JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 7, July 2011, p. 883 - 886

Research on synthesis of barium hexaferrite powders processed by mechanical alloying

I. ŞTEFAN*, R. CHIRIAC[a], C. NICOLICESCU[b], M. CIOBANU[c]
University of Craiova, Faculty of EMTS, Romania
[a]*Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS−Université Claude Bernard Lyon 1, France*
[b]*University of Craiova, Faculty of EMTS, Romania*
[c]*University of Craiova, Faculty of EMTS, Romania*

The paper presents the experimental research results regarding barium hexaferrite powders $BaFe_{12}O_{19}$ produced by mechanical alloying. Fe_2O_3 and $BaCO_3$ were used as starting materials. SiO_2 was used as quartz with mineralized role. The mixture thus formed was subjected to mechanical alloying process using a high energy ball mill Pulverisette 4 in wet medium for 5 and 20 hours, respectively. The aim of this paper is to follow the solid phase transformation that occurs in the synthesis of barium hexaferrite using thermo gravimetric analysis.

(Received March 10, 2011; accepted July 25, 2011)

Keywords: Hexaferrite, Mechanical alloying, Solid phase transformation

1. Introduction

Mechanical treatment of ferrite materials has become very important in many processes in the technology of magnetic materials during the last few decades.

Hard magnetic barium ferrites maintain their strong position on the magnet market, due to their low cost and chemical resistance [5]. Recently nanocrystalline ferrites attract substantial attention due to their prospective applications for magnetic recording [2].

Barium hexaferrite synthesis strongly depends on the grain size [3].

Nanocrystalline barium ferrite can be obtained by mechanical alloying of initial materials [4].

The process uses Fe_2O_3 and $BaCO_3$ powders as starting components and comprises two stages:

- high energy ball milling of the powders and
- annealing (ferritization) of the milling product.

M type barium hexaferrite is formed by subjecting the homogeneous stoichiometric mixture of $BaCO_3$ and $\alpha - Fe_2O_3$ as starting material powders to thermal treatment operation of presintering (ferritising, calcining).

Barium hexaferrite was noted in the paper like FBM, because in the ternary diagram BaO-FeO- Fe_2O_3 this compound is rated M.

The ternary equilibrium diagram is presented in Fig. 1.

Also, an important influence occurs, namely, mineralization action in different proportions which largely mark the chemical composition and properties of the final product.

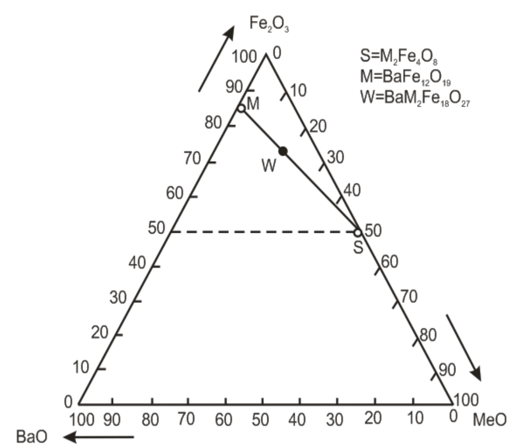


Fig. 1. Equilibrium diagram of FeO-BaO-Fe_2O_3 system

Barium hexaferrite is obtained by heating the stoichiometric homogeneous mixture of $BaCO_3$ and $\alpha - Fe_2O_3$ initial powder according to the reaction below:

$$BaCO_3 + 6Fe_2O_3 \rightarrow BaFe_{12}O_{19} + CO_2 \qquad (1)$$

This reaction occurs at elevated temperatures.

To do this successfully the thermo gravimetric analysis was used. Thus the research presented in the paper studies the mechanical alloying application process for 5 and 20 hours, respectively, on stoichiometric homogeneous mixture of $BaCO_3$ and $\alpha - Fe_2O_3$ as based powders with addition of SiO_2 in the form of quartz with mineralized effect.

2. Materials and experimental procedures

$BaCO_3$, α – Fe_2O_3 and SiO_2 powders were used as starting materials for the experiments. For obtaining FB-M, it is necessary to have a molar ratio n = FeO / BaO of 6 with the using of physico-chemical features shown in Table 1.

Table 1. Physico-chemical features of initial materials

Raw materials	Purity [%]	Particle size [μm]
Fe_2O_3	99,56	1,1
$BaCO_3$	99,38	1,2
SiO_2	96,88	1,2

To analyze the status of initial materials, we used the following types of powder mixtures, namely:

- stoichiometric homogeneous mixture of $BaCO_3$ and α – Fe_2O_3 micronic powders using Pulverisette 6 mill.
- stoichiometric homogeneous mixture of $BaCO_3$, α – Fe_2O_3 and SiO_2 micronic powders which was subjected 5 and 20 hours of milling, respectively, in a wet medium using a high energy ball mill Pulverisette 4.

To study the evolution of barium hexaferrite synthesis temperature reduction, SiO_2 was used with mineralized effect in concentration of 1 % from hematite content of the reaction mixtures.

We used this substance because it has several allotropic transformations during the heating process. The other forms, tridimit and cristobalit have not this property and presents a temperature close to solid phase reaction temperature of FB-M (870°C) synthesis as seen in Fig. 2 and by the other hand the quartz is forming an eutectic with hematite.

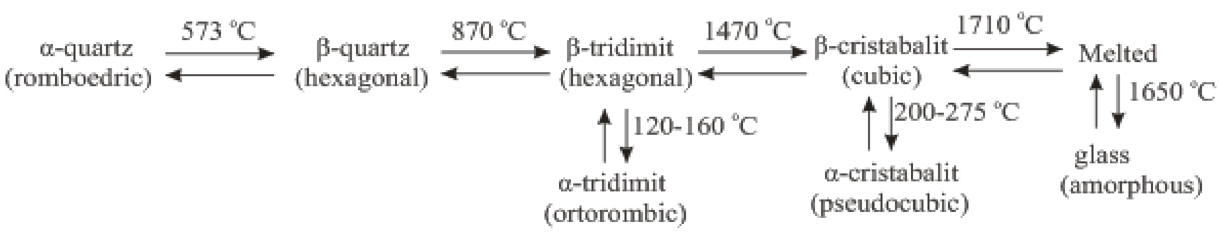


Fig. 2 . Allotropic transformation of quartz.

A BROOKHAVEN 90PLUS was used to determine the particle size distribution and a SHIMATZU SS-550 electron microscope was used for the powder granules study.

The thermodynamic processes occurring in the solid phase reaction was evaluated by thermo gravimetric analysis using a derivatograph.

3. Results and discussions

Regarding the determination of the particle size distribution, the stoichiometric homogeneous mixture of $BaCO_3$, α – Fe_2O_3 and SiO_2 micronic powders resulting from 5 and 20 hours of mechanical alloying, respectively, have the following results:

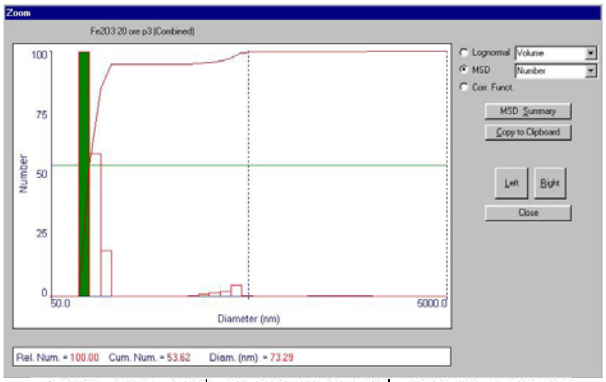
- the particle size distribution of stoichiometric homogeneous mixture after 5 hours of mechanical alloying is presented in figure 3 and shows two dimensional intervals namely [271.8, 368.2] nm and [1239.3,1678.6] nm, respectively.

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
200.7	0	0	462.3	0	94	1064.9	0	94
216.5	0	0	498.7	0	94	1148.8	0	94
233.6	0	0	538.0	0	94	1239.3	2	95
252.0	0	0	580.4	0	94	1337.0	7	97
271.8	42	12	626.2	0	94	1442.3	7	99
293.3	72	33	675.5	0	94	1556.0	2	99
316.4	100	62	728.7	0	94	1678.6	2	100
341.3	68	82	786.2	0	94	1810.9	0	100
368.2	40	94	848.1	0	94	1953.6	0	100
397.2	0	94	915.0	0	94	2107.5	0	100
428.5	0	94	987.1	0	94	2273.6	0	100

Fig. 3. Particle size distribution of Fe_2O_3, $BaCO_3$ and SiO_2 stoichiometric homogeneous mixture after 5 hours of mechanical alloying.

Most of the particles are in the first interval period, with an average size of 316.4 nm. The presence of the second period is due to powder agglomeration.

- after 20 hours of milling, the powder particle size is within [73.3,94.4] nm as shown in Fig. 4.



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
50.1	0	0	201.6	0	95	810.9	0	100
56.9	0	0	228.8	0	95	920.3	0	100
64.6	0	0	259.7	0	95	1044.4	0	100
73.3	100	54	294.7	1	95	1185.2	0	100
83.2	58	85	334.5	1	96	1345.1	0	100
94.4	19	95	379.6	2	97	1526.5	0	100
107.1	0	95	430.8	5	100	1732.4	0	100
121.6	0	95	488.9	0	100	1966.0	0	100
138.0	0	95	554.8	0	100	2231.1	0	100
156.6	0	95	629.6	0	100	2532.0	0	100
177.7	0	95	714.5	0	100	2873.5	0	100

Fig. 4. Particle size distribution of Fe_2O_3, $BaCO_3$ and SiO_2 stoichiometric homogeneous mixture after 20 hours of mechanical alloying.

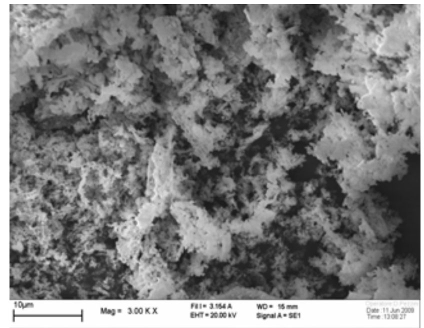
Some samples of milling in wet medium were taken from the mill after 5 and 20 hours of milling. Samples were analyzed by SEM electrons microscopy to determine the shape and size of powder nanogranules.

Micrographs of powder granules of Fe_2O_3, $BaCO_3$ and SiO_2 are presented in Fig. 5.

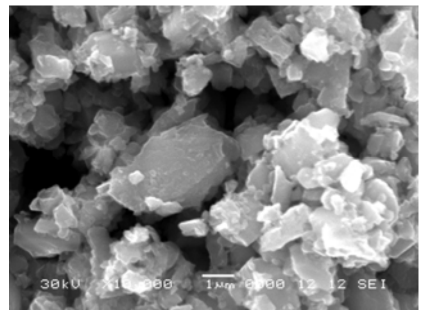
Small particle agglomerations can be observed in the SEM micrograph of the 20 h mechanical alloyed mixture.

The drawn diagram from figure 6 corresponding to the stoichiometric mixture of initial powders (unmilled) $BaOx6Fe_2O_3$ is considered the reference diagram and it can identify three thermal intervals of FB-M synthesis, namely:

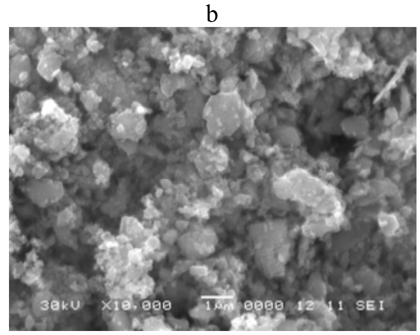
- In a heat range of 320-670^{o}C, the $BaCO_3$ decomposition occurs: $BaCO_3 \rightarrow BaO+CO_2\uparrow$
- In a heat range of 800-850 ^{o}C, the formation of barium monoferrite $BaFe_2O_4$ occurs
- In a heat range of 870-1100^{o}C, the formation of barium hexaferrite $BaFe_{12}O_{19}$ occurs



a



b



c

Fig. 5. SEM micrographs of powders milled in wet medium: a) mechanical unalloyed mixture, b) 5 h of mechanical alloyed mixture, c) 20 h of mechanical alloyed mixture.

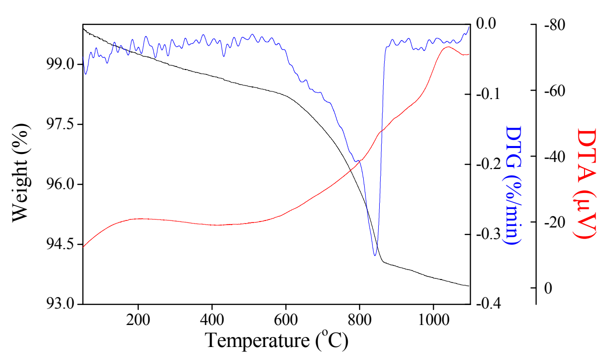


Fig. 6. Stoichiometric homogeneous mixture diagram of $BaOx6Fe_2O_3$ initial powders (unmilled) for M type ferrite

From the drawn diagram from Fig. 7, corresponding to the stoichiometric mixture of initial powders $BaOx6Fe_2O_3$ and 1 % SiO_2 concentration after 5 h of mechanical alloying, it can be identified three thermal intervals of FB-M synthesis, namely:

- In a heat range of 720°C, the $BaCO_3$ decomposition occurs: $BaCO_3 \rightarrow BaO+CO_2\uparrow$
- In a heat range of 650-750 °C, the formation of barium monoferrite $BaFe_2O_4$ occurs
- In a heat range of 810-990 °C, the formation of barium hexaferrite $BaFe_{12}O_{19}$ occurs

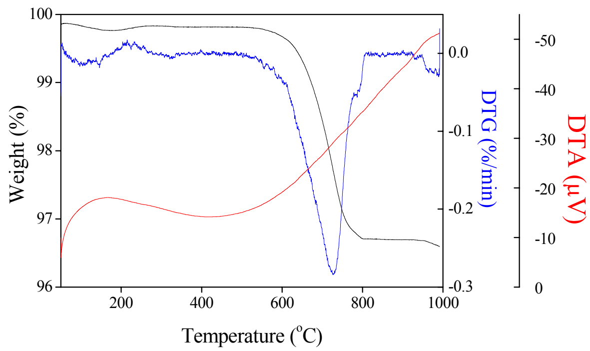


Fig. 7. Stoichiometric homogeneous mixture diagram of $BaOx6Fe_2O_3$ powders with 1% SiO_2 after 5 h of milling.

The diagram of the stoichiometric homogeneous mixture of $BaOx6Fe_2O_3$ and 1 % SiO_2 concentration after 20 h of mechanical alloying is presented in figure 8 and three thermal intervals of FB-M synthesis can be identified:

- In a heat range of 705°C, the $BaCO_3$ decomposition occurs $BaCO_3 \rightarrow BaO+CO_2\uparrow$
- In a heat range of 640-740 °C, the formation of barium monoferrite $BaFe_2O_4$ occurs
- In a heat range of 900-1080 °C, the formation of barium hexaferrite $BaFe_{12}O_{19}$ occurs

Based on data obtained from the figures 6 to 8 for the three mixtures, figure 9 shows the displacement caused by thermal effects of FBM mixture powder fineness.

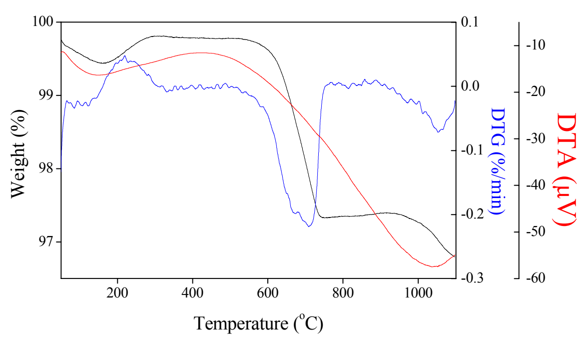


Fig. 8. Stoichiometric homogeneous mixture diagram of $BaOx6Fe_2O_3$ powders with 1% SiO_2 after 20 h of milling.

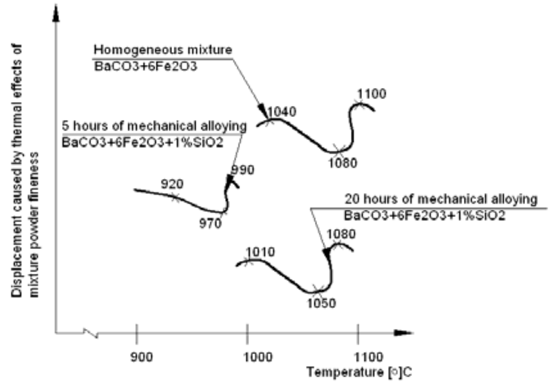


Fig. 9. Displacement caused by thermal effects of FB-M mixture powder fineness for all analyzed mixtures.

4. Conclusions

According to experimental data, we can draw the following conclusions:

- the fine division of powder mixtures is intensified with increasing of the milling time

- the use of SiO_2 mineralizator, as quartz, the temperature synthesis of M type barium hexaferrite is reduced by approximately 110°C for stoichiometric homogeneous mixture of 5 h of mechanical alloying.

After 20 h of mechanical alloying, the synthesis temperature of $BaFe_{12}O_{19}$ falls to around 1050°C due to the high fineness of the resulted mixture which tends to be crowded.

Acknowledgements

By this opportunity the authors want to give special thanks to Prof. PhD. Mihail Mangra from University of Craiova and to Engineer Rodica Chiriac from Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS−Université Claude Bernard Lyon 1, France.

References

[1] Yu. M. Vernigorov, I. N. Egorov, S.I. Egorova, Vestn. DGTU, **7**, 1(32), 31 (2007).
[2] Nobuhiro Matsushita, Kenji Noma, Shigeki Nakagawa and Masahiko Naoe, JMMM 176, 41 (1997).
[3] A. Witkowski, M. Leonowicz and W. Kaszuwara, Inzynieria Materialowa XXV (2000)140.
[4] J. Ding, W.F. Miao, P.G. McCormick, R. Street, Journal of Alloys and Compounds **281**, 32 (1998).
[5] S. Brassard, B. Champigny, ST Pierre d'Allevard, Hard ferrite in automotive motors application and their competitiveness regarding other permanent magnet materials.
[6] http://www.aacg.bham.ac.uk/magnetic materials/

*Corresponding author: stefan_iuly@yahoo.com