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Influence of Intensive Milling on Synthesis of Barium Hexaferrite Nano Particles

A. Ataie and S. Jahangir

School of Metallurgy and Materials Engineering, University of Tehran,
P.O. Box: 14395-553, Tehran, Iran

Abstract: Nano size particles of barium hexaferrite were produced by conventional mixed oxide ceramic method from $BaCO_3$ and α-Fe_2O_3 as starting materials. 3% wt. NaCl was used as a process control agent (PCA) and influence of the intensive milling has been investigated. Thermal analysis, phase composition, morphology and magnetic properties of the products were characterized using DTA/TG, XRD, SEM/TEM and VSM techniques, respectively. In all milled samples BaCO3 completely decomposed. Formation temperature of barium hexaferrite decreased in sample milled with NaCl for 10 h. NaCl is considered to be efficient in reduction of crystallite size and acceleration of barium hexaferrite reaction kinetic. Mean crystallite size of the barium hexaferrite in sample milled for 10 h in the presence of NaCl and annealed at 1000°C was measured 25 nm using TEM images. Hc and Ms in the above sample were 4.3 kOe and 52.7 emu/g, respectively.

Key words: Process control agent · Mechanical alloying · Barium hexaferrite · Nano particles.

INTRODUCTION

Nano-crystalline $BaFe_{12}O_{19}$ due to its excellent magnetic properties has significant potential for magnetic recording media, ferro-fluids and radar-absorbing coatings [1]. The preparation method strongly determines magnetic and structural properties. The conventional method to obtain barium hexaferrite particulates is the solid state reaction. This method consists of heating the mixture of hematite and barium carbonate precursors at temperature as high as 1100°C followed by milling to break up the agglomerates.

Mechanical activation of starting materials is a promising way in precursor preparation. Particle size reduction, which increases the contact surface between particles, is the direct consequence of milling. Also the energy of the system increases which results in a decrease in formation temperature of hexaferrite. Additives can strongly influence the morphology and phase composition of ball milled powder particles [2-4].

In this paper, nanometer size particles of barium hexaferrite were synthesized with high-energy ball milling of the precursors in the presence of NaCl as a process control agent. The effects of addition of NaCl on the process have been investigated.

Experimental: α-Fe_2O_3 (99% purity) and $BaCO_3$ (99% purity) powders were mixed together with a Fe/Ba molar ratio of 11. Powder mixture was milled for various times in air using planetary ball mill with 250ml hardened steel vial spinning at 300 rpm. The ball to powder weight ratio was 15. 3%wt NaCl was used to investigate the effect of PCA addition on the process. Milled samples were annealed at 600, 700, 900 and 1000°C for 1 h in a muffle furnace in air to obtain barium hexaferrite magnetic phase.

Phase composition of the samples was analyzed by Philips PW3170 XRD using Co Kα radiation. Crystallite size was measured by X-ray line broadening technique. Thermal behavior of the samples was evaluated using a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 °C /min. The morphology of the samples was studied by a Bosch Zeiss-EM-10C TEM. Vibrating sample magnetometer (VSM) was employed to evaluate the magnetic properties of the annealed sample.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the samples milled for various times without addition of NaCl. Peak broadening was happened due to the crystallite refinement and defects accumulation in powder particles,

Corresponding Author: A. Ataie, School of Metallurgy and Materials Engineering, University of Tehran, P.O. Box 14395-553, Tehran, Iran Tel: +98 912 1936361; Fax: +98 21 88006076; E-mail address: aataie@ut.ac.ir

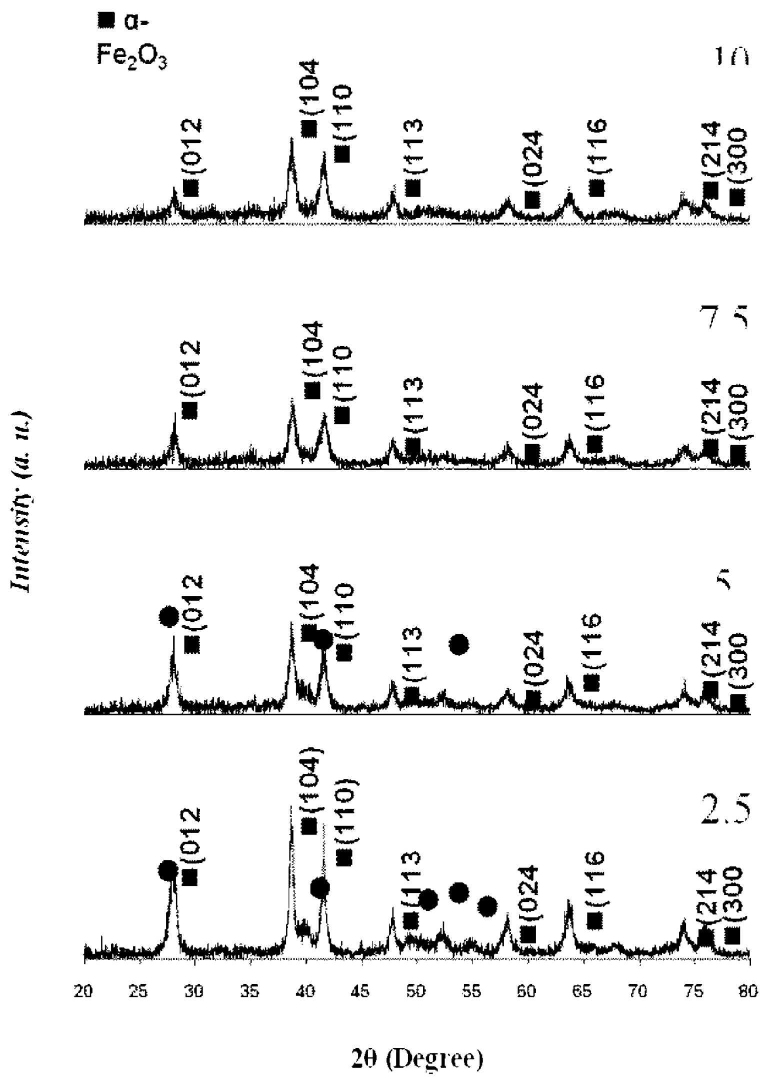

Fig. 1: XRD patterns of the samples milled for various times without addition of NaCl.

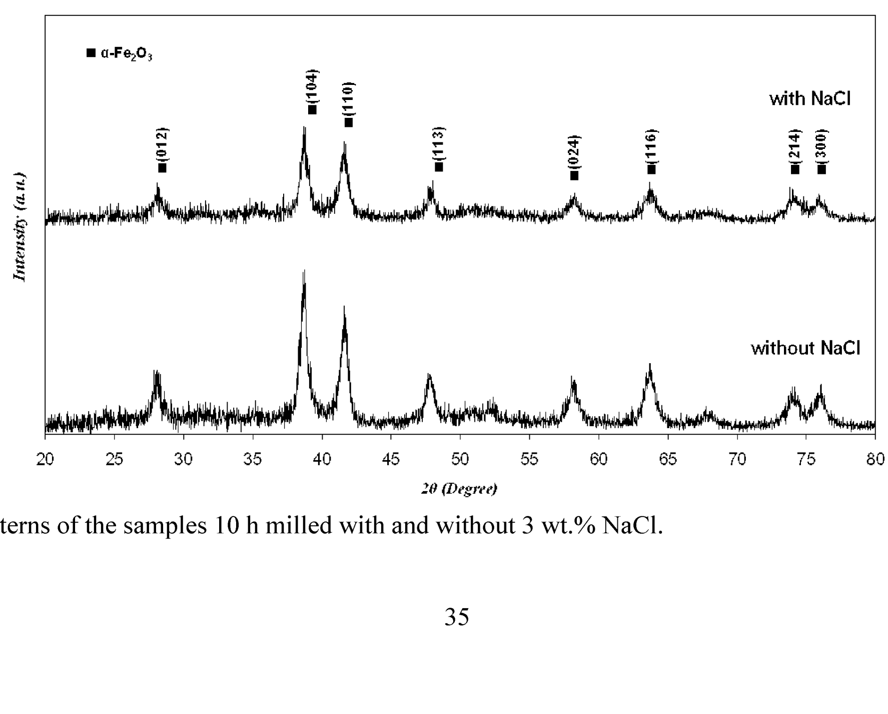

Fig. 2: XRD patterns of the samples 10 h milled with and without 3 wt.% NaCl.

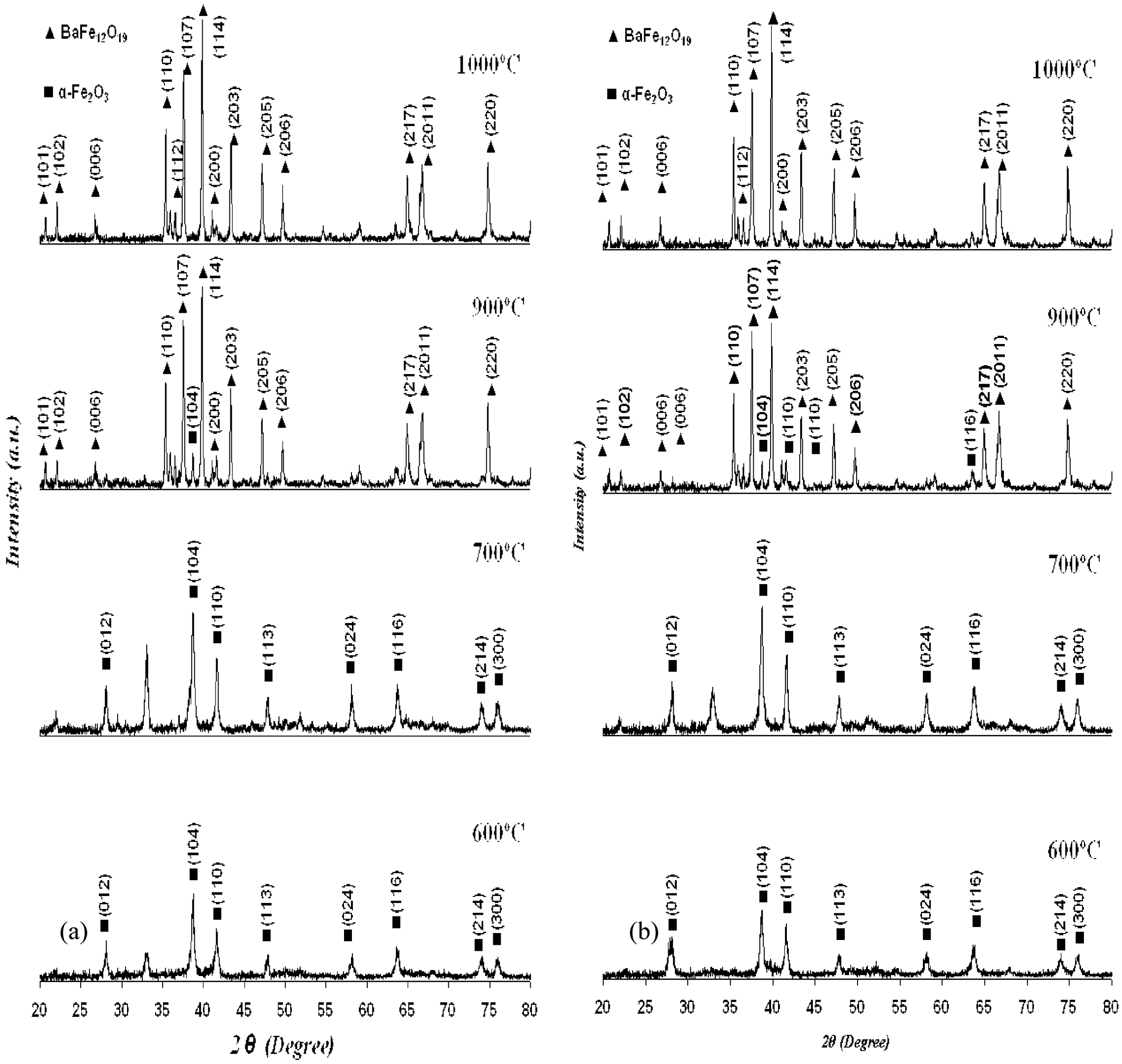

Fig. 3: XRD patterns of the samples 10 h milled with (a) and without NaCl (b) annealed at 600, 700, 900 and 1000°C

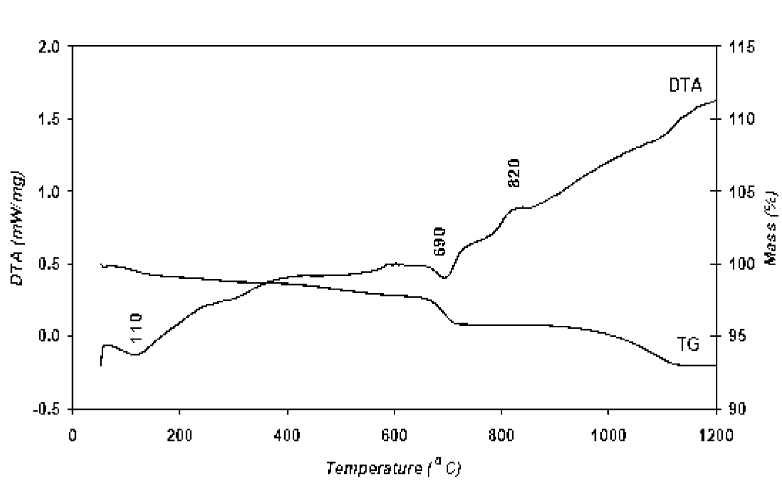

Fig. 4: DTA/TGA traces of the sample 10 h milled with 3 wt.% NaCl.

Fig. 5: SEM micrograph of 10 h milled sample in the presence of NaCl after annealing at 1000°C for 1 h

which introduce additional energy to the system in the form of interfacial and strain energy [5].

X-ray diffraction patterns of the samples milled for 10 h with and without NaCl are shown in Fig. 2. Analysis of the above patterns indicates hematite as a major phase. Barium carbonate was not detected which confirms the complete decomposition of this phase during milling process. In sample milled for 10 h in the presence of NaCl, intensity of hematite peaks significantly reduced and their width increased in comparison with the sample milled without NaCl. Mean crystallite size of hematite in 10 h milled products without and with NaCl calculated 55 and 22 nm, respectively. It seems that addition of NaCl accelerates the fracturing mechanism during milling and decreases the mean crystallite size. Even after annealing at 1000°C for 1 h, the NaCl added sample showed the nano-crystalline nature; mean crystallite size of barium hexaferrite in this sample was measured 49 nm using XRD line boardening technique.

Analysis of the XRD patterns of the samples milled for 10 h with and without NaCl and then annealed at various temperatures for 1 h (Fig. 3), indicates that at 600°C main phase is hematite while some barium monoferrite has been formed in sample milled in the presence of NaCl. Single phase barium hexaferrite has been formed at 900°C in the sample processed with NaCl while the sample milled without NaCl mainly consists of barium hexaferrite together with some hematite. Fig. 4 shows the DTA/TGA traces of the 10h milled sample in presence of 3 wt. % NaCl. An endothermic peak at around 100 °C is corresponded to the dehydration of the absorbed water. At 690 °C there is an endothermic peak with a slight change in weight which could be attributed to the formation of barium monoferrite. XRD pattern of 10h milled sample with NaCl and annealed at 700°C confirms the formation of this phase. Hematite after reaction with barium monoferrite results in formation of barium hexaferrite and the exothermic peak at 820 °C is

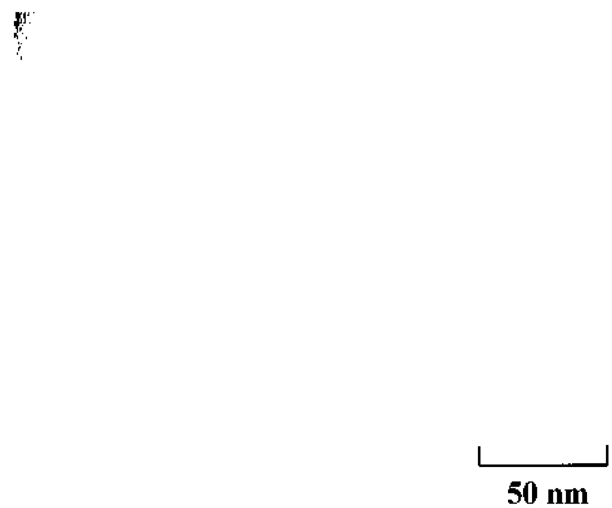

Fig. 6: TEM micrograph of 10 h milled sample in the presence of NaCl after annealing at 1000°C for 1h.

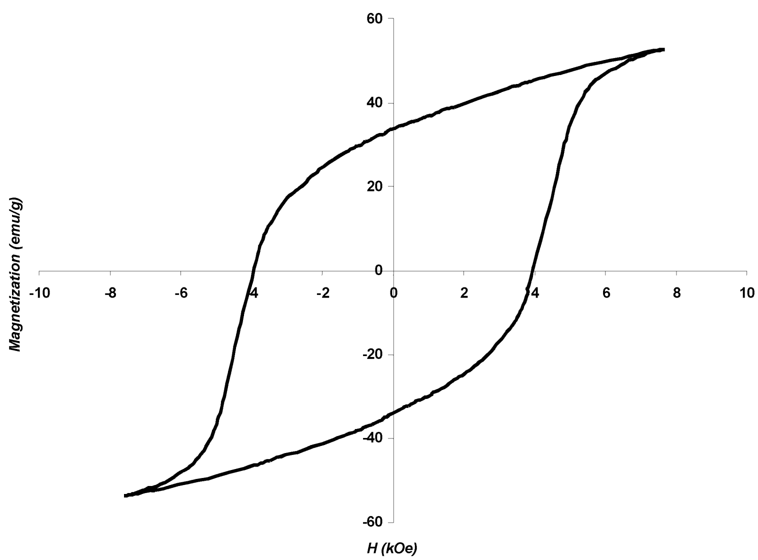

Fig. 7: Hysteresis loop of 10 h milled sample in the presence of NaCl after annealing at 1000°C for 1h.

may be due to this formation reaction which is in good agreement with XRD results. The Hexaferrite formation temperature is lowered after high-energy ball milling process.

SEM and TEM micrograph of 10h milled sample in the presence of NaCl after annealing at 1000°C for 1 h is shown in Figs. 5 and 6, respectively. The hexagonal grains with mean diameter of 150 nm could be observed in SEM micrograph. The mean crystallite size of $BaFe_{12}O_{19}$ obtained from the TEM image was 25 nm.

Fig. 7 shows the hysteresis loop of 10 h milled sample in the presence of NaCl after annealing at 1000°C for 1 h. Saturation magnetization and coercivity for this sample were measured 52.7 emu/g and 4.3 kOe, respectively.

CONCLUSION

Single phase barium hexaferrite was synthesized at a relatively low temperature of 900°C by mechanical activation of starting materials. It is shown that the using of 3%wt NaCl as a PCA lowers the formation temperature of desired phase. The mean crystallite size of $BaFe_{12}O_{19}$ in sample milled for 10h in the presence of NaCl after annealing at 1000°C for 1h was 25 nm.

REFERENCES

1. Ichnose, N., 1992. Superfine Particle Technology, Springer-Verlag.
2. Sheykhi Moghaddam, K. and A. Ataie, 2006. Role of intermediate milling in the processing of nano-size particles of barium hexaferrite via co-precipitation method. J. Alloys and Compounds. 426: 415-419.
3. Sharma, P., R.A. Rocha, S.N. de Medeiros and A. Paesano JR, 2007. Structural and magnetic studies on barium hexaferrite prepared by mechanical alloying and conventional route. J. Alloys and Compounds. 443: 37-42.
4. Zhang, Y.F., L. Lu and S.M. Yap, 1999. Prediction of the amount of PCA for mechanical milling. J. Materials Processing Technol., 89-90: 260-265.
5. Feng, H., D. Jia and Y. Zhou, 2007. Influence factors of Ball milling process on BE powders for reaction sintering of TiB/Ti_4.0Fe_7.3Mo composite. J. Materials Processing Technol., 182: 79-83.