

EFFECT OF Fe₃O₄ ADDITION ON STRONTIUM HARD FERRITES

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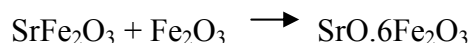
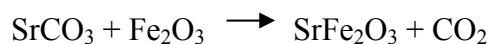
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ABSTRACT

Strontium hard ferrite (SrFe₁₂O₁₉), commonly known as the ceramic permanent magnet is conventionally prepared by using Fe₂O₃ and SrCO₃ as raw materials. In this work, we were in an attempt to replace hematite (Fe₂O₃) by magnetite (Fe₃O₄) in the synthesis of strontium hard ferrites. The ratio of the magnetite (Fe₃O₄) doped was in the range of 0.5 to 3.0. X-ray diffraction (XRD) was employed to confirm the formation of the strontium hard ferrite compound. The magnetic properties such as the maximum energy product, the remanence and the coercive force were recorded using a hysteresis tracer (B-H tracer). The results shows that it is possible to replace hematite to certain extend by magnetite without destroying the magnetic properties of the samples. The density of the samples are also reported in this paper.

INTRODUCTION

Hard ferrites are widely used in the automobile industry, electric motor, loud-speaker, toys and etc. It was reported that the demand of hard ferrites is projected to be more than 1 million metric ton per year in 2010 compared to 0.6 million metric ton in year 2000[1]. Hard magnets with high remanence after magnetization are a composition of iron and barium or strontium oxides. High magnetic permeability and magnetic flux are conducted to produce in a magnetically saturated state. This enables these so-called ceramic magnets to store stronger magnetic fields than the iron itself. The maximum magnetic field B is about 0.35 x 10⁴ Gauss and the magnetic field strength H is about 400 to 2000 oersteds (30 to 160 kiloampere turns per meter) [2-4]. The influence of the processing parameters on the magnetic properties has been studied by various researches [5-7]. Most of the researches concur that by at varying the temperature, particle size and other parameters does affecting the magnetic properties of the magnets. The permanent magnet that fabricated will contain SrFe₁₂O₁₉. These compositions are based on the reaction as follow:



Ferrite may be referred as iron or iron alloys with a body centered cubic crystal structure. Hence, ferrites permanent magnets are made in isotropic and anisotropic forms and a wide range of properties are available. As mentioned earlier, the process varies which include the size of particles, the nature of impurities, the milling sequences, the duration and the temperatures used in the reaction and sintering steps [8, 9]. The simplest process of producing magnets is isotropic magnet, in which the milled powder is dried and pressed in a mould without applying any field [10- 12]. Anisotropic magnets on the other hand can be produce using dried powder. Hence, the most promising results comes from wet slurry sample where water acts as a lubricant that promotes alignment of the powder as the magnetic field is applied in the die cavity. Shrinkage during the sintering process is common, in average of 15% due to the ceramic magnets becomes hard, where by grinding is the only practical method of machining[13-15].

Iron, cobalt and nickel are a few elements considered to be ferromagnetic at room temperature. According to quantum mechanics and the Pauli Exclusion Principle, the electrical energy within these atoms is found to be lower if the magnetic moments of the valence electrons are aligned. This makes them ferromagnetic. Each and every ferromagnet has an individual temperature called Curie temperature or Curie point which it losses its ferromagnetic properties. This is due to the tendency of thermal to disorder lowering the energy based on ferromagnetic order. A perfectly aligned ferromagnet is said to have a long-range order due to its atoms have their magnetic moments pointing at the same direction [16]. Real ferromagnets are not perfectly aligned but rather contain perfectly aligned regions, known as magnetic domains. They have their own magnetization directions. In previous paper, it has stated that one of the drawbacks of the ferrite core as compared to metal cores is its brittleness [17-19]. Being ceramic in nature, care must be taken into consideration upon handling of the cores. Powders cores are also brittle hence similar precautions are required.

It is the aim of this study to prepare ceramic magnets with magnetite in order to reinstate its hematite usage.

EXPERIMENTAL PROCEDURE

In the hard ferrite industry, pure hematite and pure strontium carbonate as starting materials are mixed in the ratio of 6:1. However, we intend to replace the hematite by magnetite in small proportion. In this work, several materials namely the pure magnetite (98%), pure hematite (99%) and pure strontium carbonate (99%) are taken into consideration to accomplish the objectives. Strontium carbonate and hematite used in this project are with CAS NO 1633-05-2 and CAS NO 1309-337-1 respectively. The samples were prepared according to the strontium carbonate, hematite and magnetite weight ratio of 1:6-x:x where x increases from 0.5 to 3.0. The samples were first wet mixed for 12h at 100 rpm. The next step was the pre-sintering process. The samples were being heated to 1150°C for 10h. The samples were then sent for high energy

milling at the speed of 350 rpm for 18h. Once the milling was completed, the samples were pressed into pellet. After the pressing process, the samples were sintered at 1200°C for 10h.

For characterization purposes, the sample was sent to the X-ray Diffraction (XRD), B-H Tracer (Hysteresis Curve) and the densitometer. X-ray diffractometer was employed for phase analysis. The analysis was performed using a Cu-K α (1.5418Å) source (40 kV, 40mA) from Siemens D-501, with a graphite secondary monochromator and scintillation counter detector. Analysis using the XRD equipment is to compare with the pure substances of SrFe₁₂O₁₉. B-H tracer was then used to analysis the magnetic properties of the magnets. The magnetic properties of the samples were obtained from hysteresis-graph and their magnetic properties were compared to the industry grade hard ferrites. Density of the samples is determined by utilizing Archimedes' Principle. The equation or sample density ρ_{sample} calculation is given as:

$$\rho_{\text{sample}} = \frac{W_a}{W_w} \rho$$

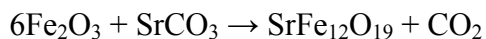
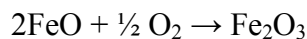
Where W_a : Weight of sample in air (g)
 W_w : Weight of water displaced by the sample (g)
 ρ : Density of water (1 g/cm³)

RESULTS AND DISCUSSIONS

Samples characterization in this work includes the XRD analysis, B-H curve analysis and density measurements.

Figure 1 shows the X-ray diffraction patterns of the magnetite doped permanent magnets compared to standard peaks of strontium hexaferrite (SrFe₁₂O₁₉). Base on the figure above, all the peak positions are basically consistent with the standard data for strontium hexaferrite phase and thus confirming the SrFe₁₂O₁₉ phase do formed in the samples. This thus shows that even magnetite was added in the sample, it does not prohibit the forming of strontium hexaferrite compound. Shortly, hematite can be replaced by magnetite to form the hard ferrites phase.

We anticipate that the formation of SrFe₁₂O₁₉ phase above involves of 3 processes, namely the decomposition of magnetite (Fe₃O₄), the oxidation of wuistite (FeO) and the forming of SrFe₁₂O₁₉. This can be summarized by the chemical reactions below:



The magnetite was first decomposed into FeO and Fe₂O₃ at temperatures between 500°C to 600°C according to Fillingham Diagram. FeO which was not stable at low temperature was then oxidized into Fe₂O₃ that is more stable. Finally the Fe₂O₃ reacted with SrCO₃ to form SrFe₁₂O₁₉ crystal. We do not expect the SrFe₁₂O₁₉ to form completely. Since the sensitivity of XRD is only 3%, we believe there are impurities which are less than 3% in the samples.

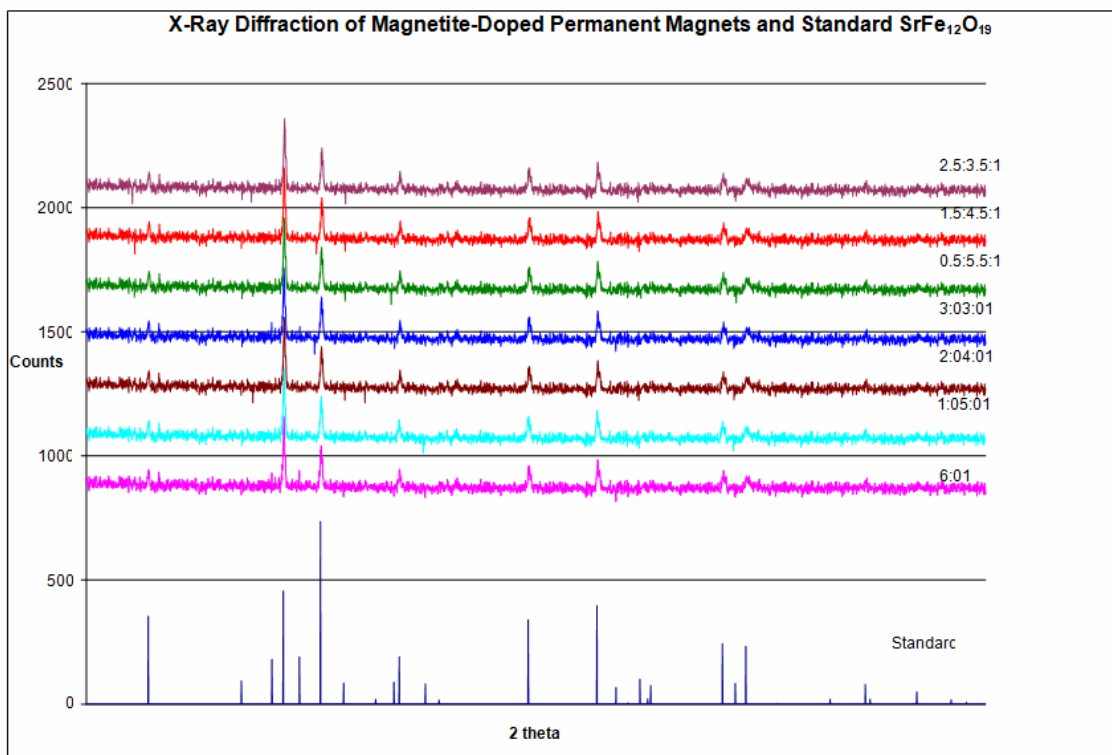


Figure 1: X-Ray Diffraction pattern of Magnetite Doped permanent magnet

The magnetic property of the samples was measured using a B-H tracer and the graphs are shown below. Basically, the magnetic property is sensitive to the formulation and the preparation processes and it is generally referred to the intrinsic and extrinsic properties. Since the milling period, the pre-sintering and the sintering temperatures were kept unchanged for all the samples, we basically assume that the change in the magnetic properties of the samples is solely due to the formulation except for certain cases.

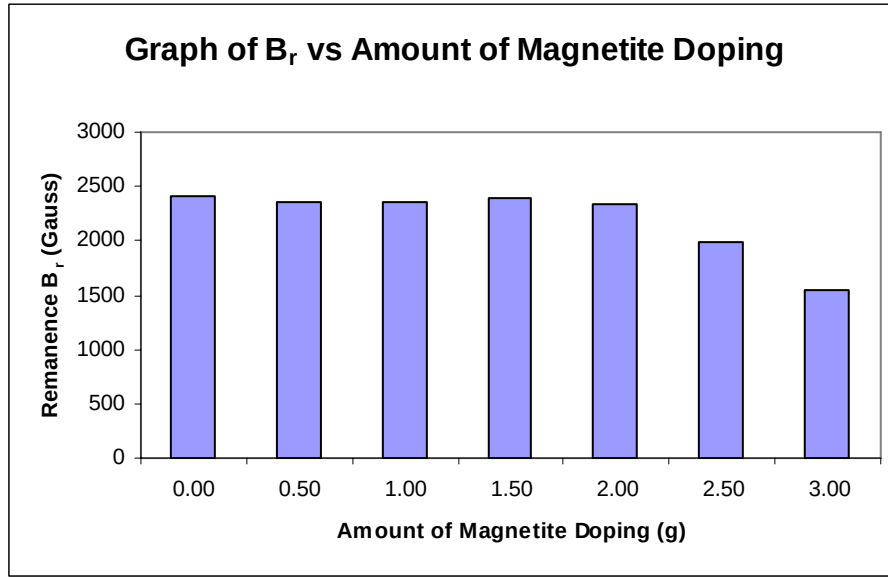


Figure 2: Graph of Remanence (B_r) versus Amount of Magnetite Doped

Figure 2 shows that the remanence of the samples remain above 2200 G for the first few samples but it starts to drop as the magnetite doped was too high. The remanence gained of the samples are still in the acceptable range that is within 1800 to 2600 Gauss (Industrial grade standard). Samples in the range of 0.00 to 2.00 magnetite doped are in are higher compared to 2.5 and 3.0 magnetite doped. However, remanence is an extrinsic property and can be improved by increasing the pre-sintering and sintering temperatures.

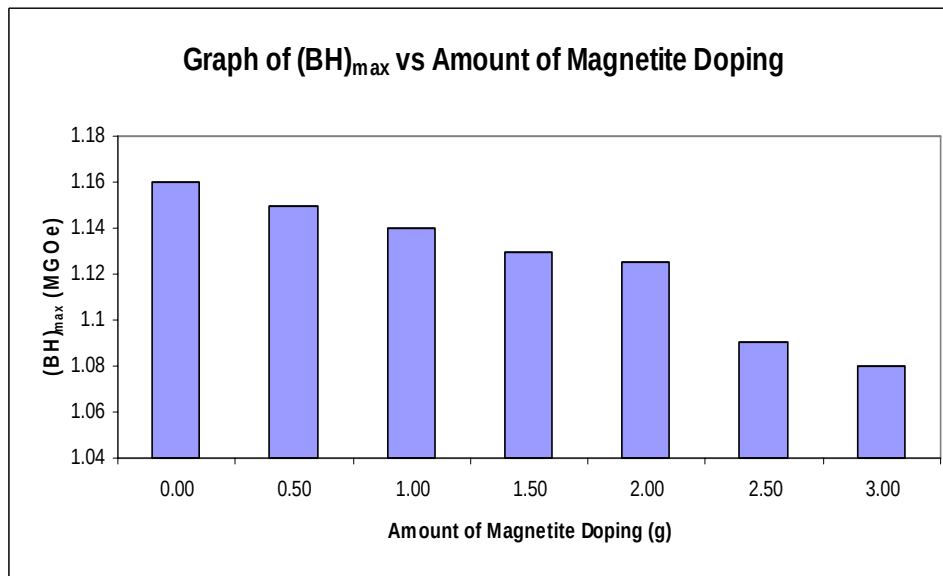


Figure 3: Graph on Maximum Energy Product $(BH)_{max}$ Versus Amount of Magnetite Doped

Correlates with the decrease of remanence, the maximum energy product, $(BH)_{\max}$ were also found to decrease with increasing mole ratio as refer in Figure 3. $(BH)_{\max}$ is an area of the second quadrant of the hysteresis loop where the value of remanence B_r and intrinsic coercivity will have the influence in it[21]. The $(BH)_{\max}$ value decrease from 1.16 to 1.08 kJ/m³ respectively with increasing amount of magnetite doped. Comparisons with the industry grade $\text{SrFe}_{12}\text{O}_{19}$, the value are still in accepted range of 0.9 to 1.19 MGOe. From the graph above, there is a slanting after 2.50 magnetite doped where added in the sample. The results continue to drop after further amount of magnetite are doped in the sample. Hence, this will show that the decreasing of the maximum energy product is due to the increasing in the ratio of the magnetite in the sample.

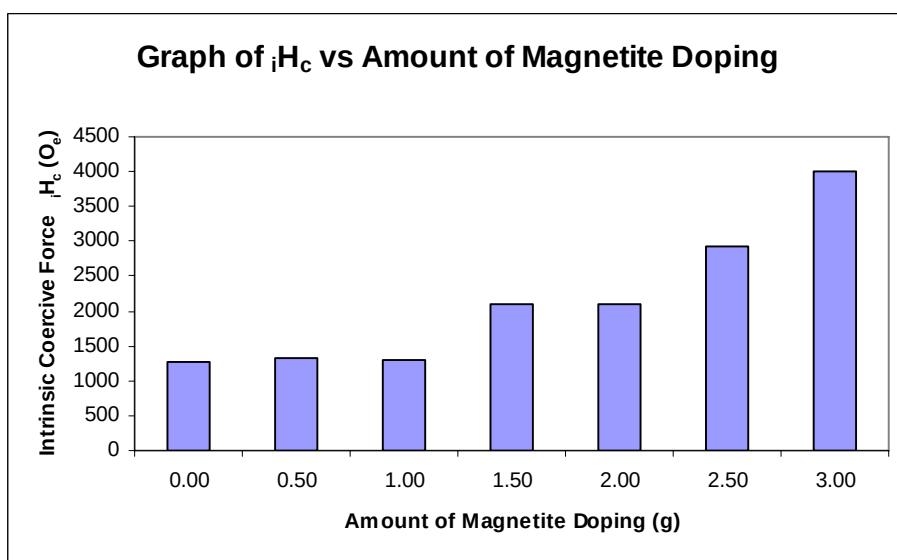


Figure 4: Graph of Intrinsic Coercivity (iH_c) Versus Amount of Magnetite Doped

In general, the intrinsic coercivity (iH_c) in Figure 4 was observed to increase with increasing amount of magnetite doped. Since the coercivity depends on the microstructure and chemical composition of the magnet, the increase in iH_c was due to the saturated interstitial site by Fe^{3+} . The increasing in the coersivity correlates with the decrease in maximum energy product obtained from earlier results. Intrinsic coercivity is the parameter to show the force required in order to rotate the moment inside the magnets. Its show how strong the magnets can retain the magnets properties from the external field. Base on the graph, the increasing of the value may due to pores or impurities found in the sample. This might be caused by the fallout of the preparation process where the mixing process is not performing at its best. Besides, internal crack that resulted by poor pelletizing technique may also resulting the increase in the values.

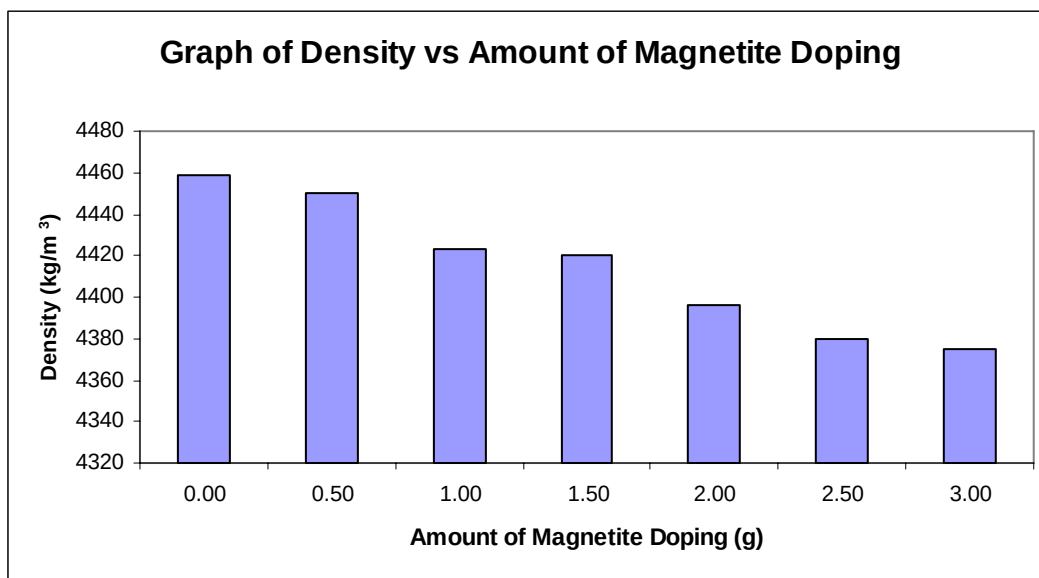


Figure 5: Graph on Sintered Density versus amount of Magnetite Doping

The density of the magnets decrease with increasing magnetite ratio added respectively as show in Figure 5. By increasing the iron oxide content, the decrease of sintered density is due to saturated Fe^{3+} at different crystallographic positions [22, 23]. Based on the results as stated earlier, the density is decreasing due to the increase of magnetite ratio. Hence, the dropped in the density also correlates to the decrease in remanence value together with the increase in intrinsic coercivity. Besides the amount of magnetite added in the sample, the pores that generate inside the sample upshot the value as above. The pores will reduce the density of the samples.

CONCLUSIONS

Based on the findings, magnetite doped in our samples was successfully to a certain extent in maintaining the quality of the strontium hexaferrite fabricated. It is clear from the results that magnetite doped magnets can be implemented in certain ratio to ensure the magnetic properties are the same as the industrial grade strontium hexaferrite magnets. However, certain aspects in sample preparation and processes needs to be improved in order to achieved a better quality of magnets and to reduce the composition of impurities in the samples.

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