Enhancement of Magnetic and Microwave Absorbing Properties of \([\text{Ba (Fe, Mn, Ti)}_{12}\text{O}_{19}]_{1-x} - [\text{CoFe}_{12}\text{O}_{4}]_x\) (x = 0.2; 0.5; 0.8) Composites

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Abstract. In this paper, we report magnetic and microwave absorbing properties of magnetic based nanocomposite, which synthesized through mechanically alloyed the magnetic crystalline powders. The first component of composite was Mn-Ti doped Barium hexaferrite(BaFe12O19) or BHF obtained through a mechanical alloying process which was mixed with the second component of mechanically alloyed the CoFe2O4 magnetic compound to form composites of \([\text{Ba (Fe, Mn, Ti)}_{12}\text{O}_{19}]_{1-x} - [\text{CoFe}_{12}\text{O}_{4}]_x\) (x = 0.2; 0.5; 0.8) compositions. Prior to composite the two magnetic components, the remanence and saturation magnetization of the components were obtained optimally. Before Mn-Ti doping, the BHF has remanence (Mr) and saturation magnetization 0.206 T and 0.42 T respectively, with the corresponding coercivity (Hc) was 263.1 kA/m. On the other hand, CoFe2O4 (CFO) which has a high saturation magnetization(0.48 T) but with a low coercivity(16.22 kA/m). In form of magnetic composite, the high remanence was almost retained, but with the coercivity value decreased further to the lowest 80.82 kA/m. These two main properties (high remanance and low coercivity) were led the composite being good candidates for microwave absorbing materials. Microwave absorbing characteristics of \([\text{Ba(Fe, Mn, Ti)}_{12}\text{O}_{19}]_{1-x} - [\text{CoFe}_{2}\text{O}_{4}]_x\) (x = 0.2; 0.5; 0.8) composites were discussed in this paper relation with their corresponding magnetic properties for designing the best microwave absorbing materials.

1. Introduction
Barium hexaferrite or BHF with a chemical formula BaFe12O19 has been widely known as a magnetic compound which commonly used as permanent magnets because of its high coercivity and high remanence (Hc = 3335 Oe, Mr = 34.2 emu / g) [1]. In addition to such superior properties, the compound is an oxide-based material having a high resistivity value reaching 4340 \(\Omega\cdot\text{cm}[2, 3\). The combination between good magnetic properties and high resistivity values owned by the compound, has led the BHF to be developed for microwave absorbing applications. However, in order to obtain maximum and effective performances as a microwave absorber, the coercivity of BHF must be reduced to fall in the range of typical coercivity values of soft magnets with no sacrificing in remanent magnetization. According to reports of previous work, it was shown that the coercivity value of BHF significantly reduced when iron (Fe) ions were partially substituted by manganese (Mn) and titanium (Ti) ions. Based on this experimental fact, Mn-Ti substituted BHF has been developed for microwave absorbing applications [4-7].
Another magnetic compound like cobalt ferrite with a chemical formula CoFe2O4 possesses a soft magnetic behaviour with a low coercivity ($H_c = 575.43$ Oe), but it has a higher saturation value than BHF (77.53 emu / g) [8]. Furthermore, the cobalt ferrite is also a good dielectric material [9, 10]. With such magnetic and dielectric properties, the cobalt ferrite can also be a good candidate for microwave absorbing applications. Combining the two magnetic phases, namely BHF doped with Mn and Ti and CoFe2O4 in a composite structure, the value of remanence and saturation magnetization of the composite can be expected to increase. With the presence of the cobalt ferrite phase in the composite structure, the coercivity should be reduced further [11]. Hence, with such magnetic properties of composite systems, we can expect that the microwaves absorbing properties would increase the microwave absorbing capacity of composite material. In this paper, the magnetic properties and microwave absorbing characteristics of Mn-Ti substituted BHF – CoFe2O4 composite system is discussed.

2. Material and Method

2.1. Preparation of Ba(Fe, Mn, Ti)$_{12}$O$_{19}$

BHF phase was synthesized by powder metallurgy method with BaCO$_3$ and Fe$_2$O$_3$ powder as precursors. The precursor's weight was measured according to stoichiometry calculation and mass conservation law. Then, precursors were mixed and milled with alcohol media, using planetary ball milling for 10 hours. After milling processes, the precursor mixed powder was dried in oven at temperature 120°C and then sintered at 1200°C for 2 hours. After sintering process, BHF phase was obtained and then it was substituted with Mn and Ti.

For substitution of Mn and Ti, BHF crystalline phase was mixed and wet milled with MnCO$_3$, TiO$_2$, and BaCO$_3$ powder for 6 hours. The mixed powder, then dried at 120°C and sintered again at 1200°C for 2 hours. After sintering process, Ba(Fe, Mn, Ti)$_{12}$O$_{19}$ (BHFMTO) was obtained. The crystalline powder of BHFMTO then compacted to form pellets using a hydraulic compaction machine with 10 ton total force for 2 minutes. Then, pellets were sintered at 1300°C for 2 hours to densified and increasing grain interaction. Pellets then evaluated its magnetic properties by perмагraph device.

2.2. Preparation of CoFe$_2$O$_4$

Cobalt ferrite (CFO) phase was synthesized by the mechanical alloying method, with precursor cobalt (Co) powder and Fe$_3$O$_4$ powder. These powders were mixed by planetary ball milling for 20 hours. Then, the mixing powder were sintered in temperature 900°C for 12 hours. This sintering was important in order to form cobalt ferrite crystalline phase. After 12 hours of sintering, the crystalline of cobalt ferrite was palletized by the compaction method using the hydraulic compaction machine, with 10 tons total force for 2 minutes. Then, pellets were sintered in temperature 1200°C for 2 hours to densification and enhanced the grain interaction. Then, the sintered pellets would be tested by perмагraph to evaluate these magnetic properties.

2.3. Preparation of composite [Ba(Fe, Mn, Ti)$_{12}$O$_{19}$]$_{1-x}$/[CoFe$_2$O$_4$]$_x$

Composite was prepared with three different compositions between BHFMTO and CFO which was 20:80, 50:50, and 80:20 (x = 0.8; 0.5; and 0.2). Each composite powder were mixed using an ultrasonic mixing device for 10 minutes. After that, the powder was compacted with 10 tons total force for 2 minutes. Then, the pellets were sintered in temperature 1200°C for 2 hours. And then, using permagraph, the pellets were evaluated its magnetic properties. And the other composite powder would be evaluated for its microwaves absorbing properties using VNA.
3. Result and Discussion

3.1. $\text{Ba(Fe, Mn, Ti)}_{12}\text{O}_{19}$ and CoFe$_2$O$_4$ Phases

3.1.1. XRD Pattern
Figure 1 shows the XRD pattern of BHFMTO ($\text{BaFe}_{12-\alpha}\text{Mn}_{\alpha/2}\text{Ti}_{\alpha/2}\text{O}_{19}$) $\alpha = 0.3$ sintered at 1200°C for 2 hours (Fig. 1a) and CFO (CoFe$_2$O$_4$) sintered at 900°C for 12 hours. Phases identification of those XRD patterns show that either BHFMTO $\alpha = 0.3$ or CFO are single phase material, due to their matching with reference data[4, 8].

![XRD pattern of Ba(Fe, Mn, Ti)$_{12}$O$_{19}$ and CoFe$_2$O$_4$](image)

Figure 1. XRD pattern of Ba(Fe, Mn, Ti)$_{12}$O$_{19}$ (a) and CoFe$_2$O$_4$ (b)
3.1.2. Magnetic Properties
Figure 2 show the hysteresis loop of BHFMTO (x = 0.3) compared with the CFO. From this result, BHFMTO show the hard magnetic properties, while CFO is soft magnetic due to its low coercivity 16.22 kA/m. However, even have low coercivity, CFO phase have high magnetic saturation 0.47 T compare to BHFMTO that only have magnetic saturation 0.41 T, but has high coercivity 103.3 kA/m. This data is also confirmed that magnetic phase appears after sintering at 1250°C for BHFMTO and 1200°C for CFO.

![Figure 2. Hysteresis loop of Ba(Fe, Mn, Ti)12O19 (black) and CoFe2O4 (red) measured at room temperature.](image)

3.2. \([\text{Ba(Fe, Mn, Ti)}_{12}\text{O}_{19}]_{1-x}/[\text{CoFe}_2\text{O}_4]_x\), Composite System

3.2.1. XRD Pattern
Three different composites were made with composition in wt% as shown in Table 2. From XRD result, shown, in Figure 3, the two phase material is obtained after mechanical alloying and sintering process. These three samples show differences in peak intensity, which is indicated differences composition between BHFMTO and CFO phases. From refinement data we get the information of the sample's composition. The result shows that the composition of samples is same with the composition during material preparation, with goodness of fit (GoF) value between 0.89 and 1.

| Code | \(\text{Ba(Fe, Mn, Ti)}_{12}\text{O}_{19}\) [wt%] | \(\text{CoFe}_2\text{O}_4\) [wt%] |
|------|------------------|------------------|
| C1   | 20               | 80               |
| C2   | 50               | 50               |
| C3   | 80               | 20               |
3.2.2. Magnetic Properties
Composite pellets was evaluated for its magnetic properties using VSM. The hysteresis loop of each type of composite in Figure 4, show the hard magnetic properties, due to the high coeversity of BHFMTO phase. In the other hand, there are also increasing of magnetization along with increasing of cobalt ferrite’s mass concentration. Hence, increasing of CoFe2O4 phase will reduce BHFMTO’s coercivity, but increasing the corresponding remanence. To calculate the saturation, Law of approach to saturation was carried out[11]. Table 2 shows the resume of magnetic properties from each composites.

![Hysteresis loop of BHFMTO/CFO composite system](image)

**Figure 4.** Hysteresis loop of BHFMTO/CFO composite system.

| Composite | Hc [kA/m] | Mr [T] | Ms [T] |
|-----------|-----------|-------|--------|
| C1        | 80.85     | 0.26  |        |
| C2        | 101.1     | 0.242 |        |
| C3        | 150.0     | 0.23  |        |

3.2.3. Microwaves Absorbing Properties
Composites are evaluated for its reflection lose using a vector network analyzer (VNA) at frequency range from 8 GHz to 12 GHz. Figure. 5, show the result of reflection lose from three different
composite of BHFMTO-CFO. The result shows that composite with code C1 has the highest reflection lose about 21.3 dB at 10.78 GHz. For C2 composite, has maximum reflection lose 13.7 dB at 10.047 GHz and C3 composite has 16.025 dB of maximum reflection loss at 10.067 GHz.

Figure 5. Reflection lose of $[\text{Ba(Fe, Mn, Ti)}_{12}\text{O}_{19}]_{1-x}[\text{CoFe}_{2}\text{O}_{4}]_{x}$ composites

4. Conclusion
We have successfully synthesized BaFe12O19 hard magnetic phase and partially substituted it with Mn and Ti, and also we have successfully synthesized CoFe2O4 soft magnetic phase of the mechanical alloying method. The crystalline samples of these magnetic phases were obtained after 1200°C and 900°C sintering respectively. The result of magnetic properties of the composite has the highest magnetization 0.26 T with coesivity 80.85 kA/m, for composition 20:80. The result of reflection loss characterization show this composite type has the highest RL 21.3 dB at 10.9 GHz frequency.

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