SYNTHESIS AND PROPERTIES OF ACICULAR BARIUM HEXAFERRITE

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SYNTHESIS AND PROPERTIES OF ACICULAR BARIUM HEXAFERRITE

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Abstract. – The barium hexaferrite crystallizes in the hexagonal system of the magnetoplumbite type. The particles, generally prepared by solid state reactions, coprecipitation, crystallisation ion a glass or by growth under a flux, usually appear in the form of hexagonal platelets. We have prepared the barium hexaferrite in the acicular form, which may be of some considerable interest for high density recording. We present in this paper the results obtained from an original process, namely the impregnation of acicular "ferrous hydroxide" by a barium alcoholate. During the course of formation of $BaFe_{12}O_{19}$, the acicular morphology is conserved, while maintaining a high magnetization of about 60 emu/g and the coercive field of around 5200 oersteds.

1. Introduction

The tremendous technological advances observed in the recording head field and recording field as well as the urgent need to increase the storage density of supports of an always smaller size require the preparation of highly efficient magnetic materials with remarkable physical characteristics, namely, a good magnetization, a high coercive field and a monodisperse granulometry.

Presently, among all oxide-based magnetic pigments, barium or strontium hexaferrite alone can satisfy these requirements. Moreover, this compound presents an easy magnetization axis most suitable for perpendicular recording.

The crystallization processes of $BaFe_{12}O_{19}$ in hexagonal platelets with controlled sizes are globally well mastered. Numerous researches and industrial patents are based on them.

Willing to innovate in the field, we considered, by anology with soft-type ferrite such as stabilized $Fe_2O_3\nu$, synthesizing barium hexaferrites in an acicular structure. This morphology is of great interest for high-density perpendicular recording.

2. Synthesis

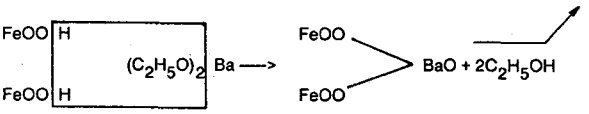
The preparation of $BaFe_{12}O_{19}$ has been performed in several steps, which will be described in this section.

The firts step is the synthesis of FeOOH "goethite" in an acicular morphology. For that purpose, we took example on a well known synthesis process [1] that consists in oxidizing, under control, ferrous sulfate dissolved in water. This process gives fine FeOOH acicular particles with a mean size of about 0.5 μm.

The second step is to introduce barium into the structure along an original impregnation process [2, 3] based on an exchange reaction between the alcohol group and the hydroxyl group. The schematic reaction is as follows:

$$12FeOOH + Ba\,(C_2H_5O)_2 \rightarrow \rightarrow 10FeOOH, Fe_2O_3, BaO + 2C_2H_5OH \quad (1)$$

and we suppose the exchange mechanism to be:



The thermogravimetric analysis (T.G.A.) of FeOOH before and after barium introduction (Fig. 1) clearly indicates a weight loss in complete accordance with the schematic reaction (1) suggested above, that is to say: consumption of one H_2O molecule for 12 FeOOH molecules.

The compound goes through a thermal treatment that produces a particular type of barium hexaferrite whose crystallographic, magnetic and morphological properties have been analysed. The paper presents the results observed according to barium content.

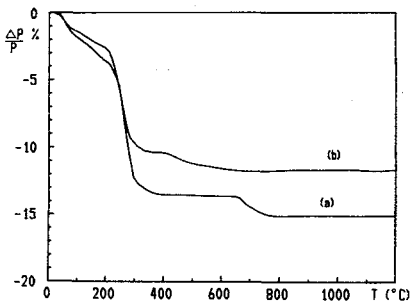


Fig. 1. – Thermogravimetric analysis: (a) $FeOOH_\alpha$, (b) $FeOOH_\alpha$ impregnated.

3. Physical analysis and discussion

From the X-ray analyses of the product annealed at various temperatures (Tab. I), we can infer an exchange reaction similar to the one usually observed when applying the classical ceramic processing, apart from the fact that $BaFe_{12}O_{19}$ formation temperature was lowered to 800 °C instead of the usual 1 200 °C.

Magnetic measures confirm the X-ray analysis' results. Indeed, below 700 °C no interesting development can be observed. Beyond that temperature and, more especially, around 750 °C and 800 °C, the com-

Table I. – *Detected phases after different thermal treatments.*

Thermal Treat.	Existing Phases
No annealing	$FeOOH\_BaCO_3$
300 °C_500 °C	$Fe_2O_3\_BaCO_3$
600 °C_700 °C	$BaFe_2O_4\_Fe_2O_3$
750 °C_800 °C	$BaFe_{12}O_{19}\_Fe_2O_3$

pound reaches a magnetization value of 46 emu/g and a high coercive field of 5 200 Oe (Fig. 2).

Varying the barium impregnation level, we obtained a maximum magnetization value for a barium impregnation rate of 1.7 moles for 12 Fe moles. Figure 3 shows magnetization evolution according to barium impregnation content.

After a 40 minutes thermal treatment at 800 °C, X-ray analyses of the product show the complete disappearance of Fe_2O_3, but also the presence of a minor quantity of $BaFe_2O_4$, which is easily eliminated by means of a 10 % -dissolved acetic acid solution. Under these conditions, we obtain a good magnetization of 62 emu/g and a high coercive field of 4 600 Oe.

Transmission electron microscopic observations enable to follow the particles' evolution at various stages of the thermal treatment (Fig. 4).

Up to 800 °C, the acicular structure is preserved. Beyond 900 °C, it completely disappears and is replaced with a platelet morphology.

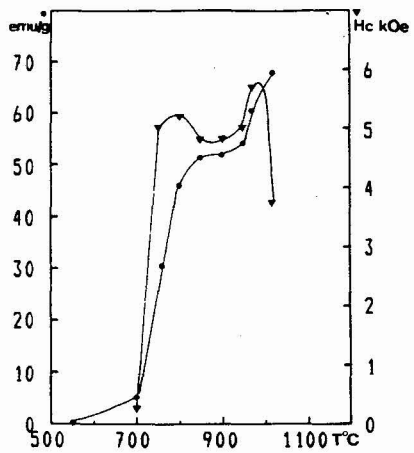


Fig. 2. – Variation of magnetization and coercivity with temperature for acicular $BaFe_{12}O_{19}$.

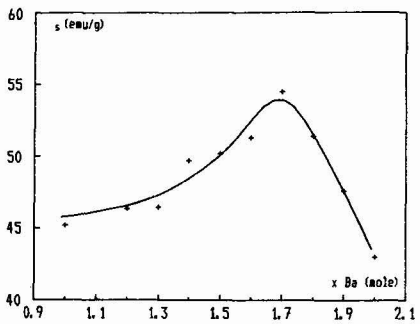


Fig. 3. – The variation of magnetization as a function of the barium content.

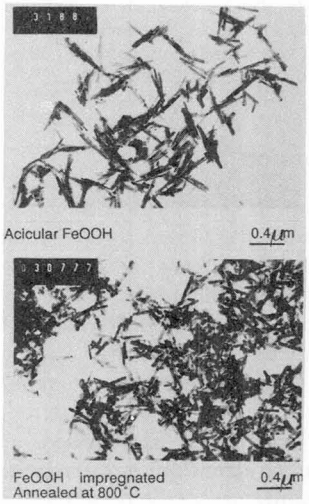


Fig. 4. – Electronic microdiffraction and schematic arrangement of hexagonal microcrystals.

4. Conclusion

By impregnation, starting from hydroxide powders with acicular morphology, it is possible to obtain Barium ferrite powders suitable for magnetic pigments.

The powders' characteristics, such as a specific area between 15 and 20 m^2/g, a mean size value of 0.2-0.1 μm with an acicularity ratio of $5 < R < 10$ for needles, and a particle-size distribution comparatively narrow, are compatible with the particle needs for magnetic media. Varying the barium content we obtained a high magnetization value 60 emu/g and a coercive field of 5 200 Oe.

Acknowledgments

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[1] Kuo, P. C., Chang, C. V., Wu, T. S., Chang, Y. H., Hsu, T. K., *J. Mater. Sci.* **1** (1982) 137-140.

[2] Najmi, M., Poix, P., Bernier, J. C., Pingaud, B., French Patent 86149937.

[3] Najmi, M., Thesis Doctorat, Université Strasbourg I (1986).