Preparation and characterization of Fe-Mn-doped Barium Hexaferrite permanent magnet

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Abstract. Barium Hexaferrite-based permanent magnets (BaFe₁₂O₁₉) was known for its high magnetic anisotropy and suitability in broad applications. Some dopants and atomic substitutions have been utilized to improve its properties for special purposes. In this paper, the Fe-Mn system was used as a dopant for preparing Fe-Mn-doped barium hexaferrite permanent magnet using mechanical alloying method. The physical properties of the samples, such as bulk density, and porosity were examined to study the effect of the dopant. In addition, the crystal structure and magnetic properties of the samples were analyzed using X-Ray Diffractometer (XRD) and Vibrating Sample Magnetometer (VSM), respectively. It is found that the addition of Fe-Mn into barium hexaferrite contributes on the appearance of minor phases such as iron oxide-based magnetite and hematite. In addition, the XRD peak shifted to smaller angle which is likely due to Mn ion substitution and lattice strain within the hexaferrite crystal. It is also observed that the magnetic properties of Fe-Mn-doped barium hexaferrite was inferior to that of the undoped samples. It means that the formation of magnetite and hematite from Fe-Mn dopant during the sintering process is dominant and results to the reduction of hard magnetic properties of the samples.

1. Introduction

Barium hexaferrite-based ferromagnetic materials (BaFe₁₂O₁₉) have been investigated for many applications such as permanent magnet, microwave absorber, and magnetic recording media [1,2]. Barium hexaferrite is a long lasting research area for nearly a century due to its high magnetocrystalline anisotropy, chemical stability, excellent frequency, and Curie temperature [3]. In recent years, the study focused on the effect of elemental substitution to M-hexaferrite structure in correlation with its magnetic and electrical properties. The addition of rare-earth element e.g. Samarium contributes to the decrease of remanence, with the slight increase of coercivity of M-hexaferrite structure [4]. In other studies, the addition of Cerium into M-hexaferrite structure produces an enhancement of magnetization and coercivity, which makes it suitable as a microwave absorbing material [5,6]. The common addition of Ti-based ion generally increase the electromagnetic properties such as permeability and permittivity [7,8].

On the other hand, the development of nanocomposite-based magnets is also interesting due to its useful magnetic characteristics, which can be achieved by employing the exchange-spring interaction...
between hard and soft magnetic structure [9,10]. As an example, the combination of ferromagnetic and anti-ferromagnetic oxide have revealed a new property which is important for magnetic recording and permanent magnet applications [11].

In this paper, we investigated the effect of Fe-Mn alloy addition to M-type structure of barium ferrite on the physical and magnetic properties of the barium hexaferrite-based magnet.

2. Experimental Method

The starting materials used for this experiment were commercial barium hexaferrite and Ferromanganese (Fe-Mn) powders. Based on the XRD data, the barium hexaferrite powder has major phase of $\text{BaFe}_{12}\text{O}_{19}$ and minor phase of $\text{Fe}_2\text{O}_3$. Whereas, the ferromanganese powder is composed by $\alpha\text{-Fe}$ and $\text{MnO}_2$. At first, barium hexaferrite and ferromanganese powder were processed separately using dry-ball mill for 24 hours and wet-high energy milling method for 1 hour, respectively, to refine the particle size. The as-milled powders were then blended in a shaker mill for 15 minutes in order to obtain the homogeneous mixture. The as-blended powder was compacted in a magnetic field press machine under 40 kgf/cm$^2$ pressure and 3.6 kOe parallel magnetic field. The magnetic field was utilized in the compaction process to produce magnetically-anisotropic samples and increase the magnetization. The as-compacted samples were sintered in a furnace at 1100, 1150, 1200, and 1250 °C, respectively, for 2 hours.

The particle size distribution was determined using optical microscope with the assistance of imageJ software [12], by measuring the particle sizes and estimating them to get the size distribution. The crystal structure of the mixed powders were analyzed using X-Ray Diffratometer (Rigaku Smartlab). The crystallite size of different phases were calculated using the Debye-Scherer equation [13]:

$$d = \frac{0.9\lambda}{\beta\cos \theta}$$

Where $d$ is the crystal size, $\lambda$ is the X-ray wavelength, $\beta$ is the Full Width at Half Maximum (FWHM) value of the related diffraction peak, and $\theta$ is the diffraction angle.

The magnetic properties were analyzed using Vibrating Sample Magnetometer (VSM-250) under external magnetic field of 2 Tesla. The physical characteristics were measured using Archimedes density and porosity measurement method according to ASTM C-373.

3. Results and Discussions

The particle sizes of the as-milled powders were determined using optical microscope which is equipped with CCD camera Pax-Cam (40x objective lens magnification). Size analyses were performed using ImageJ analysis software to produce size distribution data as displayed in figure 1. The particle size of doped and undoped-barium hexaferrite shows a Gaussian distribution with average value of 126, 121, and 120 nm for undoped, 3 wt% Fe-Mn, and 7 wt% Fe-Mn, respectively. Interestingly, the size distribution of milled Fe-Mn alloy shows irregular shape with average size value of 93 nm.

After compacted and sintered, the bulk density and porosity of the-doped barium hexaferrite samples were characterized using Archimedes method. By measuring the ratio of dry and wet mass (ASTM C373), the density and porosity of the samples can be depicted in Figure 2. The figure shows that the addition of Fe-Mn alloy into hexaferrite structure gives the decrease of density as well as the increase of porosity. The optimum value of density and porosity are 4.81 g/cm$^3$ and 20.7 %, respectively, which was achieved by 3 wt% Fe-Mn doped sample, sintered at 1200 °C. Based on figure, 2, the density and porosity values are affected by sintering temperature. It shows that, in general, the densification processes are inversely proportional with the pore formation during sintering step. The effective sintering process is needed to obtain higher sintered density and minimize porosity in order to increase the magnetic properties [14].
The XRD analyses of the sintered samples were performed to characterize the microstructural effect of Fe-Mn addition. The polycrystalline structure was observed, with BaFe$_{12}$O$_{19}$ as the main phase. Figure 3 shows the diffraction profiles, which concludes that the hexaferrite structure is still preserved after the addition of Fe-Mn alloy. The Fe-Mn alloy itself is composed by α-Fe and MnO$_2$ structure, which are marked with star (*) and hole-circle (o), respectively, in the diffraction profile. Meanwhile, the starting barium hexaferrite powder is composed by BaFe$_{12}$O$_{19}$ structure and Fe$_2$O$_3$ as a minor phase (~ 13%). Figure 3 reveals the increase of iron-oxide formation as Fe-Mn composition increases. The magnetite (Fe$_3$O$_4$) and hematite (Fe$_2$O$_3$) peak was observed for 3 and 7 wt% Fe-Mn addition, respectively. The α-Fe phase from Fe-Mn alloy was expected to be oxidized during sintering process and form the more stable oxide structure.

![Figure 1](image1.png)

**Figure 1.** Particle size distribution of (a) undoped, (c) 3wt% Fe-Mn, and (d) 7 wt% Fe-Mn barium hexaferrite, compared to (b) the milled Fe-Mn alloy.
Figure 2. Bulk density and porosity values of 3 wt% (red mark) and 7 wt% (blue mark) Fe-Mn-doped barium hexaferrite.

Based on equation (1), the crystallite size of all samples are in nanometer scale, ranged from 33.5 to 44.4 nm. The average values of hexaferrite crystallite size for 4 major peaks at (110), (008), (107) and (114) planes are 40.28 nm, 40.27 nm, and 39.68 nm for undoped, 3 wt% and 7 wt% Fe-Mn, respectively. It means that the addition of Fe-Mn alloy into hexaferrite structure slightly reduces the crystalline size, which become significant as the Fe-Mn addition increased.

MnO$_2$ phase, which is originated from the starting Fe-Mn alloy, does not appear in the diffraction profile for 3 and 7 wt% addition. However, the peak shift is detected for this addition value. The inset (right profile) of figure 3 shows that the (110), (008), (107) and (114) planes shift to smaller 2θ as Fe-Mn composition increases. The lattice parameters ($a$ and $c$) of hexagonal ferrite crystals can be determined for (110) and (008) planes using following equations:

\[
a = \frac{\lambda}{\sqrt{3} \sin \theta} \sqrt{h^2 + hk + k^2}
\]

and

\[
c = \frac{\lambda}{2 \sin \theta} l
\]

where $\lambda$ is x-ray wavelength and $\theta$ is selected diffraction peak position for specified ($h \ k \ l$) planes. The calculated lattice constant ($a$ and $c$) for undoped, 3 % and 7 % Fe-Mn-doped barium hexaferrite are 5.854 Å (22.941 Å), 5.881 Å (23.158 Å), and 5.88 Å (23.180 Å), respectively. It means that the addition of Fe-Mn alloy also increases the lattice constant (both $a$ and $c$) as the Fe-Mn addition increases. The Mn$^{2+}$ ions might partly substitute the Fe$^{2+}$ ions in hexagonal structure since the ionic radii of Mn$^{2+}$ (0.66 Å) is slightly larger than Fe$^{2+}$ (0.63 Å). Therefore, we believe that these substitutions contribute to the increase of lattice constant as the Fe-Mn addition increases.

Figure 3. XRD profile of the Fe-Mn-doped barium hexaferrite samples. Inset (right profile) shows peak shift of the doped and undoped samples.
The magnetic properties of sintered Fe-Mn-doped barium hexaferrite samples were analyzed using vibrating sample magnetometer as displayed in figure 4. The hysteresis graph shows that Fe-Mn-doped barium hexaferrite is a permanent magnet. The effects of Fe-Mn addition are described as the change in the magnetic characteristics, which are magnetic saturation ($\sigma_s$), remanence ($\sigma_r$), and coercivity field ($H_c$). Figure 4 shows that the magnetic properties slightly decrease as the Fe-Mn composition increases. The reduction of magnetic characteristics is correlated with the crystal structure formed during addition and sintering process. The iron-oxide formations with soft magnetic characteristics contribute to the magnetic properties reduction of Fe-Mn-doped hexaferrite. The increase of iron-oxide, such as in the 7 wt% Fe-Mn-doped barium hexaferrite, lowers the remanence and coercivity. From the inset, the remanence (coercivity) of samples have a decreasing trend with the value of 33.8 (3.8), 31.4 (3.0) and 29.3 emu/g (2.73 kOe) for undoped, 3, and 7 wt% Fe-Mn-doped barium hexaferrite, respectively.

![Figure 4. Magnetic properties of undoped (rectangle-black curve) and Fe-Mn-doped barium hexaferrite samples.](image)

Based on the above data, we find that the addition of Fe-Mn alloy into barium hexaferrite structure contributes to the magnetic properties reduction due to the iron-oxide (Fe$_2$O$_3$ and Fe$_3$O$_4$) formation during sintering process [15,16]. We expect that the nanocomposite formation of Fe-Mn and barium hexaferrite should be free from the humid environment. Thus, the iron as a ferromagnetic intergrain phase will raise the exchange interaction and enhance its magnetic properties. The Mn ion also play an important role in the lattice structure modification and the increase of magnetic anisotropy. We propose to consider this study for the development of high properties composite permanent magnet.

4. Conclusion
In this experiment, the Fe-Mn-doped barium hexaferrite permanent magnet has been prepared by mechanical alloying method. The as-milled powder of commercial barium hexaferrite and ferromanganese (Fe-Mn alloy) was employed in the study. Based on the microstructure analyses, the addition of Fe-Mn into barium hexaferrite contributes to the appearance of minor phase such as iron
oxide-based magnetite and hematite. In addition, the Mn ion shifts the XRD peak into smaller angle which is correlated with lattice strain within hexaferrite crystal lattice. The magnetic properties of Fe-Mn-doped barium hexaferrite were smaller than that of the undoped sample. This means that the iron oxide formation during sintering process plays the important role in the reduction of hard magnetic properties of the samples. Moreover, the environmental condition need to be considered for the development of high properties composite permanent magnets.

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