PARTICLE SIZE AND MAGNETIC PROPERTIES OF $\text{BaFe}_{12}\text{O}_{19}$ PREPARED BY THE ORGANOMETALLIC PRECURSOR METHOD

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Résumé - Des particules monodomaine de $\text{BaFe}_{12}\text{O}_{19}$ ont été préparées par la méthode des précurseurs organométalliques à basses températures de frittage. On montre que la taille des particules peut être facilement contrôlée à partir de la température et du temps de réaction. L'aimantation à saturation des grains fins diminue avec la diminution de la taille. La variation du champ coercitif avec la taille des particules peut être expliquée avec la théorie du superparamagnétisme et la nucléation des domaines. On montre qu'il n'y a pas de comportement superparamagnétique dans l'échelle des temps de la spectroscopie Mössbauer.

Abstract - Single domain $\text{BaFe}_{12}\text{O}_{19}$ particles have been prepared by using the organometallic precursor method with low reacting temperatures. It is found that an easy control of particle size may be obtained by controlling the firing temperature and reaction time. Saturation magnetization of the fine particles decreases with decreasing particle size. The dependence of the coercive field on particle size may be understood from superparamagnetic theory and multidomain nucleation formation. It is found that no superparamagnetic behaviour does exist in the Mössbauer characteristic time.

I - INTRODUCTION

In recent years a large effort has been devoted to the preparation methods of polycrystalline M-type $\text{BaFe}_{12}\text{O}_{19}$ hexagonal ferrite. This is so because a strict control of homogeneity, particle size and shape and magnetic characteristics are required for technological applications such as perpendicular magnetic recording /1/. Besides the classical ceramic method /2/, other preparative methods have been analyzed: chemical coprecipitation /3/, hydrothermal synthesis/4/ and glass-crystallization /1/. However, very recently a new method with very promising features has been proposed by Licci and Besagni /5/. The method consists in the formation of a solidified organometallic solution with the desired stoichiometry of metallic ions which is then reacted to get the desired oxide. As it has been pointed out by these authors the advantage of the method is an improved reactivity together with a good particle homogeneity and size control.

In this work we present a preliminar study of the dependence of magnetic properties of $\text{BaFe}_{12}\text{O}_{19}$ particles prepared by this method on the particle size and thermal treatments.

II -SYNTHESIS PROCEDURE AND STRUCTURAL CHARACTERIZATION

Several $\text{BaFe}_{12}\text{O}_{19}$ samples have been prepared by the organometallic precursor method proposed by Licci and Besagni /5/. The Fe ions were introduced as nitrates which were

dissolved in distilled water, precipitated with an ammonium solution and washed with water until neutrality. A stoichiometric mixture of this precipitate and Ba carbonate were dissolved in citric acid with ethylene-glycol added in order to increase the viscosity. Finally, this amorphous organic solid was decomposed at 723 K, and different thermal treatments were performed. In table I we report the different treatments to which the samples were subjected. All the samples between B and G had cumulative thermal treatments, while those named H and I were directly prepared from stage A.

Table I

Sample	Firing temperature	Firing time	Size (Å) (+)		S (m ² /g)
			T.E.M.	X. R.	
A	723 K	-	-	-	-
B	823 K	17 h	-	-	-
C	923 K	1 h	350	500	8
D	1073 K	1 h	650	790	7
E	1173 K	0.5 h	1000	-	-
F	1273 K	0.08 h	1250	950	-
G	1273 K	72 h	2300	-	-
H	923 K	42 h	300	-	12
I	973 K	10	500	-	-

(+) The size measured by T.E.M. correspond to the mean diameter of platelet-like particles, while that reported from X-ray diffraction is the diameter of spheres used in the Scherrer formula.

The identification of the M-structure was made from X-ray diffractograms while the correct chemical composition of samples were ascertained by means of X-ray fluorescence and atomic absorption analysis. The particle shape and size were determined from transmission electron micrographs. The mean particle size was studied both from the 205 diffraction line broadenings, using an Ag powder as instrumental standard, and the classical Scherrer formula. Finally, the B.E.T. specific surface area of the particles was measured for several samples. The minimum temperature at which we got a complete transformation to M phase was 923K. Nevertheless, if the reaction temperature is augmented to 973K the time necessary to complete the reaction is strongly reduced.

In figure 1 we show some characteristic electron microscopy photographs from which the mean particle size reported in table I were determined. We note that a fairly good agreement is obtained for the sizes determined from T.E.M. and X-ray diffraction. Our results show that a full correlation among particle size, heating temperature and firing time does exist.

Figure 1 - Electron microscopy photographs of samples C, E, and G.

Thus, it is clear that the present preparative method allows to control the particle diameter above about 300 Å. Moreover, the electron micrographs show that a good homogeneity is obtained and that the sintering process among the particles begins

only at about 1273 K. Finally, the measured B.E.T. specific surface areas ranged from 7 to 12 m²/g, which are much lower than those reported by Kubo et al. for particles with similar sizes prepared by the glass-crystallization procedure /6/. Thus, it seems that the present method provides samples with lower porosity.

III - MAGNETIC PROPERTIES

The saturation magnetization and coercive fields were deduced from room temperature hysteresis loops measured by means of a vibrating sample magnetometer in magnetic fields up to $H = 60$ KOe. Several room temperature ⁵⁷Fe Mössbauer spectra were also recorded in a conventional spectrometer using a 10 mCi ⁵⁷Co:Rh single line source. In figure 2 we represent the dependence of saturation magnetization and coercive field on the mean particle diameter, as obtained from T.E.M. photographs. It may be observed that a decrease of saturation magnetization does appear when the particle diameter is reduced below about 1250 Å. This is a common phenomenon in fine particles and may be understood as arising from spin non-collinearity at the surface of the crystals /7/. The experimental dependence of the coercive field on the particle size is very similar to those previously observed by Kubo et al. /6/ in BaFe₁₂O₁₉ particles prepared by the glass crystallization method. The coercive field is maximum at a diameter of about 1000 Å while it decreases at smaller and larger diameter values. The decrease of H_c below 1000 Å may be interpreted in the scope of the superparamagnetic theory of uniaxial fine particles /8/, while the H_c decrease of particles with higher diameter is associated to domain wall nucleation /6/.

Figure 2 - Dependence of saturation magnetization and coercive field on mean particle diameter.

Finally, we recorded several room temperature Mössbauer spectra in order to get a microscopic characterization of the samples. For instance, Mössbauer spectroscopy would enable us to know if the BaFe₁₂O₁₉ fine particles obtained by the present method show superparamagnetic behaviour. In figure 3 the room temperature Mössbauer spectrum of sample C is shown. In spite of being the sample with smallest size the fitted hyperfine parameters are very similar to those found in BaFe₁₂O₁₉ bulk samples and sharp absorption lines are obtained. Thus, we may conclude that no spin relaxation appears within the Mössbauer characteristic time (about 10⁻⁸ s). The thermal activation of spins responsible for the decrease of coercive field will have a higher relaxation time.

Figure 3 - Room temperature Mössbauer spectrum of sample C

As a final conclusion we may state that the organometallic precursor method provides homogeneous single domain $\text{BaFe}_{12}\text{O}_{19}$ particles at low reacting temperatures with good magnetic properties and with an easy control of particle size.

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REFERENCES

- /1/ Kubo O., Ido T., Yokoyama H., IEEE Trans. on Mag. MAG-18 (1982) 1122
- /2/ Kojima H., "Ferromagnetic Materials", vol. 3, E.P. Wohlfarth ed., North-Holland (1982) p. 305
- /3/ Kaneda K., Miyakawa C., Kojima H., J. Am. Ceram. Soc. 57 (1974) 354
- /4/ Kiyama M., Takada T., Nagai N., Horriish N., 4th Int. Conf. Ferrites, San Francisco (1984), Adv. in Ceram. ("in the press")
- /5/ Licci F., Besagni T., IEEE Trans. on Magn. MAG-20 (1984) 1639
- /6/ Kubo O., Ido T., Yokoyama H., Koike Y., Magn. Mater. Conference, San Diego (USA) (1984), J. Appl. Phys. ("in the press")
- /7/ Morrish A. H., Kaneda K., J. Magn. Mater. 35, (1983) 105
- /8/ Herpin A., "Theorie du Magnetisme", Presses Universitaires de France (1968)