

# Collapse of the Magnetic Hyperfine Structure of Barium Hexaferrite by Mechanochemical Activation

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The collapse of the magnetic hyperfine structure of barium hexaferrite as an effect of mechanochemical activation was investigated. The various inequivalent sites and phases present in the milled material were studied by transmission Mössbauer spectroscopy. Barium hexaferrite nanoparticles were obtained after only 2 h of milling time and were found to coexist with iron oxide particles for longer times of exposure to mechanochemical activation. The milled samples were then subjected to thermal annealing, in order to test the reversibility of the collapse of the hyperfine structure. The thermal annealing performed (700°C, 1 h) was partly successful in restoring the magnetic hyperfine structure of milled hexaferrite. Complementary information was obtained using transmission electron microscopy (TEM) and electron diffraction (ED).

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**KEY WORDS:** Barium hexaferrite; mechanochemical activation; Mössbauer spectroscopy; hyperfine structure; nanoparticles.

## 1. INTRODUCTION

Barium hexaferrite is a hard magnetic material with large crystalline anisotropy and high intrinsic coercivity. It has already found applications in permanent magnets or microwave devices. Fine particles of BaFe<sub>12</sub>O<sub>19</sub> are used in high density perpendicular magnetic recording media. The particle size factor plays a significant role in the macroscopic magnetic properties of dispersed systems. The size of the particles can be controlled during preparation, depending on the production method, or after preparation, by mechanical [1, 2] or thermal treatments [3–5].

In this paper we present results for the BaFe<sub>12</sub>O<sub>19</sub> powder, which was the subject of mechanical grinding using a high-energy ball mill. Phase transformations of the BaFe<sub>12</sub>O<sub>19</sub> powder were studied by Mössbauer spectroscopy, transmission electron microscopy (TEM), and electron diffraction (ED). These measurements allowed the characterization of the structural and magnetic properties of the barium hexaferrite particles as a function of ball milling time. Thermal treatment was performed for the as-milled samples. This was recognized to have a great influence on recovering both structural and magnetic properties of fine particles [4, 5].

## 2. EXPERIMENTAL

The barium hexaferrite (BaFe<sub>12</sub>O<sub>19</sub>) was synthesized by the hydrothermal process [6]. A vibratory Spex 8000 mixer mill with steel vial and balls (type 440, four of 0.25-in diameter, and two of 0.5-in diameter) was used to process the starting barium hexaferrite. The milling process was performed in air for milling times up to 60 h. The samples were collected after 2, 27, 41, and

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60 h of milling. The powders were then annealed at 700°C for 1 h in air.

The samples were characterized by Mössbauer spectroscopy, TEM, and ED before and after annealing.

The Mössbauer spectra were measured at room temperature using a 25 mCi  $^{57}\text{Co}$ -in-Rh source and analyzed with the NORMOS-SITE program. The isomer shifts are given with respect to  $\alpha$ -Fe.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the Mössbauer spectrum of the as-prepared barium hexaferrite, which is well fitted with five sextets related to the five nonequivalent crystallographical iron sites in the magnetoplumbite structure [7]. The hyperfine fields of 51.60 T, 49.46 T, 47.28 T, 41.81 T, and 40.40 T detected in the spectrum correspond to the  $4f_2$ , 2a,  $4f_1$ , 12k, and 2b sites, respectively. These values are in good agreement with the literature powder data [1].

The changes in the structure of barium hexaferrite induced by the ball-milling process can be already seen in the spectrum recorded for the sample collected after 2 h of milling (Fig. 2). A quadrupole-split doublet with broad lines ( $\Gamma = 0.8$  mm/s), quadrupole splitting, QS, of 1.09 mm/s and isomer shift,  $\delta$ , of 0.28 mm/s dominates the spectrum. It contributes to about 32% to the total spectral area. The origin of this doublet is discussed later in this paragraph. The five sextets related to the magnetoplumbite structure of barium hexaferrite, observed in the

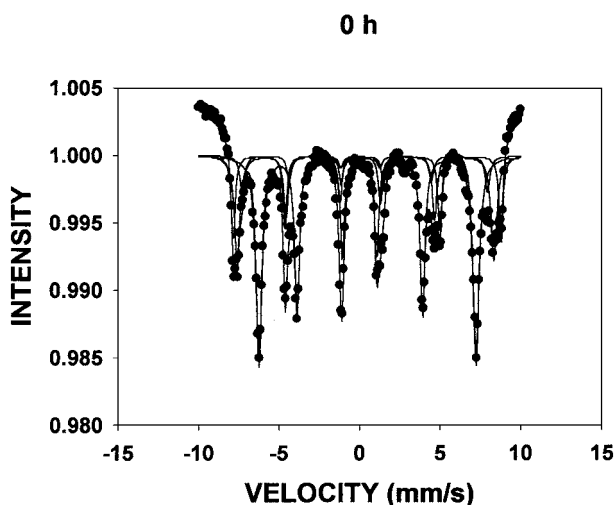


Fig. 1. Mössbauer spectrum of the as-prepared  $\text{BaFe}_{12}\text{O}_{19}$  powder.

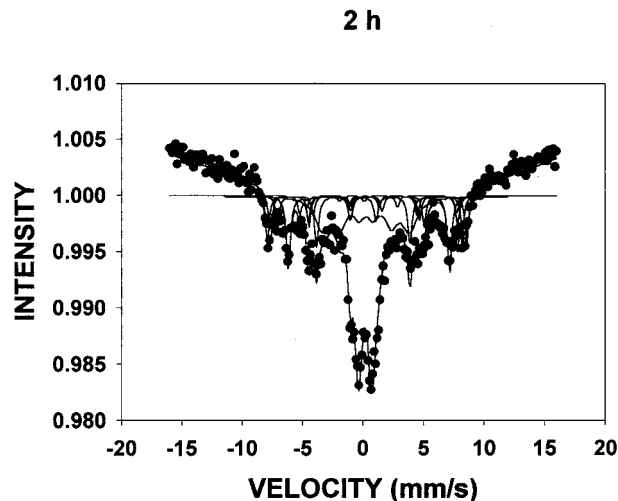


Fig. 2. Mössbauer spectrum of the  $\text{BaFe}_{12}\text{O}_{19}$  after milling for 2 h.

as-prepared sample are still seen in the spectrum shown in Fig. 2. However, their hyperfine fields are somewhat smaller than in the starting sample (Table I). Their relative contribution to the total spectral area is about 42%. The decreased values of the hyperfine fields of the five sextets indicate that the structure becomes more refined due to milling. The correlation between the Mössbauer parameters and the size of barium ferrite particles was observed in [3] and [8]. In particular, the hyperfine fields, related to the different iron sites, decreased with a gradual decrease of particle size. Besides the QS doublet and five sextets, an additional sextet with broad lines and the hyperfine field of 22.35 T is detected in the spectrum of the sample milled for 2 h. A similar broadened sextet was observed for the  $\text{BaFe}_{12}\text{O}_{19}$  powder after low-energy ball milling [1]. The broad lines indicate a distribution of hyperfine fields. This component is probably related to disordered or distributed local environments in the barium ferrite phase, caused by the mechanical grinding.

The increase of milling time to 27 and 41 h leads to a gradual degradation of the magnetic hyperfine structure (Figs. 3 and 4). The relative contribution of the QS doublet increases with the milling time to about 48% of the total spectral area at the expense of the five well-defined sextets, whose hyperfine fields decrease constantly (Table I). The quadrupole splitting increases from 1.09 mm/s for the sample collected after 27-h milling to 1.26 mm/s for 41 h. The doublet line width increases correspondingly. The relative contribution of the broad-

**Table I.** Hyperfine Fields,  $H_{hf}$ , and Relative Areas, A, of the Subspectra Representing Five Iron Sites of the Barium Hexaferrite Determined from the Room Temperature Mössbauer Spectra Obtained for the Milled and Annealed Samples as Indicated

Site	As-prepared		2 h		27 h		41 h	
	$H_{hf}$ [T]	A [%]	$H_{hf}$ [T]	A [%]	$H_{hf}$ [T]	A [%]	$H_{hf}$ [T]	A [%]
12k	41.81	51.5	41.38	16.5	41.29	7.0	40.38	9.0
4f <sub>1</sub>	47.28	7.0	46.15	6.0	45.02	7.5	44.97	7.5
2a	49.46	22.5	49.25	7.0	47.61	5.0	47.51	6.0
4f <sub>2</sub>	51.60	15.5	51.15	9.0	51.10	2.5	49.69	2.0
2b	40.40	3.5	40.32	3.5	38.50	1.0	38.00	1.5

Site	700°C, 1 h		700°C, 1 h		700°C, 1 h	
	$H_{hf}$ [T]	A [%]	$H_{hf}$ [T]	A [%]	$H_{hf}$ [T]	A [%]
12k	41.38	38.0	41.17	17.5	41.39	24.5
4f <sub>1</sub>	46.79	6.5	45.99	15.0	46.10	11.0
2a	49.20	12.5	48.91	18.0	49.11	17.5
4f <sub>2</sub>	51.12	21.5	51.44	23.5	51.48	22.0
2b	40.40	2.5	39.00	2.0	39.00	2.0

<sup>a</sup>The errors in the parameters are  $\pm 0.5$  T and  $\pm 0.5\%$ .

ened sextet with hyperfine field of 25.00 T remains at the 29% level.

After 60 h of milling, there is no evidence of the magnetic structure of barium hexaferrite in the Mössbauer spectrum (Fig. 5). There are two sextets observed: one with hyperfine field of 49.56 T and isomer shift of 0.36 mm/s, which can be attributed to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles (10% of the total spectral area) and the other with hyperfine field of 33.18 T and isomer shift of 0.00 mm/s, which corresponds to  $\alpha$ -Fe (most probably coming from the steel balls). The central part of the spectrum differs from the previous cases. It consists of two

quadrupole split doublets: the one observed before with  $QS = 1.30$  mm/s and  $\delta = 0.67$  mm/s, and a new one with  $QS = 0.40$  mm/s and  $\delta = 0.49$  mm/s.

The origin of the quadrupole doublet with QS varying from 1.09 to 1.30 mm/s may be explained in terms of the superparamagnetic behavior, as suggested by other studies. The appearance of the broadened doublet instead of the magnetic hyperfine structure after ball milling in air of the BaFe<sub>12</sub>O<sub>19</sub> powder prepared by different methods [1, 2, 4, 8] was observed. The reduction of the relative fraction of the magnetic hyperfine splittings and the simultaneous appearance of the QS doublet are proba-

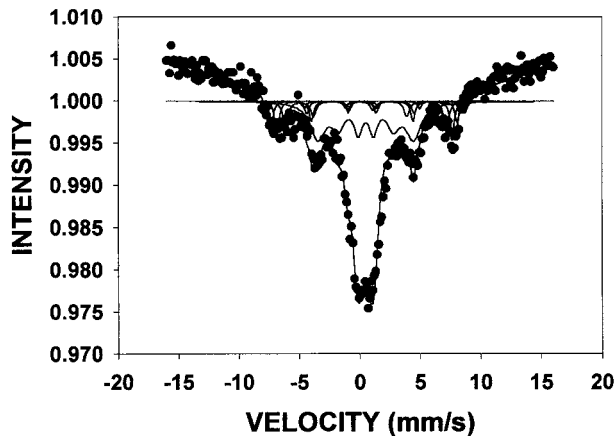


Fig. 3. Mössbauer spectrum of the BaFe<sub>12</sub>O<sub>19</sub> after milling for 27 h.

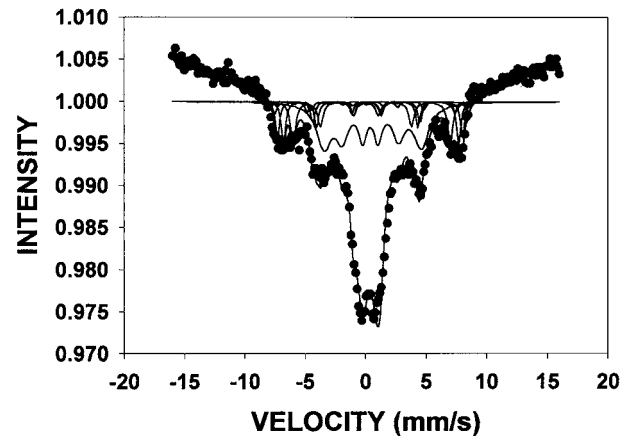


Fig. 4. Mössbauer spectrum of the BaFe<sub>12</sub>O<sub>19</sub> after milling for 41 h.

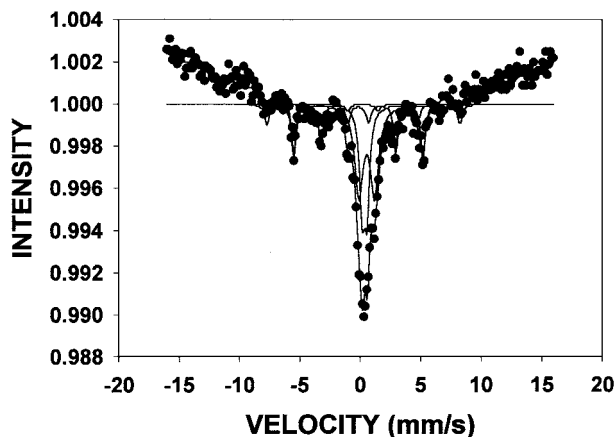


Fig. 5. Mössbauer spectrum of the  $\text{BaFe}_{12}\text{O}_{19}$  after milling for 60 h.

bly related to the relaxation effects associated with small particles. However, the formation of an amorphous like phase cannot be excluded, since its hyperfine parameters are close to those obtained in the present study [3, 9]. The broad lines of this doublet indicate a distribution of quadrupole splittings, typical for both small particles with size distribution and amorphous phase. The other doublet with  $QS = 0.40$  mm/s observed after 60-h milling can be assign to fine  $\alpha\text{-Fe}_2\text{O}_3$  particles with grain sizes of about 18 nm [10], which also exhibit the superparamagnetic behavior.

In order to complement the phase analysis, we performed annealing for the as-milled samples at  $700^\circ\text{C}$  for 1 h in air. The Mössbauer spectra of the annealed powders are shown in Figs. 6–8. There is no evidence of

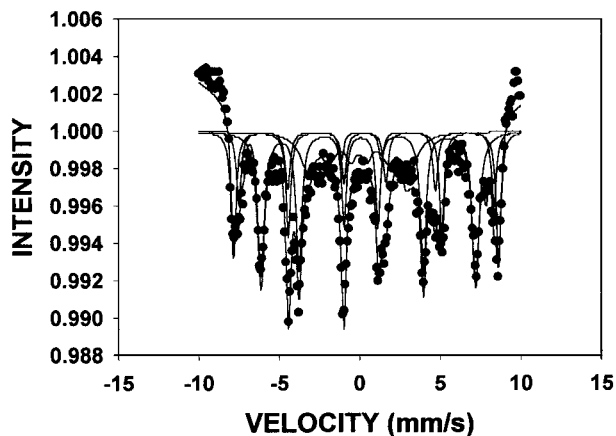


Fig. 6. Mössbauer spectrum of the  $\text{BaFe}_{12}\text{O}_{19}$  milled for 2 h and annealed at  $700^\circ\text{C}$ .

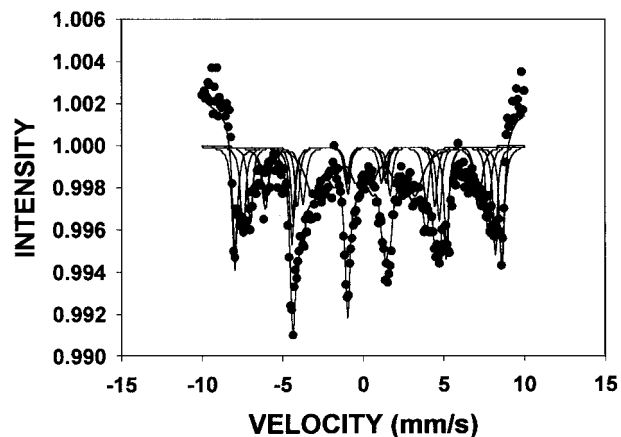


Fig. 7. Mössbauer spectrum of the  $\text{BaFe}_{12}\text{O}_{19}$  milled for 27 h and annealed at  $700^\circ\text{C}$ .

any quadrupole split doublet, indicating that the sizes of the particles are now large enough (after annealing-induced growing) to prevent superparamagnetism to be observed, or that the amorphous phase crystallized due to annealing. The spectrum of the sample obtained after 2 h of milling and annealed for 1 h (Fig. 6) reflects the one recorded for the as-prepared barium hexaferrite (Fig. 1). The hyperfine fields of the five sextets corresponding to the magnetoplumbite structure are very close to those of the starting sample, but still slightly lower (Table I). However, the increased relative contribution of the component with the hyperfine field of 51.12 T, as compared to the  $\text{BaFe}_{12}\text{O}_{19}$  (Table I), suggests the presence of another phase, which can be  $\alpha\text{-Fe}_2\text{O}_3$ , since the

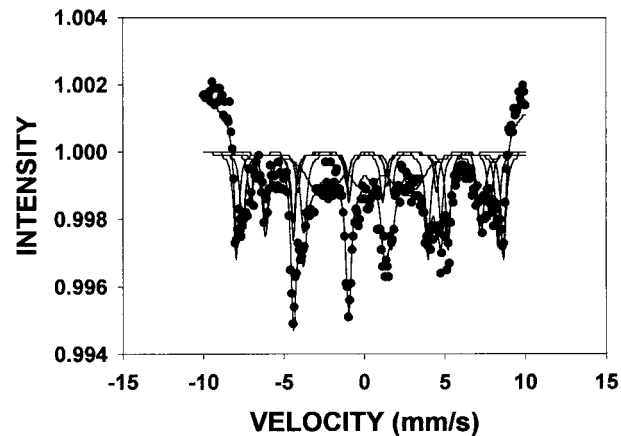


Fig. 8. Mössbauer spectrum of the  $\text{BaFe}_{12}\text{O}_{19}$  milled for 41 h and annealed at  $700^\circ\text{C}$ .

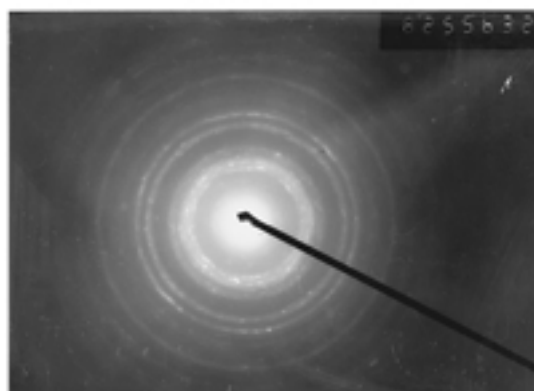
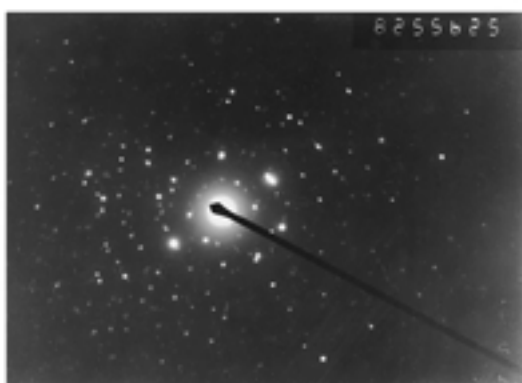
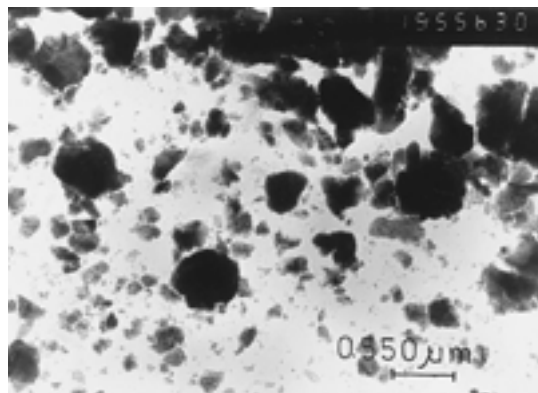
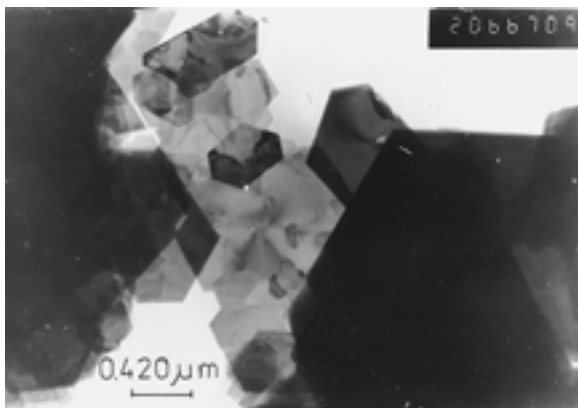


Fig. 9. TEM and ED of the as-prepared  $\text{BaFe}_{12}\text{O}_{19}$  powder.

Fig. 10. TEM and ED of the  $\text{BaFe}_{12}\text{O}_{19}$  after milling for 2 h.

anneals were performed in air. Beside these components, there is also a certain amount (about 18%) of the remaining disordered particles of barium ferrite, revealed by the presence of the broadened sextet with the hyperfine field of 19.53 T in the spectrum of Fig. 6. This amount is, however, lower than in the as-milled samples.

The spectra recorded for the annealed samples milled for 27 and 41 h are very similar to each other and qualitatively correspond to the spectrum of the sample milled for 2 h. They reveal about 24% of the component assigned to the disordered particles. Comparing the spectra of the annealed samples (Figs. 6–8) with the spectrum of the as-prepared  $\text{BaFe}_{12}\text{O}_{19}$  (Fig. 1), one can observe a gradual decrease of the intensity of the lines belonging to the sextet with the hyperfine field of 41.8 T with increasing the milling time. This affects the relative contribution of this component, which represents one of three octahedral positions (12k).

The annealing at 700°C for 1 h does not seem enough (either the temperature is too low or the anneal-

ing time too short) to fully recover the structure of barium hexaferrite after all milling conditions. However, the recovering process can be observed by analyzing the Mössbauer spectra.

These results were nicely confirmed by the electron microscopy data. Thus, Fig. 9 shows the TEM and ED micrographs of the original barium hexaferrite sample. It may be noted that the powder consists of hexagonal crystals with a diameter of 0.5 to 2  $\mu\text{m}$  and a thickness of 0.1  $\mu\text{m}$ . The TEM and ED patterns of the barium hexaferrite powder milled for 2 h are given in Fig. 10. It can be seen that the ferrite powder consists now of nanoparticles (with an average diameter of 66 nm), which are agglomerated and exhibit a lower degree of crystallization compared to the precursor.

The TEM/ED photographs shown in Fig. 11 correspond to the barium hexaferrite powder milled for 17 h or longer. In addition to the barium hexaferrite nanoparticles in aggregates, the images support the presence of iron oxide phases in the milled material. This result was

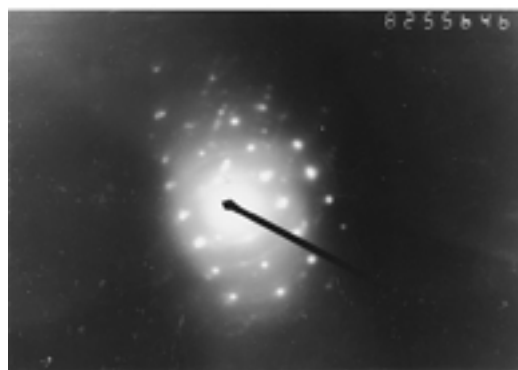
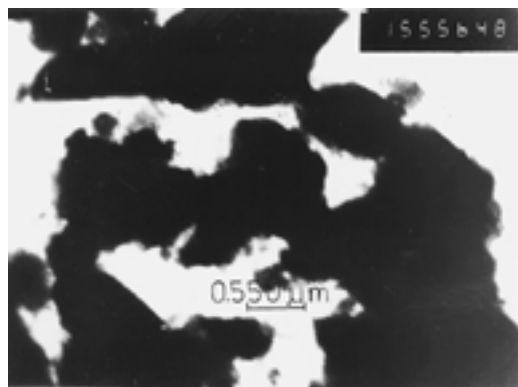


Fig. 11. TEM and ED of the  $\text{BaFe}_{12}\text{O}_{19}$  after milling for 17 h.

confirmed by X-ray diffraction and the previously presented results of Mössbauer spectroscopy.

#### 4. CONCLUSIONS

Samples of barium hexaferrite powder obtained by hydrothermal synthesis were subjected to mechano-

chemical activation for 2 to 60 h of milling time. The effect of ball milling on the magnetic and structural properties was studied by Mössbauer spectroscopy and electron microscopy. The formation of barium hexaferrite nanoparticles and iron oxide phases was investigated from the viewpoint of their effect on the magnetic hyperfine structure. This structure was partly recovered by conventional thermal annealing.

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