

The effect of mechanical milling on the solid state reactions in the barium oxalate–iron(III) oxide system

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Abstract

The formation of barium hexaferrite, BaFe₁₂O₁₉, from a 1:6 molar ratio mixture of barium oxalate and iron oxide has been investigated. Thermogravimetry (TGA), high temperature X-ray powder diffraction (HT-XRPD), differential scanning calorimetry (DSC) and micro-Raman spectroscopy have been used to determine the effect of mechanical activation on the solid state reactions occurring during heating. The resulting magnetic properties were investigated measuring hysteresis loops. For the activated mixtures, the mass loss is over at ≈600 °C i.e. well below the temperature where BaCO₃ spontaneous decomposition is complete ($T > 850$ °C). Such a noticeable temperature lowering is a consequence of the high energy milling enhancing the formation of BaFe₂O₄. After heating the milled mixture to 850 °C, BaFe₁₂O₁₉ was rapidly formed from the BaFe₂O₄ and residual Fe₂O₃. Starting from an unmilled mixture, only minor amounts of BaFe₁₂O₁₉ were formed by heating to 850 °C. The favourable formation of barium hexaferrite, when starting from milled powders, has been confirmed by micro-Raman spectroscopy. The powder from the activated sample was shown to have far better magnetic properties than the unactivated sample. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: BaFe₁₂O₁₉; Chemical synthesis; Magnetic properties; Mechanical activation

1. Introduction

Barium ferrites are widely employed for various applications due to their good chemical stability and magnetic properties. In particular, BaFe₁₂O₁₉ (barium hexaferrite) is extensively used as a permanent magnet in microwave devices and in magnetic recording media.¹ Among the different synthetic routes² leading to barium ferrites, mechanical milling³ is an economical one, since the starting materials are usually commercially available and inexpensive. Production of barium ferrites is traditionally achieved by calcining stoichiometric mixtures of hæmatite (Fe₂O₃) and witherite (BaCO₃) at temperatures above 1000 °C. Such high temperatures result in BaFe₁₂O₁₉ with low coercivity (H_c), although this can be improved by producing particles smaller than the single domain size (≈1 µm), e.g. by mechanically acti-

vating coprecipitated precursors of barium and iron(III) hydroxides that were subsequently annealed at 800 °C.^{4,5} Indeed, it is well known that mechanical activation enhances homogeneity in the precursors and lowers the reaction temperature.⁶ In a recent work Steier et al.⁷ investigated the formation of barium hexaferrite starting from mechanically activated, stoichiometric mixtures of BaCO₃–Fe₂O₃. They found that BaFe₂O₄ formation was rapid and started at 600–750 °C while BaFe₁₂O₁₉ formation was slower and occurred at 720–900 °C. The kinetics of BaFe₂O₄ formation from BaO₂ and α-Fe₂O₃ has been studied by Watanabe⁸ who found evidence of BaFe₂O₄ at 500 °C.

The aim of this investigation is to study the effect of mechanical activation on the solid state reactions occurring in the BaC₂O₄–6 Fe₂O₃ (for BaFe₁₂O₁₉) system. Such a study was performed by high resolution thermogravimetric analysis (Hres-TGA), differential scanning calorimetry (DSC) and high temperature X-ray powder diffraction (HT-XRD). Micro Raman

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spectroscopy was used to show the phase composition and homogeneity in the system. Finally, the magnetic properties and the microstructure of the hexaferrite from both milled and unmilled powders were compared.

2. Experimental

The starting chemicals were BaC_2O_4 (Sigma Aldrich, Italy, 98%) and $\alpha\text{-Fe}_2\text{O}_3$ (Sigma Aldrich, Italy, 99.9%). A physical mixture (i.e. not mechanically activated) with a molar ratio 1:6 ($\text{BaC}_2\text{O}_4\text{:Fe}_2\text{O}_3$) was prepared by weighing the appropriate amounts of the two starting materials and mixing them in an agate mortar for about 10 min. The powders were then suspended in acetone, stirred for 3 h and the solvent evaporated at 60 °C.

About 1 g of the physical mixture was mechanically activated by high energy milling for up to 72 h in a planetary mill (Pulverisette 7, Fritsch, Germany). The milling conditions were: 400 rpm with agate balls (12 mm diameter) in agate jars (ball/sample mass ratio 10:1).

- TGA measurements were made using a 2950 thermogravimetric analyser connected to the TA5000 computer (TA Instruments Inc. USA). About 12 mg of each powder sample was heated under a nitrogen flow of 100 ml/min between 25 and 850 °C at 2 K/min and with a resolution parameter of 5 using a dynamic rate approach,⁹ the sample was then maintained at 850 °C for 12 h and finally cooled.
- DSC measurements were performed using about 30 mg of the sample heated to 1000 °C at 5 K/min under a nitrogen flow of 60 ml/min in a DSC1500 (Stanton Redcroft, UK).
- Samples of both milled and unmilled mixtures were heated at 2 K/min under nitrogen flow up to 850 °C in a high-temperature chamber (Anton Paar HTK1200) fitted into a X-ray powder diffractometer (Bruker D5005) equipped with a goniometer and a graphite bent crystal monochromator. The XRD spectra were recorded in step scan mode using a count time of 3 s per 0.02° step over a 2θ range of 10–65°. The average crystal size was estimated from the broadening of the $\text{BaFe}_{12}\text{O}_{19}$ peaks using the Scherrer formula; the instrumental line broadening was determined using a polycrystalline silicon standard.
- Micro-Raman measurements were carried out at room temperature with a Labram Dilor Raman spectrometer, equipped with the Olympus microscope HS BX40. The beam of a He–Ne laser at 632.8 nm was focussed on a spot with a diameter of 2 μm . The laser power onto the sample was kept low enough to avoid overheating of the probed volume.

- Magnetic properties were studied by means of a SQUID Quantum Design MPMS-7 magnetometer, hysteresis loops were measured at room temperature in fields ranging from 0 to ± 15000 Oe.
- The morphology of the final powders was examined, after sputtering them by graphite, using a Jeol 2600 scanning electron microscope.

3. Results and discussion

3.1. Pure BaC_2O_4

To assess the effect of mechanical activation, if any, on the decomposition of barium oxalate, high resolution TGA measurements were performed both on commercial samples of BaC_2O_4 and on samples ball milled for different times (4, 27 and 46 h). Fig. 1 reports the TGA thermogram of the sample milled for 46 h. Two mass loss stages are completed during the heating ramp while a third one, though starting at ≈ 700 °C, mostly takes place during the isotherm at 850 °C. The first stage up to 250 °C is due to dehydration. Actually the commercial barium oxalate was found to be slightly hydrated ($\text{BaC}_2\text{O}_4 \cdot 0.15\text{H}_2\text{O}$) and, although 2 months of storage in the laboratory did not result in noticeable changes of hydration, 46 h of milling resulted in a hydration increase up to $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$.

The two further stages of mass loss correspond respectively to the near-quantitative decomposition of oxalate to carbonate ($\text{BaC}_2\text{O}_4 \rightarrow \text{BaCO}_3 + \text{CO}$) and to the loss of CO_2 as barium oxide forms. This last reaction is very slow up to 850 °C and even at the end of the isothermal stage, only reached 94% of the theoretical value. Clearly, mechanical activation only affects the degree of hydration of barium oxalate and not its decomposition.

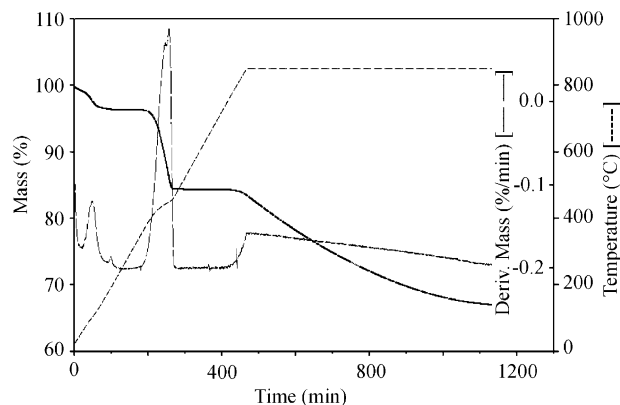


Fig. 1. TGA thermogram of a BaC_2O_4 sample milled for 46 h. The mass (%), its time derivative ($\% \text{min}^{-1}$) and the temperature (°C) are reported as a function of time (min).

3.2. $BaC_2O_4 + 6Fe_2O_3$ mixtures

3.2.1. TGA measurements

The TGA curves of $BaC_2O_4 + 6Fe_2O_3$ mixtures milled for various times are shown in Fig. 2 and the results are summarized in Table 1.

Fig. 2 shows that milling results in mass loss processes taking place at lower temperatures: indeed the mass loss during the isothermal period is only significant in the case of the unmilled mixture where the decomposition of $BaCO_3$ begins at a slightly lower temperature ($\approx 650^\circ C$) than in the pure BaC_2O_4 milled samples. This is clearly the consequence of the reaction with iron(III) oxide which then goes to completion during the isothermal period at $850^\circ C$. The milled mixtures show a mass loss which is complete at $\approx 620^\circ C$ as a consequence of high energy milling enhancing the formation of barium ferrite.

From Table 1 it is evident that the extent of hydration of barium oxalate, which increases with milling time, attains a higher level than milled pure barium oxalate does. It may be that iron oxide enhances the mechanical stress put on barium oxalate so to further increase its surface area and, in turn, the absorbed water amount. Indeed the enhanced effect of milling on the softer of two phases has been demonstrated previously.⁶ Furthermore, by increasing the milling time, ΔM_2 increases while ΔM_3 decreases: the milled samples show mass losses in the second stage (ΔM_2) which are greater than expected (ΔM_2^{calc}) for the oxalate-carbonate transfor-

mation while, in turn, the third step of mass loss (ΔM_3) is less than that calculated for the carbonate-oxide transformation (ΔM_3^{calc}). This demonstrates that a different reaction mechanism is operating in the milled powder.

Further TGA measurements were performed to determine the minimum temperature where the mass loss is complete in the longer milled samples. In these measurements, samples were heated to temperature at $20^\circ C/min$, isothermally heated for 12 h and then heated at $2^\circ C/min$ up to $850^\circ C$ to evaluate the residual mass loss (likely due to $BaCO_3$ decomposition). The lowest isothermal temperature has been fixed at $460^\circ C$ which corresponds to the onset temperature of the third stage of mass loss in the dynamic run reported in Fig. 2. These measurements are shown in Fig. 3 where it can be seen that an isothermal annealing of 12 h at $550^\circ C$ results in complete mass loss. These data allow an estimate of the activation energy of the reaction by plotting $\ln(\Delta M_{iso})$ vs. $(1/T)$. This yields an activation energy of 39.4 kJ/mol.

3.2.2. XRD measurements

To assess what phases were actually formed at $550^\circ C$, XRD powder patterns were collected on the milled mixture after it has been heated under nitrogen flow at $2^\circ C/min$ to $550^\circ C$ in the high temperature chamber of the diffractometer. Fig. 4 reports the spectrum (a) of the starting mixture where only broad diffraction humps due to Fe_2O_3 are visible (the sharp peak at $2\theta \approx 25^\circ$ is due to the alumina sample holder). The figure also

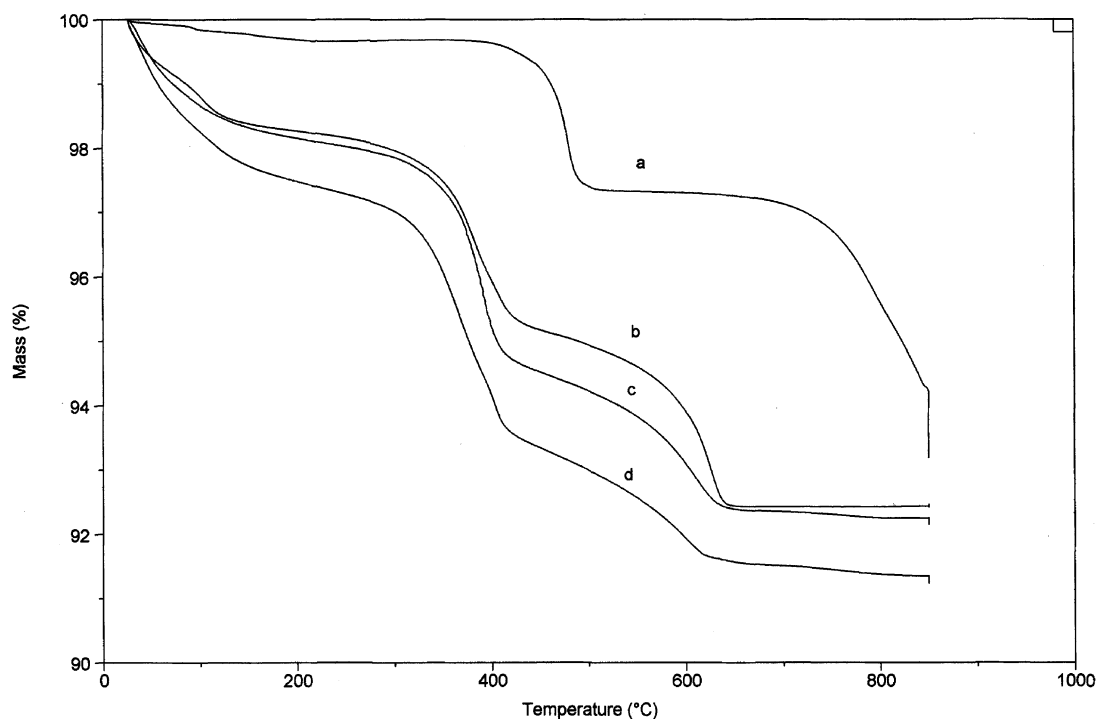


Fig. 2. TGA thermograms (mass% vs. temperature) of $BaC_2O_4 + 6Fe_2O_3$ mixtures: (a) physical mixture; (b) mixture ball milled for 20 h; (c) mixture ball milled for 32 h; (d) mixture ball milled for 46 h.

Table 1
TGA measurements performed on barium oxalate–iron(III) oxide mixtures (molar ratio 1:6)

t (h)	ΔM_1	T_1	n H ₂ O	ΔM_2	T_2	ΔM_2^{calc}	ΔM_3	ΔM_3^{calc}	ΔM_{tot}
0	-0.32	358	0.21	-2.36	573	-2.36	-3.71	-3.71	-6.81
20	-1.70	184	1.14	-3.10	445	-2.33	-2.78	-3.66	-7.58
32	-1.87	211	1.25	-3.36	417	-2.32	-2.52	-3.65	-7.85
46	-2.54	205	1.74	-4.20	462	-2.31	-2.02	-3.62	-8.76

t (h) represents the milling time; ΔM_1 and T_1 represent the first stage of mass loss (%) and its final temperature (°C). n H₂O is the hydration extent of barium oxalate. ΔM_2 and T_2 represent the second stage of mass loss (%) and its final temperature (°C). ΔM_2^{calc} represents the mass loss calculated for the decomposition oxalate → carbonate. ΔM_3 (%) is the mass loss of the third stage. ΔM_3^{calc} represents the mass loss calculated for the decomposition carbonate → oxide. ΔM_{tot} is the total mass loss recorded at the end of the 12 h isothermal period at 850 °C.

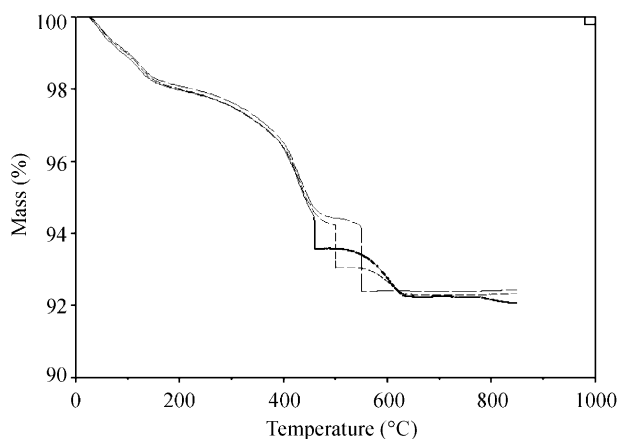


Fig. 3. TGA thermograms of BaC₂O₄ + 6Fe₂O₃ mixtures milled 46 h and heated 12 h at different isothermal temperatures. Full line: isothermal temperature 460 °C. Short-dashed line: isothermal temperature 500 °C. Long-dashed line: isothermal temperature 550 °C.

shows a time series of XRD spectra collected at 550 °C. From these it can be seen that the peaks of Fe₂O₃ narrowed considerably due to thermal recrystallisation. The hump at $2\theta \approx 28^\circ$ stems from the two most intense reflections of BaFe₂O₄ while the third one is hidden under the (quite broad) Fe₂O₃ peak at $2\theta \approx 33.2^\circ$. It can be seen that the intensities of all the reflections in the spectra do not vary appreciably. Since each spectrum took approximately 2 h to collect, it can be seen that annealing for 12 h at 550 °C does not affect the phase composition of the system. Therefore, in the milled sample, the mass loss process at 550 °C corresponds to the formation of a poorly crystalline BaFe₂O₄ rather than to BaFe₁₂O₁₉. Therefore the activation energy value (39.4 kJ/mol) refers to barium monoferrite formation: such a value is considerably lower than that (≈ 82 kJ/mol) reported by Watanabe⁸ who, however, prepared BaFe₂O₄ starting from BaO₂ and α -Fe₂O₃.

Fig. 5 shows the XRD patterns of a sample of unmilled BaC₂O₄–6Fe₂O₃ mixture. After heating the sample (under nitrogen flow at 2 °C/min) to 550 °C, only BaFe₂O₄ and Fe₂O₃ reflections were evident (a). A time series collected at 850 °C (b–e) showed that weak reflections for BaFe₁₂O₁₉ were present in addition to those of BaFe₂O₄ and Fe₂O₃, which are the main phases produced after a prolonged annealing of the unmilled mixtures at 850 °C.

Fig. 6 shows a similar XRD time sequence for milled powders heated up to 850 °C. While the spectrum collected at 550 °C (a) shows only peaks pertinent to BaFe₂O₄ and Fe₂O₃, after heating to 850 °C (Fig. 6 b–g) peaks for BaFe₁₂O₁₉ replace those of BaFe₂O₄ and weak peaks for Fe₂O₃ remain. The phase composition does not seem to be affected by the time of annealing and the continued presence of Fe₂O₃ is a consequence of the hydration of the starting BaC₂O₄ not being accounted for thereby resulting in an excess of Fe₂O₃. This was confirmed by the absence of any further change after annealing the sample for 24 h at 1000 °C. Barium hexaferrite formation has reached the equilibrium after quite a short time at 850 °C. Formation of barium hexaferrite in the sample heated at 1000 °C was confirmed by the presence of an energetic event at 456 °C in a DSC run which corresponds to the Curie temperature of BaFe₁₂O₁₉.¹⁰

3.2.3. DSC measurements

The solid state reactions were also studied by DSC. Fig. 7 shows the DSC trace of the BaC₂O₄ + 6Fe₂O₃ mixture milled for 46 h. The small endothermic peak between 400 and 500 °C corresponds to the sum of the endothermic oxalate-carbonate decomposition and the exothermic oxidation of the carbon monoxide to carbon dioxide (the latter was confirmed by TG/FT-IR). A broad endothermic peak shows up between 580 and 700 °C whose associated enthalpy is ≈ 53 kJ/mol of oxalate. No further thermal effects were present at higher temperatures. A run performed on pure barium oxalate milled 46 h, gives an endothermic enthalpy of 15.8 kJ/mol oxalate for the carbonate decomposition. The XRD spectrum of a sample after a DSC run up to 750 °C (end of the main peak) showed the presence of only BaFe₂O₄ and Fe₂O₃. Thus, the difference between the two enthalpy values provides an estimate of ≈ 37 kJ/mol for the enthalpy of BaFe₂O₄ formation from barium and iron(III) oxides. The absence of thermal effects at $T > 750$ °C stems from the fact that hexaferrite formation is too slow to generate a DSC peak.

3.2.4. Micro-Raman measurements

The enhancement of barium hexaferrite formation due to mechanical activation is clearly supported by micro-Raman measurements of the different ferrite phases coexisting in the powder.^{5,11} Fig. 8 reports the Raman spectra (180–900 cm⁻¹ region) of the milled and unmilled mixtures after annealing at 850 °C.

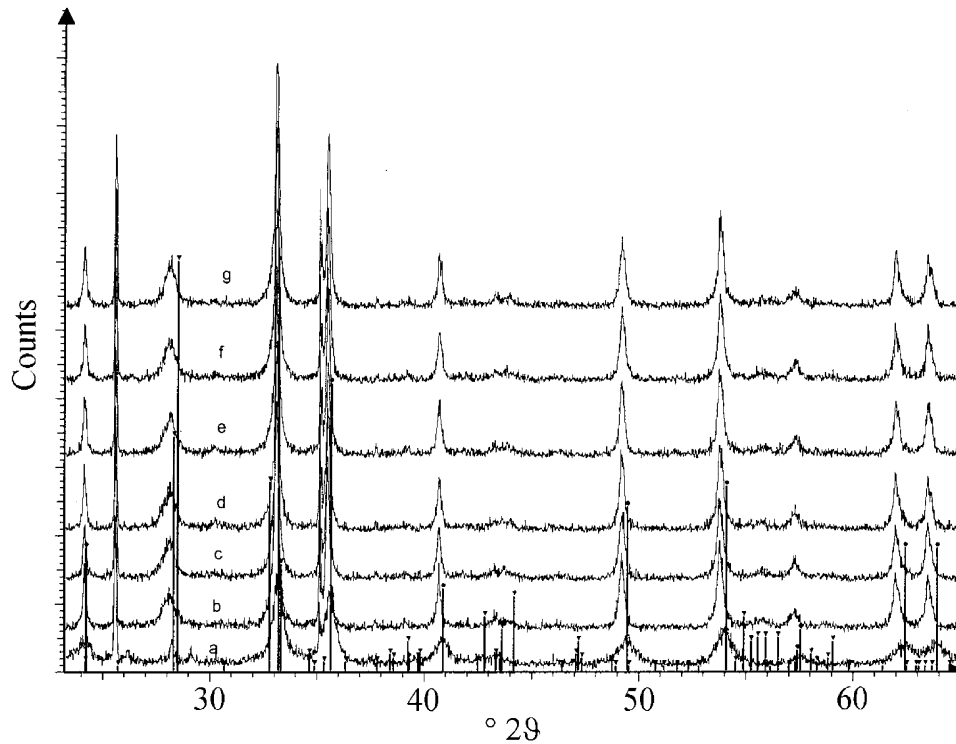


Fig. 4. HT-XRPD spectra collected on a $\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$ mixture milled 46 h. Spectrum (a) has been taken at 25°C while spectra (b–g) have been successively taken at 550°C . The markers refer to Fe_2O_3 (circles) and to BaFe_2O_4 (triangles).

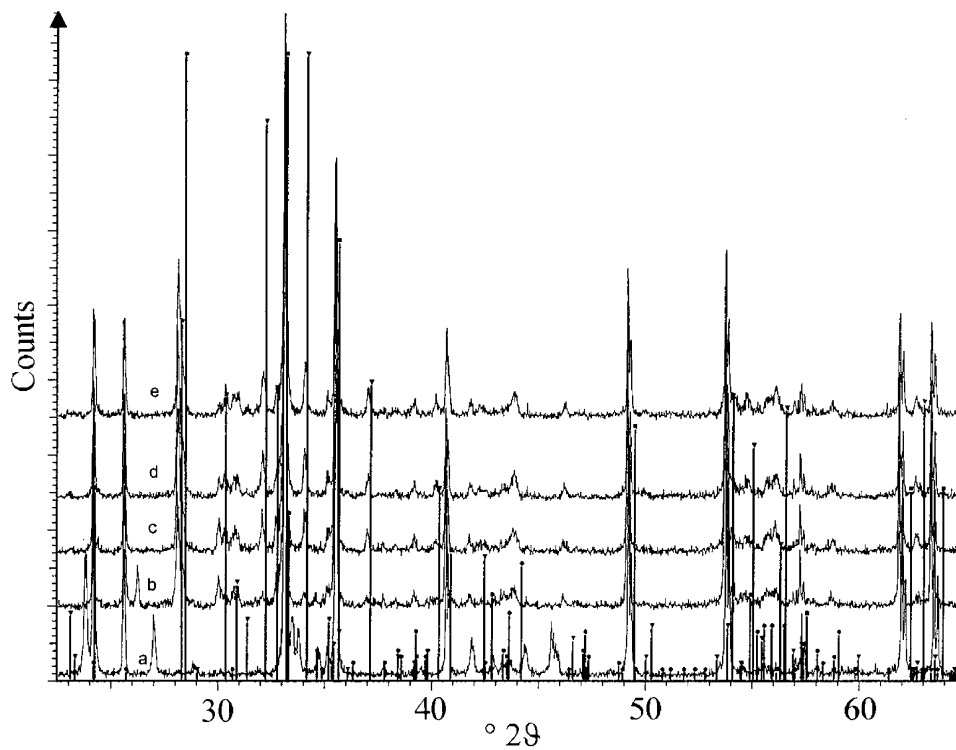


Fig. 5. HT-XRPD spectra collected on a $\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$ physical mixture. Spectrum (a) has been taken at 550°C while spectra (b–e) have been successively taken at 850°C . The markers refer to Fe_2O_3 (squares) to BaFe_2O_4 (circles) and to $\text{BaFe}_{12}\text{O}_{19}$ (triangles).

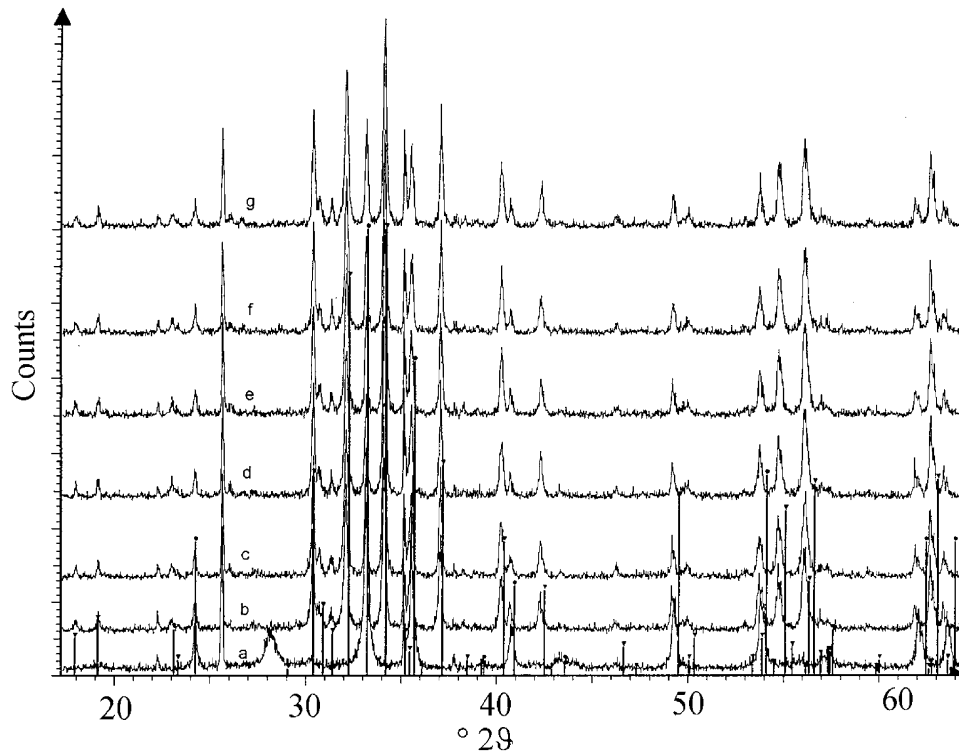


Fig. 6. HT-XRPD spectra collected on a $\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$ mixture milled 46 h. Spectrum (a) has been taken at 550°C while spectra (b–g) have been successively taken at 850°C . The markers refer to Fe_2O_3 (circles) and to $\text{BaFe}_{12}\text{O}_{19}$ (triangles).

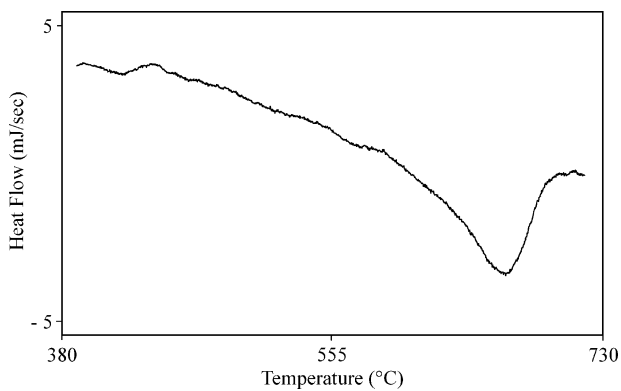


Fig. 7. DSC thermogram of a $\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$ sample milled 46 h.

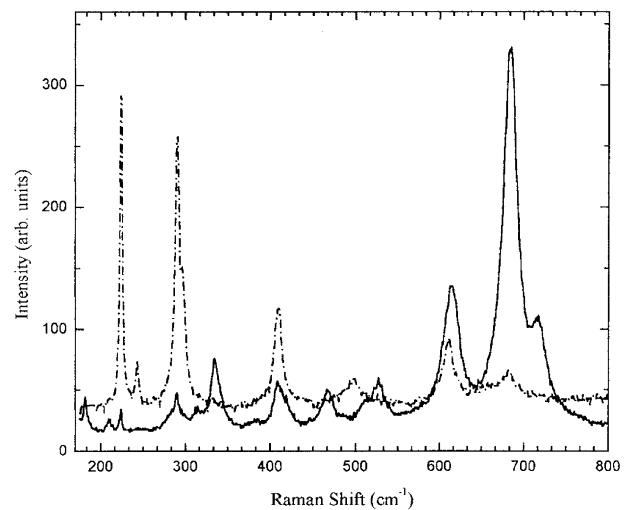


Fig. 8. Micro-Raman spectra at room temperature of the physical mixture ($\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$) annealed at 850°C (dashed line) and of the same mixture milled before annealing at 850°C (solid line).

Comparison of these results with those reported in the literature^{5,12} shows that the Raman spectrum of the annealed physical mixture displays strong $\alpha\text{-Fe}_2\text{O}_3$ peaks in the low energy region at 224, 290 and 410 cm^{-1} respectively, whereas the spectrum of the mechanically activated sample is consistent with barium hexaferrite structure, as it is evident from the presence of modes at 613 and 685 cm^{-1} with the shoulder at 717 cm^{-1} . Furthermore, the position and the narrow line-width of the modes confirm the large crystallite size and homogeneity of the powder. The low intensity of the $\alpha\text{-Fe}_2\text{O}_3$ peaks is indicative that the $\alpha\text{-Fe}_2\text{O}_3$ content of this

sample is extremely low, allowing for the high Raman scattering of this phase.

The Raman signal of the ball milled sample was uniform throughout the sample but that of the unmilled sample varied with spot position (the ratio of the peaks at 685 and 613 cm^{-1} changes). Clearly, the formation of barium hexaferrite is far from being complete in the physical mixture, with hematite being the predominant

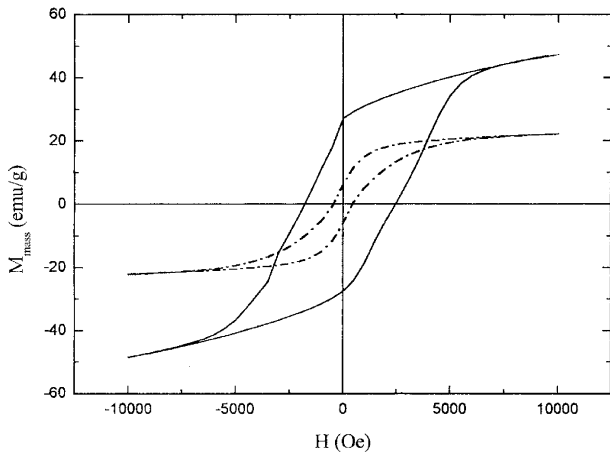


Fig. 9. Hysteresis loops at room temperature obtained from the unmilled (dashed line) and milled (solid line) $\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$ mixtures annealed at 850°C .

phase. In addition in this sample the broad and weak signal around 500 cm^{-1} could suggest the presence of a small quantity of $\gamma\text{-Fe}_2\text{O}_3$.¹¹ The Raman scattering of neither sample shows signals attributable to BaFe_2O_4 .

3.2.5. Magnetic measurements

The magnetic properties of the products of the solid state reaction occurring in the $\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$ system have been determined by measuring the hysteresis loops. It is known that pure $\text{BaFe}_{12}\text{O}_{19}$ is characterized by a well defined hysteresis loop with high coercivity value ($H_c > 5.5\text{ kOe}$) and saturation magnetization $M_s \approx 70\text{ emu/g}$.^{5,11} It has been shown that the magnetic properties of $\text{BaFe}_{12}\text{O}_{19}$ can be significantly depressed by the presence of phases such as antiferromagnetic hematite ($\alpha\text{-Fe}_2\text{O}_3$) and paramagnetic monoferrite BaFe_2O_4 . Furthermore one has to consider the effect of the

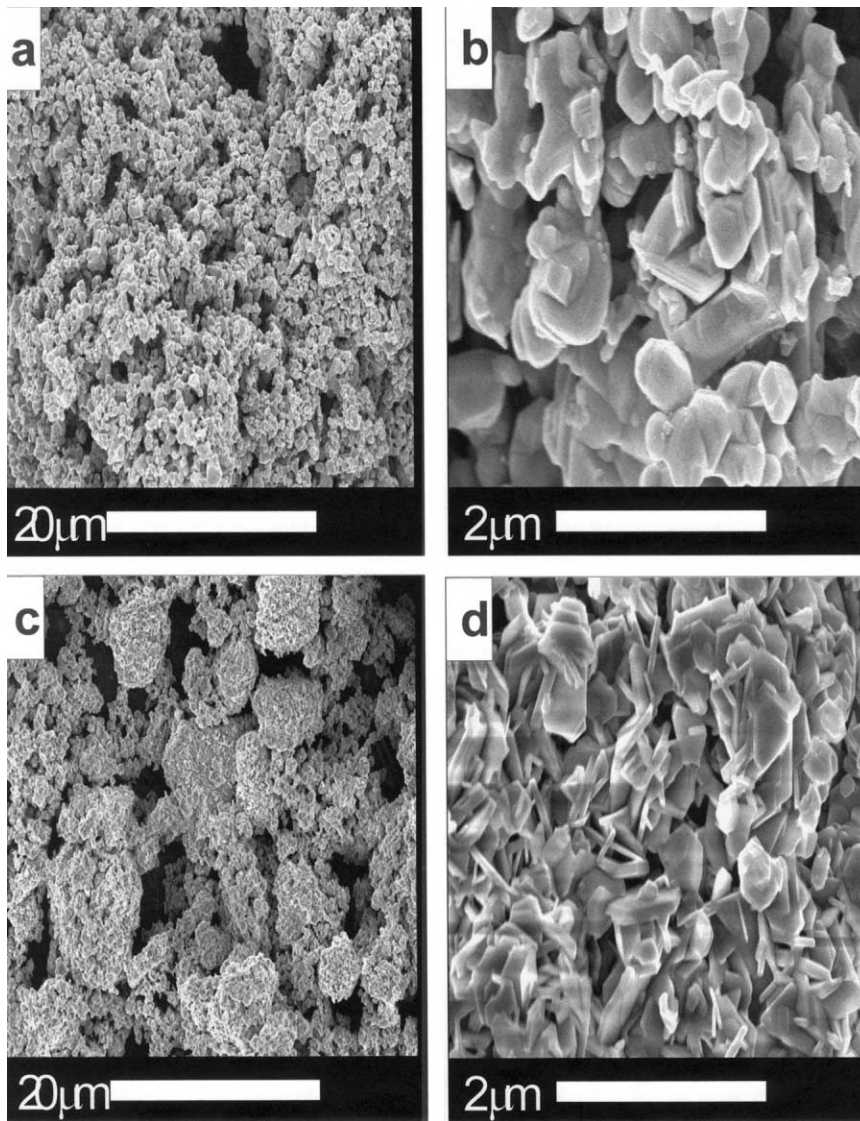


Fig. 10. SEM micrographs of the physical mixture ($\text{BaC}_2\text{O}_4 + 6\text{Fe}_2\text{O}_3$) annealed at 850°C (a and b) and of the same mixture milled before annealing at 850°C (c and d).

crystalline size. Indeed the highest coercivities require a particle size of less than 1 μm to ensure they are single crystal. However, when the domain size approaches the nanometer scale a ferrimagnetic material can exhibit superparamagnetic behaviour.

Fig. 9 compares the hysteresis loops obtained at room temperature for the two powders. It is clear that the loop for the milled sample is well defined, with a value of saturation magnetization (M_s reached at ≈ 12 kOe) greater than 50 emu/g, while for the unmilled sample the hysteresis loop exhibits a distorted shape and $M_s \approx 20$ emu/g. We observe that the M_s value of the milled sample is lower than the saturation magnetization for “pure” Ba hexaferrite phase, though it is comparable with the values obtained for samples prepared by mechanical alloying and annealing at the same temperature.³

The reduction of the crystallite size can lead to higher coercivity values but the obtained H_c is in any case an indication of the good magnetic properties of the sample which has been milled prior to annealing. On the contrary, the narrow loop and the small values of M_s and H_c resulting from the sample obtained by the physical mixture are consistent with the presence of different phases with different magnetic behaviour.

3.2.6. Morphological observations

To examine in detail the morphology of the particles, XRD was performed on the annealed powders and for $\text{BaFe}_{12}\text{O}_{19}$ a total of 19 peaks were fitted for peak position and full width at half maximum; those peaks which overlapped with hematite were discounted (as it has already said some hematite remained, even after 18 h at 850 °C). From the peak widths, the Scherrer crystallite size of 149 ± 111 nm ($\pm 2\sigma$) was determined accounting for the instrumental line broadening.

Scanning electron micrographs are shown in Fig. 10 of the annealing products of both unmilled (a and b) and milled powders (c and d). The unmilled powder (a) shows the presence of very large clusters of particles, the milled powder (c) has small aggregates ranging up to ~ 10 μm in diameter. Closer examination of the unmilled powder (b) shows a range of particle sizes and morphologies with < 300 nm rounded particles, 370 nm equiaxed crystals and a range of irregular particles > 1 μm all evident. It is probable that the rounded particles were unreacted hematite, the crystals either $\text{BaFe}_{12}\text{O}_{19}$ or BaFe_2O_4 both of which were detected by XRD and the larger particles a partially sintered combination of phases.

After milling and annealing, the morphology is much more uniform with flat hexagonal plates evident throughout the sample (d): this morphology is typical of phases from the $\text{P6}_3/\text{mmc}$ space group. The plates are typically 200 nm in diameter and around 60–80 nm thick, although there are both larger and smaller crystals evident in the powder. The size of the plates is similar to the crystallite size of 149 ± 111 nm implying

that the plates are single crystals, the high standard deviation is due to the high aspect ratio of the crystals.

4. Conclusions

The effect of mechanical milling on the formation of barium hexaferrite, $\text{BaFe}_{12}\text{O}_{19}$ from barium oxalate and hæmatite has been investigated. The main points can be listed as follows:

- Milling of the pure oxalate resulted in an increase in the hydration from 0.165 to ~ 0.5 water molecules. In the presence of hæmatite the hydration increased to 1.7.
- Thermogravimetric analysis shows that mechanical activation of $\text{BaC}_2\text{O}_4\text{--}6\text{Fe}_2\text{O}_3$ mixtures results in the mass loss being complete at ≈ 600 °C i.e. well below the temperature where BaCO_3 (the more common barium precursor) spontaneous decomposition is complete ($T > 850$ °C).
- The formation of the hexaferrite was found to comprise two steps: formation of the monoferrite (BaFe_2O_4), followed by reaction between the monoferrite and hæmatite. Monoferrite formation was completed by 550 °C and corresponded to the full extent of mass loss. Both activation energy (by TGA experiments) and enthalpy (by DSC experiments) of this reaction have been determined. Reaction between the ferrite and hæmatite was only evident above 600 °C and completed by heating to 850 °C.
- Starting from a physical mixture of the powders, BaFe_2O_4 was the main phase formed. Indeed, even after several hours at 850 °C, residual Fe_2O_3 was still evident.
- The preferential formation of barium hexaferrite from milled mixtures has been confirmed both by HT-XRD and by micro-Raman spectroscopy.
- Magnetic characterisation of this powder showed a well defined hysteresis loop with a saturation magnetization of > 50 emu/g, whereas the unmilled sample is characterised by a distorted hysteresis loop with $M_s \approx 20$ emu/g.
- The product hexaferrite powder was made of plate-like hexagonal crystals typically 200 nm in diameter and around 60–80 nm thick. XRD of this powder showed a crystallite size of 149 ± 111 nm suggesting that the plates are single crystals.

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