Effect of additive Na$_2$O on sintering temperature, crystal structure and magnetic properties of BaFe$_{12}$O$_{19}$ magnet

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Abstract. The BaFe$_{12}$O$_{19}$ magnet has been made at several sintering temperature (1100, 1150, 1200, 1250 and 1300°C) and various additive Na$_2$O (0, 1, 2 and 3 % of weight) by using Powder Metallurgy. The BaFe$_{12}$O$_{19}$ powder and NaHCO$_3$ powder as Na$_2$O source were mixed with ethanol until homogeneous by using magnetic stirrer, dried at 80°C and calcined at a temperature 1000°C for 1 hour. The calcined powders were milled by using a ball mill in dry condition. Then, the powders were mixed with 3 % PVA as a binder, then, the powder is put into a dies mold and pressed with a pressure of 30 MPa. The disc samples were sintered by using furnace Thermolyne. The characterization of the sintered sample was done such as measurement of density and porosity, analysis of crystal structure and measurement of magnetic properties. The characterization results show that the optimum sintering temperature is 1200°C with additive 1% of Na$_2$O, if more than 1 %, the physical and magnetic properties decrease. The composition of additive N$_2$O at the sintering temperature 1200°C does not influence the crystal structure.

1. Introduction

Barium ferrites are well known hard magnetic materials, which are based on iron oxide. They are also called as ferrite magnets and could not be easily replaced by any other magnets [1]. Hexagonal barium ferrite having the chemical formula of BaFe$_{12}$O$_{19}$ are widely used in magnetic recording media, microwave devices, and electromagnetic shielding fields [1]. The barium ferrite is attractive materials for permanent magnet due to their large uniaxial anisotropy, high chemical stability and corrosion resistance [2]. The Magnetic saturation of Barium hexaferrite is 380 emu/cm$^3$ or 72 emu/g at room temperature and the Curie point is 450°C [3]. Many methods of synthesis have been developed to obtain a low production cost of powder particles of barium ferrite. There are many methods such as powder metallurgy method and chemical routes (sol-gel or co-precipitation). The powder metallurgy method is preparation process by using solid-solid mixing, and continued with sintering process. Sintering is a heat treatment applied to a powder compact in order to impart strength and integrity. The temperature used for sintering is below the melting point of the major constituent of the Powder Metallurgy material [4]. The properties of final product can be influenced by impurity of raw materials, mole ratio BaO to Fe$_2$O$_3$ and particle size or grain size and sintering temperature [4,5]. The sintering temperature of Ba-Ferrite is high enough about 1300°C [5], and during the sintering process, the grain will be growth. The development of grain size after sintering process can influence of magnetic properties, where the grain size becomes bigger, the magnetic properties will reduce [6]. To prevent grain size does not grow rapidly after the sintering process it is necessary to add ingredients additive. Some additives may be used such as silica (SiO$_2$), Al$_2$O$_3$, Na$_2$O, Fe$_2$O$_3$ [7]. Not only
dampen the grain growth, but those additives can also serve lower the sintering temperatures [7]. The aim of this paper is to know the effect of Na$_2$O additive on sintering temperature, the crystal structure and magnetic properties of BaFe$_{12}$O$_{19}$ prepared by Powder Metallurgy.

2. Methodology
The raw materials used in this work were barium hexa ferrite BaFe$_{12}$O$_{19}$ powder (purity 99.0%) and NaHCO$_3$ powder (purity 99.90 %) as a Na$_2$O source. The sintering aid Na$_2$O was varied as 0, 1, 2 and 3 wt% in the raw material mixture. The raw materials were weighed in calculated amount and mixed with ethanol until homogeneous by using magnetic stirrer, then they are dried at 80$^\circ$C and calcined at a temperature 1000$^\circ$C with holding time 1 hour by using Thermolyne Furnace. The calcined powders were milled by using a ball mill in dry condition for 24 hours. The fine powders were mixed with 3 % PVA as a binder, then, they are put into a dies mold and compacted with a pressure of 30 MPa. The disc samples were sintered by using Thermolyne Furnace with heating rate about 8$^\circ$C/minute from room temperature to 400$^\circ$C, and hold for 1 hour, then the temperature was increased from 400$^\circ$C to sintering temperatures (1100, 1150, 1200, 1250 and 1300$^\circ$C) with heating rate of 10$^\circ$C/minute , and at those temperature were hold for 1 hour. The sintered samples were measured for density and porosity by using Archimedes method. The phase identification study of sintered samples was carried out by X-ray diffractometer. Magnetic properties of the barium hexa ferrite samples were measured by using Gauss meter and vibrating sample magnetometer (VSM).

3. Results and Discussion
The XRD results of the samples that have been sintered at a temperature of 1200$^\circ$C are shown in figure 1.

![Figure 1. XRD- patterns of 1200$^\circ$C sintered samples with variation of Na$_2$O additives.](image-url)
The XRD analysis is performed only on samples using additives and without additives and had been sintered at a temperature of 1200°C. The results of X-ray diffraction pattern show that all the samples have the same diffraction pattern, as presented in figure 1. Based on ICDD card No. 00-027-1029 that peaks that formed an BaO6Fe2O3 phase with a hexagonal crystal structure and have lattice parameters a = b = 5.892 Å, c = 23 198 Å, cell volume = 697.44 Å³. The addition of additives to 3% by weight Na2O does not give effect to changes in the crystal structure.

The measurement result of bulk density of sintered pellets is shown in figure 2. The curve shows that the value of bulk density of sintered sample with 0 % wt.Na2O increases sharply from sintering temperature 1100°C to 1300 °C. However the bulk density values of samples with Na2O additives (1% and 2 %) also tend to increase the sintering temperature range between 1100 to 1200 °C, and tend to be slightly down between 1200 to 1300°C. But sample with 3 % Na2O tends to increase the sintering temperature range between 1100 to 1200 °C and tends to decline sharply at the sintering temperature range between 1200 to 1300 °C.

![Figure 2](image2.png)

**Figure 2.** The bulk density of sintered sample as function of sintering temperature.

Based on the results shown in figure 2, the densification process samples without additive has been required high temperatures up to 1300°C to obtain maximum bulk density value (4.55 g/cm³). Meanwhile, the maximum bulk density of samples with addition of Na2O (1% to 3 % Na2O) can be achieved at sintering temperature 1200°C. In this case that the Na2O additive has a function as flux materials so as to lower the melting temperature of a materials, which consequently, the sintering temperatures can be reduced.

Figure 3 shows a curve of porosity of sintered samples as function of sintering temperature. The value of porosity tends to decrease for all sample, it is due to a mechanism of sintering process.

![Figure 3](image3.png)

**Figure 3.** The curve of porosity sintered sample with variation of Na2O additives.
Densification and grain growth occur during a sintering process at high temperature, this can cause shrinkage and pore reduction [8]. The porosity value of sample with Na₂O additives is lower compared to sample without Na₂O additive. The lowest porosity value (1.12 %) is achieved on sample with 1% Na₂O at a temperature sintering 1200 °C, but the porosity values of samples with Na₂O additive greater than sample1% tends to increase again. The value of porosity of samples with Na₂O additive tends to be slightly down at sintering temperature more than 1200°C. Na₂O additive capable of depressing the value of the porosity and improve densification to a temperature of 1200°C, but to a temperature above 1200°C tends to diminish the level of densification, because the grain growth during the sintering process to a temperature of 1200°C can be prevented. And grain will grow up again at sintering temperatures above 1200°C.

The measurement results of magnetic properties of sintered samples show at figure 4 and figure 5. Figure 4 shows a flux magnetic (FM) value with variations of sintering temperature. The flux magnetic is a magnetic strength on surface material or amount of magnetic flux in an area taken perpendicular to the magnetic flux's direction and it is measured by using Gauss meter.

![Figure 4. Flux magnetic curves for sintered samples with variation of sintering temperature.](image)

Where value of FM for samples with 0 wt% Na₂O tends to increase with increasing of sintering temperature, the maximum value of FM is 610 Gauss at sintering temperature 1300°C. The value of FM of samples with Na₂O additive tends to increase from temperature sintering 1100°C until 1200°C. Because all samples with the additive at this condition have maximum densification, and the grain growth can be prevented by using the Na₂O additive. But the FM value of samples with Na₂O additive tend to decrease at temperature sintering more than 1200°C, it is due to lower bulk density value. The highest value of FM is about 620 Gauss for the sample with 1 wt% Na₂O and at sintering temperature 1200°C. Figure 5 shows hysteresis curve of 1200°C sintered sample with the variation of Na₂O additives.

![Figure 5. Hysteresis curve of 1200°C sintered sample with variation of Na₂O additives.](image)
The hysteresis curve as seen in figure 5 shows that the Na$_2$O additive composition can influence the hysteresis loops. The area of hysteresis loops trends smaller and it indicates that magnetic properties such as magnetic saturation (ms), remanence (mr) and coercivity (Hc) become lower. According to the measurement results of bulk density and porosity, the Na$_2$O additive can significantly influence the densification until sintering temperature 1200$^\circ$C. It means that there are not grain growth until temperature 1200$^\circ$C. According to the research results of J. Topfer et.al. [7], the magnetic properties tend to increase as the grain size decreases. Further, they reported a decrease in saturation magnetization with decreased grain size [7]. It can be proved that based on table 1, samples without additives Na$_2$O have magnetic saturation value (ms) is higher than the ms value of the sample with additives Na$_2$O. That means grain growth does not occur in accordance with the level of densification tends to increase.

The Na$_2$O additive value gives significantly effect on the value of ms and mr, and coercivity value (Hc) is nearly constant. Table 1 shows the value of parameter-parameter magnetic properties according to results of hysteresis loop graph. The sample without Na$_2$O additive has the highest value of mr (48.50 emu/g) compared to other samples, but value Hc, ms and energy product BH$_{max}$ are near constant.

### Table 1. Value of Remanence (mr), coercivity (Hc), magnetic saturation (ms) and energy product (BH)$_{max}$ of 1200$^\circ$C sintered sample with variation of Na$_2$O additives.

| Sample                | mr (emu/g) | Hc (kOe) | ms (emu/g) | BH$_{max}$ (MGOe) |
|-----------------------|------------|----------|------------|------------------|
| BaFe$_{12}$O$_{19}$   | 48.50      | 1.322    | 61.07      | 0.144            |
| BaFe$_{12}$O$_{19}$ + Na$_2$O 1% | 42.15 | 1.314 | 52.18 | 0.135            |
| BaFe$_{12}$O$_{19}$ + Na$_2$O 2% | 25.72 | 1.282 | 47.24 | 0.129            |
| BaFe$_{12}$O$_{19}$ + Na$_2$O 3% | 18.14 | 1.252 | 41.28 | 0.119            |

### 4. Conclusion

In this study, the effect of Na$_2$O additive has been investigated on the densification, magnetic properties and crystal structure of barium ferrite by solid state sintering method. It was observed that Na$_2$O additive can influence significantly on densification and magnetic properties, but it does not give effect on the crystal structure. The optimum percentage of additive is 1 % wt.of Na$_2$O, and the sintering temperature becomes lower at this condition. Permanent magnet BaFe$_{12}$O$_{19}$ with 1 % wt. of Na$_2$O and sintered at 1200$^\circ$C has properties such as : bulk density = 4.67 g.cm$^{-3}$, porosity = 1.21 %, flux magnetic = 620 Gauss, remanence =42.15 emu/g, coercivity =1.314 kOe and energy product =0.135 MGOe.

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