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Synthesis and characterization of small $BaFe_{12}O_{19}$ particles

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Abstract

Fine particles of $BaFe_{12}O_{19}$ have been successfully prepared using a combustion method and annealed at 700, 750, 850 and 1000°C to obtain particles with average diameter in the range 50–200 nm. The structural properties observed by X-ray diffraction in conjunction with the hyperfine characteristics estimated from room temperature Mössbauer spectra explain well the magnetic behavior of the small particles.

1. Introduction

Hexagonal magnetic hard ferrites as $BaFe_{12}O_{19}$ have received much attention because of their potential applications: permanent magnets, microwave devices and perpendicular magnetic recording media. In other aspects, peculiar magnetic properties are expected in the case of small particles (< 0.1 μm), as compared to those observed for crystalline samples [1]. One can expect an increase of the coercive field and a decrease of the magnetic losses. Various procedures have been recently developed to obtain ultrafine oxide particles, as mechanical milling, solid state reaction, etc. The combustion process was successfully applied to $BaFe_{12}O_{19}$ and we report here on the magnetic properties obtained by Mössbauer spectroscopy and magnetic measurements.

2. Experimental section

$BaFe_{12}O_{19}$ particles were synthesized by the combustion process resulting from the exothermic behavior of the redox reaction between the corresponding metal nitrate (oxidant) and oxalic acid dihydrazide (ODH) fuel [2]. The chemical conditions are detailed elsewhere [3]. In the present paper, we report on the results obtained on 4 samples labelled O1, O2, O3 and O4. They correspond to samples resulting from annealing treatment at 700, 750, 850 and 1000°C, during 100 h respectively.

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3. Structural characterization

X-ray diffraction was performed at room temperature using Cu Kα radiation. The presence of very well-defined Bragg peaks is significant of a good crystalline state of the samples. The main crystallographic data are reported in Table 1. The lattice parameters which were refined using the $P6_3/mmc$ space group, remain independent of the annealing treatment of the samples and are in good agreement with the most common published data [4]. In addition, let us mention for the as-prepared sample, the presence of an additive component attributed to the hematite α-Fe_2O_3 phase impurity induced during the synthesis. One can suspect also the presence of $BaFe_2O_4$, but it was not evidenced from X-ray diffraction. The morphology of the powders was studied by transmission electron microscopy at 120 kV. The particles are agglomerated due to effective sintering and the particle size, which is less than 0.1 μm in the case of the low temperature annealing state, then increases with the higher temperature annealing treatments (see Table 1).

4. Magnetic results and discussion

^{57}Fe absorption Mössbauer spectroscopy was carried out on the different samples only at room temperature at which the different magnetic sextets can be better distinguished. The spectra were refined keeping all the hyperfine parameters free during the fitting procedure and assuming the presence of five iron components (12k, $4f_1$, $4f_2$, 2a and 2b) in agreement with the assignment proposed by Evans et al. [5]. Two additive components corresponding to α-Fe_2O_3, hematite, and $BaFe_2O_4$, barium monoferrite, were

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Table 1
Crystallographic data and magnetic properties for $BaFe_{12}O_{19}$ particles. H_c and M_s were measured at room temperature, for $H_{max} = 13.5$ kOe

Sample	Annealing temperature (°C)	Lattice parameters		% α-Fe_2O_3	Average particle size (μm)	H_c (Oe)	M_s (emu/g)
		$a = b$ (Å)	c (Å)				
O1	700	5.888	23.205	2.5	< 0.1	5208	54.3
O2	750	5.892	23.203	1.4	0.05–0.15	5256	55.7
O3	850	5.892	23.194	0	0.15–0.20	5285	57.8
O4	1000	5.892	23.190	0	0.15–0.50	5145	59.0
Ceramic	1100	5.891	23.201	0	> 2	1925	57.5

Table 2
Hyperfine parameters of $BaFe_{12}O_{19}$ samples: isomer shifts DI (mm/s), quadrupole splittings 2ϵ (mm/s), magnetic hyperfine fields CH (T) and relative areas (%) of subspectra

Position	12k				$4f_1$				$4f_2$				2a				2b			
Param.	DI	2ϵ	CH	%	DI	2ϵ	CH	%	DI	2ϵ	CH	%	DI	2ϵ	CH	%	DI	2ϵ	CH	%
Error	±0.01	±0.01	±0.4	±2	±0.01	±0.01	±0.4	±2	±0.01	±0.02	±0.4	±3	±0.01	±0.05	±0.4	±2	±0.01	±0.05	±0.4	±2
O1	0.35	0.40	41.5	50.3	0.27	0.26	48.9	21.0	0.43	0.11	51.3	16.3	0.27	−0.02	51.0	5.9	0.34	2.20	41.2	6.5
O2	0.36	0.40	41.4	50.8	0.26	0.18	48.9	18.3	0.40	0.15	51.3	18.1	0.29	−0.03	51.1	7.9	0.28	2.21	40.2	4.9
O3	0.36	0.39	41.4	50.2	0.26	0.20	49.0	20.9	0.40	0.16	51.5	14.6	0.32	0.03	50.9	9.3	0.28	2.24	40.0	5.0
O4	0.37	0.40	41.5	49.2	0.27	0.20	49.1	19.7	0.40	0.23	51.5	13.0	0.34	−0.04	51.1	11.2	0.30	2.16	39.7	6.9
Ceramic	0.35	0.40	41.4	50.4	0.27	0.21	48.9	16.1	0.39	0.19	51.4	19.4	0.31	−0.02	50.6	8.9	0.30	2.20	40.0	5.2
% theor.				50.0				16.7				16.7				8.3				8.3

also introduced in the fitting procedure. The contribution of hematite phase is not easy to estimate because the values of their hyperfine parameters are very close to those of the $4f_2$ iron site. In addition, the second impurity was not observed (the weight in iron atoms was estimated at less than 0.5%).

Except for those of the quadrupole shift, the final values of the hyperfine parameters are very similar to those obtained on well-characterized and well-crystallized $BaFe_{12}O_{19}$ samples prepared from high purity starting materials (see Table 2). In addition, one can note a small discrepancy on the relative populations for the iron sites by comparing to the expected values: this difference could be attributed to stacking faults of RSR^*S^* blocks.

The magnetic measurements were made with a vibrating sample magnetometer VSM in the temperature range $77\ K \leq T \leq 1100\ K$. Hysteresis loops were recorded and the corresponding values of coercive fields and saturation magnetizations are given in Table 1. The increase of the saturation magnetization with the annealing temperature is attributed to improved purity and crystallinity of the $BaFe_{12}O_{19}$ phase, as defined by the X-ray and Mössbauer spectroscopy data. The coercive field shows high values in all cases ($H_c > 5$ kOe), which are similar to those expected for monodomain hexaferrite particles [6], with a tendency to increase with the annealing temperature up to 850°C, but at higher temperatures, H_c drops, due to the increase of the grain size, i.e. to the presence of polydomain particles.

The critical temperature has been measured by thermogravimetric analysis, TGA, in the presence of a magnetic field and by VSM magnetometry and similar values to those of ceramic samples have been observed, although a slight decrease of T_N is found for the smaller particles.

The results highlight the compromise that the aim to obtain crystalline pure monodomain particles represents, although good results may be obtained with the combustion method, followed by an annealing operating at approximately 850°C.

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