Manufacture of barium hexaferrite (BaO3.98Fe2O3) from iron oxide waste of grinding process by using calcination process

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Abstract. The utilization of iron oxide waste of grinding process as raw materials for making barium hexaferrite has been completed by powder metallurgy method. The iron oxide waste was purified by roasting at 800 °C temperature for 3 hours. The method used varying calcination temperature at 1000, 1100, 1200, and 1250 °C for 3 hours. The starting iron oxide waste (Fe2O3) and barium carbonate (BaCO3) were prepared by mol ratio of Fe2O3:BaCO3 from the formula BaO3.98Fe2O3. Some additives such as calcium oxide (CaO), silicon dioxide (SiO2), and polyvinyl alcohol (PVA) were added after calcination process. The samples were formed at the pressure of 2 ton/cm2 and sintered at the temperature of 1250 °C for 1 hour. The formation of barium hexaferrite compounds after calcination is determined by X-Ray diffraction. The magnetic properties were observed by Permagraph-Magnet Physik with the optimum characteristic at calcination temperature of 1250 °C with the induction of remanence (Br) = 1.38 kG, coercivity (HcJ) = 4.533 kOe, product energy maximum (BHmax) = 1.086 MGOe, and density = 4.33 g/cm3.

1. Introduction
Barium hexaferrite is one of the ferrite permanent magnets with a complex hexagonal magnetoplumbite structure and general formula of MFe12O19, where M = Ba, Sr, Pb [1]. This magnet is the most extensively investigated material among the family of hard ferrites because it has high curie temperature, relatively large magnetization, excellent chemical stability, and corrosion resistivity, whereas its magnetic and electrical properties should be modulated to satisfy different applications [2]. There are many applications of barium hexaferrite in electronic devices such as automotive industry, magnetic recording media, microwave devices, electric generators and in many magnetically operated devices such as magnetic levitations, telephone ringers, receivers, etc [3].

The main raw material for making barium ferrite is iron oxide. There are many sources of iron oxide materials in Indonesia, such as iron sand and iron oxide waste from production process of steel industry. The use of local resources as materials for research is highly recommended by the government (in accordance with national development program) [4]. This is due to the high cost of imported chemicals and the entry restriction of these chemicals to Indonesia.

The waste material is often a problem because it can damage and pollute the environment. The problem needs research and technology to optimize it so that the waste can be utilized into a more useful product. One of the waste that can be processed into utilizable raw materials is iron powder waste from the grinding process. In grinding process, the iron is cut using a grinding eye and produce the residual iron in the form of coarse powder. There are plenty of iron and steel industries that
produce tools and components from iron. They produce a lot of waste iron that has not been utilized. Iron waste taken from the rest of the grinding process can be seen in figure 1.

![Figure 1. Pieces of waste iron from the grinding process.](image)

Laurent et al reported that iron oxide commonly known in 3 forms, i.e. hematite ($\alpha$-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), and maghemite ($\gamma$-Fe$_2$O$_3$) [5]. There are many studies that have been developed to obtain iron oxide; powder metallurgy is one of the common technique used. The other methods that are mentioned by Teja et al. and Cheng et al. that often used are sol-gel, co-precipitation, microemulsion and thermal decomposition [6, 7]. Iron oxide can be applied in many area, such as on the development of sensors and actuators, material to produce inorganic pigments, main materials for making magnetic materials, adsorbent of wastewater treatment an so on [8]. Considering many uses of iron oxide, research to prepare the oxide as a main raw material to make magnetic materials is interesting.

This paper will introduce the manufacture of permanent magnet barium hexaferrite from iron waste of the grinding process by a powder metallurgy method. This research is a preliminary study to find out whether the iron waste from the grinding process can be used as a raw material for the manufacture of magnetic materials.

2. Experiment

The experiments were carried out in two stages: the preparation of iron oxide and the manufacture of barium hexaferrite magnets from iron oxide waste.

2.1 Preparation of iron oxide

The iron powder obtained from the rest of the grinding process must be prepared to increase the purity before being used. Characterization result of waste using X-Ray diffraction before purification process can be seen in figure 2. On the curve we can see the waste iron contains magnetite (Fe$_3$O$_4$) compound $= 81.8\%$, silicone (Si) $= 4.2\%$, Nickel (Ni) $= 12.9\%$, and Zinc (Zn) $= 11\%$.

This waste still contains many impurities that must be removed through several processes. To improve the purity of waste, we have done three purification processes: separation, roasting, and milling. The iron waste is separated from non-magnetic material by magnetic bars. Magnetic materials and metals stick on bars, while non-magnetic and non-metallic materials are left. Furthermore, the iron powders are washed with water to remove dust and other impurities. The iron powders are burned at 800 °C for 3 hours, then milled using a milling machine for 50 hours to produce a fine iron oxide powder (Fe$_2$O$_3$) that is ready for use as the main raw material for making barium hexaferrite permanent magnets.
The purity of iron oxide waste increased, as seen from the color change of the powder into a dark black color. The iron oxide powder of purification process result can be seen in figure 3. After being roasted and milled by grinding machine, the iron oxide waste contains hematite (Fe₂O₃) and maghemite (Fe₃O₄). There is no Si, Ni, and Zn anymore.

2.2 Manufacture of barium hexaferrite magnet

The raw main materials for making barium hexaferrite magnets are iron oxide and barium carbonate. Both materials are weighed on the weight percent Fe₂O₃: BaCO₃ = 85.00 wt%: 15.00 wt%. Next, the raw materials are mixed in a milling machine using steel balls in alcohol media for 6 hours. After that, the materials are calcined at varied temperatures of 1000, 1100, 1200, and 1250 °C for 3 hours of holding time. The variation of the calcination temperature was performed to determine the optimal temperature of initial formation of the barium hexaferrite compound. After the calcination process, the mixture is dried, weighed, and then some additives such as calcium oxide (CaO), silicon dioxide (SiO₂), and polyvinyl alcohol (PVA) of about 0.75 to 1.5 wt% of the weight of calcine powder are added. Mixing process of calcine powders and additives are performed in a milling machine for 16 hours. The mixture is then dried at 100 °C temperature until it dries and is then filtered with 400 mesh sieve shaker to make the powder homogeneous and has the same particles size so it is ready to be pressed. The samples are pressed at 2 ton/cm² by using hydraulic press in a round shape. The samples that have been pressed are sintered at temperature of 1250 °C for 1 hour. The process of calcination...
and sintering are done using a furnace Yamato 1700 °C. Magnetic properties are characterized using the Physik Magnetic Permagraph, and the formation of barium hexaferrite compounds using X-Ray Diffraction Maxima. The experimental details of preparation of iron oxide and manufacturing of barium hexaferrite can be seen in figure 4.

Figure 4. Flow chart of preparation of iron oxide and manufacturing of barium hexaferrite.

3. Results and discussion
The experimental utilization of iron waste from the grinding process to become the raw material for making permanent magnets has been completed. The characterization results shown by the test of barium hexaferrite compound formation using XRD, and magnetic properties test by using Permagraph. The characterization results using XRD shows that the calcination temperature influences the forming of barium hexaferrite compounds.

Curves 1-4 have similar pattern with different percentages of barium hexaferrite compound formation. On curve 1, formation percentage of barium hexaferrite (BaFe$_{12}$O$_{19}$) is 86.7% while hematite ($\alpha$-Fe$_2$O$_3$) is 13.3%. Curve 2 showed 98.7 formation of BaFe$_{12}$O$_{19}$ and 1.3% magnetite(Fe$_3$O$_4$). On curve 3, BaFe$_{12}$O$_{19}$ formation is 99.6%, Fe$_3$O$_4$ = 0.4%, and the percentage of BaFe$_{12}$O$_{19}$ and Fe$_3$O$_4$ on curve 4 is almost the same with curve 3. The percentage of barium hexaferrite formation is increasing with the increase of calcination temperatures. Magnetic properties has reached the maximum at 1200 °C temperature, therefore that at temperature of 1250 °C it remains unchanged. The patterns of formation of barium hexaferrite can be seen in figure 5.
Several other studies have also investigated by Sumangala et al. and Prengki et al. about the effect of calcination temperature on structures, microstructures, and magnetic properties of magnesium ferrite and nickel ferrite \[9, 10\]. Gharagozlou [11] observed the effect of calcination temperature on crystallinity and particle size of cobalt ferrite nanoparticle. It is known that crystallinity and particle size of ferrite increase at higher calcination temperature. The morphological changes to the cobalt ferrite magnet due to differences in calcination temperature have also been observed by Sezer [12]. The calcination process is performed by heating the solid material at a high temperature which aims to reduce impurities, removing volatile substances, and oxidizing an elements or compounds as reported by Rachel et al [13].

Hysteresis curve of barium ferrite at varying temperature were analyzed using Permagraph as shown in figure 6. It can be observed that the sample curve calcined at temperature of 1250 °C is larger than the other samples. This curve shows the magnitude of the maximum energy product of the sample. This magnetic properties are influenced by the level of sample crystallinity that are affected by the calcination temperature.

Figure 6. Hysteresis Curve.
The magnetic characteristic of samples such as induction of remanence (Br), coercivity (HcJ), maximum energy product (BHmax), and density are shown in table 1. The higher calcination temperature is, the Br value increases as well as the values of Hc, BHmax, and density.

**Table 1. Magnetic properties and density of the barium hexaferrite with variation of calcination temperatures.**

| Magnetic Properties and Density | 1000 °C | 1100 °C | 1200 °C | 1250 °C |
|--------------------------------|---------|---------|---------|---------|
| Br (kG)                        | 1.27    | 1.26    | 1.36    | 1.38    |
| HcJ (kOe)                      | 3.067   | 4.089   | 4.540   | 4.533   |
| BHmax (MGOe)                   | 0.35    | 0.34    | 0.39    | 1.086   |
| ρ (g/cm³)                      | 4.24    | 4.29    | 4.31    | 4.33    |

The magnetic characteristic values increase because at higher calcination temperature the formation of ferrite compound and crystallinity are better. Grain growth at higher calcination temperature reduces porosity and increases density. Porosity is one factor that can disrupt the magnetization process. The higher the density, the magnetic properties will be better.

The magnetic characteristics obtained from these experimental results approached the previous experiment of making barium hexaferrite magnets from iron oxide waste by Novrita et al [14], where the remanent induction value is about 1.5 kG. Standard Specifications for Permanent Magnet Materials compares with the characteristics of commercial barium hexaferrite magnets on the market that range between 2.4 kG - 4 kG [15]. The magnetic strength value of this magnet still needs to be improved again, so further experiments are needed to improve the generated magnetic characteristics.

4. Conclusion

In summary, a preliminary research of the utilization of iron waste from the grinding process has been carried out with powder metallurgy technology. The results show that the magnetic characteristics of barium hexaferrite are almost similar with the previous experiments of ferrite magnets from other iron oxide wastes. The calcination temperature affects the magnetic characteristic of barium hexaferrite, where the optimum condition is obtained at calcination temperature of 1250 °C. This experiment still requires further research because there are still many conditions of process that will affect the characteristics of the magnet such as iron waste purification process, composition, grain size, and sintering temperature.

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