The 4th International Conference
"Advanced Composite Materials Engineering "
COMAT 2012
18- 20 October 2012, Brasov, Romania

RESEARCH ON MECHANICAL ALLOYING EFFECTS ON MAGNETIC PROPERTIES OF BARIUM FERRITE TYPE M

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Abstract: *The paper presents the effects of mechanical alloying process of $BaCO_3$ and αFe_2O_3 powders on the magnetic properties of barium ferrite type M.*
For preparation of the magnetic ferrite powders was used a physical method as mechanical ball milling method.
The powders magnetic property was characterized with a Vibrating Sample Magnetometer. The phase's structure was presented by an X-ray diffractometer. The morphology of the powder was observed with a particle size analyzer and a scan electron microscope.
There was observed a significant increase in remanence magnetization and coercive field of barium ferrite samples obtained by mechanical alloying.
Keywords: *barium ferrite, mechanical alloying, remanence, coercive field.*

1. INTRODUCTION

Barium ferrite type M is widely used in the fabrication of commercial permanent magnets, computer data storage, high density perpendicular magnetic and magneto-optic recording, magnetic fluids and microwave devices [1–3].
This type of ferrite is termed as hard ferrite due to their high coercive force, high saturation magnetization, high Curie temperature, chemically inert and mechanically resilient [4].
Mechanical alloying is one of the suitable processing techniques for synthesis of ferrite powders.
Homogenous distribution of the powder particles after mechanical alloying is an important factor which affects the ferritization process and the magnetic properties of ferrites. From this point of view, milling in water should be beneficial for the material properties, because distribution of particles size is narrower than in the case of milling in air [5]. For this reason, all the experiments of this work were carried out in water.
This present work aims to study the mechanical alloying effects of iron oxide Fe_2O_3 and barium carbonate $BaCO_3$ powders on magnetic properties of barium ferrite type M. Were studied three powder mixtures.
The first mixture, also known as reference mixture (denoted RM) was performed by mixing the Fe_2O_3 and $BaCO_3$ powders for 30 minutes in a planetary mill. The other two mixtures were carried out by mechanical alloying process for 4 to 12 hours (denoted MA4 and MA12). All the mixtures were heated to the same temperature and we pursued the influence of the mechanically alloyed powders on their magnetic properties.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

For synthesis of barium ferrite $BaFe_{12}O_{19}$, mixture of iron oxide Fe_2O_3 (99% purity) and barium carbonate $BaCO_3$ (99% purity) powders was used with composition $BaCO_3 + 6Fe_2O_3$ (Figure1).

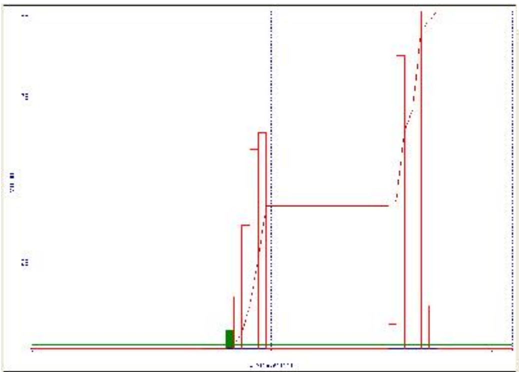
a) Fe_2O_3 **b)** $BaCO_3$

Figure 1: Fe_2O_3 and $BaCO_3$ powders used for mechanical alloying process

The used powders were weighed out in stoichiometric proportion in order to form the desired composition.
These starting materials were mixed by a mechanical activation process. Ball milling process was carried out in a vibratory mill type Pulverisette 4 for 4 and 12 hours in water medium. A mass ratio ball to powder was 4:1. The mill generated vibrations of balls and the material inside the container during which their collisions occur [6,7].
After milling process the initial powders were analyzed by thermal analysis in air atmosphere. The phases structure were presented by an X-ray diffractometer.
The morphology of the powder was observed with a particle size analyzer and a scan electron microscope.
The magnetic hysteresis loops of obtained powder material were measured by a Vibrating Sample Magnetometer.

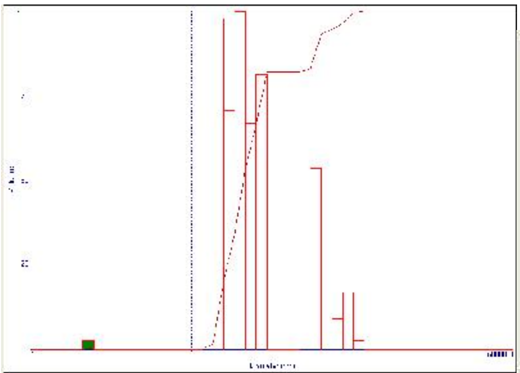
3. RESULTS AND DISCUSSIONS

There were analyzed from morphological point of view the initial materials used to form barium ferrite type M and the mixtures resulting from mechanical alloying too. Thus, in figure 2 and 3 are presented the particle size distribution of $BaCO_3$ and Fe_2O_3 powders and in figures 4 and 5 are shown the mechanically alloyed mixtures of $BaCO_3x6Fe_2O_3$ powders for 4 and 12 hours.



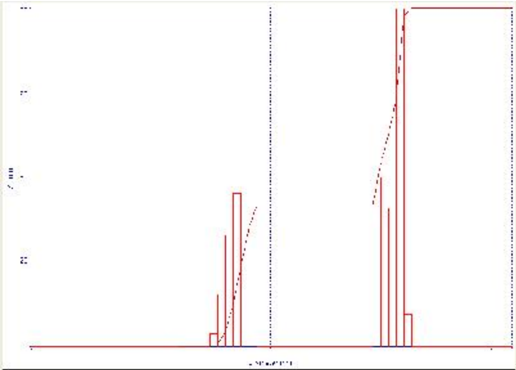
d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
264.2	0	0	621.6	0	42	1462.8	0	42
285.6	0	0	671.9	0	42	1581.1	7	44
308.7	0	0	726.3	0	42	1709.0	87	64
333.6	5	1	785.1	0	42	1847.3	28	71
360.6	15	5	848.6	0	42	1996.8	100	95
389.8	36	13	917.2	0	42	2158.3	11	97
421.3	59	27	991.4	0	42	2332.9	13	100
455.4	64	42	1071.6	0	42	2521.6	0	100
492.3	0	42	1158.3	0	42	2725.6	0	100
532.1	0	42	1252.0	0	42	2946.1	0	100
575.1	0	42	1353.3	0	42	3184.5	0	100

Figure 2: Particle size distribution of $BaCO_3$ initial powders



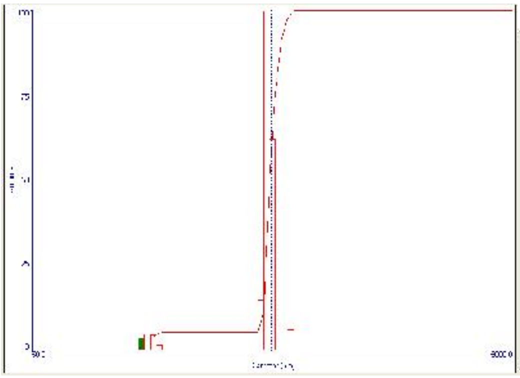
d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
60.6	0	0	334.3	0	0	1845.2	0	82
70.7	0	0	390.4	0	0	2155.2	0	82
82.6	0	0	456.0	0	0	2517.3	5	83
96.5	0	0	532.7	0	0	2940.2	54	93
112.7	3	0	622.1	6	2	3434.2	6	95
131.6	0	0	726.7	98	20	4011.2	9	96
153.8	0	0	848.8	70	34	4685.2	17	100
179.6	0	0	991.4	100	53	5472.4	2	100
209.8	0	0	1157.9	67	66	6391.8	0	100
245.0	0	0	1352.5	81	82	7465.8	0	100
286.2	0	0	1579.7	0	82	8720.1	0	100

Figure 3: Particle size distribution of Fe_2O_3 initial powders



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
215.3	0	0	485.8	0	42	1096.0	0	42
231.8	0	0	523.0	0	42	1180.1	0	42
249.6	0	0	563.2	0	42	1270.7	0	42
268.8	0	0	606.4	0	42	1368.3	50	54
289.4	4	1	653.0	0	42	1473.3	35	63
311.6	15	5	703.1	0	42	1586.5	41	73
335.6	33	13	757.1	0	42	1708.3	100	98
361.3	45	24	815.3	0	42	1839.4	9	100
389.1	44	35	877.9	0	42	1980.6	0	100
419.0	26	42	945.3	0	42	2132.7	0	100
451.1	0	42	1017.8	0	42	2296.4	0	100

Figure 4: Particle size distribution of $BaCO_3xFe_2O_3$ powders after 4 hours of milling



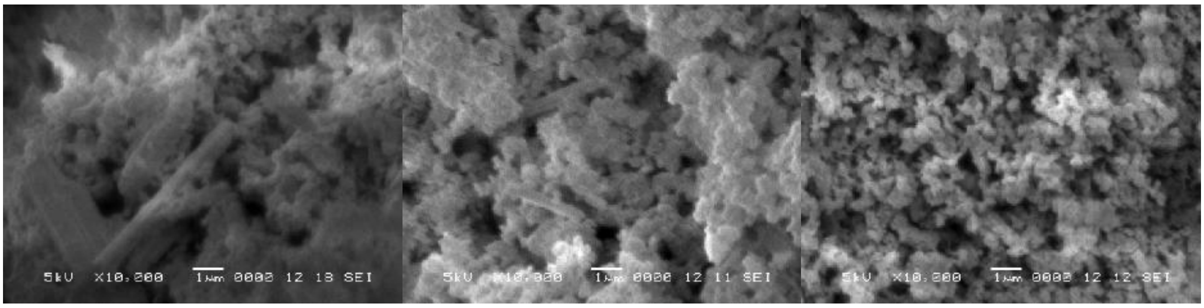
d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
120.2	0	0	225.2	0	5	422.1	0	5
127.2	0	0	238.4	0	5	446.9	14	11
134.7	0	0	252.4	0	5	473.1	100	51
142.6	3	1	267.3	0	5	500.9	62	76
151.0	4	3	283.0	0	5	530.4	39	91
159.9	4	5	299.6	0	5	561.5	16	98
169.3	1	5	317.2	0	5	594.5	6	100
179.2	0	5	335.9	0	5	629.5	0	100
189.7	0	5	355.6	0	5	666.5	0	100
200.9	0	5	376.5	0	5	705.6	0	100
212.7	0	5	398.6	0	5	747.1	0	100

Figure 5: Particle size distribution of $BaCO_3xFe_2O_3$ powders after 12 hours of milling

Particle size ranges and maximum size of analyzed powder particles were systematized in table 1 and in figure 6 are shown the SEM micrographs of the $BaCO_3xFe_2O_3$ samples mechanically alloyed and unalloyed.

Table 1: Particle size ranges and maximum particle size of materials

Sample No.	Initial materials used in mixtures of BFM	Granulometric ranges [nm]	Maximum size of particles [nm]
1	$BaCO_3$	[333.6 – 455,6] [1581,1 - 2332,9]	1996,8
2	Fe_2O_3 unmilled	[622,1 – 1352,5] [2517,3 – 5472,4]	991,4
3	$BaCO_3xFe_2O_3$ milled 4 hours	[289,4 – 419,0] [1368,3 – 1839,4]	1708,3
4	$BaCO_3xFe_2O_3$ milled 12 hours	[142,6 – 169,3] [446,9 – 594,5]	473,1



a) **b)** **c)**

Figure 6: SEM micrographs of the $BaCO_3xFe_2O_3$ samples: **a)** unmilled; **b)** milled for 4 h; **c)** milled for 12 h

From the obtained data, it can be seen that powders particle size decreases with increasing of mechanical alloying time. The SEM micrograph of the milled sample for 12 hours, shows that the size of powder particles belongs to the submicron field.
In order to determine the heating temperature of $BaCO_3$ and Fe_2O_3 powders was performed the thermogravimetric analysis using a MOM derivatograph device. Heating process was performed with 10°C/min. The diagram of the $BaCO_3x6Fe_2O_3$ mixture is shown in figure 7.

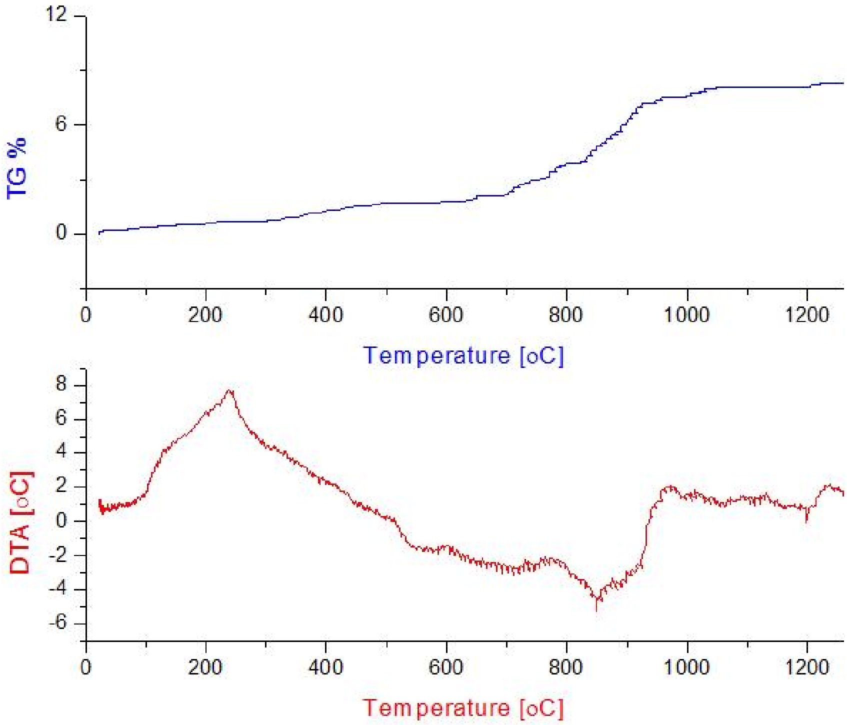


Figure 7: Diagram of $BaCO_3x6Fe_2O_3$ mixture: cuves TG and DTA

Analyzing the TG and DTA curves obtained from heating the mixture of $BaCO_3x6Fe_2O_3$ powders it can be observed two pronounced endothermic peaks at temperatures of 850 and 1100°C. The peak from temperature of 850oC placed on the DTA curve is related to weight loss slope from TG curve at the same temperature where a reaction product is formed. In order to identify the reaction product, a mixture of $BaCO_3x6Fe_2O_3$ was heated up to a temperature of 850oC, then was suddenly cooled in water and was subjected to X-ray diffraction, and is observed in the diffractogram from figure 8 that at this temperature is born barium monoferrite, $BaFe_2O_4$.
On the DTA curve is also observed another peak at 1200oC corresponding to the formation of a new phase which was identified by X-ray diffraction (figure 9) as barium ferrite (BFM).

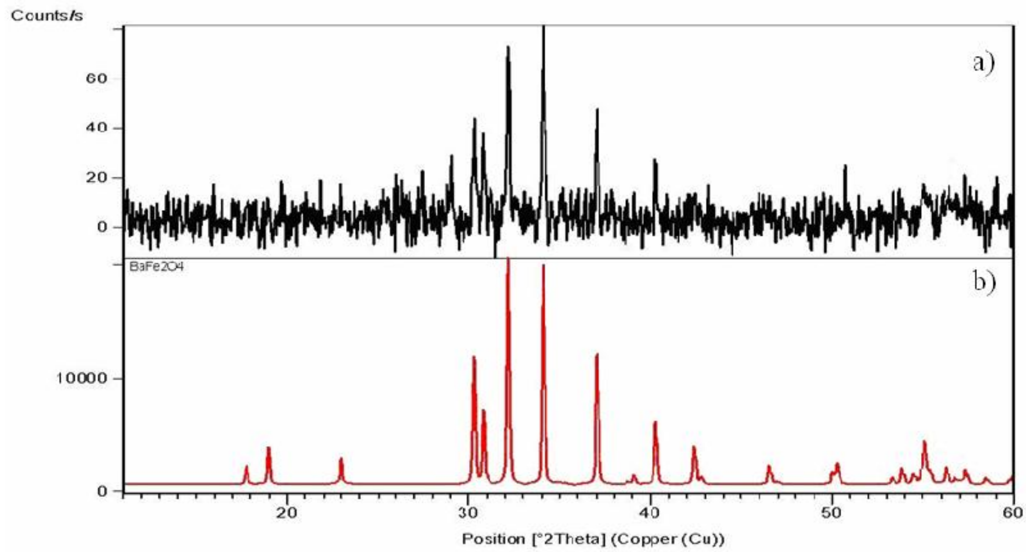


Figure 8: X-ray diffraction of $BaCO_3x6Fe_2O_3$ sample heated at 850°C: a) sample; b) monoferrite phase

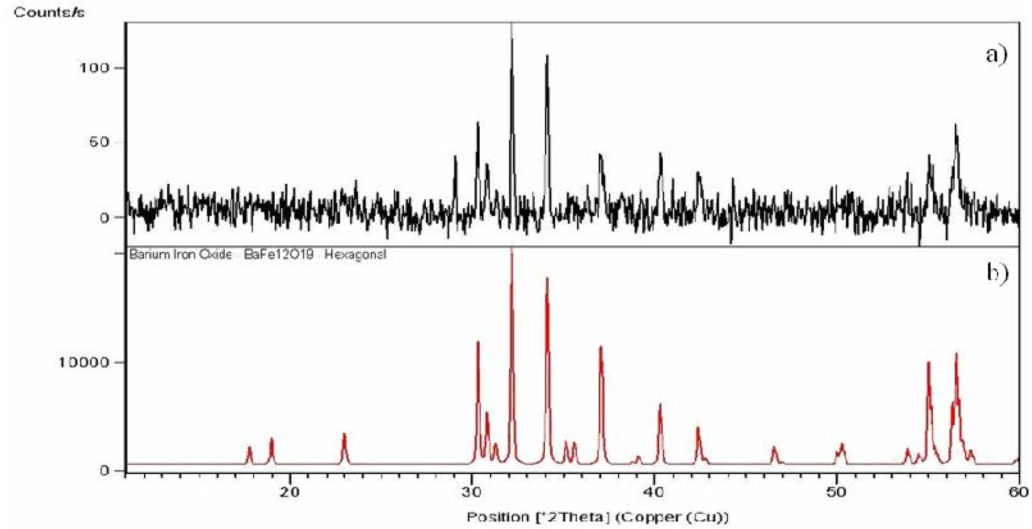
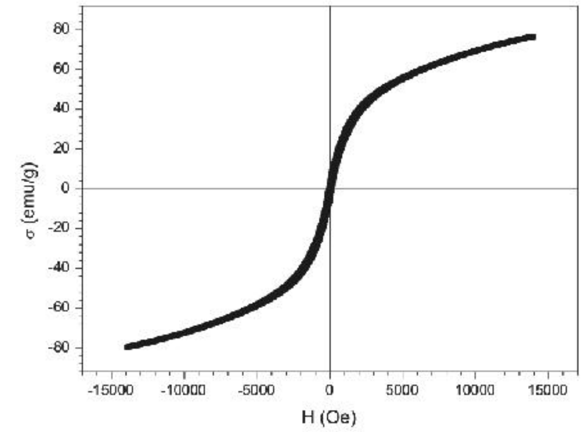
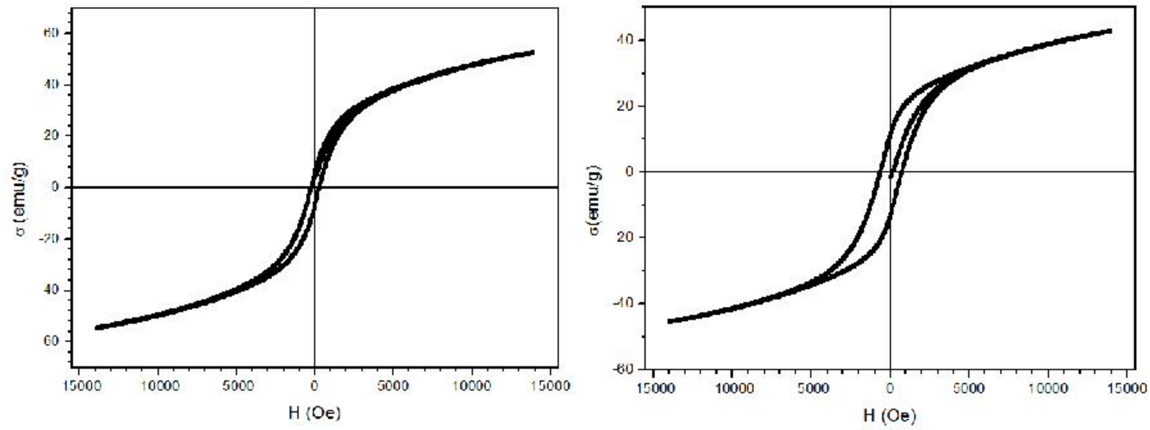


Figure 9: X-ray diffraction of $BaCO_3x6Fe_2O_3$ sample heated at 1200°C: a) sample; b) ferrite phase

The magnetic hysteresis loops of obtained barium ferrite were measured by a Vibrating Magnetometer and there are presented in figure 10.



a)



b) c)

Figure 9: Magnetic hysteresis loops of $BaCO_3xFe_2O_3$ samples: **a)** unmilled; **b)** milled for 4 h; **c)** milled for 12 h

The magnetic characteristics of obtained ferrite are presented in table 2. From hysteresis loops and from table 2 is observed an increase in magnetic properties once with increasing of mechanical alloying time. Remanent magnetization σr reaches the value of 8 emu/g and coercive field has a value of 250 Oe for $BaCO_3x6Fe_2O_3$ sample mechanically alloyed 4 hours.

The mechanical alloyed sample for 12 hours shows much higher values of remanent magnetization and the coercive field, respectively 12 emu/g and 800 Oe.

Table 2: The magnetic characteristics of barium ferrite samples

Sample / Mag. Param.	MA4	MA12
σ_r /emu/g	8	12
Hc/Oe	250	800

4. CONCLUSIONS

Analyzing the results from experimental research can conclude the following:

- increasing of mechanical alloying time for $BaCO_3$ and Fe_2O_3 mixtures lead to a reduction of powders particle size starting from micron field and reaching in the submicron field after 12 hours of mechanical alloying;
- mechanical alloying time influence the magnetic characteristics of barium ferrite type M samples;
- it can be seen that ferrite derived from mechanically alloyed mixture for 12 hours has the highest amount of remanent magnetization, namely σr =12 emu/g;
- regarding to the coercive field value it is found that this increases to a value of 800 Oe for ferrite obtained by mechanical alloying for a longer time. As it is known, the coercive field is influenced by the particle size of the magnetic powder.

The more the mechanical alloying time increases, or the more particle size of $BaCO_3$ and Fe_2O_3 powders tend to the nanometer field, the better the magnetic properties are.

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