Heat treatment of mechano-chemically produced BaFe$_{12}$O$_{19}$/Fe$_3$O$_4$ magnetic nano-composites

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Abstract. Barium hexaferrite (BaFe$_{12}$O$_{19}$) magnetic powder was synthesized via ceramic route by mixing of Fe$_2$O$_3$ and BaCO$_3$ and subsequent calcination of the mixed powder in air at 1150°C. The synthesized barium hexaferrite was mixed with graphite to be treated mechano-chemically in high energy ball mill in air atmosphere for various times. Subsequently, the milled samples were subjected to high temperature in argon atmosphere. XRD patterns of the milled samples revealed that graphite partially reduced barium hexaferrite to Fe$_3$O$_4$ after 15 hours of milling, resulted in a magnetic nano-composite of BaFe$_{12}$O$_{19}$/Fe$_3$O$_4$. Extending milling time to 80 hours promoted the reduction process to FeO. Heat treatment of the milled samples resulted in different magnetic composites. Iron was seen in XRD pattern of the 40 hours milled sample that was heated at 680°C. SEM images showed that after heat treatment, fine particles in agglomerates grew and larger particles formed. As a result, mean particle size increased due to the heat treatment of the milled powder.

Keywords: Barium hexaferrite; magnetic nano-composite; ball milling; partial reduction, heat treatment

1. Introduction
Hexagonal ferrites, especially barium hexaferrite (BaFe$_{12}$O$_{19}$) have been used for different applications such as permanent magnets, magnetic recording media, magneto-optic materials and microwave filters. These materials exhibit high saturation magnetization and high values of coercivity as well. High Curie temperature and chemical stability are other advantages [1, 2].

Due to recent interest for production and application of hexaferrite nanoparticles, many researchers have employed different methods such as co-precipitation, sol–gel combustion, micro-emulsion, hydrothermal and self-propagating high temperature synthesis to produce this type of nano-materials [3-6].

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Low values of coercivity can be achieved by heat treatment of hexaferrite materials under carbon containing gases, nitrogen and hydrogen or a combination of these gases at high temperatures. Lower coercivity makes these materials suitable for magnetic recording media such as hard disks, video tapes, and etc. where a lower coercivity is necessary for easier data re-writing [7-10]. Here, the effect of milling of barium hexaferrite and graphite mixture in a high energy ball mill and subsequent heat treatment on magnetic properties has been investigated.

2. Experimental procedure
Hematite (>99% purity) and barium carbonate (>99% purity) were mixed in a jar mill and calcinated at 1150 °C for 2 hours. The molar ratio of Fe₂O₃/BaCO₃ was 5.5/1. The synthesized barium ferrite was mixed with graphite. The molar ratio of C/O was 1.1 in the mixture. The powder blend milled for different times in a high energy planetary ball mill with ball to powder mass ratio and rotating speed of 35 and 300 rpm, respectively. Heat treatment of the samples carried out under argon atmosphere in an electrical tube furnace with heating rate of 10 °C/min and dwell time of 10 minutes at the desired temperature. Then, the samples were furnace-cooled under argon atmosphere. Phase identification was done with a Philips PW-1730 XRD machine with Co-Kα radiation. Powder crystallite size was calculated according to Williamson-Hall method [11] (see appendix). DTA analysis (Differential Thermal Analysis) performed in a NETZSCH STA 409 PC/PG calorimeter with Al₂O₃ crucible and heating rate of 10 °C/min under flowing argon atmosphere. Magnetic properties measurements were done by a LakeShore Model 7307 VSM. Philips XL30 SEM was used to study particle size and morphology of the powder.

3. Results and discussions
The XRD patterns of milled barium hexaferrite and graphite mixtures are shown in figure 1. It can be seen that during milling, Fe₃O₄ and then FeO phases have been produced from BaFe₁₂O₁₉. In fact BaO·6(Fe₂O₃) is reduced to lower iron oxides in high energy ball milling. The reduction process makes it possible to obtain a BaFe₁₂O₁₉/Fe₃O₄ magnetic composite during milling. The particles of barium hexaferrite which is a brittle ceramic material fractures repeatedly in the milling medium to reach the nanoscale. The soft graphite which surrounds these particles makes a nano-reactor [12] for the reduction process of barium hexaferrite to lower iron oxides.

![Figure 1. XRD patterns of barium hexaferrite and graphite mixtures milled under air atmosphere for different times; 10, 15, 20, 40, and 80 hours.](image-url)
After 15 hours of milling, the intensity of Fe$_3$O$_4$ peaks in the XRD patterns increases and that of BaFe$_{12}$O$_{19}$ decreases with milling time. Long milling times up to 80 hours result in an improvement in reduction process and appearance of FeO peaks in the XRD patterns. XRD peak broadenings show that the crystallite size of barium hexaferrite is 41 and 14 nm for 10 and 20 hours milled samples, respectively. This parameter is 7 nm for FeO in 80 hours milled sample. Therefore, increasing milling time results in decreasing crystallite size of barium hexaferrite in the milled samples.

Figure 2 represents DTA curves of un-milled and 40 hours milled mixtures of barium hexaferrite and graphite. The endothermic peak at 992 °C in the curve of unmilled sample which relates to the reduction of barium hexaferrite to iron and other Ba containing compound(s) decreases to 748 °C after 40 hours milling of the mixture. This decrease in the peak temperature is a result of accumulation of energy and inducing crystalline defects into the powder particles due to the milling.

Figure 3 represents XRD patterns of un-milled and 40 hours milled samples that are heat treated at 680 °C. These patterns illustrate that for un-milled sample, reduction process proceeds to FeO due to the heat treatment. Heat treatment of the 40 hours milled sample resulting in a new composite consisting of Fe, Fe$_3$O$_4$, BaFe$_{12}$O$_{19}$, FeO, C, BaFe$_2$O$_4$, and Ba$_3$Fe$_2$O$_6$ phases.

![Figure 2. DTA diagrams of barium hexaferrite and graphite mixtures for un-milled and 40 hours milled samples.](image)

![Figure 3. XRD patterns of heat treated samples at 680 °C; (a) un-milled and (b) 40 hours milled.](image)
Figure 4 shows the hysteresis loops of as-produced and heat treated samples. By heat treating the 40 hours milled sample, coercivity of the initial hard magnetic material decreases because of the formation of a new magnetic composite of BaFe$_{12}$O$_{19}$ (hard magnetic material), Fe (soft magnetic material), Fe$_3$O$_4$ and some other non-magnetic phases. The intrinsic coercivity, $H_{ci}$, decreases from 2020 Oe for as-produced powder to 477 Oe for milled and heat treated powder.

Figure 5 shows SEM images of 40 hours milled samples before and after heat treatment and also 80 hours milled powder. Figures 5(a) and 5(b) show that each larger agglomerate consists of fine particles. The mean particle size for 40 and 80 hours milled samples is 94 and 56 nm, respectively. It can be seen in figure 5(c) that after heat treatment, fine particles in agglomerates of milled powder adhered to each other and grew to form larger particles.

![Hysteresis loops of as-produced and heat treated samples.](image)

**Figure 4.** Hysteresis loops of as-produced and heat treated samples.

![SEM images of barium hexaferrite and graphite mixture.](image)

**Figure 5.** SEM images of barium hexaferrite and graphite mixture; (a) milled for 40 hours, (b) milled for 80 hours and (c) milled for 40 hours and then heat treated at 680 °C.

4. **Conclusions**

According to the results of the present research, the following conclusions were drawn.

1. By milling of BaFe$_{12}$O$_{19}$ and graphite, a nano-crystalline magnetic composite consisting of BaFe$_{12}$O$_{19}$ and Fe$_3$O$_4$ was formed after 15 hours. Extending milling time resulted in increasing the amount of Fe$_3$O$_4$ in this composite.

2. FeO phase observed in the 80 hours milled sample due to the reduction process. The crystallite size of this phase was 7 nm at this stage.
3. Heat treatment of the un-milled mixture for 10 minutes at 680 °C promoted the reduction process to FeO phase. This heat treatment for 40 hours milled sample promoted the reduction process up to iron and made a magnetic composite consisting of Fe/Fe₃O₄/BaFe₁₂O₁₉ beside other phases. The coercivity decreased as a result of heat treatment of the milled sample.

4. The particle size of the milled samples reached to 94 and 56 nm after 40 and 80 hours of milling, respectively. Furthermore, heat treatment resulted in particle size increments.

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Appendix
Williamson-Hall [11] method for crystallite size measurements relies on the principle that the contribution of size broadening, $\beta_L$, and strain broadening, $\beta_e$, of the XRD peaks width varies with Bragg angle as follow:

$$\beta_L = \frac{k\lambda}{L \cos \theta}$$

$$\beta_e = C \varepsilon \tan \theta$$

The contribution of $\beta_L$ varies with $1/\cos \theta$ and that of $\beta_e$ varies with $\tan \theta$. Total contribution of size broadening and strain broadening will be:

$$\beta_{tot} = \beta_e + \beta_L = \frac{k\lambda}{L \cos \theta} + C \varepsilon \tan \theta$$

Or

$$\beta_{tot} \cos \theta = C \varepsilon \sin \theta + \frac{k\lambda}{L}$$

By plotting $\beta_{tot} \cos \theta$ versus $\sin \theta$ for different peaks, $C \varepsilon$ and $k\lambda/L$ can be obtained from a linear fit as the slope and intercept, respectively.

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