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BaFe₁₂O₁₉ SMALL PARTICLES: FORMATION. PARTICLE SIZE AND MAGNETIC PROPERTIES

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Abstract. – Small particles of BaFe₁₂O₁₉ are prepared at low temperature by a liquid mix technique. By using X-ray diffraction, Mössbauer, and magnetic measurements we show that this method allows an easy control of the size and shape (400 Å–3 000 Å) of the particles, which display essentially bulk magnetic properties.

Hexagonal-ferrite small particle are being widely considered as interesting materials for high density magnetic recording media. A great effort is then being performed on preparing materials with proper size, crystal size homogeneity and controlled magnetic properties. In recent works [1] it has been shown that the liquid mix technique is an interesting synthesis method for this purpose. It seems then necessary to study the relationship among thermal treatments, phase formation, crystal size and magnetic properties. In this work we extend previous reports dealing with the relationship among all these items.

Samples of BaFe₁₂O₁₉ composition were prepared by the liquid mix technique. Detailed procedure can be found elsewhere [1]. Here we only mention that the investigated samples were prepared with different thermal treatments, from $T = 450^\circ\text{C}$ to $T = 1\,150^\circ\text{C}$ for different periods of time (t). X-ray diffraction analysis was carried out by using a Siemens 2θ -diffractometer and Cu – K α_1 radiation. The Rietveld profile analysis method was used, both to refine structural parameters and to deduce the relative concentration of the different phases when present.

Electron microscopy photographs show that particles have an hexagonal platelet-like shape and allows a measure of the averaged size perpendicular to hexagonal axis but does not provide any estimation of the highness along this axis. The broadening of the X-ray diffraction peaks (H) permits a measure of the particle size in a direction perpendicular to H . Thus from X-ray diffraction a reasonable measure of the averaged particle size along some directions and the shape of the particles can be obtained. The reflections (006) (104) (110) (008) (112) (107) (114) (203) (205), (206) and (220) have been used to evaluate the particle size and shape according to the method of Cox [2]. Mössbauer spectroscopy was used to perform phases analysis as well as to characterize the hyperfine parameters of these phases, which usually are in a small particle form.

A SQUID magnetometer was used to obtain hysteresis curves.

X-ray (XRD) and Mössbauer spectroscopy (MS) analysis lead to the following conclusions. (1) The spinel phase γ – Fe₂O₃ is formed at $T > 150^\circ\text{C}$. (2) At $T \approx 450^\circ\text{C}$ small particles of the magnetoplumbite M-phase exist as can be observed by MS but not by XRD. At this temperature BaFe₂O₄ oxide is detected by XRD but it is not observable by MS at least when the reported hyperfine parameters [3] for BaFe₂O₄ are considered. As shown in figure 1 the severe overlapping of the spectra may cause the failure to observe BaFe₂O₄ by MS. (3) When samples are heated again at 700°C for $t = 2$ h the concentration of the M-phase increases further at expense of the BaFe₂O₄ oxide.

Fig. 1. – Room-temperature Mössbauer spectra of sample prepared at $T = 600^\circ\text{C}$, $t = 1$ h.

The concentration of the spinel phase [S], as observed by MS, decreases when increasing the annealing temperature. At $T = 450^\circ\text{C}$, $[S]/[M] \approx 2$, but at $T = 750^\circ\text{C}$, $[S]/[M] \approx 0.07$ where $[M]$ denotes the relative concentration of the M-phase. (4) At this tem-

perature ($T < 800^\circ\text{C}$) the particle size is not very sensitive to the annealing time " t ". By using the Cox line-broadening analysis we got, (for $T = 750^\circ\text{C}$, $t = 1$ h), $D \approx 695 \text{ \AA}$, $H \approx 508 \text{ \AA}$ but $D \approx 826 \text{ \AA}$, $H \approx 517 \text{ \AA}$, for $T = 750^\circ\text{C}$ $t = 6$ h. (5) When the sample is heated at higher temperature, say $T > 800^\circ\text{C}$, no BaFe_2O_4 is observed by XRD. $\alpha\text{-Fe}_2\text{O}_3$ oxide is formed by oxidation of the preexisting spinel phase, but its concentration never exceeds 12 %. The particles size increases rapidly for longer annealing times. At $T = 1\,000^\circ\text{C}$, $t = 1$ h, $D \approx 2\,320 \text{ \AA}$, $H \approx 1\,133 \text{ \AA}$, but at this temperature the rate of growing is about three times faster than at 700°C . (6) The concentration of $\alpha\text{-Fe}_2\text{O}_3$ decrease when samples are heated at $T > 900^\circ\text{C}$ but it is still present ($< 3\%$) for $T \approx 1\,000^\circ\text{C}$. From the magnetic point of view the analysis of the samples has revealed the following prominent features. (7) The saturation magnetization (M_s) increases when the annealing temperature T or the annealing time t increases, approaching to the expected 100 emu/gr for $T > 1\,000^\circ\text{C}$. (8) The coercitive magnetic field as deduced from the hysteresis loops, versus the mean size of the particles (D) shows a maximum around 4-5 KOe for $D \approx 1\,000 \text{ \AA}$, decreasing above and below this size. (9) The superimposed susceptibility at high fields decreases when T and/or t increases. (10) Mössbauer spectra have revealed that the hyperfine magnetic fields for the M-phase increases slightly when samples are annealed at higher T or longer t , thus pointing to bulk values. (11) Even for the samples prepared at low temperatures when the particle size is smaller ($< 400 \text{ \AA}$) the Mössbauer spectra does not reveal any superparamagnetic effect. A lower limit for particle size could be obtained by using the Neel law. When the appropriate anisotropy constant is used ($\approx 4.5 \times 10^6 \text{ erg cm}^{-3}$ for bulk material) a particle size not larger than $100 \text{ \AA}$ is found.

From XRD and Mössbauer data we may conclude that the hexaferrite is formed according to the following scheme. At $T < 150^\circ\text{C}$ $\gamma\text{-Fe}_2\text{O}_3$ and BaFe_2O_4 oxides are formed. At higher T the solid state reaction between both oxides leads to the M-phase forma-

tion. The existence of a small amount of $\alpha\text{-Fe}_2\text{O}_3$ reveals that some Ba was preexisting in a different form (BaO , ...), both oxides reacting at high temperature, and leading to a lowering of the $\alpha\text{-Fe}_2\text{O}_3$ phase as observed. It is to be remarked that at 750°C , $[M] \approx 90\%$ and the particle size can be easily controlled.

The magnetic data can be interpreted as follows. The dependence of M_s on particle size reveals spin-reduction effects at the surface of the grains [4] which also accounts for the existence of the superimposed magnetic susceptibility. The same argument holds for Mössbauer data. It is worth to comment the non observance of any sizeable relaxation effect, thus showing that the axial magnetic anisotropy is strong enough to avoid spin relaxation (at 300 K) in the Mössbauer time scale.

On the other hand, measured coercitive magnetic fields ranging from 2-5 KOe are exceedingly high for magnetic recording purpose, and some cationic substitution is in order.

Summarizing, we can conclude that liquid mix technique allows low-temperature M-phase synthesis with controlled particle size and shape. The magnetic properties of this particles are essentially coincident with those of bulk materials except, perhaps, the effects associated to surface spin-reduction.

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