Factors Affecting the Synthesis and Formation of Single-Phase Barium Hexaferrite by a Technique of Oxalate Precursor

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Abstract: Problem statement: Barium hexaferrite (BaFe$_{12}$O$_{19}$), is of great importance as permanent magnets, particularly for magnetic recording as well as in microwave devices. Approach: The aim of this study was to synthesize Stoichiometric and single-phase barium hexaferrite through a technique of oxalate precursor. Effects of different Fe$^{3+}$/Ba$^{2+}$ mole ratio and annealing temperature on the particle size, microstructure and magnetic properties of the resulting barium hexaferrite powders has been studied and reported in the presented research. The annealing temperature was controlled from 900-1200°C, while the Fe$^{3+}$/Ba$^{2+}$ was controlled from 12-8.57. Results: The resultant powders were investigated by Differential Thermal Analyzer (DTA), X-Ray Diffractometer (XRD), Scanning Electron Microscopy (SEM) and Vibrating Sample Magnetometer (VSM). Single phase of well crystalline BaFe$_{12}$O$_{19}$ was first obtained at Fe$^{3+}$/Ba$^{2+}$ mole ratio of 9.23 and 8.57 at annealing temperature 1100°C. Moreover, at annealing temperature 1200°C the single phase BaFe$_{12}$O$_{19}$ appeared at all different Fe$^{3+}$/Ba$^{2+}$ mole ratio. The SEM results showed that the grains were regular hexagonal platelets. In addition, maximum saturation magnetization (70.25 emu g$^{-1}$) was observed at mole ratio 10 and annealing temperature 1200°C. However, it was found that the coercivety of the synthesized BaFe$_{12}$O$_{19}$ samples were lower than the theoretical values. Conclusion: The barium hexaferrite was synthesized at annealing temperature 1200°C with a single phase using oxalate as precursor route.

Key words: Barium hexaferrite, annealing temperature, mole ratio, magnetic properties, oxalate precursor

INTRODUCTION

Permanent magnet materials are essential in devices for storing energy in a static magnetic field. Ferrite is a class of ceramic materials with useful electromagnetic properties and the electromagnetic properties for ferrite materials is affected by operating conditions such as temperature, pressure, field strength, frequency and time. Ferrites play an important role in the field of electronics industry because they are relatively inexpensive, more stable and easily manufactured. Ferrites are widely used in microwave devices, permanent magnets, high density magnetic and magneto-optic recording media and telecommunications devices. Hexagonal ferrites, MFe$_{12}$O$_{19}$ (where M = Ba, Sr and/or Pb) are a group of magnetic compounds, which all have high resistivity, magneto-crystalline anisotropy and saturation magnetization, low dielectric losses and are thermally stable well above their Curie temperature (Kojima and Wohlfarth, 1982; Smit and Wijn, 1959; Ogawara and Oliveira, 2000). As a result of its specific magnetic properties, barium hexaferrite and its derivatives can be used for permanent magnets, magnetic recording media and microwave applications (Hessien et al., 2008). BaFe$_{12}$O$_{19}$ (BaM) and its derivatives are currently magnetic material with great scientific and technological interest, due to its relatively high Curie temperature, high coercive force and high magnetic anisotropy field as well as an excellent chemical stability and corrosion resistivity (Kojima and Wohlfarth, 1982). Barium hexaferrite (BaFe$_{12}$O$_{19}$) has a complex hexagonal unit cell and belonging to the magnetoplumbite structures (Richerson, 1992). Magnetoplumbite are of the type A$^{2+}$O$_1$.6B$_2$ 3+O$_1$. The arrangement of the 12 Fe$^{3+}$ ions in the unit cell is as follows: Two ions in the tetrahedral sites (four nearest O$^{2-}$ neighbors), nine ions in the octahedral sites (six nearest O$^{2-}$ neighbors) and one ion in the hexagonal site.
Matutes-Aquino et al. used various Fe series of ferric chloride and barium chloride solution as starting materials. A commercial ceramic method (solid-state reaction) which involves the firing of stoichiometric mixture of barium carbonate and iron oxide at high temperatures (about 1200°C) was applied for the preparation of Barium hexaferrite. In this respect, several low-temperature chemical methods were investigated for the formation of ultrafine ferrite powders. The oxalate precursor method was used to synthesize nanocrystalline barium ferrite with high saturation magnetization. Effects of Fe3+/Ba2+ mole ratios and the annealing temperature on the synthesis of ferrite powders were investigated. The annealing temperature was controlled from 900-1200°C, while Fe3+/Ba2+ mole ratios were controlled from 12-8.57.

**RESULTS**

Figure 1 shows the Differential Thermal Analysis (DTA) plot (a and b) of the synthesized mixture of barium-iron oxalates precursors at two different Fe3+/Ba2+ mole ratios 12 and 8.57 respectively. It can be seen in peaks I-IV that an endothermic reaction occurred at around (95.11, 158.52, 182.45 and 232.15°C) which corresponds to the dehydration of iron and barium oxalates. This is consistent with earlier findings suggesting that, two different crystals hydrate types namely MeC2O4·2H2O and MeC2O4·3H2O (Me = metal ion) were significantly related to the anhydrous oxide mixture decomposition into both metal oxide and gases (CO2 and CO). Figure 1b shows that the VI peak has higher intensity in the case of Fe3+/Ba2+ mole ratio 8.57 as compared with mole ratio 12. This is most likely due to the increase of barium oxalate amount. Peak VIII in the plot at (956.90°C), showed the initial step to form BaFe12O19. Moreover, the intensity and sharpness of peak VIII in (plot b) was also increased, indicating that the stability of the formed barium ferrite will be increased with increasing content of barium oxalate ratio. Therefore, the DTA results indicate that barium ferrite cannot form before 956.90°C.
Fig. 1: Thermal profiles (DTA) of mixtures of barium-iron oxalates precursors at Fe$^{3+}$/Ba$^{2+}$ mole ratios (a) 12 and (b) 8.57.

Fig. 2: XRD patterns of BaFe$_{12}$O$_{19}$ from barium-iron oxalate precursor with Fe$^{3+}$/Ba$^{2+}$ mole ratio 8.57 thermally treated at different temperatures (900-200°C) for 2 h.

Figure 2 shows the XRD patterns of the calcined powder of BaFe$_{12}$O$_{19}$ obtained from barium-iron oxalate precursor solutions, with Fe$^{3+}$/Ba$^{2+}$ mole ratio 8.57 thermally treated at different temperatures (900-1200°C) for 2 h. On the start of the annealing process at (900°C), a complete absence of M-type barium ferrite phase. Instead, the hematite Fe$_2$O$_3$ phase appears as a major phase, which is consistent with DTA results. But at (1000°C) the concentration of the hematite phase decreases and barium ferrite phase was detected. Increasing the annealing temperature to 1100°C, enhanced the formation of barium hexaferrite phase and decreased the hematite Fe$_2$O$_3$ phase. At the calcinations temperature (1200°C), single phase of barium hexaferrite (BaFe$_{12}$O$_{19}$) evidently was formed.

Fig. 3: XRD patterns of BaFe$_{12}$O$_{19}$ from barium-iron oxalate precursor with different Fe$^{3+}$/Ba$^{2+}$ mole ratio and thermally treated at 900°C for 2 h.

Fig. 4: XRD patterns of BaFe$_{12}$O$_{19}$ from barium-iron oxalate precursor with different Fe$^{3+}$/Ba$^{2+}$ mole ratio and thermally treated at 1000°C for 2 h.

XRD analysis was carried out in this study to investigate the effect of Fe$^{3+}$/Ba$^{2+}$ mole ratios of the powders thermally treated at different temperatures (900-1200°C) for 2 h and the results are presented in Fig. 3-6. The results in Fig. 3 indicate that the thermal calcination of barium-iron oxalate precursor at 900°C has not yielded barium ferrite phase BaFe$_{12}$O$_{19}$ in any case. Instead iron oxide (Fe$_2$O$_3$) phase has appeared clearly in all the Fe$^{3+}$/Ba$^{2+}$ ratio. These results confirm the DTA results, which showed no sign of BaFe$_{12}$O$_{19}$ formation at 900°C. Figure 4 shows XRD patterns at annealing temperature 1000°C, formation of barium ferrite was observed for all mole ratios.
As expected, increasing the Fe$^{3+}$/Ba$^{2+}$ mole ratio enhanced the formation of barium ferrite phase (i.e., decreasing the amount of Fe$_2$O$_3$). Figure 5 showed the XRD patterns of BaFe$_{12}$O$_{19}$ precursor powders at 1100°C. The formation of barium ferrite phase was highly enhanced for all mole ratios, while the Fe$_2$O$_3$ formation diminished significantly. It can be also observed that single phase of well crystalline BaFe$_{12}$O$_{19}$ was first obtained at Fe$^{3+}$/Ba$^{2+}$ mole ratio of 9.23 and 8.57 at annealing temperature 1100°C. Raising the calcination temperature for the precursor up to 1200°C (Fig. 6), the single phase BaFe$_{12}$O$_{19}$ appeared at all different Fe$^{3+}$/Ba$^{2+}$ mole ratio. At the same time no sign of iron oxide (Fe$_2$O$_3$) appeared. Figure 7 shows the effect of various mole ratios on the crystalline size of the obtained powders. It can be observed that increasing the annealing temperatures helps significantly agglomeration of the particles and grains growth during calcination course. This leads to the increase of grain size and formation of single phase barium hexaferrite powders.

Figure 8 displays SEM micrographs of BaFe$_{12}$O$_{19}$ powders obtained from oxalate precursors with Fe$^{3+}$/Ba$^{2+}$ mole ratio of 9.23 and annealed for 2 h.

Clearly, it appears that increasing calcination temperature (900-1200°C) has a substantial effect on the microstructure of synthesized BaFe$_{12}$O$_{19}$ powders.
Fig. 9: Effect of Fe<sup>3+</sup>/Ba<sup>2+</sup> mole ratios on the microstructure of synthesized BaFe<sub>12</sub>O<sub>19</sub> powders obtained from oxalate precursors and annealed at 1000°C for 2 h. (a) Fe<sup>3+</sup>/Ba<sup>2+</sup> = 12; (b) Fe<sup>3+</sup>/Ba<sup>2+</sup> = 10.9; (c) Fe<sup>3+</sup>/Ba<sup>2+</sup> = 10; (d) Fe<sup>3+</sup>/Ba<sup>2+</sup> = 9.23 and (e) Fe<sup>3+</sup>/Ba<sup>2+</sup> = 8.57

In Fig. 8a, fine precipitated particles, with random grain orientation. This confirms the previous results of XRD and DTA, which showed no sign of BaFe<sub>12</sub>O<sub>19</sub> growth at 900°C. However, as the annealing temperatures increased to 1000°C Fig. 8b, individual particles possess a plate-like hexagonal shape containing a few numbers of spherical small particles. At annealing temperature 1100°C (Fig. 8c), the ferrite powders showed uniform coarse structure with a well-clear hexagonal shape.

As the Ba<sup>2+</sup> ion concentration increased in the composition of the samples (Fig. 9c-e), uniform and coarse structure with clear homogeneous microstructure become more pronounced. Moreover, a well-clear crystalline micro-structure containing a fewer numbers of spherical small particles can be seen in these SEM micrographs. As the annealing temperature increased to 1100°C (Fig. 10a-e), the produced powders of BaFe<sub>12</sub>O<sub>19</sub> possessed very well-defined plate-like hexagonal shape.

**DISCUSSION**

Table 1 and Fig. 11-14 present the magnetic properties of the synthesized barium ferrite powders, which were obtained at room temperature under an applied field of 10 kOe. The results showed that the saturation magnetization of the produced powders increased by increasing the temperatures. Figure 11 display the effect of annealing temperature on the hysteresis loop of BaFe<sub>12</sub>O<sub>19</sub> powders obtained from oxalate precursors at Fe<sup>3+</sup>/Ba<sup>2+</sup> mole ratio 10. This is likely due to the presence of single domain of BaFe<sub>12</sub>O<sub>19</sub> particles. In line with SEM results, the change in magnetic properties can be attributed to the presence of well crystalline BaFe<sub>12</sub>O<sub>19</sub> microstructures, as the annealing temperature of the powders was increasing gradually to reach optimum conditions.
Table 1: Effect of Fe$^{3+}$/Ba$^{2+}$ mole ratios and annealing temperature on the magnetic properties of Barium hexaferrite

| Fe$^{3+}$/Ba$^{2+}$ mole ratio | Temp. (°C) | Ms (emu g$^{-1}$) | Mr (emu g$^{-1}$) | $H_c$ (Oe) |
|-------------------------------|-----------|------------------|------------------|---------|
| 12                            | 900       | 3.667            | 1.3710           | 666.0   |
|                               | 1000      | 33.010           | 1.0710           | 250.0   |
|                               | 1100      | 62.440           | 21.4100          | 662.6   |
|                               | 1200      | 82.212           | 13.0000          | 503.8   |
| 10.91                         | 900       | 2.074            | 0.8269           | 643.7   |
|                               | 1000      | 34.220           | 3.0660           | 235.4   |
|                               | 1100      | 67.150           | 21.0100          | 641.6   |
|                               | 1200      | 67.210           | 13.6900          | 387.5   |
| 10                            | 900       | 1.702            | 0.6210           | 653.0   |
|                               | 1000      | 37.400           | 5.5310           | 381.1   |
|                               | 1100      | 67.590           | 18.4500          | 556.6   |
|                               | 1200      | 70.250           | 16.6400          | 451.3   |
| 9.23                          | 900       | 1.733            | 0.6292           | 653.3   |
|                               | 1000      | 46.820           | 3.4710           | 172.6   |
|                               | 1100      | 65.440           | 20.8300          | 837.8   |
|                               | 1200      | 68.450           | 15.1100          | 480.6   |
| 8.57                          | 900       | 2.728            | 2.7280           | 808.7   |
|                               | 1000      | 44.800           | 3.5070           | 240.8   |
|                               | 1100      | 64.960           | 19.1200          | 620.8   |
|                               | 1200      | 67.230           | 18.7700          | 536.7   |

Figure 11: Effect of annealing temperature on the M-H hysteresis loop of synthesized BaFe$_{12}$O$_{19}$ powders obtained from oxalate precursors at Fe$^{3+}$/Ba$^{2+}$ mole ratio 10

This was likely due to the presence of single domain of BaFe$_{12}$O$_{19}$ particles. Such high saturation magnetization for barium ferrite at 1200°C can be attributed to the high-phase purity and well-defined crystalline structure of BaFe$_{12}$O$_{19}$. In contrast, the coercive force $H_c$ results of BaFe$_{12}$O$_{19}$ powders, which is produced by the oxalate precursor method were lower than the theoretical value of (6700 Oe). In addition, these results might be related to the residual Fe$_2$O$_3$ having a high intrinsic coercive force (Hessien et al., 2008).
Fig. 14: Effect of Fe$^{3+}$/Ba$^{2+}$ mole ratio on the M–H hysteresis loop of synthesized BaFe$_{12}$O$_{19}$ powders obtained from oxalate precursors and annealed at 1200°C for 2 h

However, clearly this technique is a promise for providing BaFe$_{12}$O$_{19}$ with the highest saturation magnetization value. Figure 11-13 and Table 1, display effect of Fe$^{3+}$/Ba$^{2+}$ mole ratio on the M–H hysteresis loop of synthesized BaFe$_{12}$O$_{19}$ powders obtained at different annealing temperatures.

Figure 12 showed that at annealing temperature 1000°C decreasing the Fe$^{3+}$/Ba$^{2+}$ mole ratios from 12-8.57 increased the saturation magnetization of the formed BaFe$_{12}$O$_{19}$ particles from 33.01-44.8 emu g$^{-1}$. This is mainly due to increasing formation of well crystalline BaFe$_{12}$O$_{19}$ powders and decrease of the presence of non-magnetic species of Fe$_2$O$_3$ as the mole ratio percentage went up. These results are in substantial agreement with the previous XRD and SEM results, which was shown in Fig. 4 and 8. However, the effect of Fe$^{3+}$/Ba$^{2+}$ mole ratio on the M–H hysteresis loop of synthesized BaFe$_{12}$O$_{19}$ powders obtained at 1100°C and 1200°C was less significant in Fig. 13 and 14. This suggests that the Fe$_2$O$_3$ particles diminished dramatically at temperature 1100°C and 1200°C, which lend support to the XRD and SEM results corresponding to these temperatures in Fig. 5 and 10, where the crystallinity of BaFe$_{12}$O$_{19}$ powders were very evident.

**CONCLUSION**

The structural and magnetic properties of newly prepared barium hexaferrite powders were studied in a comparative way. The results from DTA, XRD, SEM and VSM studies can be summarized as follows:

- Differential Thermal Analysis (DTA) plots of the synthesized mixture of barium-iron oxalates precursors showed that the initial step to form BaFe$_{12}$O$_{19}$ started at (956.90°C)
- Single phase of well crystalline BaFe$_{12}$O$_{19}$ was first obtained at Fe$^{3+}$/Ba$^{2+}$ mole ratio of 9.23 and 8.57 at annealing temperature 1100°C while at annealing temperature 1200°C the single phase BaFe$_{12}$O$_{19}$ appeared at all different Fe$^{3+}$/Ba$^{2+}$ mole ratio
- The morphology of the particles at 1000 and 1100°C are hexagonal platelet crystal. By increasing the temperature up to 1200°C, grains have coalesced to form larger grains
- The oxalate precursor route has proven to produce pure barium ferrite powders with good magnetic properties with maximum saturation magnetization value of (70.25 emu g$^{-1}$) and coercivity force (451.3 Oe)
- Regarding the particles size, it can be seen that, the minimum particle size appeared at (1000°C) and the maximum size was found at (1200°C), which most likely explained by the formation of the single phase of barium hexaferrite (BaFe$_{12}$O$_{19}$)

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