

CHARACTERIZATIONS OF CERAMIC MAGNETS FROM IRON SAND

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ABSTRACT

Ceramic magnets with the chemical composition of barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) were obtained through the synthesis of magnetite powder from iron sand taken from the Southern Coast of Yogyakarta in Indonesia. The iron sand was dissolved and then synthesized to produce magnetite powder. Subsequently, the magnetite powder was oxidized at temperatures of 700, 900, and 1100°C for five hours to produce hematite. The un-oxidized magnetite and the magnetite which was oxidized at the different temperatures were each mixed with barium carbonate, respectively. The mixtures were then calcined at 1100°C for two hours. The calcined products were compacted and then sintered at 1100°C for one hour to produce sintered ceramic magnets. X-ray diffraction (XRD), a vibrating sample magnetometer (VSM), a scanning electron microscope (SEM) with an energy dispersive X-ray spectroscopy (EDS), and thermogravimetry analysis (TGA) were used to characterize the ceramic magnets. The results showed the magnetite that was directly calcined, compacted, and sintered had a $\text{BaFe}_{12}\text{O}_{19}$ phase and also had the presence of a Fe_2O_3 phase with a $\text{BH}(\text{max})$ of 0.26 MGOe, H_c of 1.27 kOe, and M_s of 31.421 emu/g. The sintered ceramic magnet which was initially oxidized at a temperature of 900°C had a $\text{BaFe}_{12}\text{O}_{19}$ phase with a $\text{BH}(\text{max})$ of 0.78 MGOe, H_c of 1.95 kOe, and M_s of 46.970 emu/g. These results indicate satisfactory results as a permanent magnet. Thus, the iron sand from the Southern Coast of Yogyakarta in Indonesia has potential for the production of ceramic permanent magnets.

Keywords: Barium hexaferrite; Ceramic magnets; Hematite; Iron sand; Magnetite

1. INTRODUCTION

A ferrite permanent magnet or ceramic magnet is a major supporting component of electronic devices, and is widely used in applications such as speakers, electric motors, generators, etc. The needed magnetic materials in Indonesian manufacturing are currently imported, mostly from Japan and China (Sardjono et al., 2012). However, iron sand, a raw source of magnetic materials, is available in abundance on the Southern Coast of Yogyakarta in Indonesia. The iron sand can be synthesized to obtain magnetic and hematite (Mastuki et al., 2012) and then calcined to form barium hexaferrite, which is a main component of ceramic magnetic materials

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(Nowosielski et al., 2007). Wide applications of these materials are mainly due to their low cost, high saturation magnetization, high Curie temperature and high coercivity, associated with excellent chemical stability, corrosion resistance (Janasi et al., 2002; Rashad et al., 2011), and interesting magnetic properties (Choi et al., 2012). The ceramic magnet is still extensively used although it has a lower magnetic strength than that of rare earth magnets (Nowosielski et al., 2007). The purpose of this research was to determine the development potential of the iron sand from the Southern Coast of Yogyakarta as a materials substitution for the production of ceramic magnets obtained via the synthesis of magnetite from iron sand.

2. EXPERIMENTAL PROCESS

The base material in this research was iron sand from the Southern Coast of Yogyakarta Indonesia. The iron sand was crushed in a milling machine to obtain fine particles (size: <74 μm). The fine particles were dissolved using HCl (from Sigma-Aldrich) to produce ferrous and ferric salts in an aqueous solution. The NH_4OH (ammonium hydroxide) was added to the solution until it reached a pH of 8, at the temperature of 80°C . A black powder precipitate formed immediately during the reaction. The precipitate was washed with distilled water to remove any remaining solution. Subsequently, the precipitate was then oxidized at various temperatures of 700, 900, and 1100°C for five hours at standard atmospheric pressure. There were four groups of samples: the black powder precipitate that was obtained from the reaction (designated as S1), and the samples of S1 that were oxidized at the various temperatures of 700, 900 and 1100°C , designated as S2, S3, and S4, respectively. Each sample was mixed with barium carbonate (BaCO_3) in stoichiometric ratio until homogeneous. The homogeneous mixtures were calcined at 1100°C for two hours in a furnace at standard atmospheric pressure. The calcined samples were mixed with binder of polyvinyl acetate (PVA of 3% by weight) and were then uniaxially compacted with a pressure of 30 MPa to produce cylindrical green compacts. The samples were then sintered at 1100°C for one hour at standard atmospheric pressure. The sintered samples were magnetized into a ceramic permanent magnet.

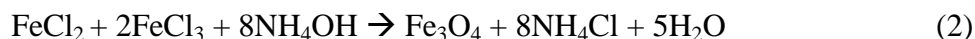
Characterization of the phases were investigated by a Shimadzu XRD-6000 diffractometer using nickel-filtered Cu-K α radiation ($\lambda=1.54056 \text{ \AA}$). The magnetic properties such as remanence magnetization (Mr), saturation magnetization (Ms), and coercivity (Hc) were characterized using a VSM OXFORD 1.2H machine with an applied magnetic field between -10 kOe and 10 kOe . The JEOL JSM-6510LA SEM with EDS was used to analyse the chemical composition of the surface elements. Thermogravimetry (TGA) was performed on a sample of the green materials using a Mettler Toledo TGA over the temperature range of standard room temperature to 1100°C .

3. RESULTS AND DISCUSSION

The iron sand was milled to a fine powder in order to make the chemical reaction process more effective. The fine powder was dissolved using HCl (hydrochloride) at a temperature of 80°C . The chemical reaction is showed in Equation 1.



The aqueous solution of iron (II), chloride iron (III) chloride and dissoluble waste material were obtained. The solution was separated from the waste material through filtering. The aqueous solution of iron (II) chloride and iron (III) chloride was then reacted with NH_4OH (ammonium hydroxide). The formation of Fe_3O_4 from iron (II) chloride and iron (III) chloride were reacted with NH_4OH , is presented by the co-precipitation reaction (Equation 2).



It is generally known that stoichiometric amounts of ferrous and ferric ions reacted to produce Fe_3O_4 (magnetite). The magnetite was then oxidized at various temperatures at standard atmospheric pressure. The chemical reaction is presented in Equation 3.



The XRD patterns of the black powder (S1) and the oxidized samples (S2, S3, and S4) are shown in Figure 1. The peaks of 2-theta of the black powder sample (S1) clearly shows the typical pattern for Fe_3O_4 according to the Joint Committee on Powder Diffraction Standards/JCPDS number 19-629. All of the oxidized samples show the typical pattern of the $\alpha\text{-Fe}_2\text{O}_3$ phase (JCPDS number 73-3825 for $\alpha\text{-Fe}_2\text{O}_3$ (alpha hematite phase) and the $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) phase (JCPDS number 089-5894). The magnetite was not only successfully synthesized from the iron sand, but it was also successfully oxidized at these temperatures to form alpha hematite. As Chirita et al. (2009) mentioned, the phases Fe_2O_3 are polymorphs that Fe_2O_3 exist in the form of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$.

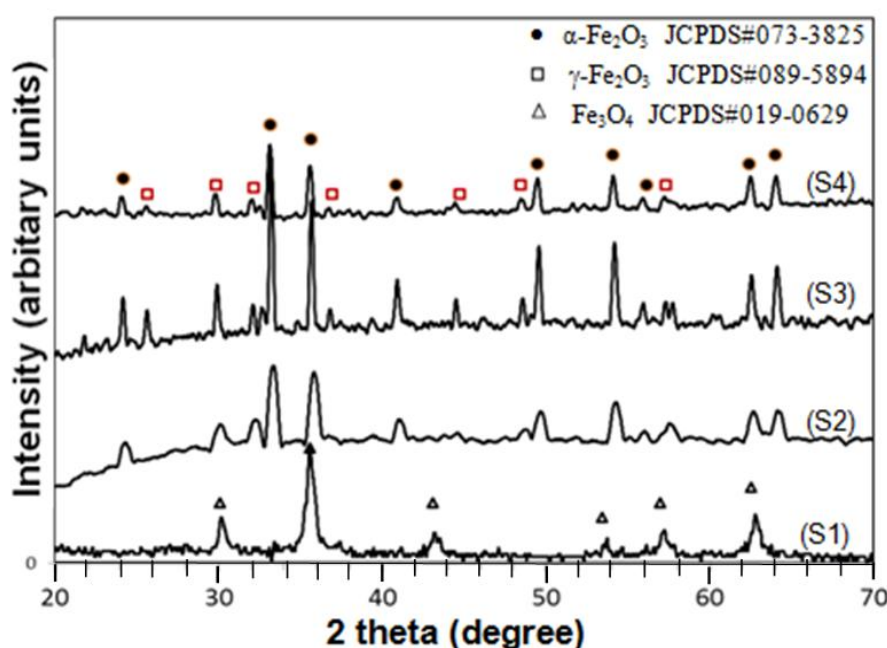


Figure 1 The XRD patterns of the magnetite S1 sample and the oxidized magnetite S2, S3, and S4 samples

The XRD patterns of the sintered samples are shown in Figure 2. The XRD pattern of the sintered S1 sample showed two phases of barium hexaferrite and hematite. The sintered S1 sample was obtained from a calcinated mixture of magnetite (S1) and barium carbonate. The resulting hematite was created by the oxidization of the magnetite that did not react with the barium carbonate. The magnetite could not be directly reacted with barium carbonate to form barium hexaferrite during the calcination process. The magnetite was first oxidized to hematite at standard atmospheric pressure at a high temperature; the chemical reaction is shown in Equation 3. The barium carbonate decomposed to barium oxide and carbon dioxide, also at high temperature (Ştefan, 2011). A large fraction of the hematite reacted with barium oxide to form barium hexaferrite, with a small fraction of the hematite phase left as an excess. The XRD pattern of the sintered S1 sample was indicated by weak peaks of 2-theta of the hematite among peaks of 2-theta

of the barium hexaferrite. The XRD pattern of the sintered S1 sample agrees with the research of Nowosielski et al., (2007). Nowosielski et al. (2007) reported the X-ray investigations of Fe_2O_3 and BaCO_3 mixture was annealed at temperature 950°C enabled the identification of hard magnetic $\text{BaFe}_{12}\text{O}_{19}$ phase. They also found that the Fe_2O_3 phase exists in the $\text{BaFe}_{12}\text{O}_{19}$ phase. The Fe_2O_3 phase was a rest of Fe_2O_3 that was not react with BaCO_3 in which forms a compound of $\text{BaFe}_{12}\text{O}_{19}$. The XRD patterns of the sintered S2, S3, and S4 samples show a clear peak of barium hexaferrite. However, the XRD pattern of the sintered S2 sample of an initial oxidation at 700°C shows low intensity for the peak of barium hexaferrite. The barium hexaferrite shows a typical pattern as according to JCPDS number 27-1029.

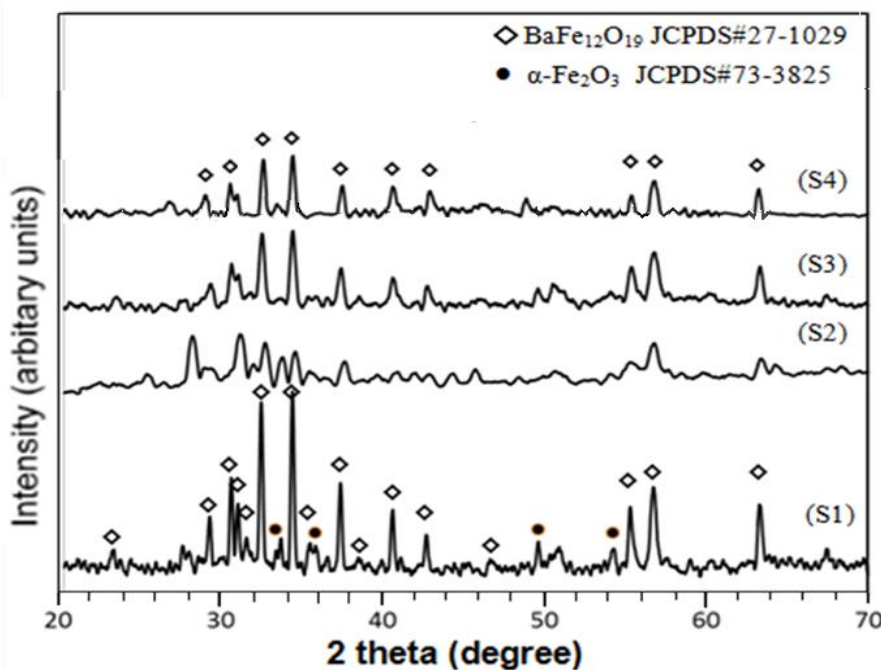


Figure 2 The XRD patterns of the sintered sample (S1) and the sintered samples with initial temperatures oxidation of 700°C (S2), 900°C (S3), and 1100°C (S4)

Rashad et al., (2011) reported the XRD patterns of barium hexaferrite powders that were annealed at different temperatures from 800 to 1200°C for two hours, indicating the synthesis of barium hexaferrite as a major phase. The barium hexaferrite was formed by a reaction of BaO and Fe_2O_3 at a high temperature. Barium hexaferrite, as one of the permanent magnet materials of the ferrite magnet type, has ferromagnetism behaviour. The reaction that forms barium hexaferrite is showed in Equation 4 (Ştefan et al., 2011).

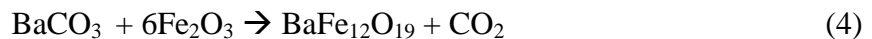


Figure 3 shows the hysteresis curve of the magnetite S1 sample and the oxidized samples. The magnetite sample (S1) has a higher M_s than that of the oxidized samples. The narrow hysteresis curve of the S1 sample indicates superparamagnetic materials. The superparamagnetic system is the state where clusters or nanoparticles possess magnetic anisotropy (Faraji et al., 2010). The oxidized samples show a low saturation magnetization, with the saturation magnetization decreasing as the temperature of oxidation increases. A low saturation magnetization indicates an antiferromagnetic property. The antiferromagnetic structure corresponds to a disappearing total magnetization when no external field applied. As mentioned by Chirita (2009), hematite exhibits a strong antiferromagnetic property.

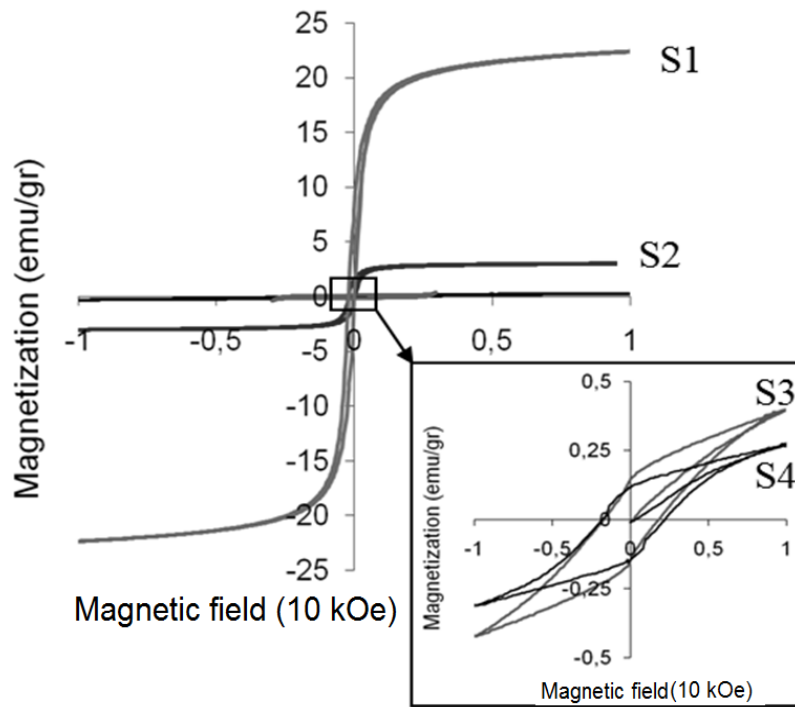


Figure 3 Hysteresis curves of magnetite S1 sample and oxidized magnetite S2 sample, inset picture shows hysteresis curves of S3 and S4 samples

Figure 4 shows the hysteresis curves of the calcined-sintered samples. The sintered S3 sample exhibits the highest saturation magnetization. A wide hysteresis curve is desirable for permanent magnets. The typical sample with high saturation magnetization and high coercivity indicates ferromagnetic properties (Janasi, 2002).

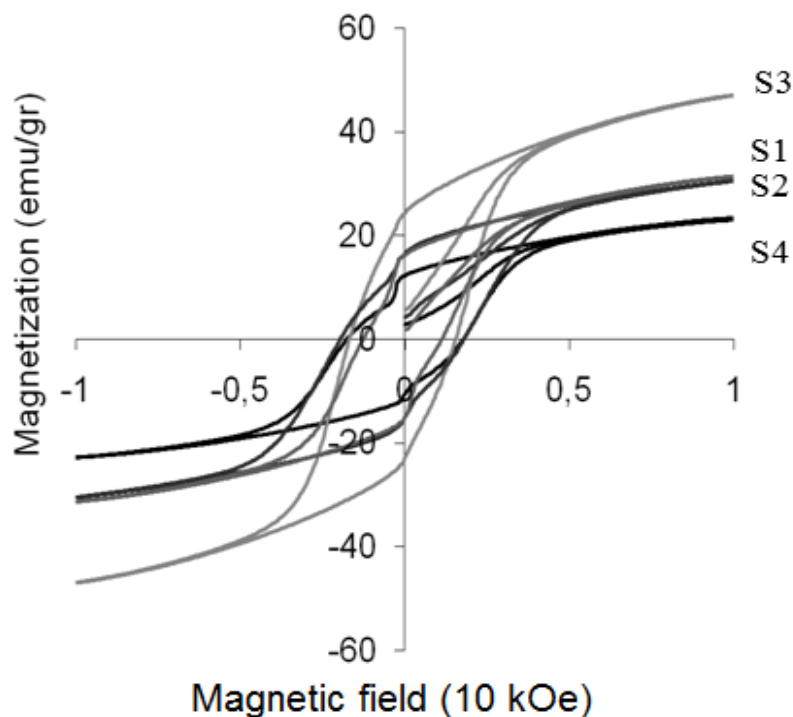


Figure 4 Hysteresis curves of the calcined-sintered of S1, S2, S3, and S4 samples

The barium hexaferrite phase synthesized from iron sand has a ferromagnetic property as a permanent magnetic material. The sintered S3 sample has the highest Ms of 46.97 emu/g, Hc of 1.95 kOe, and BH(max) of 0.78 MGOe. The sample has good magnetic properties as compared to the China standard Y10 and Y10T of hard ferrite (ceramic) magnets with Hc of 1.57-2.01 kOe and BH(max) = 0.8-1.2 MGOe. The information of all the hysteresis curves in Figures 3 and 4 is summarized in Table 1.

Table 1 Summary of magnetic properties of the oxidized samples and calcined-sintered samples

Samples	Magnetic properties		
	Energy product BH(max) (MGOe)	Saturation Magnetization Ms (emu/g)	Coercivity Hc (kOe)
S1	0.03	22.39	0.20
S2	0.01	3.03	0.20
S3	0.01	0.39	1.72
S4	0.01	0.28	1.86
Sintered S1	0.26	31.42	1.27
Sintered S2	0.46	30.62	1.68
Sintered S3	0.78	46.97	1.95
Sintered S4	0.25	22.99	1.75

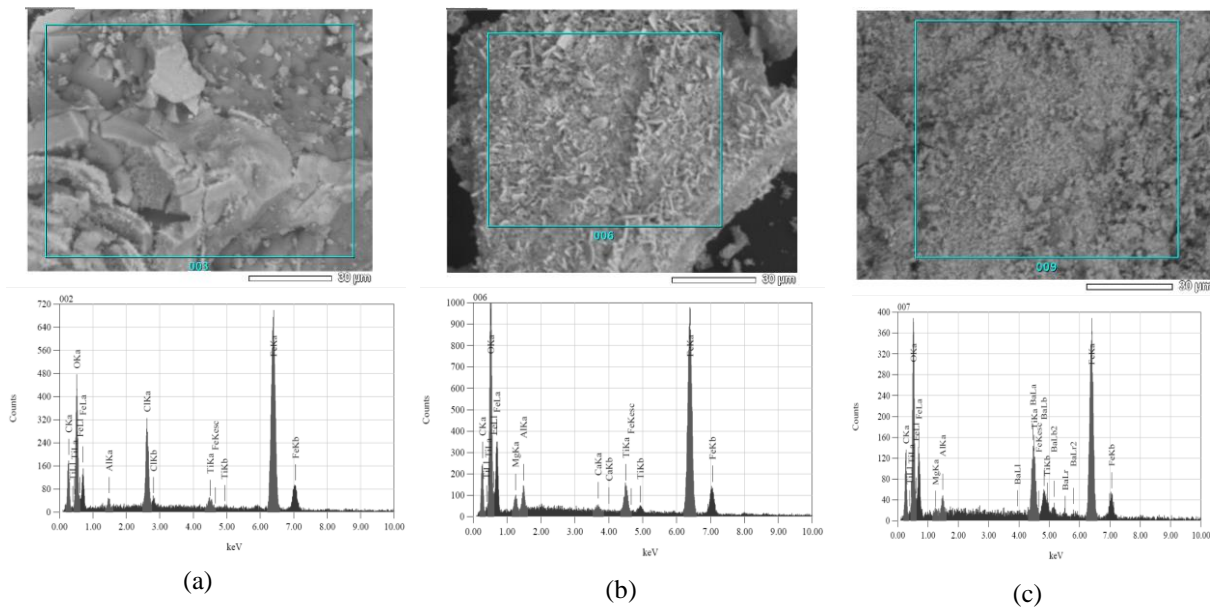


Figure 5 SEM images and EDS quantitative elements analysis of samples: (a) magnetite phase (S1 sample); (b) hematite phase (S3 sample); (c) barium hexaferrite phase (sintered S3 sample)

The SEM with EDS was used to analyse the chemical composition of elements at the surface of S1, S3 and sintered S3 samples as shown in Figure 5. The EDS analysis of the S1 sample showed a large quantity of Fe and O, indicating a magnetite phase. The magnetite was oxidized at temperatures of 900°C to form hematite (S3 sample), which is seen by the increase of the oxygen in atomic percentage from 36.79% to 44.61%. The EDS data of the calcined-sintered S3 samples show elements of Ba, Fe, and O, which were obtained by calcinating with a stoichiometry ratio of BaCO₃ and Fe₂O₃. Formation of barium hexaferrite occurred through the chemical reaction as described in Equation 4. The EDS also showed other elements in small quantities, *i.e.*, Al, Ti, Mg, and Ca. These elements are the materials that bind to the iron oxide in the iron sand.

Figure 6 shows the TGA curve of the barium hexaferrite precursor which is heated from temperature range of standard room temperature to 1100°C. The TGA curve shows the weight loss of the sample at temperatures between 550°C and 1000°C. This weight loss may be due the decomposition of barium carbonate to barium oxide and carbon dioxide gas. The completion of formation of the barium hexaferrite is shown to occur around 1100°C with a total weight loss of 4%. This weight loss corresponds in the Equation 4 where the loss of carbon dioxide gas is also 4%. The formation of the barium hexaferrite was identified using X-ray diffraction on the calcined-sintered S3 sample and the X-ray diffraction pattern of the sample can be seen in Figure 2.

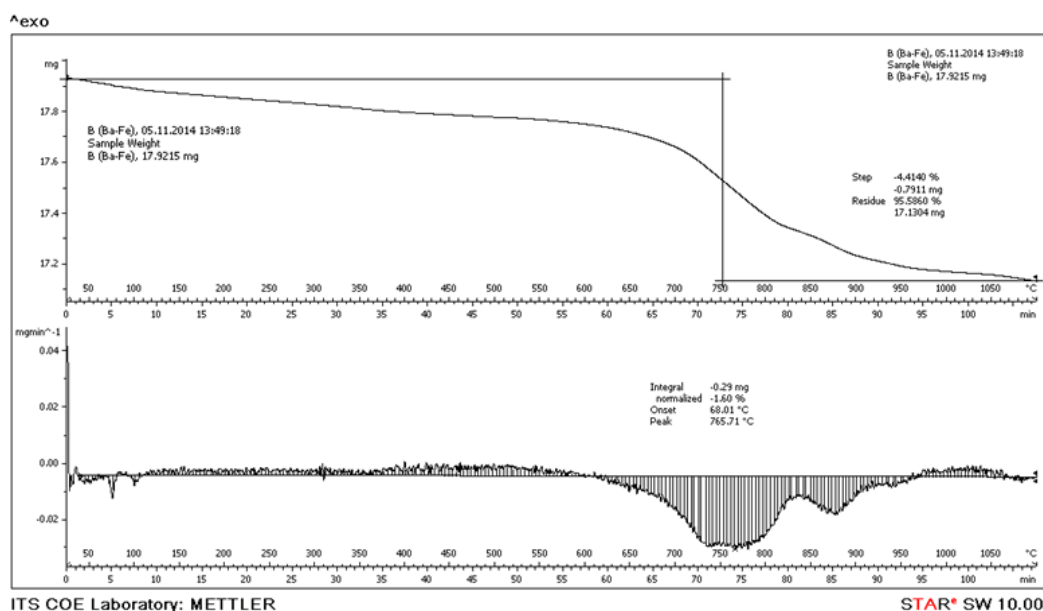


Figure 6 Thermogravimetry (TGA) of the barium hexaferrite precursor

4. CONCLUSION

The magnetite and barium hexaferrite materials were successfully synthesized from iron sand. The XRD analysis of the magnetite that was oxidized at various temperatures indicated the hematite phase. The magnetite that was oxidized at 900 °C, then calcined, compacted, and sintered, gave clear results of a good ceramic magnet material. Thus, the iron sand from the Southern Coast of Yogyakarta in Indonesia has potential as a source for ceramic magnet materials.

5. ACKNOWLEDGEMENT

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