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Thermogravimetric studies on the BHF synthesis of $BaCO_3$ and α-Fe_2O_3 mixtures processed by mechanical alloying

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The paper presents the results of experimental research regarding barium hexaferrite synthesis from $BaCO_3$+6α-Fe_2O_3 powders processed by mechanical alloying for 5 and 20 hours. The influence of the mechanical alloying time on synthesis temperature of barium hexaferrite (BHF) was determined by thermogravimetric analysis. Research has revealed that using stoichiometric mixtures prepared by mechanical alloying leads to a significant reduction of BHF synthesis temperature. The obtained results shows a reduction of BHF synthesis temperature by 4 % in case of mechanically alloyed mixture for 5 hours and by 12 % in case of mechanically alloyed mixture for 20 hours.

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Keywords: Hexaferrite, Mixture, Mechanical alloying, Hematite

1. Introduction

Nowadays, the demand for the development of new magnetic materials has increased extraordinarily, owing to their applications in new emerging technologies. This relates to the big research effort carried out on barium hexaferrites, $BaFe_{12}O_{19}$, used mainly for the permanent magnets [1].

Recently, there are various routes of synthesis of barium hexaferrite and its magnetic properties are very much dependent on the processing routes and microstructures [2,3,4,5].

A ball milling technique has been widely used to prepare hard ferrite powders [6,7]. This is a simple route to produce hexaferrite powders of very small particles and morphology [8].

The aim of the paper is to obtain barium hexaferrite by using α-Fe_2O_3 and $BaCO_3$ mechanically alloyed powders in wet medium for 5 respectively 20 hours. For this purpose, the thermogravimetric analysis of obtained mixtures was made. Thus, it was obtained a reduction of BHF synthesis temperature up to 12 % for mechanically alloyed mixture a longer time in wet medium compared with the homogenized mixture in dry medium for 30 minutes (mixture used in paper as reference work).

Experimental research results have revealed that using $BaCO_3$ and α-Fe_2O_3 powders in stoichiometric ratio prepared by mechanical alloying, significantly reduce the temperature of BHF synthesis.

2. Materials and experimental procedures

Barium carbonate $BaCO_3$ and iron oxide Fe_2O_3 (hematite) are the initial materials used in the manufacture of barium hexaferrite by calcination process.

In table 1 are presented the materials used in research and the main elements needed to calculate the composition of barium hexaferrite mixtures. Thus, for experiments were made three mixtures, the first mixture is formed by $BaCO_3$ and α-Fe_2O_3 powders which was homogenized in a ball mill Pulverisette 6. The second and the third mixtures are formed by $BaCO_3$ and α-Fe_2O_3 mechanically alloyed powders for 5 respectively 20 hours in a ball mill Pulveristte 4.

Table 1 Mixtures used for research

Sample codes	Mixture type	Ratio Fe_2O_3/BaO	Purity α-Fe_2O_3 [%]	Purity $BaCO_3$ [%]	BaO in $BaCO_3$	Initial mixture composition	
						α-Fe_2O_3	$BaCO_3$
						%	%
HM	Homogeneous mixture	6	99.56	99.38	77.23	82.96	17.04
MA5h	Mechanically alloyed mixture 5 hours						
MA20h	Mechanically alloyed mixture 20 hours						

$BaCO_3$ and α-Fe_2O_3 powders were homogenized for 30 minutes in dry medium while mechanically alloyed mixtures were carried out in wet medium using distilled water and daxad solution.

It was used wet working medium, because it provides a better homogeneity and a significant reduction of powders particle size. The mixing ratio of powder/balls was 1:2.

After 5 respectively 20 hours of effective milling, slurries obtained were dried in an oven and then uncrowded for 3 minutes in a planetary ball mill.

After homogenization and mechanical alloying, the mixtures of $BaCO_3$ and α-Fe_2O_3 powders were analyzed from morphology point of view using a BROOKHAVEN 90PLUS device.

A SHIMATZU SS-550 electron microscope was used for the powder granules study.

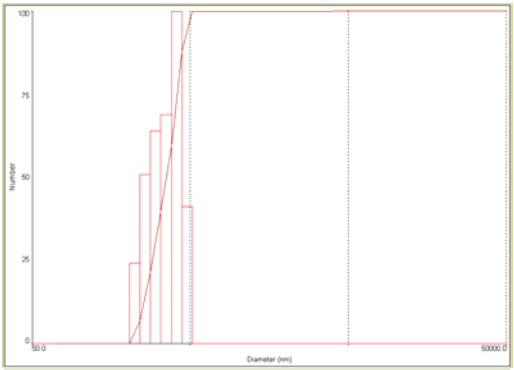
Slurries resulted from mechanical alloying process were air dried and then were dosed by weighing using an analytical balance and placed in a derivatograph MOM Budapest for thermogravimetric analysis.

Phase identification of the samples was carried out by X-ray diffractometer (D8 Discover (Bruker)) in θ–2θ geometry using Cu Kα radiation of wavelength 1.5418 Å and a step size of 0.05°.

3. Results and discussions

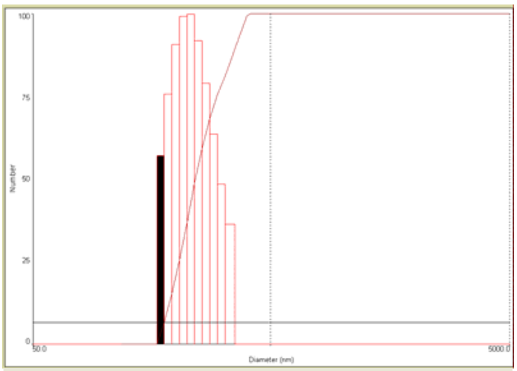
3.1. Powder morphology

The data regarding particle size distributions of the $BaCO_3$ and α-Fe_2O_3 initial powders and mechanically alloyed mixtures for 5 and 20 hours are shown in figure 2.



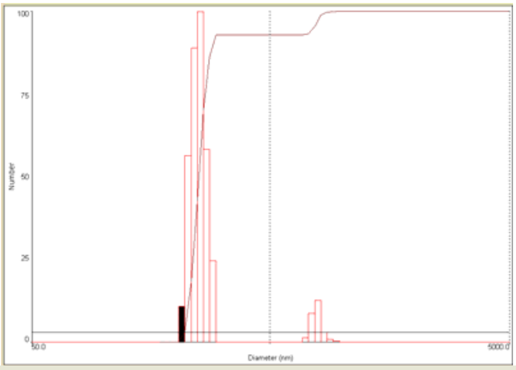
d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
76.2	0	0	407.5	0	88	2178.6	100	100
88.8	0	0	474.6	0	100	2537.2	41	100
103.4	0	0	552.8	0	100	2954.9	0	100
120.4	0	0	643.8	0	100	3441.3	0	100
140.2	0	0	749.7	0	100	4007.8	0	100
163.3	0	0	873.1	0	100	4667.6	0	100
190.2	0	0	1016.9	0	100	5435.9	0	100
221.5	0	7	1184.3	24	100	6330.7	0	100
258.0	0	21	1379.2	51	100	7372.9	0	100
300.5	0	40	1606.3	64	100	8586.5	0	100
349.9	0	59	1870.7	69	100	10000.0	0	100

a)



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
193.5	0	0	335.6	0	7	581.7	0	7
203.5	0	0	352.8	0	7	611.6	58	7
213.9	0	0	370.9	0	7	643.0	74	8
224.9	0	0	389.9	0	7	675.9	85	12
236.4	0	1	409.9	0	7	710.6	98	27
248.5	0	2	430.9	0	7	747.1	100	69
261.3	0	4	453.0	0	7	785.4	88	97
274.7	0	6	476.2	0	7	825.7	68	100
288.8	0	7	500.7	0	7	868.0	48	100
303.6	0	7	526.4	0	7	912.5	38	100
319.2	0	7	553.4	0	7	959.4	0	100

b)



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
62.5	0	0	204.3	10	9	668.1	0	88
69.6	10	0	227.6	13	9	744.1	0	88
77.5	58	0	253.4	5	10	828.7	0	90
86.3	93	3	282.3	3	14	922.9	0	91
96.1	100	7	314.3	2	23	1027.8	0	94
107.1	66	9	350.1	0	37	1144.7	0	96
119.2	23	9	389.9	0	61	1274.9	0	97
132.8	0	9	434.2	0	88	1419.9	0	100
147.9	0	9	483.6	0	88	1581.3	0	100
164.7	0	9	538.6	0	88	1761.2	0	100
183.5	3	9	599.9	0	88	1961.4	0	100

c)

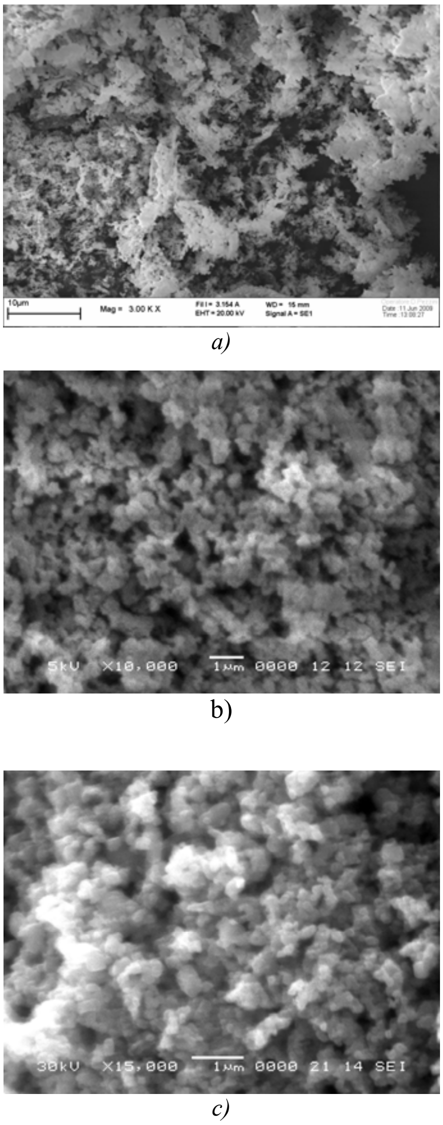
Fig. 2. Particle size distributions of $BaCO_3x6\alpha$-Fe_2O_3 mixtures: a) homogeneous stoichiometric mixture; b) mechanically alloyed mixture for 5 hours; c) mechanically alloyed mixture for 20 hours

The results regarding particle size distribution of the analyzed samples are presented in table 2:

Table 2. Particle size ranges and maximum size of particles for BHF mixtures.

Sample No.	Stoichiometric mixtures	Particle size ranges [μm]	Maximum size of particles [μm]
1	HM	[1.18 – 2.53]	2,17
2	MA5h	[0.61 – 0.91]	0,74
3	MA20h	[0.069 – 0.11] [0.18 – 0.31]	0,096

It appears that for the initial powder mixture was obtain a size range between 1,1 and 2,5 μm where the most particles have a size of 2,1 μm.



a)

b)

c)

Fig. 3 SEM images for mixed $BaCO_3x6\alpha\text{-}Fe_2O_3$ powders: a) homogeneous stoichiometric mixture; b) mechanically alloyed mixture for 5 hours; c) mechanically alloyed mixture for 20 hours.

The majority size fraction for mechanical mixture resulted after 5 hours of milling (MA5h) show a size range with values between 0,61 - 0,91 μm where the maximum particles fits at the value of 0,74 μm, which shows that the powder is in submicron area. After 20 hours of mechanical alloying (MA20h) were recorded two particle size classes with values between 0,069 – 0,11 μm and 0,18-0,31 μm, and the maximum particles fit to the value of 0,096 μm. There are very fine powders with particles located in the nanometer area.

Some samples milled 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 particles. Micrographs of $BaCO_3x6\alpha\text{-}Fe_2O_3$ mixtures are presented in fig. 3.

The microscopic aspects reveal the presence of polygonal-shaped grains for both samples mechanically alloyed for 5 and 20 hours. Irregular edges powder particles are likely to provide good compressibility of powders resulted by mechanical alloying. Small particles can be observed in the SEM micrograph for the mechanical alloyed mixture 20 h.

3.2. Thermogravimetric analysis and XRD

Barium hexaferrite is obtained by heating the mixture of $\alpha\text{-}Fe_2O_3$ and $BaCO_3$ powders. Heating was carried out using a MOM Budapest derivatograph.

The heating parameters of the derivatograph for $BaCO_3x6\alpha\text{-}Fe_2O_3$ powders were:

- heating up to 1500°C with a constant speed of 10°C/min;
- DTA sensitivity = 1/13;
- TG sensitivity = 200.

The drawn diagram at resistive heating for $BaCO_3x6\alpha\text{-}Fe_2O_3$ reference stoichiometric mixture HM (resulted by 30 minutes of homogenization in dry conditions) is shown in figure 4, and according to the diagram, there is found on the TG curve a significant decrease of sample weight in the heat range between (680-870)°C and is due to the decomposition of barium carbonate and CO_2 loss.

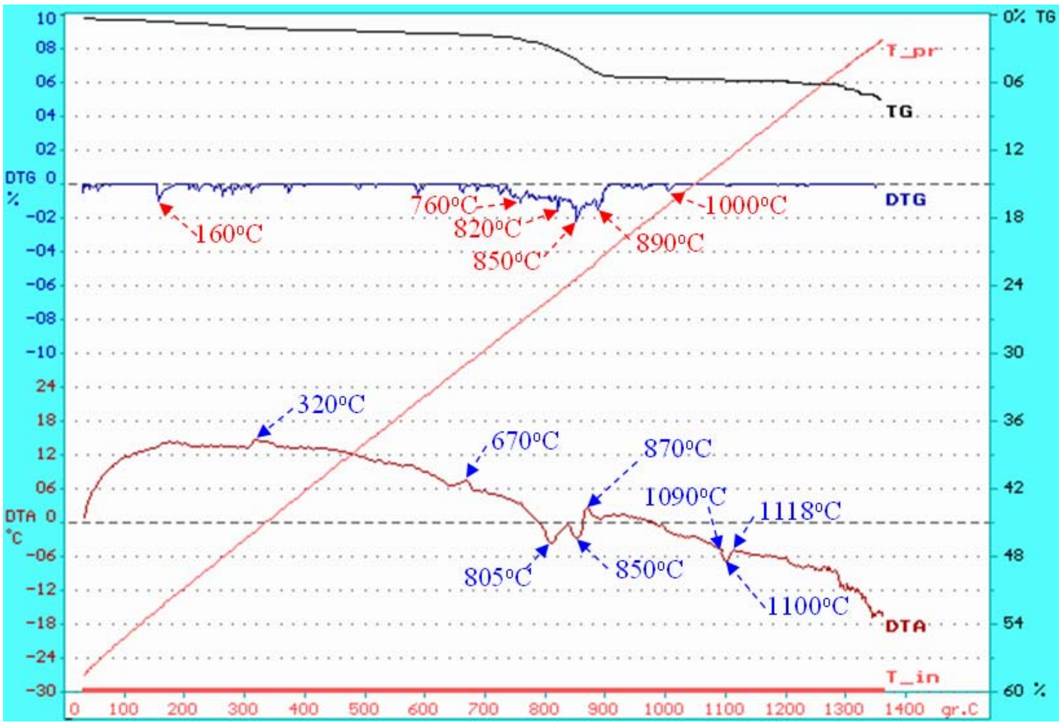


Fig. 4. The diagram of homogeneous mixture, HM

It can be seen from the obtained diagram an endothermic peak at 805°C, attributed to a crystalline transition of $BaCO_3$ remained unreacted (undecomposed) up to this temperature in the time interval specific to the heating rate. Correlated with this transition, occurs another peak of weight loss at 850°C where a reaction product is formed. This peak is visible both on the DTG and DTA curve and represents the formation of barium monoferrite, $BaFe_2O_4$.

DTA curve also presents an exothermic peak at 870°C, which after XRD investigation, was found that this presents the beginning of barium hexaferrite synthesis.

On the DTA curve is observed a peak at 1100°C corresponding to formation of a new phase that was identified by X-ray diffraction (figure 5) as being barium hexaferrite (BHF).

According to the diagram and to the thermal values on the DTA curve, the thermal range of hexaferrite synthesis (BHF) is (1090-1118) °C and the peak from 1100°C is due to the maximum intensity of phase transformation, namely, BHF synthesis.

Further, in the figure 6 is presented the corresponding diagram for $BaCO_3$x6α-Fe_2O_3 mixture resulting from mechanical alloying for 5 hours.

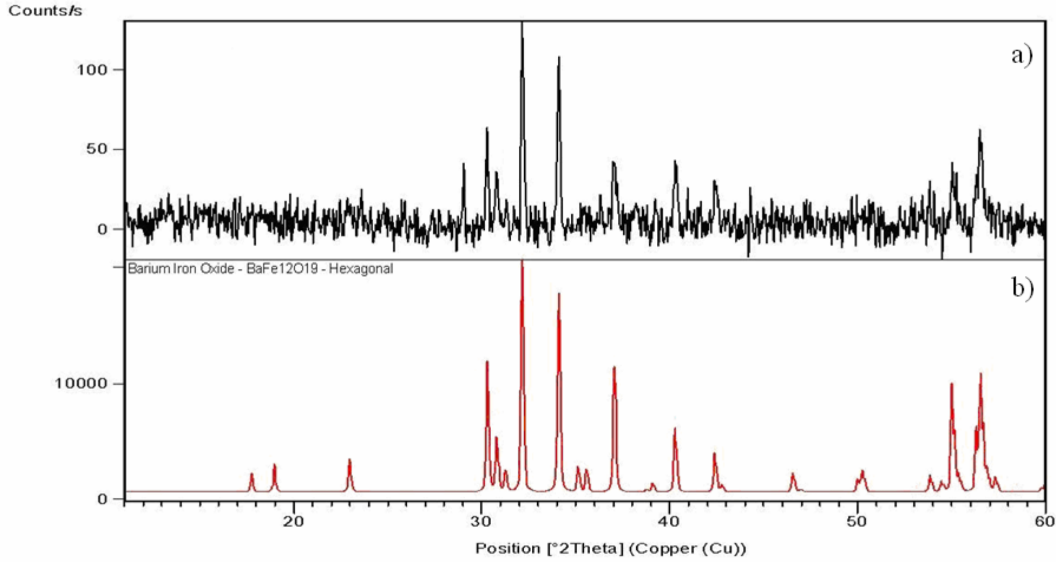


Fig. 5 XRD patterns of homogeneous mixture (HM): a) sample; b) hexaferrite phase

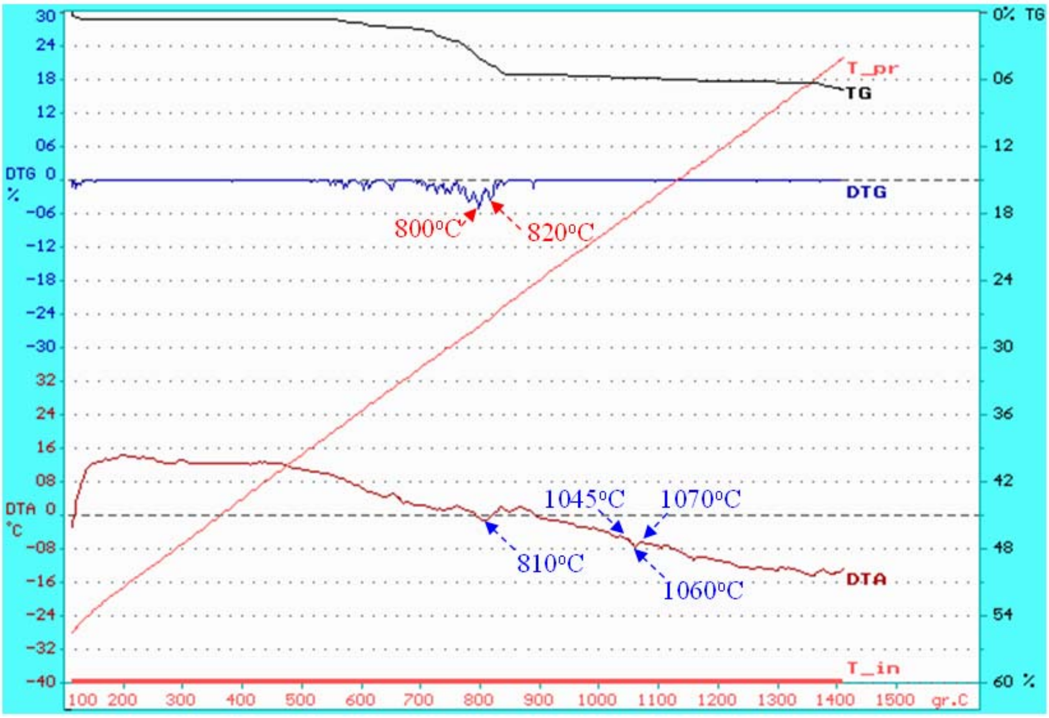


Fig. 6 The diagram of mechanically alloyed mixture, MA5h

On this diagram, we identify the endothermic peak from temperature of 810°C corresponding to monoferrite formation and another peak at 1060°C corresponding to barium hexaferrite synthesis according to the X-ray diffraction from figure 7. Total weight loss at heating process of this powder is 7 %.

Further, is presented in the figure 8 the diagram corresponding to $BaCO_3x6\alpha\text{-}Fe_2O_3$ mixture resulting from mechanical alloying for 20 hours.

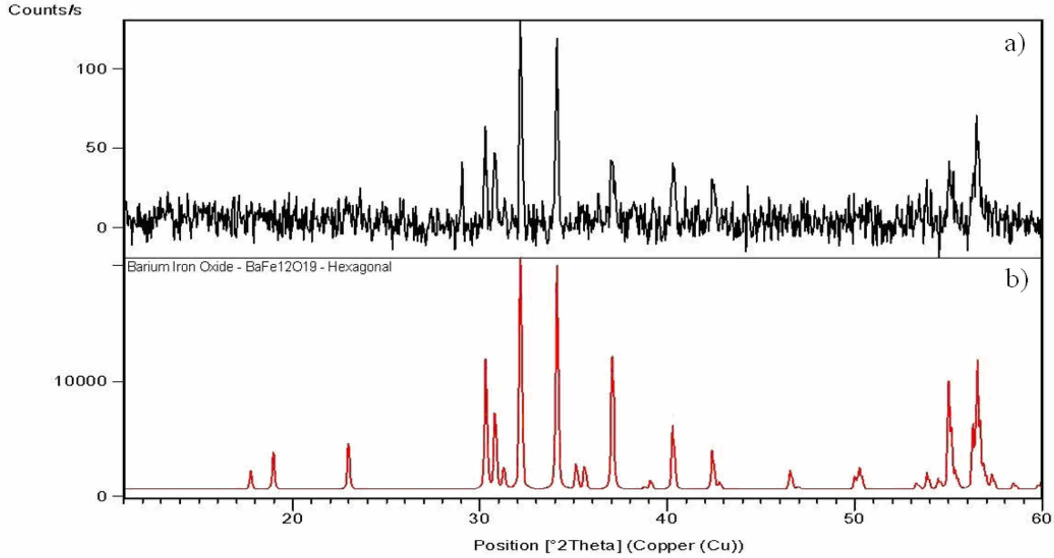


Fig. 7 XRD patterns of mechanically alloyed mixture for 5 hours (MA5h) heated at 1060°C: a) sample; b) hexaferrite phase

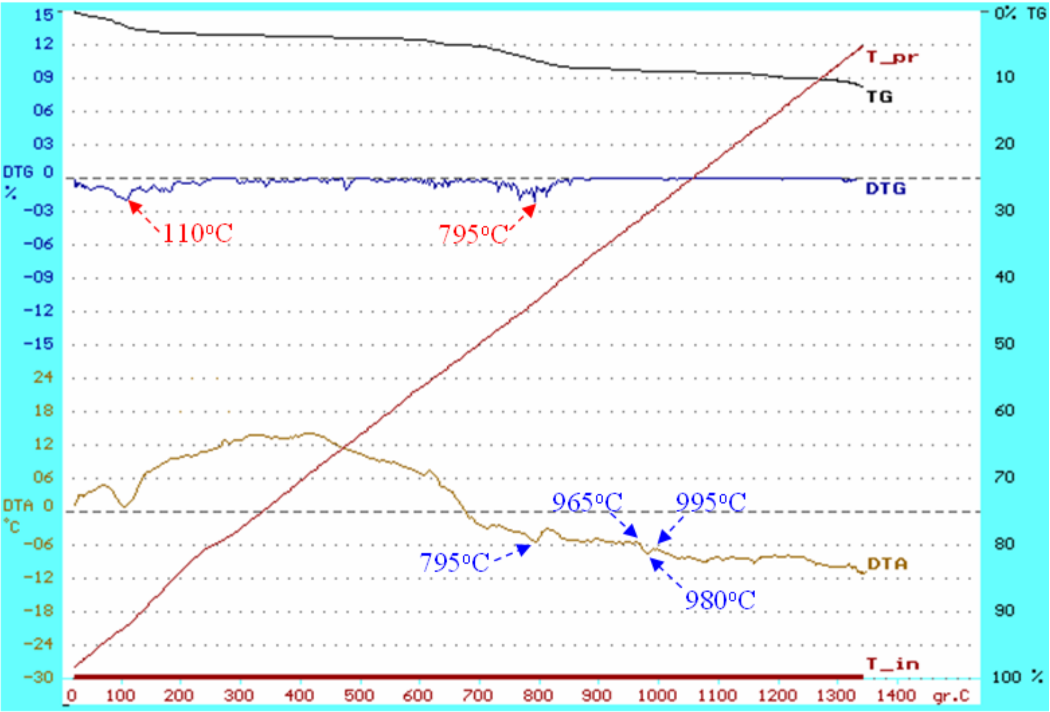


Fig. 8 The diagram of mechanically alloyed mixture, MA20h

On the DTA curve, we identify the peak at 795°C corresponding to barium monoferrite formation and further the peak at approximately 980°C corresponding to maximum intensity of reaction for barium hexaferrite synthesis , according to the X-ray diffraction from Fig. 9.

Total weight loss at heating process of this sample is 11 %.

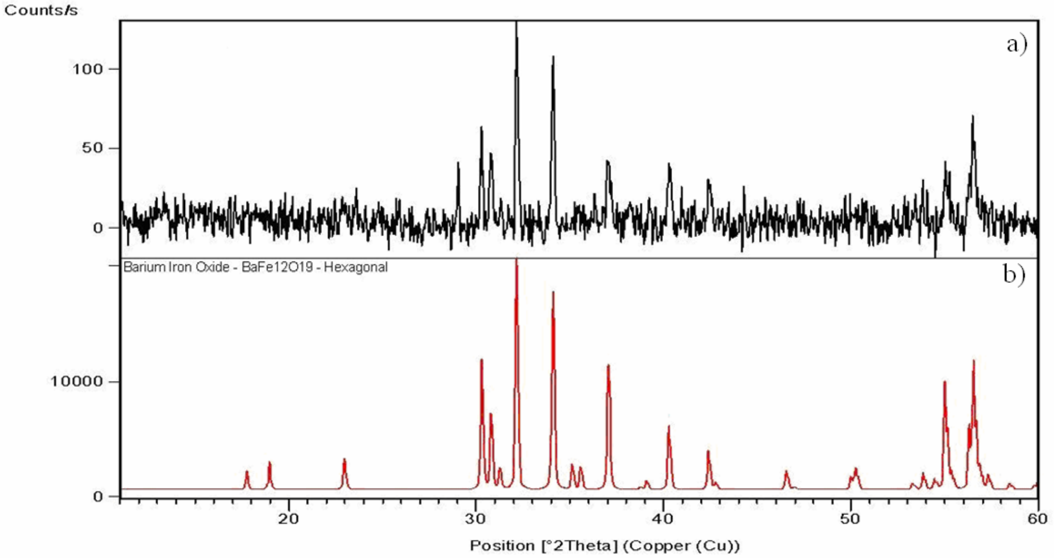


Fig. 9 XRD patterns of mechanically alloyed mixture for 20 hours (MA20h) heated at 980°C:
a) sample; b) hexaferrite phase

In Table 3, are presented the values of phase transformations at the formation of barium monoferrite and BHF by ferritisation of mechanically alloyed mixtures compared with the reference mixture, HM.

Table 3. Values of phase transformations at BHF synthesis

Sample No.	Sample code	Values of phase transformations for monoferrite (°C)	Values of phase transformations for hexaferrite (°C)			ΔT	
			Start reaction	Maximum reaction	End reaction	°C	[%]
1	HM	**850**	**1090**	**1100**	**1118**	**0**	**0**
2	MA5h	810	1045	1060	1070	40	3,64
3	MA20h	795	965	980	995	120	10,91

Compared with the reference mixture, HM, it can be observed a decreases of the synthesis temperature of barium hexaferrite up to 10,91 % for the mechanical mixture. It can also be seen that, when the mechanical alloying time increase then is reduced the synthesis temperature of BHF by 40°C for MA5h respectively 120°C for MA20h.

Therefore, an important observation for industrial application is that, mechanical alloying of stoichiometric mixture leads to significant thermal reductions of barium hexaferrite synthesis.

4. Conclusions

Regarding to the particle size distribution, thermogravimetric and XRD analysis can be drawn the following conclusions:

- Using the milling process for 5 hours, it was obtain a reduction of powders particle size up to 66 % compared to the initial powders;
- Using milling process for 20 hours, a very fine powder is located in sub-micron domain and presents a reduction of powders particle size up to 95 % compared to the initial powder. So, in conclusion, it appears that increasing the mechanical alloying time of powders decreases the particle size.
- According to the XRD analysis, it was observed that for the mechanically alloyed mixture for 5 hours, the synthesis temperature of BHF decreased with 4 % in comparation with the initial powder mixture. For the mechanically alloyed mixture 20 hours it was obtain a reduction of BHF synthesis temperature with approximately 12 % compared to the initial powder mixture and 8 % compared to the mechanically alloyed mixture for 5 hours.

Therefore, it can be seen that the temperature of BHF synthesis is reduced with increasing of mechanical alloying time, namely, once with decreasing of powders particle size.

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