# Magnetic properties enhancement of M-Ba ferrites embedded in a SiO$_2$ matrix

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## Abstract

M–Ba ferrite powders prepared by the coprecipitation method were embedded, using the sol–gel technique, in an inert silica xerogel matrix. Samples were analysed by X-ray diffraction and vibrating sample magnetometry. We compare the magnetic and structural properties of pure ferrite samples and those embedded in the inorganic matrix. The mixed samples had a proportion of 30% BaFe$_{12}$O$_{19}$:70% SiO$_2$ in weight. We observed an enhancement of the coercive force in ferrite powders, embedded in the SiO$_2$ matrix, accompanied by a decrease of the saturation magnetization, with respect to pure samples.

Keywords: Barium ferrite; Sol‑gel; Magnetic properties; Chemical coprecipitation; Silicate glasses.

Hexagonal ferrites are widely used as permanent magnets, high-density magnetic recording media and microwave devices; they are prepared using standard ceramic methods [1], chemical coprecipitation [2], sputtering technique [3], microemulsion [4], liquid mix technique [5], glass crystallization method [6] and the sol–gel method [7]. The preparation method strongly determines their magnetic and structural properties.

Some of the technological applications require materials with strict control of homogeneity, particle size and shape, properties that govern the magnetic behavior. In

particular, hexagonal barium ferrite has been investigated for magnetic recording media. One technical challenge for applying barium ferrite to high-density recording media is to reduce their grain size. In order to reduce the grain size we propose embedding the M-Ba ferrite prepared by chemical coprecipitation in an insulating matrix prepared by the sol–gel method. Sol–gel processing is now well accepted as a technology to prepare coatings and thin films with thicknesses lower than 1 µm.

Inorganic matrix, as host for nanoparticles, can be an effective medium to incorporate particles with uniform size and determinate morphology having control over the homogeneous dispersion of ultrafine clusters of metal oxides. Different systems dispersed in insulating matrices, like silica, have been fabricated by sputter deposition, ball milling, evaporation and chemical methods [8–11]. These materials presented considerable changes in the magnetic properties when compared with their counterpart pure, bulk material. The sol–gel process has some advantages in making inorganic composite materials containing highly dispersed magnetic fine particles; the process facilitates a good and homogeneous dispersion of the particles into the inorganic matrix.

We deal in this paper with the structural and magnetic study of M-Ba ferrites embedded in silica xerogel matrix. Special attention is given to the magnetic effects caused by the adopted experimental conditions.

Powder M-Ba ferrite was prepared using the chemical coprecipitation method. A solution of $FeCl_3 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$, in water, was poured into $NaOH/Na_2CO_3$ alkaline solution. Thermal treatment of the obtained coprecipitates was performed at 1130°C for 2 h in order to for the ferrite. The obtained powder was embedded in a silica xerogel matrix prepared by the sol–gel method. The starting solutions of the silica

xerogel matrix were prepared by mixing tetraethyl orthosilicate (TEOS), water and ethanol. The mole ratios of ethanol to TEOS and water to TEOS were 4:1 and 1167:1, respectively. Added amounts of $BaFe_{12}O_{19}$ were calculated in order to obtain final composites of $BaFe_{12}O_{19}$–$SiO_2$ with a concentration of 30% of $BaFe_{12}O_{19}$ in weight. Soft pieces of the gels were obtained after about 48 h.

Those pieces were ground to form a fine powder. For subsequent annealing the samples were placed in an oven at the desired temperature for 30 min in air. The powders were analyzed by VSM and Xray diffraction (XRD) to determine the obtained magnetic and structural properties.

XRD results of the $SiO_2$ sample added with MBa ferrite show well-defined peaks assigned to barium hexaferrite, $BaFe_{12}O_{19}$, without noticeable changes when samples were heat treated over the temperature range from 200°C to 1000°C. In all cases, a broad diffraction band located at the left part of the diffractogram, corresponding to the amorphous $SiO_2$ matrix, is present.

Samples heat treated at 1100°C show a change of phase, indicating the decomposition of M-Ba ferrite into haematite phase ($\alpha$-$Fe_2O_3$), and the minor phase, barium monoferrite, $BaFe_2O_4$. Structural modification of amorphous silica into cristobalite and quartz has also been observed. The ferrite cluster sizes, estimated using Scherrer's equation [12], are indicated in Table 1. These values are noticeably reduced in comparison with the grain size of about 150 nm for the pure M-Ba ferrite.

Saturation magnetization and coercivity values are represented in Table 1. The phase change at 1100°C is accompanied by a drastic decrease of the saturation magnetization and the coercivity value. The measured low values of magnetic

parameters are due to the change of phase occurring in temperatures above 1000°C and can be explained by the occurrence of a-$Fe_2O_3$ and $BaFe_2O_4$ phases.

Table 1
Magnetic parameters of coprecipitated M-Ba ferrite embedded in silica xerogel in terms of heat treatment

| Temperature (°C) | Cluster size M-Ba ferrite (nm) | Magnetization saturation $\sigma_s$ (emu/g) | Remanence $\sigma_r$ (emu/g) | Coercive force $H_c$ (Oe) | Squareness $\sigma_r/\sigma_s$ |
|---|---|---|---|---|---|
| RT | — | 11.78 | 6.48 | 5468 | 0.55 |
| 200 | 37.94 | 12.56 | 6.90 | 5483 | 0.54 |
| 400 | 38.92 | 12.21 | 6.72 | 5505 | 0.55 |
| 600 | 36.74 | 13.18 | 7.28 | 5496 | 0.55 |
| 800 | 35.23 | 12.57 | 6.92 | 5477 | 0.55 |
| 900 | 35.61 | 13.76 | 7.54 | 5562 | 0.54 |
| 1000 | 36.10 | 13.22 | 7.29 | 5522 | 0.55 |
| 1100 | 41.58 | 0.68 | 0.49 | 5405 | 0.72 |

The grain size of pure M-Ba ferrite is about 150 nm (S. Palomares-Sánchez, et al., Scripta Mater. 34 (1996) 1195).

The obtained coercivity values were improved with respect to values obtained for the pure coprecipitated ferrite sample. The coercivity value measured for the pure coprecipitated ferrite is 3151 Oe, whereas the value measured in our sample, embedded in a silica xerogel matrix, is 5562 Oe. Fig. 1 shows the hysteresis loops of the pure coprecipitated ferrite and the sample with the powder embedded in the silica matrix. Other typical values for M-Ba ferrites prepared via the sol–gel route are 4699 Oe, and when the precursors are milled the values increase to 4951 Oe [13]. From the results we can observe that the coercivity value are improved in our samples. This improvement in coercivity can be ascribed to a reduction of the sizes of the particles.

A noticeable decrease in the saturation magnetization of the M-Ba ferrite embedded in silica matrix, compared with the pure ferrite sample, is observed in all the ranges of heat treatment temperature. The reduction on the saturation magnetization of samples embedded in a silica xerogel matrix is expected since this parameter depends on the total mass of the magnetic material and the concentration of M-Ba ferrite

embedded is 30% in weight. The reduction of this value may be caused by non-colinearity of the magnetic moments at the surface of the nanoparticles, resulting in a decrease of the saturation magnetization for small particles.
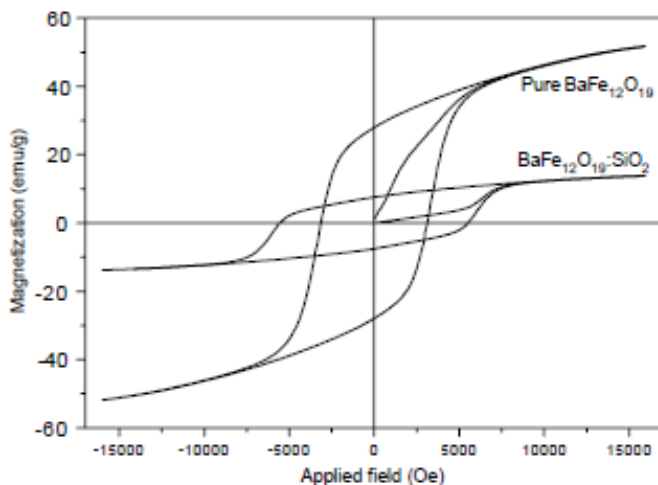


Fig. 1. Hysteresis loops of the pure coprecipitated M-Ba ferrite and of the sample with the coprecipitated M-Ba ferrite embedded in the silica matrix.

For the sample heat treated at 1100°C the saturation magnetization is reduced to about 0.68 emu/g, 4.9% lower than the saturation magnetization for the sample heat treated at 1000°C. We believe that the ferrite–glass interface could strongly influence the coercivity and saturation magnetization of our nanocomposites. Since our samples contain very small particles, a large fraction of ions is at or near the surface so that the interaction between the ferrite particles and the silica matrix may play a determinant role.

In the range of temperatures from room temperature to 1000°C, the squareness ratio $\sigma_r = \sigma_s$ values are comparable to the theoretical value of $\sigma_r = \sigma_s = 0{:}5$ according to the Stoner– Wohlfarth model for noninteracting monodomain magnetic particles [14]. At

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1100°C this value suffers a noticeable change due to the decomposition of the ferrite in hematite and Ba-monoferrite.

The magnetic parameters for the sample heat treated at 1100°C show little change in their hope comportment. This situation is related to a structural change produced by the interaction of the ferrite nanocluster with the silica gel matrix. At this temperature crystallite cristobalite and quartz begin to appear in the matrix as well as hematite and monoferrite phase.

From the results we can observe that the grain size is diminished ten times, the coercivity values are improved in our samples, whereas the saturation magnetization decreases with respect to the pure coprecipitated hexaferrite. This material has potential application as magnetic recording media, due to useful characteristics such as high coercivity, small grain size and the great facility that guarantees the sol–gel method to make thin films without subsequent heat treatment.

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