Effect of Nd$^{3+}$ substitution on the BH$_{\text{max}}$ properties of barium-strontium hexaferrite permanent magnet

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Abstract. This paper describes the effect of the substitution of Nd$^{3+}$ ions in Barium-Strontium Hexaferrite (Ba$_{0.6}$Sr$_{0.4}$)$_{1-x}$Nd$_x$Fe$_{12}$O$_{19}$ with $x = 0.01, 0.03$ and $0.05$, on the energy of the product. All samples were made from raw materials of barium (II) carbonate, strontium (II) carbonate, neodymium (III) oxide, and iron (III) oxide which each have a purity of > 99% which was processed by the solid-state reaction method using high energy milling with a rotating speed of 750 rpm. The crystal structure and phase formed are characterized using an X-ray diffractometer. Scanning electron microscopy is used for surface morphology analysis and permagraph is used for hysteresis characterization so that the product energy can be calculated. X-ray diffraction analysis showed that all phase samples have an orthorhombic structure and space group P nma. Surface morphology is almost homogeneous with heterogeneous shapes and the average particle size ranges from 200-800 nm. The maximum product energy obtained is 165.4kGOe in the sample $x = 0.05$.

1. Introduction
Permanent magnets have a very important role in everyday life, for example in industry, communication, and defense tools. To improve its energy product, there are two ways that can be taken, namely increasing extrinsic properties through its nanostructures, and increasing intrinsic properties through its atomic structure. With nanostructures, rare-earth substitution can rarely increase the energy product [1]. In addition to having high coercivity, it must also have high magnetic saturation which is a necessary condition for the application of permanent magnets.

In the last decade, permanent magnet based on NdFeB is still the primadonna in its application [2]. However, recently M-type hexaferrite-based magnetic materials have begun to gain the attention of many researchers [3-10, 11]. This is due to the properties of this material, high magnetic saturation, chemical stability, suitability with microwave absorbers, high performance at relatively high temperatures and low cost [8-9]. Some efforts that have been made to improve performance include substitution on Fe atoms with Mg$^{2+}$-Al$^{3+}$ [3], Ti$^{4+}$ [8], the substitution of the Ce$^{3+}$ ion on the Sr$^{2+}$ ion (Sr$_1$Ce$_x$Fe$_{12}$O$_{19}$) [4] or simultaneously by reducing the particle size. Magnetic saturation and coercivity are influenced by particle size. The smaller the particle size, the higher the coercivity [10]. When substituted with Ce$^{3+}$, the product energy (BH)$_{\text{max}}$ will increase if $0 < x \leq 0.15$, while it will decrease if $0.15 < x \leq 0.30$ (BH)$_{\text{max}}$ [4]. Sr$_{0.5}$Ca$_{0.2}$Nd$_{0.3}$Fe$_{12}$, Al$_{0.5}$Co$_{0.5}$Fe$_{12}$, O$_{19}$ (BH)$_{\text{max}}$ will increase if $0 < x \leq 0.2$ and will decrease to $0.2 < x \leq 0.5$ [7]. These different results can be the subject for further discussion.
Several methods that have been used to produce permanent magnetic materials include solid state reaction methods using planetary ball-mill [3, 6], conventional ceramic processes [4, 6-7, 11] or high energy milling [8, 10, 12] and the sol-gel method [13]. Solid state reaction method is a method that is relatively easier and cheaper. Solid state reaction method using high energy milling can be done in dry or wet conditions.

This paper will discuss the effects of substitution of Nd$^{3+}$ ions on the system $(\text{Ba}_{0.6}\text{Sr}_{0.4})_{1-x}\text{Nd}_x\text{Fe}_{12}\text{O}_{19}$ with the values $x = 0.01, 0.03$ and 0.05 on the energy of the product as a permanent magnet. Samples were processed by the solid-state reaction method with mechanical alloying using wet milling.

2. Methods
With stoichiometric calculations, samples $(\text{Ba}_{0.6}\text{Sr}_{0.4})_{1-x}\text{Nd}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0.01; 0.03$ and 0.05) are made from raw materials consisting of barium (II) carbonate, strontium (II) carbonate, neodymium (III) oxide, and iron (III) oxide, each of which has a purity of > 99%. The sample was then ground using High Energy Milling (HEM) in wet conditions using ethanol for seven hundred and fifty rotations per minute for twenty hours. After drying in an oven at 80 $^\circ$C, then the sample is pressed with a pressure of 5 tons so that it is shaped as a pellet with a diameter of about 1.5 cm. Then the samples were sintered for five hours at 1000 $^\circ$C. X-ray diffraction is used to analyze the crystal structure and phases formed. Surface morphology and grain size were analyzed using Scanning Electron Microscopy (SEM), while permeagraph was used to analyze product energy.

3. Result and Discussion
The results of the analysis of XRD characterization found that all samples were in phase. All samples have orthorhombic crystal structures with the P nma space group. The substitution of Nd$^{3+}$ ions in the Ba$^{2+}$/Sr$^{2+}$ position does not change the crystal structure. The same result was also obtained by Y. Yang et al., where Nd$^{3+}$ was substituted on Sr$^{2+}$/Ca$^{2+}$ ions [7]. The refinement results of X-Ray Diffraction measurements with diet programs for the three samples $(\text{Ba}_{0.6}\text{Sr}_{0.4})_{1-x}\text{Nd}_x\text{Fe}_{12}\text{O}_{19}$ with a value of $x = 0.01; 0.03$ and 0.05 can be seen in figure 1. The complete results of XRD analysis can be seen in Table 1. The greater the value of x, the greater the lattice parameter and lattice volume. This is due to the radius of the atom Nd = 2.06 Å. It is smaller than the radius of the Ba atom = 2.53 Å, but greater than the radius of the atom Sr = 2.00 Å. So, the more the x value increases, the bigger the volume of the lattice [14]. There is a decrease in the value of the density of the sample. This is because the addition of Nd atoms results in an increase in bulk volume.

![Figure 1. Refinement results of X-Ray Diffraction measurements on samples $(\text{Ba}_{0.6}\text{Sr}_{0.4})_{1-x}\text{Nd}_x\text{Fe}_{12}\text{O}_{19}$ (a) $x = 0.01$; (b) $x = 0.03$ and (c) $x = 0.05$.](image-url)
### Table 1. Lattice parameters, R-factor and $\chi^2$.

| $x$ | Lattice parameters | $a = \beta$ | $\gamma$ | Vol | $W_{R0}$ | $\rho$ | $\chi^2$ |
|-----|-------------------|-------------|----------|-----|---------|-------|---------|
|     | $a$ (Å) | $b$ (Å) | $c$ (Å) | ($^\circ$) | ($^\circ$) | $(\text{Å}^3)$ | $(\text{g/cm}^3)$ |       |
| 0.01 | 5.8736 | 5.8736 | 23.1403 | 90 | 120 | 691.373 | 0.0385 | 11.912 | 0.6057 |
| 0.03 | 5.8829 | 5.8829 | 23.1567 | 90 | 120 | 694.063 | 0.0464 | 11.866 | 0.7389 |
| 0.05 | 5.8843 | 5.8843 | 23.1673 | 90 | 120 | 694.707 | 0.0467 | 11.855 | 0.9908 |

The surface morphology observations using the scanning electron microscope are shown in Figure 2. Although the surface morphology seems quite clear and there is no agglomeration, the shape and size of the grain is still heterogeneous with an average size between 200-800 nm. These results indicate that the milling process using high energy milling produces relatively smaller grain sizes compared to planet ball-mill, which is an average of 500 nm [3] and in the size range of 400-2,200 nm, with an average of 640 nm for a forty-two hours milling time [12]. In addition to the milling process, the high temperature used in the manufacturing process also affects the size of the grain produced. The higher the temperature used; the grain size will increase. A heating temperature of 1250 °C will produce a grain size of 950 nm [11]. There were several parts that have different colors. Our guess is that the different colors are not caused by impurity, but rather by charging, where the sample is less conductive and lacks vacuum.

![Surface morphology of the sample (Ba$_{0.6}$Sr$_{0.4}$)$_{1-x}$Nd$_x$Fe$_{12}$O$_{19}$](image)

**Figure 2.** Surface morphology of the sample (Ba$_{0.6}$Sr$_{0.4}$)$_{1-x}$Nd$_x$Fe$_{12}$O$_{19}$ (a) $x = 0.01$; (b) $x = 0.03$ and (c) $x = 0.05$.

Sample hysteresis curve (Ba$_{0.6}$Sr$_{0.4}$)$_{1-x}$Nd$_x$Fe$_{12}$O$_{19}$ (a) $x = 0.01$; (b) $x = 0.03$ and (c) $x = 0.05$ is shown in Figure 3. the more content Nd ($x$ increases), the “fatter” the curve will become, which results in it
having an increasing $H_c$, $M_r$ and $M_s$ value. This means that the greater the addition of Nd, the more suitable the sample is for permanent magnet material. $H_c$, $M_r$ and $M_s$ values can be seen in Table 2.

**Figure 3.** Sample hysteresis curve $(Ba_{0.6}Sr_{0.4})_{1-x}Nd_xFe_{12}O_{19}$ (a) $x = 0.01$; (b) $x = 0.03$ and (c) $x = 0.05$.

**Table 2.** The results of the magnetization analysis with permagraph.

| $x$   | $H_c$ (kOe) | $B_r$ (x100 Gauss) | $(BH)_{max}$ (kGOe) |
|-------|-------------|-------------------|---------------------|
| 0.01  | 0.210       | 0.59              | 31.4                |
| 0.03  | 0.438       | 0.52              | 36.4                |
| 0.05  | 0.399       | 1.18              | 165.4               |

The maximum product energy value $[(BH)_{max}]$ determines the quality of a permanent magnet. The value can be determined by calculating the area in the second quadrant of the B-H magnetization loop curve. The results obtained values $(BH)_{max}$ for $x = 0.01$, 0.03 and 0.05 are 31.4 kGOe, 36.4 kGOe, and 165.4 kGOe respectively. This result is better than the result obtained by M. Rianna et al., Which is 45.8 kGOe [3]. Increased value $(BH)_{max}$ indicates an increase in available energy. Thus, the remanence values ($B_r$) and magnetic induction coercivity ($H_c$) will affect the value $(BH)_{max}$ [7]. High coercivity values are associated with particles that are significantly smaller than the size of a single domain [15]. Particle size is strongly influenced by calcination temperature. A high calcination temperature can reduce porosity and increase sample density. The higher the density, the better the magnetic properties will be [16]. The value $(BH)_{max}$ is also affected by the shape of the granules. Granules in oblate form will have a greater $(BH)_{max}$ when compared to in the form of prolate [17]. This is in accordance with the opinion of F. Jimenez et al., that microstructure control, such as grain size and texture allow extrinsic manipulation through various methods for magnetic phase characteristics [18]. This is evident from our results, which are higher than 640 kGOe with a two-hour milling time [15]. The more the value of $x$ increases, the more the value $(BH)_{max}$ will increase. This is in accordance with the opinion of Y. Yang et al., where to improve the magnetic properties can be through substitution of Sr$^{2+}$ or Ba$^{2+}$ ions by rare earth elements [7].

**4. Conclusion**

We have succeeded in making samples $(Ba_{0.6}Sr_{0.4})_{1-x}Nd_xFe_{12}O_{19}$ with values of $x = 0.01$, 0.03 and 0.05 with solid state reaction method using high energy milling. All samples were in phase with orthorhombic crystal structures. The average size of particles is 200-800 nm in heterogeneous forms. As the Nd content increases, the energy of the product will also increase. The product energy obtained was 31.4 kGOe,
36.4 kGOe and 165.4 kGOe for x = 0.01, 0.03 and 0.05, respectively. Therefore, we conclude that this material can be applied as a permanent magnet.

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