Fine Powders of Co-Mn Cation Deficient Spinel Ferrites for Magneto-Optical Pigments

L. Bouet, P. Tailhades, M. Durand and A. Rousset

Laboratoire de Chimie des Matériaux Inorganiques, Université Paul Sabatier, ESR 5070 du CNRS, 118 route de Narbonne, 31062 Toulouse cedex, France

Abstract: Very small particles of Co-Mn defect spinel ferrites with acicular and spherical shape were prepared. Their magnetic and magneto-optical properties were measured in function of their oxidation state and their size. It was shown that the coercivity of acicular (AP) and spherical (SP) particles with a mean crystallite size close to 20 nm, reached 3800 and 2950 Oe respectively. The SP coercivity decreases when the grains sizes become lower than 20 nm, but remains higher than 1000 Oe for particles having crystallites close to 10-15 nm. The Curie temperature decreases also slightly when the grains are smaller than 20 nm, while the remanent Faraday rotation falls from 0.6 to 0 deg/μm when the crystallite size is reduced from 40 to 7-8 nm. The Co-Mn ferrite particles studied have interesting properties, even they have not, for now, all the required properties to be high performance pigments for magneto-optical recording.

1. INTRODUCTION

Previous studies [1] on fine powders and thin films of $\text{Co}_x\text{Mn}_y\text{Fe}_{2-x-y}\text{O}_4$ with x and y close to 0.7-0.8 and 0.12-0.13 respectively, have revealed that oxido-reduction phenomena could occur in these ferrites along thermal treatments in air from 200 to 550°C. The charges equilibria involved could be described as follow (□ cationic vacancies generated by the oxidations):

(1)	$T \approx 250^\circ\text{C}$	$4\text{Mn}^{3+} \rightarrow 3\text{Mn}^{4+} + \square$	total oxidation,
(2)	$T \approx 350^\circ\text{C}$	$3\text{Mn}^{2+} \rightarrow 2\text{Mn}^{3+} + \square$	partial oxidation,
(3)	$T \approx 450^\circ\text{C}$	$3\text{Mn}^{4+} + \square \rightarrow 4\text{Mn}^{3+}$	total reduction,
(4)	$T > 500^\circ\text{C}$	$3\text{Mn}^{2+} \rightarrow 2\text{Mn}^{3+} + \square$	total oxidation and crystallographic transformation.

The three first reactions generate defect spinel ferrites. The last, however leads to the precipitation of a corundum-type phase. The oxidations proceed from the surface to the core of the grains. When the particles are partially oxidized the highly oxidized outer part and weakly or un-oxidized inner part have small and a large unit cell respectively. In fact, the more the ferrite is oxidized, the lower its lattice constant. Simply speaking, way it may be assumed that the accommodation of the two spinel lattices thus tends to develop a tension near the surface and a compression in the core. The resulting stress, which reaches a maximum at around half oxidation, can be responsible of an enhancement of the coercive force due to induced magneto-elastic effects and probably also to the creation of a directional order (DO). In fact, the DO can be created by applying a mechanical stress to magnetized ferro/ferrimagnetic materials. As the DO establishment kinetic is very low, special heat treatments are generally required to create it completely. In defect spinel ferrites, the highest increases in coercivity were obtained after slow coolings (#10°C/hour) of the samples from their oxidation temperature to room temperature. By this method, coercivities close to 4000 Oe were already reached for different fine powders of spinel ferrites [3].

For the present study, very small particles of Co-Mn ferrites were prepared and their magnetic and magneto-optical properties were measured. The purpose of this work was to know if high coercivity and remanent Faraday rotation can be retained in this kind of powders, when the mean particle size is about 10 or 20 nm. This information is especially important in evaluating the potential interest of the Co-Mn ferrites pigments for use as particulate magneto-optical storage media, as has been proposed by Abe and Gomi [4][5]

2. EXPERIMENTAL AND SAMPLES

The submicronic powders of Co-Mn ferrites were prepared by "chimie douce" with different controlled morphologies. The acicular particles (AP) were obtained by thermal decomposition of mixed oxalic precursors as described in previous works [6]. The hydroxide route in strongly alkaline medium was used to synthesized "spherical" particles (SP). The precursors (acicular and spherical) were first decomposed under air in the range 150 to 600°C. The resulting product was a oxide mixture composed of spinel and corundum-type phases. The stoichiometric ferrite was then obtained after an annealing at around 330°C, in a reducing $\text{H}_2\text{-N}_2\text{-H}_2\text{O}$ atmosphere. The mean crystallite size of the particles was adjusted by annealings at different temperatures ($330 < T < 600^\circ\text{C}$) under nitrogen. The elongated particles were approximatively 70 nm long and had an acicular shape ratio of 2. The mean crystallite sizes of the spherical particles varied from 10 to 40 nm according to their thermal history.

Figure 1: Coercivity (H_c) versus oxidation temperature for acicular (AP) and spherical (SP) particles having crystallite sizes close to 20 nm.

Figure 2: Coercivity (H_c) versus crystallite size (d) for spherical particles quenched (Q) or slowly cooled (SC) (10°C/h) after oxidation at 400°C .

Figure 3: Remanent Faraday rotation ($\theta_{F,R}$) and Curie temperature (T_c) versus crystallite size (d) for spherical particles quenched (Q) or slowly cooled (SC) (10°C/h) after oxidation at 400°C .

The chemical analyses gave the following compositions: $\text{Co}_{0.8}\text{Mn}_{0.14}\text{Fe}_{2.06}\text{O}_4$ for AP, and $\text{Co}_{0.8}\text{Mn}_{0.15}\text{Fe}_{2.05}\text{O}_4$ for SP. X-ray diffraction was used to control the phase purity and to determine the mean crystallite size by the Scherrer method. The magnetic properties were measured on packed samples (packing density $\approx 1\text{g/cm}^3$) with a M2000 (S21S) hysteresisometer. The Faraday rotation was measured at 780 nm wavelength. For these measurements, the ferrite powders were dispersed in a NaCl matrix. The Faraday rotation was taken as $\theta_{F,R} \cdot f^{-1}$ ($\theta_{F,R}$: Faraday rotation of the mixture, f^{-1} : volume fraction of ferrite particles).

3. RESULTS AND DISCUSSION

The figure 1 shows the curves of the coercivity versus the oxidation temperature for both AP and SP powders having a mean crystallite size close to 20 nm. All the samples were oxidized for two hours at a given temperature and quenched after this dwell time. The curves show two peaks centred at 250°C and 400°C . The tops of these peaks appear close to the temperatures where half the Mn^{3+} and Mn^{2+} ions respectively, were oxidized, as it was already demonstrated for other Co-Mn spinel ferrites thin films and fine powders. Above 450°C , the reduction of the Mn^{4+} ions brings a decrease in coercivity.

Because the samples were quenched, their coercivity was not optimized. In fact, this last could be strongly increased when the powders were slowly cooled (10°C/hour) after the oxidation. This enhancement is due to the creation of a DO which induces a magnetic anisotropy in the monodomain particles during the slow cooling. By this way, the coercivities of AP and SP oxidized at 400°C , went from 2300 and 1850 Oe to 3800 and 2950 Oe respectively. Because of their shape anisotropy the acicular particles had always the highest coercive forces. Otherwise, the increase rate $\Delta H_c/H_c$, due to the DO was also the strongest for this kind of particles ($\approx 65\%$ for AP and $\approx 60\%$ for SP). In spite of the very interesting magnetic properties of the AP samples, the study of the variation of the coercivity in function of the crystallite size, was not done on AP but on SP powders oxidized at 450°C for 2 hours. In fact, the annealing carried out to adjust the crystallite size, modified also the acicular ratio of the particles in the case of AP. In contrast, any significant change in shape is observed for SP.

The SP coercivity drastically decreased, when the crystallite size became smaller than 15-20 nm, and vanished when the particles had a superparamagnetic behaviour at room temperature, for a critical size valued at 7-8 nm (fig. 2). In spite of his important fall for particles sizes below 20 nm, the SP coercivity remained high (>1000 Oe) even for very small particles (10-15 nm). The AP coercivities should be still higher for acicular particles. The Curie temperature decreased also slightly for particles sizes below approximately 20 nm, but the decrease of the remanent Faraday rotation occurred, at least, from 40 nm, leading to low rotations (0.1-0.2 $\text{deg}/\mu\text{m}$) for the very small particles (10-15 nm)(fig. 3).

For a potential application in particulate magneto-optical media, mixed valence defect spinel ferrites studied can, for the time being, be evaluated as follow. The 20 nm particles can have strong coercivity and good remanent Faraday rotation at 780 nm, but their Curie temperature is high. Thermomagnetic recording would seem possible using these particles only with shorter wavelengths (400-500 nm), for which the optical absorption of the spinel ferrites ($>50\,000\text{ cm}^{-1}$) is not too low. Smaller grain sizes would make thermomagnetic recording easier and avoid media noise during magneto-optical reading. However, in spite of their high coercivity (>1000 Oe) the 10-15 nm particles have low remanent Faraday rotation at 780 nm. It will be interesting to measure the remanent Faraday rotation of these powders at shorter wavelengths. In fact, the spinels ferrites generally have better magneto-optical properties for green or blue radiations [1].

References

- [1] Bouet L., Tailhades Ph., Rousset A., J. Mag. Mag. Mater. 153, (1996), 389-396.
- [2] Néel L., J. Phys. Rad. 15, (1954), 225-239.
- [3] Tailhades Ph., Bouet L., Gillot B., Mollard P., Rousset A. Proceedings of ICF 6, Japan, (1992), 991-994.
- [4] Abe M., Gomi M., J. Magn. Soc. Jpn., 15 (S1), (1991), 259-261.
- [5] Gomi M., Abe M., J. Magn. Soc. Jpn., 15 (S1), (1991), 227-229.
- [6] Tailhades Ph., Chassaing I., Bonino J.P., Rousset A., Mollard P., Proceedings of ICF 6, Japan, (1992) 421-424.