Magnetic and Electromagnetic Wave Absorption Characteristics of BaFe\textsubscript{11}Ti\textsubscript{0.5}Zn\textsubscript{0.5}O\textsubscript{19} in X Band

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Abstract. Research has been made on BaFe\textsubscript{11}Ti\textsubscript{0.5}Zn\textsubscript{0.5}O\textsubscript{19} compound by high energy milling (HEM) with variation of milling t = 2, 8, and 12 hours. This research was conducted to find out the influence of milling time on magnetic and electromagnetic wave absorption properties of BaFe\textsubscript{11}Ti\textsubscript{0.5}Zn\textsubscript{0.5}O\textsubscript{19} compound. Materials were characterized by X-Ray Diffraction (XRD), Permagraph C, Scanning Electron Microscope (SEM), and Vector Network Analyzer (VNA). XRD patterns of bulk sample had shown the material forms a single phase BaFe\textsubscript{12}O\textsubscript{19} (Barium hexaferrite). A SEM image of bulk sample shows hexagonal structure. A VNA spectrum obtained from 12 hours milling exhibit the highest electromagnetic wave absorption compared with 2 and 8 hours milling, with 99.19\% absorption at frequency 11.7 GHz in X-band. Agglomeration occurs on the sample powder may due to electrostatic force among particles and a SEM image confirmed it. Based on that results, the addition of milling time can improve the electromagnetic wave absorption of BaFe\textsubscript{11}Ti\textsubscript{0.5}Zn\textsubscript{0.5}O\textsubscript{19} powder.

Keywords: Barium hexaferrite, High energy milling, Electromagnetic wave absorption.

1. Introduction

The ferrite-based magnets are proven to be effective for electromagnetic wave absorbing materials (EWAMs) applications that work at frequencies from hundreds MHz to GHz. EWAMs can convert Radar-emitted electromagnetic waves into heat energy. As a result, the wave reflected and received by the receiver becomes very weak. The hexaferrites, notably BaFe\textsubscript{12}O\textsubscript{19} (BaM) is able to reduce power and radiation on the Radar due to their high values of saturation magnetization (Ms) and coercivity (Hc) along with low cost, excellent chemical stability and corrosion resistance [1].

A wide range of possible compositions of these ferrites were synthesized by various preparation techniques and different substitutions. As cation substitutions is one of the ways to modify the...
properties of BaM in order to meet the requirements, especially for EWAMs. Previous researchers have modified and improved the properties of M-ferrites by replacing Ba$^{2+}$ by Sr$^{2+}$, La$^{2+}$, Pb$^{2+}$ ions or substituting Fe$^{3+}$ ions by trivalent, divalent, and tetravalent cations [2–5].

Here, we reported the milling time effect of high energy milling (HEM) on magnetic properties and electromagnetic wave absorption of Barium hexaferrite doped with Ti$^{4+}$ and Zn$^{2+}$ element of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ compound in X-band.

2. Experimental method

BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ samples were synthesized by mechanical alloying method via high energy milling (HEM). Iron oxides (Fe$_2$O$_3$), Barium carbonate (BaCO$_3$), Magnesium oxide (MgO) and Titanium oxide (TiO$_2$). These oxides in proper stoichiometric were commercially procured from Merck. All of oxides were mixed with dry milling in HEM machine for 2 hours and calcinated at 900°C for 3 hours. Calcinated powder were sieved up to 425 mesh and pelletized using hydraulic press machine in stainless steel dies of 12 mm diameter and further sintered at 1200°C for 3 hours. Magnetic properties of sintered tablets were measured by Permagraph C (Magnet-Physik Dr. Steingroever GmbH). After that sintered tablets were pulverized with HEM machine in various milling time for 2, 8, and 12 hours, respectively. X-Ray diffraction (XRD) pattern of pulverized powder was performed with Rigaku Ultima IV diffractometer with Cu-Kα radiation. Grain morphology characterized using Scanning Electron Microscope (SEM, Hitachi SU3500). X-Ray Energy Dispersive Spectroscopy (EDS) was also carried out. The microwave properties conducted with Vector Network Analyzer (VNA, ADVANCE TEST R3770). Microwave absorption properties were evaluated by reflection loss (RL) which can be calculated by the equation:

\[
\text{Return Loss (dB)} = -20 \log |\Gamma|
\]

\[
\Gamma = 10\left(\frac{-\text{Return Loss}}{20}\right)
\]

\[
\text{Absorption (}% = (1 - \Gamma) \times 100\%
\]

3. Results and discussion

The XRD pattern of pulverized powder sample in Figure 1 shows a typical structure of BaM with P63/mmc space group (ICCD: 98-004-7018). All peaks of substituted BaM with milling time variation appear in 2, 8 and 12 milling.

![XRD pattern of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ milled powder.](image)
The magnetic properties for bulk sample are shown in Figure 2. The results show that the undoped BaM has largest intrinsic coercivity ($H_c$) of 230,434 kA/m, and drastically $H_c$ decreased as Fe$^{3+}$ ions substituted by Ti and Zn ions.

![Hysteresis curves of BaFe$_{12}$O$_{19}$ and BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$](image)

**Figure 2.** Hysteresis curves of BaFe$_{12}$O$_{19}$ and BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$.

Table 1 represent the magnetic properties of BaFe$_{12}$O$_{19}$ and BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ with their bulk density. The saturated magnetization (Ms) of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ increased to 66.01 emu/g from 51.46 emu/g of BaFe$_{12}$O$_{19}$, and vice versa the coercivity decreased due to Fe$^{3+}$ ion substituted by Ti-Zn ions.

| Compound         | Mr (emu/g) | Ms (emu/g) | Hc (kOe) | Bulk density (g/cm$^3$) |
|------------------|------------|------------|----------|------------------------|
| BaFe$_{12}$O$_{19}$ | 34.29      | 51.46      | 2.869    | 4.849                  |
| BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ | 27.71      | 66.01      | 0.623    | 4.941                  |

A SEM image of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ pellet shown in Figure 3a, some pores were exhibited on the surface of sample due to lack of holding time (3 hours) during the sintering process, so then bulk density (BD) value of sample didn’t achieve to 5.20 g/cm$^3$ as theoretical density of Ferrite. Hexagonal structural exhibited in the sample as shown in the Figure 3a, and has random orientation.

It has been proven that BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ synthesis through mechanical alloying method is able to form a hexagonal crystal structure with an incomplete angle due to the addition of Ti$^{4+}$ and Zn$^{2+}$ element as doping. Hexagonal crystals with perfect angles may be achieved with appropriate stoichiometric calculations as well as changes in process parameters during sintering.

Figure 3b shown the morphology of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ powder on 10,000x magnification of a SEM image, it shows the presence of agglomeration in the sample which has been pulverized for 12 hours, according to Lerocch et al. [6]; agglomeration occurs due to Van der Waals bonding, coulomb force, and electrostatic forces between particles.
Figure 3. SEM images of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ tablet and as powder for 12 hours of milling time.

The microwave absorption properties of BaFe$_{12}$O$_{19}$ and BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ have been measured by VNA, compared to reflection loss (RL) of BaFe$_{10}$TiZnO$_{19}$ from reference [7]. The RL results shown in Figure 4 and Table 2, with 2 hours pulverizing time shown fluctuating in RL values, with the highest RL was -13.9247 dB at frequency 10.8 GHz, which the absorption value of the wave was reached to 79.87%. The absorption percentage is much better than that of the pre-tested metal plate which is shown in Table 2. In 8 hours pulverizing sample, the highest RL value was -24.0395 dB at frequency 11.92 GHz and calculated wave absorption achieved to 93.72% and 6.28% reflect back. For 12 hours pulverizing results shows the highest RL value upto -41.851 dB at frequency 11.7 GHz and calculated of electromagnetic wave absorption was 99.19%. This sample has a better wave absorption value than previous results that only reached -25 dB [7].

Figure 4. Reflection loss (RL) of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ and other samples as comparison.

These results increase considerably compared to BaFe$_{12}$O$_{19}$ sample due to doping effect of Ti and Zn elements and pulverizing BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ particle by longer milling time. Also, these results suggest that the mechanical alloying process can produce a good EWAM. The EWAM is a material...
that not only has a large electromagnetic wave absorption value, but also has a wide band of absorption due to the EWAM can absorb in many frequency ranges [8]. The more absorption values that are formed means the uptake of the EWAM is getting better. Other factors that may affect the results of VNA testing are sample density, sample surface condition, and preparation process prior to testing. Solid and flat surface samples without air gaps will provide more accurate test results. The absorption mechanism of electromagnetic waves can be explained through two overviews; the magnetic and the conductive aspects. Both of these aspects cause the penetrated electromagnetic waves into the EWAM will lose its energy. When electromagnetic waves reach the conductive material, the electric field of the wave will be absorbed and cause a Coulomb force. The existing Coulomb force on the conductive material will interact and subsequently produce an electric current and convert to heat and kinetic induction energy. The kinetic induction occurs due to the emergence of a magnetic field. The magnetic field arising from the conductive material will be reinforced by the magnetic properties of the EWAM.

### Table 2. Wave absorption values of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ powder.

| Sample                                      | Reflection Loss(dB) | Frequency (GHz) | $\Gamma$ | Wave absorption (%) |
|---------------------------------------------|---------------------|-----------------|----------|---------------------|
| Steel plate 3 mm                            | -1.0310             | 10.6            | 0.8881   | 11.19               |
| BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ 2h milled powder | -13.9247            | 10.8            | 0.2013   | 79.87               |
| BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ 8h milled powder | -24.0395            | 11.92           | 0.0628   | 93.72               |
| BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ 12h milled powder | -41.8510            | 11.7            | 0.0081   | 99.19               |

### 4. Conclusion
Based on research results, it has been concluded that mechanical alloying process succeeds in forming a hexagonal crystal structure as BaFe$_{12}$O$_{19}$. The electromagnetic wave absorption values of BaFe$_{11}$Ti$_{0.5}$Zn$_{0.5}$O$_{19}$ powder keep increasing along with the length of milling time, with the highest reflection loss (RL) value is 12 hours milling time which is equal to -41.851 dB at frequency 11.7 GHz with wave absorption achieved to 99.19%.

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### References
[1] S. Singhal, T. Namgyal, J. Singh, K. Chandra, S. Bansal, “A comparative study on the magnetic properties of MFe$_{12}$O$_{19}$ and MAIFe$_{11}$O$_{19}$ (M = Sr, Ba and Pb) hexaferrites with different morphologies”, Ceramics International 37 (2011) 1833–1837.
[2] P.A. Marino-Castellanos, A.C. Moreno-Borges, G. Orozco-Melgar, J.A. Garcia, E. Govea-Alcaide, “Structural and magnetic study of the Ti4+-doped barium hexaferrite ceramic samples: theoretical and experimental results”, Physica B 406 (2011) 3130–3136.
[3] A. Gonzalez-Angeles, J. Lipka, A. Gruskova, J. Slama, V. Jancarik, V. Slugen, “Magnetic comparison of BaCa and BaSr substituted Hexaferrite powders”, Journal of Physics: Conference Series 217 (2010) 1–5.
[4] T.M. Meaz, C.B. Koch, “X-ray diffraction and Mossbauer spectroscopic study of BaCo$_{0.5}$Zn$_{0.5}$Ti$_x$Fe$_{12-2x}$O$_{19}$ (M- type hexagonal ferrite)”, Egypt Journal of Sol–Gel Science and Technology 26 (2003) 197–203.

[5] A. Septiani, T. Kristianto, Dedi, N. Idayanti, Y. Taryana, “Magnetic and microwave absorbing properties of Al and Zn substituted barium hexaferrites in X-band region”, 2016 International Conference on Radar, Antenna, Microwave, Electronics and Telecommunications, (ICRAMET) 149-151.

[6] S. Leroch and M. Wendland, “Influence of Capillary Bridge Formation onto the Silica Nanoparticle Interaction Studied by Grand Canonical Monte Carlo Simulations”, Langmuir (2013) 29 (40), 12410-12420.

[7] Nenni, M. Delina, W. A. Adi, Y. Taryana, “Pengaruh Substitusi Ion Ti-Zn Terhadap Sifat Kemagnetan dan Sifat Penyerapan Gelombang Elektromagnetik Material Sistem BaFe$_{12-x}$Ti$_x$Zn$_x$O$_{19}$”, Spektra: Jurnal Fisika dan Aplikasinya, Universitas Negeri Jakarta, (2017) (In Indonesia)

[8] N. Awalin, “Studi Penyerapan Gelombang Elektromagnet Rentang X-Band Dengan Menggunakan Penyerap PANi Konduktif dan Barium M-Heksaferit Terdoping Ion Zn (0.3<X<0.9)“, Undergraduate Theses, Surabaya: FMIPA – Institut Teknologi Sepuluh November, (2017) (In Indonesia)