

Magnetic Characterization of Manganese doped-Barium Hexaferrite in Fe Sites of $\text{Ba}(\text{Fe}_{1-x}\text{Mn}_x)_{12}\text{O}_{19}$

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Abstract—Barium hexaferrite is a magnetic material that has been widely used in various applications as it is relatively more stable than other magnetic materials. Several previous efforts attempted to increase the magnetic properties of barium hexaferrite. In this report, barium hexaferrite was successfully substituted by Mn for $\text{Ba}(\text{Fe}_{1-x}\text{Mn}_x)_{12}\text{O}_{19}$ via solid state reaction, where x was 0.1, 0.2, 0.3, 0.4, and 0.5. BaCO_3 , MnO_2 , and Fe_2O_3 precursors were stoichiometrically mixed on the basis of mass composition, and the mixture was milled for 24 h using a wet ball milling technique. The milled precursor was dried for 24 h in a 100°C oven and calcined at 1200°C for 2 h. The samples were characterized by XRD for their phase identification where the new phase barium hexaferrite, manganite oxide, and manganese ferrite was formed and no trace of the origin precursor phases were observed. For characterization of the magnetic properties, the samples were crushed and filtered prior to pressing up to 5 MPa under a magnetic field condition. The pressed samples were varied under different sintering temperatures of 1050, 1100, and 1150°C before further characterization by a pherograph, a magnetization characteristic instrument. Based on the investigation, the remanence decreased to 0.025 T when the Mn concentration was increased to $x = 0.5$. The Mn atoms replaced Fe, resulting in an increase in the magnetic moment.

Keywords— Barium hexaferrite substituted Mn, Solid State reaction, XRD Characterization, Magnetic Characterization

I. INTRODUCTION

Barium hexaferrite is a magnetic material that has been widely used to many applications. Barium hexaferrite has high coercivity and remanence [1], which means it is stable to an external magnetic field. Additionally, it is heat resistant due to a high curie temperature of 700°C. Finally, barium hexaferrite can be used in a corrosive environment due to its high corrosive resistance owing to the stability of its molecular structure.

The ferrite magnet structure is $\text{MO}_6\text{Fe}_2\text{O}_3$, where M is metal atoms that can be bonded with ferrite such as Ba, Sr or Pb. The crystal structure of these magnets is hexagonal [2-4]. In addition, there is type of ferrite with a cubic crystal structure, $\text{MO}_2\text{Fe}_2\text{O}_2$, where M is a divalent metal such as Mn, Ni, Mg, Co or Fe [5].

Various efforts to increase the magnetic performance of barium hexaferrite has been performed [1], including

reducing the grain size to increase the magnetic properties [6] and adding Al_2O_3 to increase the coercivity of barium hexaferrite.

This research aims to increase the magnetic properties of barium hexaferrite by doping with Mn, which is expected to replace Fe given their similar atomic radius [7]. Additionally, Fe and Mn are both transition metals, with Fe having 4 electrons in the d subshell and Mn having 5. The magnetic moment of Mn is also greater than Fe.

Barium hexaferrite doped with Fe has been previously demonstrated. Barium hexaferrite was doped with Zn and Ti in 1998 [8, 9] and with cobalt (Co) in 2000 [10]. For absorber applications, Fe in barium hexaferrite has been substituted with magnesium and titanium [8].

In 2008, barium hexaferrite was doped with a small concentration of Mn [11], as $\text{BaFe}_{12-x}\text{Mn}_x\text{O}_{19}$, where x were 0.5, 1.0, 1.5, and 2.0. The results showed that the

coercivity was greater when the Mn concentration was larger. The lattice parameter was constant while the c parameter decreased. The change meant decreasing the lattice volume.

This research investigated the effect of the Mn substitution on the magnetic properties of barium hexaferrite, $\text{Ba}(\text{Fe}_{1-x}\text{Mn}_x)_{12}\text{O}_{19}$, with x values of 0.1, 0.2, 0.3, 0.4, and 0.5. The effect of the Mn concentration on the magnetic properties was investigated and the samples were defined by phase using XRD and correlated to the data.

II. EXPERIMENTAL METHOD

A. Sample Preparation

The sample was prepared by a solid state reaction or powder metallurgy. The raw materials were BaCO_3 , MnO_2 , and Fe_2O_3 , and were in powder form. The mass for each x value was determined by stoichiometry.

The mixed precursors were milled using a wet ball mill method. The ball mill and precursor ratio was 1:2. 100 ml of water was added and the solution was milled for 24 h. The solution was dried for 24 h in a 1000°C chamber.

The milled precursor was calcined at 30°C/min to 1200°C to form the barium hexaferrite phase. The sample was crushed, sieved with a 40 mesh, and pressed at 5 MPa to produce a ring.

The ring was sintered to remove carbon and harden the sample. The temperature stopping were 100°C, 300°C, and 600°C, each for 30 minutes. The last temperature stop was 1050, 1100, and 1150°C for 2 h. Therefore, there were three samples for each sintering temperature (one samples is: 100°C and 1050°C, one samples is: 300°C and 1100°C, etc.).

B. Sample Characterization

Phase characterization was carried out by XRD. The results were analyzed using PCPDFWIN, Xpowder, and GSAS to determine the phase and lattice parameter. The magnetic characterization was measured using a permagraph, which can be used to determine the magnetic quantities. Data was processed and expressed in a table or graph.

III. RESULT AND DISCUSSION

A. Phase Characterization

The XRD results showed that new phases were formed (**Figure 1**) and no precursor phase remained. Therefore, the reaction formed new bonding. The result was also compared with previous research [11].

The result at x = 0.1 showed that there were two phases, barium hexaferrite and iron manganite oxide ($\text{BaFe}_{11.6}\text{Mn}_{0.4}\text{O}_{19}$). Both phases were similar when verified with PCPDFWIN. The GSAS calculation for this sample with quadratic chi value was 1.987, indicating the refinement was insufficient and the error was 5–10%.

The result at x = 0.2 showed two possible phases, barium hexaferrite and manganese ferrite. At x = 0.4, there were four possible phases, magnetite, barium hexaferrite, manganese ferrite, and barium manganese oxide. There were three possible phases at x = 0.5, manganese oxide, barium iron manganite, and barium hexaferrite.

Theoretically, Mn and Fe are similar in dimension and oxidation number. It was assumed that Mn will precisely replace the Fe site. All characterized samples had barium hexaferrite and the phase occurred when the heating was greater than 1000°C.

The lattice parameter of barium hexaferrite was determined using GSAS. Table 1 illustrates the barium hexaferrite parameter length, which indicates a and b were the same, except for x = 0.5. c decreases when the Mn concentration increased. The lattice volume decreased when the Mn concentration increased.

It was the same with the situation when barium hexaferrite was doped with Cu [1]. The values of a and b were nearly the same. c increases as the concentration of Cu increases, which may be caused by magnetic shrinking of copper [1] as in Mn.

The structure of barium hexaferrite contains many layers, including oxygen and iron or manganese layers, as shown in **Figure 2**. The values of a and b are representative of the interaction between iron that has a magnetic moment. The c values represent the interaction between O atoms and iron or manganese. When the manganese increases, the c value decreases. The interaction between Fe and oxygen is weaker than manganese and oxygen. The interaction includes gravitational and coulomb interactions.

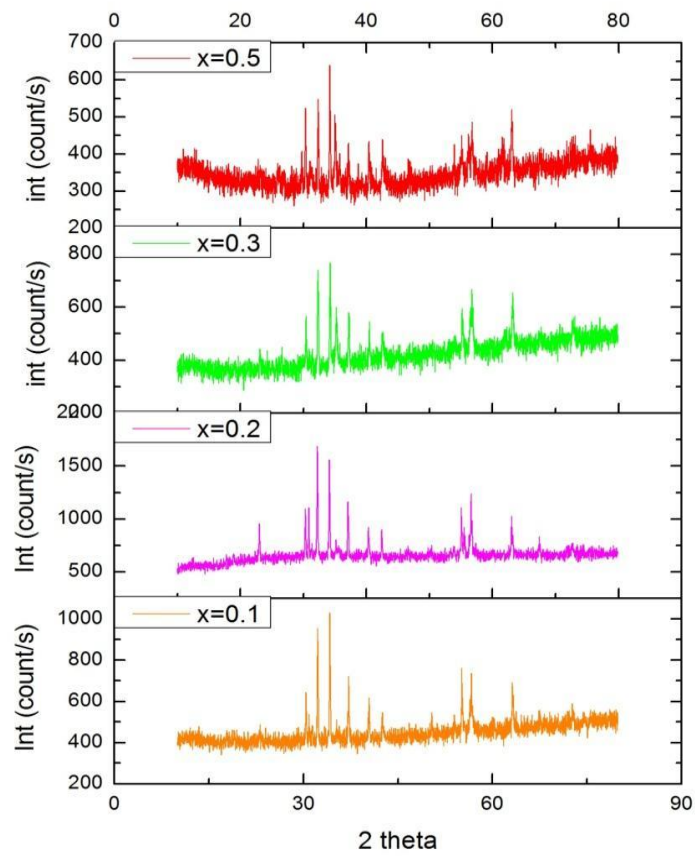

 Fig. 1 XRD result of barium hexaferrite for $x = 0.1, 0.2, 0.3,$ and 0.5

 TABLE I. LATTICE PARAMETERS FOR $x = 0.1, 0.2, 0.3,$ AND 0.5

x	a	b	c
0.1	5.88	5.88	23.15
0.2	5.89	5.89	23.16
0.3	5.88	5.88	23.19
0.5	5.90	5.90	23.08

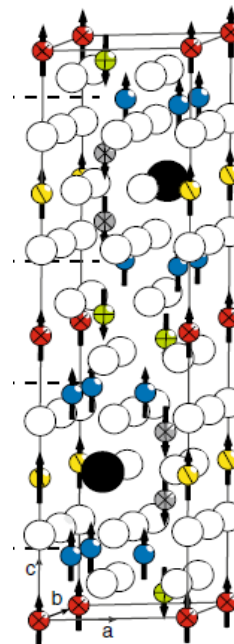


Fig. 2. Barium hexaferrite structure and magnetic moment orientation [12]

B. Magnetic Characterization

The magnetic characterization showed that the magnetic remanence decreased when the Mn concentration decreased. Mn^{+3} has 4 outer electrons with four filled orbitals. Therefore, the magnetic moment is 2 Magneton Bohr, which is weaker than iron. If manganese is replaced by Fe with an increased magnetic moment, the remanence would decrease. If it replaces iron, the magnetic moment decreases and the remanence will increase.

Compared to [11], the same magnetic property pattern was observed with increasing Mn. The magnetization decreases when the concentration increased. However, the coercivity is greater with more Mn.

Mn actually substitutes at the Fe site with the spin up and down, and the percentage is different so the magnetic properties change insignificantly.

BHmax, the energy product of the magnetic material, also decreases when the Mn concentration increases. The hysteresis of the magnetic material is related to the magnetic moment volume change. Therefore, Mn makes a smaller change than Fe.

The area of the hysteresis curves in **Figure 3** also change with the amount of Mn. The optimum area was at 0.4, in which 40% of the Fe was replaced by Mn. This area indicates the stability of the magnet: ff the area is large, it will be permanent and vice versa.

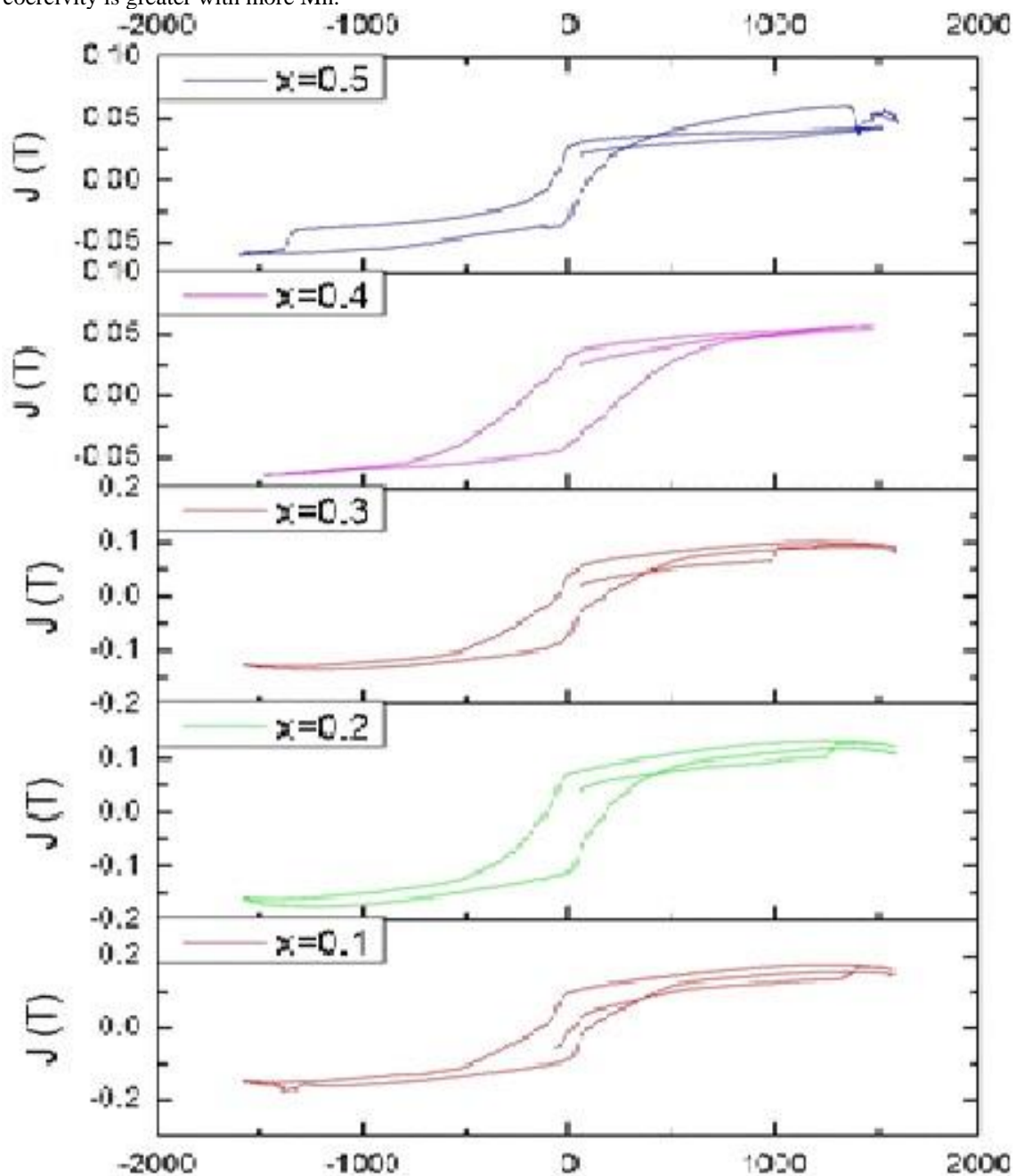


Fig. 3 Magnetic hysteresis of barium hexaferrite substituted with Mn at x = 0.1,0.2, 0.3, 0.4, and 0.5

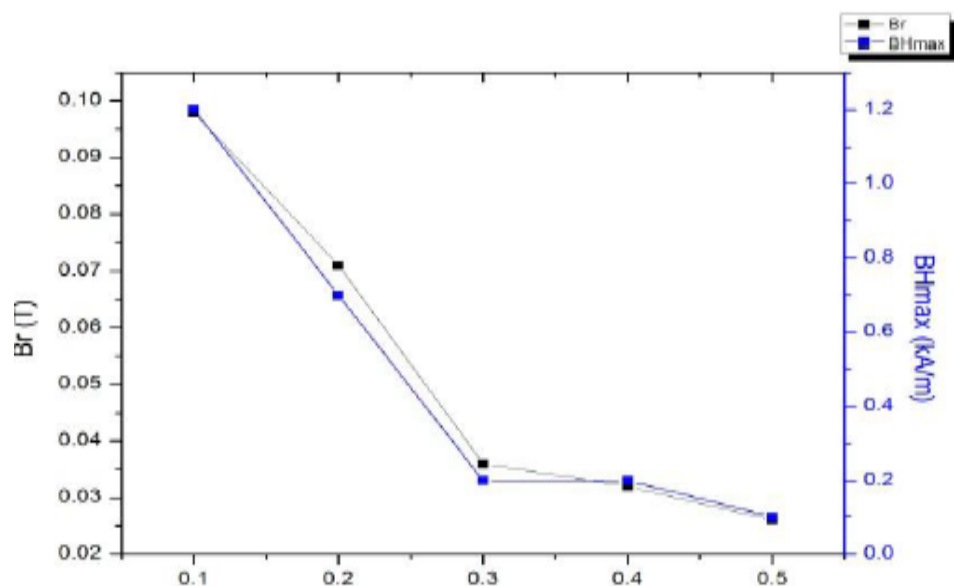


Fig. 4 Remanence of barium hexaferrite substituted with Mn at $x = 0.1, 0.2, 0.3, 0.4,$ and 0.5

IV. CONCLUSION

Barium hexaferrite with Mn at the Fe site was successfully fabricated. The XRD results showed there was no precursor phase, and new phases were formed, barium hexaferrite, manganite, magnetite, and manganese oxide. The manganese atom did not precisely replace iron. The lattice parameter c decrease because the interaction force between manganese and oxygen was stronger than that of iron and oxygen. The remanence decreased when the Mn concentration increased. The Mn replaced the Fe site with a magnetic moment up.

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