Synthesis and magnetic properties of ferromagnetic W-type hexaferrite by mechanical milling route

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Abstract. The W-type Barium hexaferrite particle have been successfully synthesized by mechanical milling route. The formation of phase BaFe18O27 through two-stage mechanism which starts with the formation of BaFe16O19. The synthetic result is tested by X-ray Diffraction (Cu(Kα) to determine a structure and formation phase. The magnetic characteristic is tested by permeagraph in saturating field up to 1.5 Tesla. The synthetic result shows that the partial substitution of Fe\(^{2+}\) ions with Co\(^{2+}\) ions influence the change in magnetic properties particularly coercivity. W-hexaferrite has a promising potential in microwave absorption application in the future especially in the range at 8 Ghz to 9.0 GHz.

1. Introduction
W-Hexaferrite was the one of the ceramic magnets which generally has the WF\(_{16}\)O\(_{19}\) phase and is formed from alkaline oxide compounds from divalent atoms of class IIA. Atoms which used to form W-Hexaferrite such as Zn, Mg, Ca, Ba, Sr and Pb as a substitute for the element W [1,2,3]. This phase is better known as the W type hexaferrite. And on it’s development, W hexaferrite has a common phase in the form of BaFe\(_{18}\)Me\(_{3}\)O\(_{27}\) with Me as a replacement ion for Fe\(^{2+}\) ion. There are some various advantages from BaMe\(_x\)Fe\(_{18-x}\)O\(_{27}\) magnetic material, such as very economical and have a high stability against the influence of external magnetic fields, chemical properties and temperature [4]. Therefore, material became a permanent class magnetism to be applied in data storage of ATM card. Some researchers developed the synthesis of M hexaferrite compounds by various methods to obtain the best properties in composition and superior in application.

Several studies have been done to obtain the formation of BaMeFe\(_{16}\)O\(_{27}\) single phase, but it is not easy even though using the composition of BaCO\(_3\) and Fe\(_2\)O\(_3\) which is stoichiometric. Follow-up phases in minor quantities such as BaFe\(_{19}\)O\(_{19}\), and Fe2O3 are often still found in synthesis results.

\[ \text{BaFe}_{18}\text{O}_{19} + \text{Fe}_2\text{O}_3 + \text{Co}_2\text{O}_3 \rightleftharpoons \text{BaMeFe}_{16}\text{O}_{27} \]  

(1)

Various methods have been applied to, such as powder metallurgy [5], plasma arch [6], as well as milling mechanics that use high energy to produce ultrafine powder. Various studies have shown that the powder metallurgy method is more effective to produce large-scale production. Nonetheless, various obstacles that occur in this method are the formation of associated phases that caused by non-stoichiometry result from synthesis. In this research, the process of forming the BaMeFe\(_{16}\)O\(_{27}\) phase is carried out through a synthesis mechanism that is based on stoichiometric composition.

2. Methods
The forming process of BaFe\(_{16}\)Co\(_{2}\)O\(_{27}\) compound begins with combining the basic compound of single phase BaFe\(_{18}\)O\(_{19}\) with Co\(_2\)O\(_{3}\) and Fe\(_3\)O\(_{4}\). The tree compounds were mixed and refined using a planetary
ball mill with a speed of 300 rpm for 8 hours. This process will produce a homogeneous alloy between two compounds with a 45micron filter size. The powder of materials was compacted 2 tons to produce a sample with 2.54 cm and 0.5 cm thickness. The sintering process at 1200°C for 4 hours in an oxygen atmosphere. Phase analysis was carried out by using the Philips PAN-analytical diffractometer equipped and a tube provided with copper anode (λ=1.5406 Å). The microstructures were observed with the scanning electron microscope (SEM) which was run at 20.0 kV and connected to energy-dispersive-spectroscopy (EDS) analysis. The applied magnetic field varied between +1200 kA/m and −1200 kA/m. The magnetic hysteresis loops of magnetization M vs. H were plotted by normalizing the M to the saturation magnetization Ms.

3. Results and discussions

3.1. Investigation of structural analysis

The substitution process of Cobalt ions derived from Co$_3$O$_4$ have divalent Co$^{2+}$ and trivalent Co$^{3+}$ ions which will replace both Fe$^{2+}$ and Fe$^{3+}$ ions. The SEM image in figure 1 shows the difference morphology of BaFe$_{12}$O$_{19}$ and BaFe$_{16}$Co$_2$O$_{27}$ after the sintering process in 1200°C. The SEM morphologies of two samples show that almost of grains size shape 2 μm to 8 μm approximately. The sample of BaFe$_{12}$O$_{19}$ had 2 μm particle size, but in BaCo$_2$Fe$_{16}$O$_{27}$ the particles exhibit elongated shape and could be observed the structurer differences in the aggregation of two samples and show that substitution with Cobalt ion had significantly affect the grain size and morphology.

![Figure 1](image)

**Figure 1** Photomicrograph SEM of sintering BaFe$_{12}$O$_{19}$ and BaCoFe$_{16}$O$_{27}$ image.

The figure 2 show the diffraction pattern of compound M-type BaFe$_{12}$O$_{19}$ and W-type of BaFe$_{16}$Co$_2$O$_{27}$. The phase of M-type (a) hexaferrite are chemical stable with $a = 5.87925$ Å and $c = 23.13619$ Å and α$_3$O$_3$ as minor phase. And W-type hexaferrite (b) of BaFe$_{16}$Co$_2$O$_{27}$ are $a = 5.76532$ Å and $c=32.96741$Å were calculated by reaveld iteration analysis and comparated by standard pattern (00-054-0106) [7]). The average crystallite size of the samples were calculated from broadening of diffraction pattern data the size of particle diameter were determined by using Debye Sherrer the formula. The crystallite sizes of BaFe$_{12}$O$_{19}$ were in range 34 nm and 50 nm for BaFe$_{16}$Co$_2$O$_{27}$. 


Figure 2 The diffraction pattern of (a) M-Type hexaferrite (BaFe$_{19}$O$_{19}$) and (b) W-Type hexaferrite (BaCo$_2$Fe$_{16}$O$_{27}$)

It’s shows that Co$^{2+}$ or Co$^{3+}$ ions making prefer orientation of crystal structure and anisotropy.

3.2. Magnetic properties
The values of Coercive field and saturation magnetization were determined from the hysteresis loops. Figure 3 shows magnetization hysteresis curves of BaFe$_{12}$O$_{19}$ and BaCo$_2$Fe$_{16}$O$_{27}$ measured at room Temperature. The coercive field strength for BaFe$_{12}$O$_{19}$ sample is about 220 kA/m. This value is smaller than the reported values for similar samples grown by different techniques [8]. The coercivity of BaCo$_2$Fe$_{16}$O$_{27}$ decreased from 220 kA/m for BaFe$_{12}$O$_{19}$, down to 0.03 kA/m. It Show that coercive field of two samples show different significantly and shows that the partial substitution of Fe$^{2+}$ ions with Co$^{2+}$ ions influence the change in magnetic properties particularly coercivity which significantly decreases as the number of Co$^{2+}$ ions. The behavior of the coercivity was consistent with the general behavior of the anisotropy field and change value of a lattice parameter of BaFe$_{12}$O$_{19}$ and BaCo$_2$Fe$_{16}$O$_{27}$. The significant drop in the coercive field of the sample is associated with the change of crystallization anisotropy from planar to uniaxial anisotropy [9]. The spontaneous of saturation magnetization for the BaCo$_2$Fe$_{16}$O$_{27}$ was
large BaFe$_{12}$O$_{19}$ from 0.32 T to 0.34 T. Although the change in value of spontaneous magnetization was not significant, but indicated change of Crystal orientation.

![Figure 3 Hysteresis BaFe$_{12}$O$_{19}$ and BaCo$_2$Fe$_{16}$O$_{27}$](image)

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3.3. Electromagnetics properties
Figure 4 shows the real part ($\epsilon'$) and imaginary part ($\epsilon''$) versus frequency for (a) BaFe$_{12}$O$_{19}$ and (b) BaCo$_2$Fe$_{16}$O$_{27}$ samples. The plot of $\epsilon'$ and $\epsilon''$ values for all the samples in the frequency range 0f 8.2-12.4 GHz. It can be observed that the value of $\epsilon'$ are large then $\epsilon''$ and imaginary part of dielectric $\epsilon''$ indicated the change of dielectric loss of the samples.
The average dielectric power loss is proportional to $\epsilon''[10]$ and the real permittivity $\epsilon'$ is an expression of polarization ability of sample which mainly arises from dipolar polarization and interfacial polarization [11].

From figure 5, the real part $\mu'$ and the imaginary part $\mu''$ of permeability as a function of frequency in the 8.2-1.4 GHz range are plotted in figure 3.4(b). $\mu'$ of BaCo$_2$Fe$_{16}$O$_{27}$ increase from 8.2 GHz to 8.7 Hz. Meanwhile $\mu'$ decreases and exhibits resonance peak with maximum value of $\mu' = 6.2$ at 8.4 GHz.

4. Conclusions
The single phase BaCo$_2$Fe$_{16}$O$_{27}$ hexaferrite powders were successfully synthesized by mechanical milling route method. Pure crystalline W-type hexaferrite powders can be achieved when the as-prepared powder is sintered at and above 1200 °C. The Surface shape morphology and grains of various shapes that have an average size increases from 2 μm to 47 μm. The substitution elements Co$^{3+}$ yield the magnetocrystalline anisotropy transition from in-plane to axial and will cause a change of soft magnetic properties to hard magnetic. Therefore, a group of magnetically soft W hexaferrite compounds with in-axial crystal anisotropy and strong magnetization is interestingly attention, suggesting that they may be potentially useful microwave absorbing materials.

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(a)  
![Figure 4](image1.png)  
(b)  
![Figure 4](image2.png)  

(a)  
![Figure 5](image3.png)  
(b)  
![Figure 5](image4.png)  

Figure 4 Magnitude of complex dielectric permittivity (a) BaFe$_{12}$O$_{19}$ and (b) BaCo$_2$Fe$_{16}$O$_{27}$

Figure 5 Magnitude of complex dielectric permittivity (a) BaFe$_{12}$O$_{19}$ and (b) BaCo$_2$Fe$_{16}$O$_{27}$
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