Crystal Structure Analysis of Electromagnetic Wave Absorber Material BaFe$_{12-x}$Ti$_x$/2Zn$_x$/2O$_{19}$ Based

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Abstract. The optimization of BaFe$_{12-x}$Ti$_x$/2Zn$_x$/2O$_{19}$ (x=2.2; 2.4; 2.6; 2.8) single phase composition have been performed. The materials were synthesized by solid state reaction method through mechanical milling technique. The materials were made from the mixture of oxide materials, which are BaCO$_3$, Fe$_2$O$_3$, TiO$_2$ and ZnO. The mixture was milled for five hours using a High Energy Milling (HEM), was dried at 100$^\circ$C in the Oven and then was sintered at 1000$^\circ$C for five hours in the Furnace. The phase identification of BaFe$_{12-x}$Ti$_x$/2Zn$_x$/2O$_{19}$ (x=2.2; 2.4; 2.6; 2.8) were carried out by using a Match Program while the crystal structure analysis were investigated by using a General Structure Analysis System (GSAS) program. The refinement results of x-ray diffraction pattern showed that the sample of x $\leq$ 2.4 have a BaFe$_{12}$O$_{19}$ single phase while the sample of $x$ > 2.4 have two phases, which are BaFe$_{12}$O$_{19}$ and ZnFe$_2$O$_4$ phases. The surface morphology of sample and the element of sample were identified through an analysis of Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) data.

1. Introduction
Barium Hexaferrite (BaFe$_{12}$O$_{19}$) has received great attention because of its applications in permanent magnet, high density magnetic recording media, and microwave devices [1,2]. This material (BaFe$_{12}$O$_{19}$) has a high saturation magnetization which is 72 emu/gr, high coercivity field which is 6700 Oe, high anisotropy field, high Curie temperature which is 450$^\circ$C, and high magnetic permeability [3-5]. Some characteristics of the material are suitable for application of electromagnetic wave absorber material. However, the high coercivity field cause its absorption ability is reduced because there is no resonance occurs between the magnetic moment with magnetic field and electric field within electromagnetic wave. So, to increase its absorption ability, the coercivity field of Barium Hexaferrite must be reduced [6]. One of the techniques to change its magnetic properties is modification of Barium Hexaferrite through ionic substitution.

Fe$^{3+}$ ions in Barium Hexaferrite are substituted by one trivalent ion or by combination of one divalent ion and one tetravalent ion [7] that have the similar size. The efficiency of substitution is depend on the difference of electronegativity and the ionic radius between the dopant and host element [8] (in this case, the host element is Fe$^{3+}$ ions). The similar ionic radius and the electronegativity make dopant to replace half of Fe$^{3+}$ ions position surely. In this research, Ti$^{4+}$ and Zn$^{2+}$ ions are used to
replace Fe$^{3+}$ ions position partially within Barium Hexaferrite. The ionic radius of Ti$^{4+}$ and Zn$^{2+}$ ions are 0.605 Å and 0.68 Å that have similar ionic radius with Fe$^{3+}$ (0.645 Å), while their electronegativity are 1.54, 1.7 and 1.83 [7-10].

In previous research, Nenni et al have analyzed about effect of substitution Ti-Zn ions on magnetic and elecro-magnetic wave absorption properties of BaFe$_{12-x}$Ti$_x$Zn$_{2y}$O$_{19}$ material system [10]. The research reported that BaFe$_{12-x}$Ti$_x$Zn$_{2y}$O$_{19}$ (x=2) material has single phase of BaFe$_{12}$O$_{19}$. Therefore, there will be optimization of BaFe$_{12-x}$Ti$_x$Zn$_{2y}$O$_{19}$ composition in this research. The crystal structure analysis of BaFe$_{12-x}$Ti$_x$Zn$_{2y}$O$_{19}$ material (with various composition x=2, 2.4, 2.6 and 2.8) using solid state reaction method will be carried out. The addition of Ti$^{4+}$ and Zn$^{2+}$ ions are predicted to replace Fe$^{3+}$ ions position partially without change the crystal structure of Barium Hexaferrite. The effect of substitution Ti$^{4+}$ and Zn$^{2+}$ ions to crystal structure and lattice parameter of samples are acknowledged by X-Ray Diffractometer (XRD). The surface morphology and the element of samples are observed by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS).

2. Material and Method
BaFe$_{12-x}$Ti$_x$Zn$_{2y}$O$_{19}$ (with various composition x=2.2, 2.4, 2.6 and 2.8) material were synthesized by solid state reaction method through mechanical milling technique. The materials were made from the mixture of BaCO$_3$, Fe$_2$O$_3$, TiO$_2$ and ZnO. Mass of each material was determined based on stoichiometric calculation then was weighed and was placed in the stainless steel vial. The mixture was added with five balls mill and ethanol. The ratio of the sample and five balls mill was 1:2. The mixture was milled for five hours using High Energy Milling (HEM) and then was dried at 100$^\circ$C in the Oven. The dried sample was mashed and was sintered at 1000$^\circ$C in the Furnace.

The X-Ray diffraction pattern of modified samples were measured by X-Ray Diffractometer (XRD) using radiation of CuK$\alpha$ ($\lambda = 1.5406$ Å). The formed phase of the samples were analyzed using Match and General Structure Analysis (GSAS) program qualitatively and quantitatively. After that, the surface morphology and the component of the samples were observed by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS).

3. Results and Discussion
The x-ray diffraction pattern of the samples were matched with x-ray diffraction pattern of standard BaFe$_{12}$O$_{19}$ phase on Match program. Figure 1 shows the results of x-ray diffraction pattern of BaFe$_{12-x}$Ti$_x$Zn$_{2y}$O$_{19}$ samples (with various composition x=2.2; 2.4; 2.6 and 2.8). The results of phase identification show that the x-ray diffraction pattern of samples x=2.2 and x=2.4 have the similar pattern with x-ray diffraction pattern of standard BaFe$_{12}$O$_{19}$ phase. Therefore, both of them have single phase of BaFe$_{12}$O$_{19}$. The result of BaFe$_{12}$O$_{19}$ phase identification is referred from Crystallography Open Database (COD) with the 96-900-8138 card number. However, there are another diffraction peak at the angle of 30$^\circ$ and between 60$^\circ$ up to 70$^\circ$ in the samples x=2.6 and x=2.8, which are ZnFe$_2$O$_4$ phase. It is caused by unbalanced reaction in the sample so that the samples x=2.6 and x=2.8 have two phases, which are BaFe$_{12}$O$_{19}$ and ZnFe$_2$O$_4$ phases.

For the sample x=2.6, identification of BaFe$_{12}$O$_{19}$ and ZnFe$_2$O$_4$ phases are indicated from COD: 96-901-4002 and COD: 96-900-510. On the contrary, identification of BaFe$_{12}$O$_{19}$ and ZnFe$_2$O$_4$ phases for the sample x=2.8 are indicated from COD: 96-900-8138 and COD: 96-900-6896. But, Match program has not given the information of structure parameters and the amount of mass fraction of BaFe$_{12}$O$_{19}$ and ZnFe$_2$O$_4$ phases so that quantitative analysis is required by using GSAS program. Figure 2 shows the refinement results of x-ray diffraction pattern of the sample (with various composition x = 2.2; 2.4; 2.6 and 2.8) using GSAS program.

Figure 2(a) and 2(b) shows that the x-ray diffraction pattern of samples x=2.2 and x=2.4 have similar pattern with the x-ray diffraction pattern of calculation. The whole diffraction peaks of samples x=2.2 and x=2.4 has been fitted and the difference between the diffraction peaks of the sample and calculation are relatively slight. It shows that both of the sample have single phase which is BaFe$_{12}$O$_{19}$.
phase. Figure 2(c) and 2(d) inform the x-ray diffraction pattern of samples x=2.6 and x=2.8. Blue and red dots show the diffraction peaks of ZnFe$_2$O$_4$ phase, so that both of those samples have two phases.

**Figure 1.** X-ray diffraction pattern of BaFe$_{12-x}$Ti$_{x/2}$Zn$_{x/2}$O$_{19}$ sample with various composition (x=2.2; 2.4; 2.6 and 2.8).

Based on these results, Fe$^{3+}$ ions have been partially substituted by Ti$^{4+}$ and Zn$^{2+}$ ions. However, this substitution has the optimum composition, which is x=2.4. It means that not all of Ti$^{4+}$ and Zn$^{2+}$ ions can replace part of Fe$^{3+}$ ions in Barium Hexaferrite. The substitution of Ti$^{4+}$ and Zn$^{2+}$ ions changes the structure parameter of BaFe$_{12-x}$Ti$_{x/2}$Zn$_{x/2}$O$_{19}$. The information about the change of structure parameter can be looked at Table 1.

Barium Hexaferrite has hexagonal structure with space group P6$_3$/mmc, lattice parameter a = b = 5.89Å, and c = 23.17 Å, α = β = 90°, γ = 120°[11]. Based on Table 1, there are changes of lattice parameter on each phase and sample. It is indicated that Fe$^{3+}$ ions have been partially substituted by Ti$^{4+}$ and Zn$^{2+}$ ions. The alteration of lattice parameter on the samples x=2.2 and x=2.4 still maintain hexagonal crystal structure of Barium Hexaferrete. There are unbalance reaction on the samples x=2.6 and x=2.8 so that Fe$_2$O$_3$ and ZnO ions were bound then formed the ZnFe$_2$O$_4$ phase. The qualities of fitting sample are determined by R factor and χ$^2$ where the value of χ$^2$ is less than 1.3 [12]. Based on Table 1, the value of χ$^2$ from each sample is corresponding to 1.3 thus we can say that the samples are fitted well.

Mass fraction of each phase of BaFe$_{12-x}$Ti$_{x/2}$Zn$_{x/2}$O$_{19}$ (x=2.2; 2.4; 2.6 and 2.8) is shown in Figure 3. Based on Figure 3, samples x=2.2 and x=2.4 have 100% BaFe$_{12}$O$_{19}$ phase. However, 3.87% ZnFe$_2$O$_4$ phase emerge on the sample x = 2.6 and increased up to 7.9% on the sample x=2.8. It shows that x=2.4 is the optimum composition of Ti$^{4+}$ and Zn$^{2+}$ ions substitution.

The results of refinement are also supported by observation of the particle’s surface morphology using SEM, as shown in Figure 4. The surface morphology of particles x=2.2 and x=2.4 are relatively uniform and evenly distributed in the entire of sample surface. The particle sizes are less than 5 μm, respectively, as shown in Figure 4(a) and 4(b). The results are equal with phase identification result by Match and GSAS that the samples x=2.2 and x=2.4 have single phase. While Figure 4(c) and 4(d) show the aggregation in the particles of the samples x=2.6 and x=2.8 because of other phases. The particle size of both samples is also less than 5μm.
Figure 2. The refinement results of x-ray diffraction pattern of BaFe$_{12-x}$Ti$_x$/2Zn$_x$/2O$_{19}$. a) $x=2.2$, b) $x=2.4$, c) $x=2.6$, d) $x=2.8$. The red, green and purple curves express the x-ray diffraction pattern of sample, x-ray diffraction pattern of calculation and the difference of them. The black, red and blue dots show the diffraction peaks of BaFe$_{12}$O$_{19}$ and ZnFe$_2$O$_4$ phases.

Table 1. Structure Parameter, RFactor, and Goodness of Fit ($\chi^2$). $R_{wp}$ (%) and $\chi^2$ are the quality of fitting factor.

| Sample $(x)$ | Phase | Lattice parameter (Å) | Crystal structure | Volume $(\text{Å}^3)$ | Density $(\text{g/cm}^3)$ | $R_{wp}$ (%) | $\chi^2$ |
|-------------|-------|-----------------------|-------------------|---------------------|---------------------------|-------------|---------|
| 2.2         | BaFe$_{12}$O$_{19}$ | a: 5.891307, b: 5.891307, c: 23.201977 | Hexagonal         | 697.395             | 11.775                    | 3.54        | 1.26    |
| 2.4         | BaFe$_{12}$O$_{19}$ | a: 5.891109, b: 5.891109, c: 23.19949 | Hexagonal         | 697.274             | 11.338                    | 3.47        | 1.28    |
| 2.6         | BaFe$_{12}$O$_{19}$ | a: 5.874818, b: 5.874818, c: 23.135712 | Hexagonal         | 691.516             | 13.529                    | 3.54        | 1.34    |
|             | ZnFe$_2$O$_4$     | a: 8.364467, b: 8.364467, c: 8.364467 | Cubic             | 585.214             | 5.427                     | 3.54        | 1.34    |
| 2.8         | BaFe$_{12}$O$_{19}$ | a: 5.892707, b: 5.892707, c: 23.206532 | Hexagonal         | 697.864             | 11.141                    | 3.65        | 1.38    |
|             | ZnFe$_2$O$_4$     | a: 8.663953, b: 8.663953, c: 8.663953 | Cubic             | 650.352             | 4.924                     | 3.65        | 1.38    |
Figure 3. Mass fraction as a function of composition. The blue and green graphs are the accretion of mass fraction of BaFe$_{12}$O$_{19}$ and ZnFe$_{2}$O$_{4}$ phases.

The elements of BaFe$_{12-x}$Ti$_{x/2}$Zn$_{x/2}$O$_{19}$ sample are known by the measurement using EDS as shown in Figure 5 and Table 2. The carbon elements in each sample are originated from carbon tip during the preparation so that they are not part of the elements of the four samples. The sample with composition of $x=2.2$ and $x=2.4$ have single phase and the similar crystal structure although their composition are different.

Figure 4. The surface morphology of a) obtained single phase BaFe$_{12}$O$_{19}$ ($x=2.2$), b) obtained single phase BaFe$_{12}$O$_{19}$ ($x=2.4$), c) obtained BaFe$_{12}$O$_{19}$ and ZnFe$_{2}$O$_{4}$ phases ($x=2.6$), d) BaFe$_{12}$O$_{19}$ and ZnFe$_{2}$O$_{4}$ phases ($x=2.8$).
Figure 5. EDS Spectrum of BaFe_{12-x}Ti_{x/2}Zn_{x/2}O_{19} after sintered at 1000°C for 5 hours a) x=2.2, b) x=2.4, c) x=2.6, d) x=2.8

Table 2. Element distribution on the BaFe_{12-x}Ti_{x/2}Zn_{x/2}O_{19}(x = 2.2; 2.4; 2.6; 2.8) was measured by EDS. Each of four samples consist of Barium (Ba), Iron (Fe), Oxygen (O), Titanium (Ti), Zink (Zn) and Carbon (C) unsur which are in 4.464 keV, 6.398 keV, 0.525 keV, 4.508 keV, 8.630 keV, 0.277 keV energy, respectively.

|          | 4.464 | 6.398 | 0.525 | 4.508 | 8.630 | 0.277 |
|----------|-------|-------|-------|-------|-------|-------|
| Ba (Ba)  | 16.72 | 51.18 | 42.23 | 26.76 | 7.63  | 3.10  |
| Fe (Fe)  | 15.28 | 43.36 | 42.23 | 26.76 | 7.29  | 3.48  |
| O (O)    | 15.28 | 43.36 | 42.23 | 26.76 | 7.29  | 3.48  |
| Ti (Ti)  | 3.86  | 3.82  | 3.82  | 3.82  | 3.82  | 3.82  |
| Zn (Zn)  | 15.28 | 43.36 | 42.23 | 26.76 | 7.29  | 3.48  |
| C (C)    | 15.28 | 43.36 | 42.23 | 26.76 | 7.29  | 3.48  |
4. Conclusion
The synthesis of BaFe$_{12-x}$Ti$_x$/2Zn$_x$/2O$_{19}$ with various composition ($x = 2.2; 2.4; 2.6; 2.8$) have been successfully performed. The refinement results of the x-ray diffraction pattern show that the samples $x=2.2$ and $x=2.4$ have single phase while the samples $x>2.4$ have two phases. Thus the substitution of Ti$^{4+}$ and Zn$^{2+}$ ions into Fe$^{3+}$ ions are only of 2.4 at.% without altering the hexagonal crystal structure of Barium Hexaferrite. The surface morphology of samples $x=2.2$ and $x=2.4$ are uniform and spread evenly.

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