 185, pp. 120–128, Sep. 2017, doi: 10.1016/j.seppur.2017.05.033.

[8] E. Mazario, N. Menéndez, P. Herrasti, M. Cañete, V. Connord, and J. Carrey, "Magnetic hyperthermia properties of electrosynthesized cobalt ferrite nanoparticles," *J. Phys. Chem. C*, vol. 117, no. 21, pp. 11405–11411, 2013, doi: 10.1021/jp4023025.
[9] S. Amiri and H. Shokrollahi, "The role of cobalt ferrite magnetic nanoparticles in medical science," *Mater. Sci. Eng. C*, vol. 33, no. 1, pp. 1–8, Jan. 2013, doi: 10.1016/j.msec.2012.09.003.
[10] P. Puspitasari, U. A. Rizkia, S. Sukarni, A. A. Permanasari, A. Taufiq, and A. B. N. R. Putra, "Effects of Various Sintering Conditions on the Structural and Magnetic Properties of Zinc Ferrite ($ZnFe_2O_4$)," *Mater. Res.*, vol. 24, no. 1, p. e20200300, 2021, doi: 10.1590/1980-5373-mr-2020-0300.
[11] P. Puspitasari, M. Chairil, S. Sukarni, and N. S. W. Supriyanto, "Physical properties and compressibility of quail eggshell nanopowder with heat treatment temperature variations," *Mater. Res. Express*, vol. 8, no. 5, p. 055008, May 2021, doi: 10.1088/2053-1591/ac0266.
[12] B. D. Cullity, *Elements of X-Ray Diffraction*, 2nd ed. Addison Wesley.
[13] H. A. Gatea, "Impact of Sintering Temperature on Crystallite size and Optical Properties of SnO_2 Nanoparticles," *J. Phys. Conf. Ser.*, vol. 1829, no. 1, p. 012030, Mar. 2021, doi: 10.1088/1742-6596/1829/1/012030.
[14] S. A. Sardjono and P. Puspitasari, "Synthesis and characterization of cobalt oxide nanoparticles using sol-gel method," 2020, p. 040046. doi: 10.1063/5.0002419.
[15] S. Dang, Z. Wang, W. Jia, Y. Cao, and J. Zhang, "Facile synthesis of rod-like nickel-cobalt oxide nanostructure for supercapacitor with excellent cycling stability," *Mater. Res. Bull.*, vol. 116, pp. 117–125, Aug. 2019, doi: 10.1016/j.materresbull.2019.04.023.
[16] S. P. John and J. Mathew, "Determination of ferromagnetic, superparamagnetic and paramagnetic components of magnetization and the effect of magnesium substitution on structural, magnetic and hyperfine properties of zinc ferrite nanoparticles," *J. Magn. Magn. Mater.*, vol. 475, pp. 160–170, Apr. 2019, doi: 10.1016/j.jmmm.2018.11.030.
[17] A. Muhammad, P. Puspitasari, and Andoko, "Properties of soft magnetic material $SmCo_5$ synthesized using low-temperature sol-gel method," Malang, Indonesia, 2019, p. 050008. doi: 10.1063/1.5115684.
[18] P. Puspitasari, A. A. Permanasari, M. S. Shaharun, and A. Muhammad, "High saturation superparamagnetic properties of low-temperature sintering of nickel oxide," Tangerang Selatan, Indonesia, 2020, p. 030024. doi: 10.1063/5.0000884.
[19] S. Xu, Y. Ma, B. Geng, X. Sun, and M. Wang, "The remanence ratio in $CoFe_2O_4$ nanoparticles with approximate single-domain sizes," *Nanoscale Res. Lett.*, vol. 11, no. 1, p. 471, Dec. 2016, doi: 10.1186/s11671-016-1691-3.
[20] O. Perales-Pérez and Y. Cedeño-Mattei, "Optimizing Processing Conditions to Produce Cobalt Ferrite Nanoparticles of Desired Size and Magnetic Properties," *Magn. Spinels - Synth. Prop. Appl.*, 2017, doi: 10.5772/66842.
[21] M. Afshari, A. R. Rouhani Isfahani, S. Hasani, F. Davar, and K. Jahanbani Ardakani, "Effect of apple cider vinegar agent on the microstructure, phase evolution, and magnetic properties of CoFe2O4 magnetic nanoparticles," *Int. J. Appl. Ceram. Technol.*, vol. 16, no. 4, pp. 1612–1621, 2019, doi: 10.1111/ijac.13224.
[22] S. Xavier, M. K. Jiji, S. Thankachan, and E. M. Mohammed, "Effect of sintering temperature on the structural and electrical properties of cobalt ferrite nanoparticles," *AIP Conf. Proc.*, vol. 1576, pp. 98–101, 2014, doi: 10.1063/1.4861992.
[23] M. Goodarz Naseri, E. B. Saion, H. Abbastabar Ahangar, A. H. Shaari, and M. Hashim, "Simple synthesis and characterization of cobalt ferrite nanoparticles by a thermal treatment method," *J. Nanomater.*, vol. 2010, 2010, doi: 10.1155/2010/907686.
[24] C. Luna, M. del P. Morales, C. J. Serna, and M. V zquez, "Multidomain to single-domain transition for uniform $Co_{80}Ni_{20}$ nanoparticles," *Nanotechnology*, vol. 14, no. 2, pp. 268–272, Feb. 2003, doi: 10.1088/0957-4484/14/2/332.