Change of Structure and Magnetic Properties of La-Substituted Barium Hexaferrite

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Abstract. The substitution of Lanthanum into barium hexaferrite (Ba1-xLaxFe12O19) for La3+ (x = 0, 0.2, 0.4, and 0.6) has been synthesized using the solid reaction method through mechanical milling. Refinement results from X-ray diffraction patterns (XRD) showed that the formation of hexagonal crystal structures with space group P63/mmc, where the lattice parameters of a = b and c decreased, while the lattice strain obtained increased with increasing La concentration in the sample. The single phase is obtained at the concentration of x = 0, while the concentration of x = 0.2, 0.4 and 0.6 are already multi-phase. The morphological observation of particles using a scanning electron microscope (SEM) shows that with the presence of the La3+ substitution results the particle size distribution varies. Saturation magnetization and magnetocrystalline anisotropy are reduced due to this La substitution. This is thought to be caused by a decrease in magnetic (Fe-O-Fe) interaction and a reduction in the barium hexaferrite phase fraction in the sample. It was concluded that the effect of La substitution on Ba1-xLaxFe12O19 resulted in changes in Crystal structure parameters, particle size distribution, and magnetic properties of the material.

1. Introduction
One type M ferrite is barium hexaferrite which is a ferromagnetic material which has the characteristics of uniaxial magnetocrystalline anisotropy with saturation magnetization very high at room temperature. Besides that, it has high electrical resistance, excellent chemical stability and is very resistant to corrosion. Because of its excellent nature so that many applications of technology that can be developed from this material include for high-density magnetic recording media, motor components, even for microwave absorbent materials [1-3]. The synthesis of this material is also very easy and inexpensive so it has the potential for its application in the world of industry [4-8].

Barium hexaferrite (BaFe12O19) has a hexagonal magnetoplumbite crystal structure with a P63/mmc space group. The transition of magnetic properties from ferromagnetic becomes paramagnetic through Curie (Tc) temperature transition, which is equal to 723 °K. Based on the characteristics of magnetocrystalline anisotropy, the a-b crystallographic axis is a hard-axis and the c crystallographic axis is known as the easy-axis [9-11]. The magnetic properties of this material are intrinsically completely dependent on cation distribution on crystallographic sites [12-13]. Therefore,
analysis of the crystal structure and its correlation with magnetic behavior at room temperature of the Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ material need to be explored more deeply in this paper [14-16]. So the purpose of this study was to determine the effect of changes in structural parameters on changes in the intrinsic properties of magnetic materials Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$.

2. Material and Method
Barium hexaferrite (BaFe$_{12}$O$_{19}$) substituted with La$^{3+}$ produces a Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ system prepared using the solid reaction method through mechanical milling with several raw materials namely BaCO$_3$ (Merck, purity 99.9%), La$_2$O$_3$ (Merck, purity 99.9%), and Fe$_2$O$_3$ (Sigma-Aldrich, purity 99.9%). The three raw materials according to each composition were mixed and milled for 5 hours in a 50 ml ethanol environment using a high energy milling PW-1000di device. Then the milling mixture is dried in an oven with a temperature of 100 °C for 6 hours. After the sample and milling balls are separated, the sample is manually crushed again using mortal agate. The resulting powder is compacted into tablet form with the compaction pressure of 7000 psi. The tablet form samples were then sintered using the Thermolyne 6000 furnace at 1200 °C for 2 hours. Furthermore, each sample was characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), and permeograph. XRD is used to determine changes in structural parameters due to the effect of La$^{3+}$ substitution. X-ray anodes use CuKα ($\lambda = 1.5406$ Å) with step 0.01. Quantitative analysis is carried out using the size of the general structure analysis system (GSAS) software. Surface morphology using SEM brand JEOL JED 350, and magnetic properties testing using permeograph brand Physik 255 with a range of -1 to 1 Tesla.

3. Results and Discussions
The X-ray diffraction patterns (XRD) of barium hexaferrite samples was substituted by La$^{3+}$ (Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$) for $x = 0, 0.2, 0.4$ and $0.6$ are shown in Figure 1. The results of qualitative analysis using Match program showed that all samples consisted of barium hexaferrite phase with hexagonal crystal symmetry (space group P63/mmc) [17]. The peaks of the XRD pattern are all very compatible with the ref data of JCPDS: 00-043-0002. However, samples that have a single phase are only in the composition $x = 0$. While the composition of $x = 0.2, 0.4$ and $0.6$ consists of multi-phase.

![Figure 1. X-ray diffraction patterns of Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ (x = 0, 0.2, 0.4, and 0.6)](image-url)

Based on the results of the identification phase it appears that the reaction has succeeded in forming a single phase Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ which is in the composition $x = 0$, while for the composition $x = 0.2$ consists of two phases, namely phase BaFe$_{12}$O$_{19}$ and Fe$_2$O$_3$, and for composition $x > 0.2$ consists of three phases, namely the phases of BaFe$_{12}$O$_{19}$, Fe$_2$O$_3$, and LaFeO$_3$. To determine changes in crystal structure parameters, the number of mass fractions formed, and the cationic distribution of La substitution results into Ba atoms quantitative analysis was carried out using the GSAS program.

Figure 2 shows the results of refinement of X-ray diffraction pattern of the sample Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ with variations in composition ($x = 0, 0.2, 0.4$ and $0.6$). Figure 2 (a) is the refinement result of the
XRD pattern for $x = 0$ which has formed a Bragg diffraction peak with a single phase $\text{BaFe}_{12}\text{O}_{19}$ structure. Figure 2 (b) is the result of refinement of the XRD pattern for $x = 0.2$ has formed a two-phase Bragg diffraction peak, the structure of $\text{BaFe}_{12}\text{O}_{19}$, and $\text{Fe}_2\text{O}_3$. Whereas Figure 2 (c-d) is the refinement result of XRD pattern for $x = 0.4$ and $0.6$ which has formed a three-phase Bragg diffraction peak, the structure of $\text{BaFe}_{12}\text{O}_{19}$, $\text{Fe}_2\text{O}_3$ and $\text{LaFeO}_3$. Qualitative analysis refers to the Crystallography Open Database with card numbers (JCPDS: 00-043-0002), (JCPDS: 00-033-0664), and (JCPDS: 00-037-1493) for $\text{BaFe}_{12}\text{O}_{19}$, $\text{Fe}_2\text{O}_3$ and $\text{LaFeO}_3$ phases, respectively.

![XRD patterns](image)

**Figure 2.** The refinement result of the X-ray diffraction patterns $\text{Ba}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0, 0.2, 0.4$ dan $0.6$).

The refinement results are also supported by observations of particle surface morphology for the two single phases using SEM as shown in Figure 3. Figure 3 shows that the particle morphology of the composition $x = 0$ has excellent and uniform particle homogeneity across the sample surface, while for the composition $x > 0$ the shape of the particles begins to vary.

Furthermore, in Figure 4 describes the results of measuring magnetic properties using permeograph. This test produces a hysteresis curve which is the relationship between magnetization ($M$) and the external magnetic field ($H$).
Figure 3. The morphology of Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ particle observed using SEM for a) x=0, b) x=0.2, c) x=0.4, and d) x=0.6

Figure 4. Kurva hysteresis of the Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$

Saturation magnetization and coercivity fields decreased with an increase in La concentration up to 20% at x = 0.2. A sample of Ba$_{0.8}$La$_{0.2}$Fe$_{12}$O$_{19}$ shows optimum saturation magnetization. Saturation magnetization decreases due to increased La substitution in barium hexaferrite. Lattice strains arise because the atomic radius is smaller than La$^{2+}$ (1.69 Å) compared to Ba$^{2+}$ (1.98 Å). Although the lattice strain increases more than 20% La substitution in barium hexaferrite, but saturation magnetization and coercivity fields decrease because the Fe site is occupied by non-magnetic La atoms.

In Figure 5, the fraction of the barium hexaferrite phase mass decreases with increasing La substitution into the material. Therefore, the discussion above shows that a decrease in magnetic properties for non-magnetic La substitution at Ba site can be obtained by 20% substitution. Thus, there is a correlation between induced magnetic force and non-magnetic La concentration in the sample.

Figure 5. Mass Fraction of Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$
This can be explained by considering the lattice strain and decreasing the exchange of Fe-O-Fe interactions due to La ion off-centering. It is noted that the saturation magnetization (Ms) is maximum for 20% La substitution samples (Ba$_{0.8}$La$_{0.2}$Fe$_{12}$O$_{19}$), where the coercivity field is the minimum for this sample. This result is similar to previous studies [20].

4. Conclusion
The synthesis of Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ with variations in composition (x = 0, 0.2, 0.4, and 0.6) was successfully carried out. The refinement results of X-ray diffraction patterns of Ba$_{1-x}$La$_x$Fe$_{12}$O$_{19}$ samples showed that the sample had a single phase in the composition x = 0 (BaFe$_{12}$O$_{19}$). The particle morphology of composition x = 0 has good and uniform particle homogeneity across the surface while for x > 0 particles vary. The lattice parameter, unit cell volume and particle size decrease with an increase in La content in the sample. All samples were crystallized in hexagonal crystal symmetry with the P63/mmc space group. The lattice parameter reduced by increasing La in the barium hexaferrite. It was concluded that magnetization was able to maintain up to 20% of La substitution and decrease with an increase in La substitution. This can be explained by considering the lattice strain and decreasing the exchange of Fe-O-Fe interactions due to La ion off-centering.

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