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Structure of cobalt and fluorine doped hexaferrites

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Hexagonal ferrites in the BaO–Fe_2O_3–CoO system have the M, Y, Z, W and S structures. $BaFe_{12-x}Co_xO_{19-x}$ prepared by the glass synthesis method crystallizes with the M structure but for $x > 0$ a few $CoFe_2O_4$(S) crystallizes at first and then is located at the core of the recovered platelets of hexaferrite M. $BaFe_{16-x}Co_{2+x}O_{27-x}F_x$ prepared in the same way has not the W structure but is a mixture of cobalt doped M and S.

1. Introduction

The applications of the barium hexaferrite are numerous and principally connected to its strong magnetization and coercive field. Under the crystalline state it looks like hexagonal platelets having a great magnetocrystalline anisotropy: the magnetization vector is perpendicular to the plane of the platelets. The coercive field varies from 2.3×10^5–4.4×10^5 Am^{-1} while the size of the crystallites varies from 0.3–3 or 4 μm. It has a maximum when the platelets reach the monodomain size, e.g. about 0.5 μm [1]. This high coercive field is an obstacle for the application of $BaFe_{12}O_{19}$ as pigment for magnetic recording. Nevertheless it could be a good product for high density perpendicular magnetic recording because of its great magnetocrystalline anisotropy. Then to decrease the coercive field we have chosen to decrease the size of the crystallites using the glass synthesis method. It consists of preparing a glass, to crystallize the compound within the glass by annealing and then recuperating the product by dissolving the matrix. In 1970, Shirk and Buessem [1] were first to present this method. In 1982, Kubo *et al.* [2] gave the complete diagram of this preparation for $BaFe_{12}O_{19}$. We have pointed out that the size of the crystallites varies more with the temperature than with the time of the annealings in the case of $LiFe_5O_8$ [3]. We have also proposed some single rules for a generalization of the glass synthesis method [4].

The optimization of the annealing conditions to decrease the coercive field has allowed us to reach only about 1.6×10^5 Am^{-1} [4]. A fast quenching with water has been tried and leads to the same results: 1.4×10^5 Am^{-1} for the lower H_c [5]. To reach coercive fields under 1.2×10^5 Am^{-1} dopings of the hexaferrite are necessary. Numerous preparations with the based substitution of two Fe^{3+} by the couple Ti^{4+}–Co^{2+} have been patented [6–9]. We have made them and have obtained the same results, but we have also worked out a doping with compensation of the electric charges on the anions like: $Fe^{3+} + O^{2-}$ and $Co^{2+} + F^-$ [10]. This work has been completed by dopings of the hexaferrite: with an excess of cobalt and fluorine, with only fluorine, with only cobalt. Thus the coercive field becomes lower than 1.2×10^5 Am^{-1} and the magnetization remains rather strong (> 60 uem CGS^{-1} g). In the end we have synthetized a ferrite W also doped with Co and F [11]:

$$BaFe_{16-x}Co_{2+x}O_{27-x}F_x \quad x = 0.5$$

During these works that we have just described, a specific problem—what are the phases which crystallize in the glass when Co and/or F are added—has received particular attention.

2. Study of BaO–Fe_2O_3–CoO system at 1050 °C

In all the non-doped preparations it is without any contestation the phase M of $BaFe_{12}O_{19}$ which crystallizes. The addition of bivalent cations in the $BaFe_{12}O_{19}$ network, particularly Co^{2+}, can induce the formation of hexagonal ferrites with very closely crystalline structures. In the BaO–Fe_2O_3–CoO ternary diagram, the M, Y, Z, W and S compositions can be found. Their characteristics are given in the Table I [12]. The identification of the recovered phases is difficult because a confusion is possible between the different phases.

We have carried out a previous study of the ferrites W, Y and Z. The classical ceramic way has been followed for the synthesis:

1. Mixing of the starting product $BaCO_3$, Fe_2O_3 and Co_3O_4.
2. Heating at 1050 °C for 5 h.

These conditions are very similar to those used for the annealings of the glass ceramic method. Analysed by X-ray diffraction measurements the phases M and Y are pure whereas the phases Z and W correspond to the mixings M + Y and M + S.

Nevertheless the saturation magnetization and the coercive fields measured at room temperature (Table II) are in agreement with the classical values

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TABLE I Magnetic (magnetization σ_s, Curie temperature T_c and coercive field H_c) and structural (parameter c) characteristics of the different phases.

Phases Formula	M $BaFe_{12}O_{19}$	Y $Ba_2Co_2Fe_{12}O_{22}$	Z $Ba_3Co_2Fe_{24}O_{41}$	W $BaCo_2Fe_{16}O_{27}$	S $CoFe_2O_4$
O_x	19	22	41	27	4
c	23.2	43.5	52.3	32.8	
σ_s	85	43	63	89	101
T_c (°C)	450	340	410		520
H_c (Am^{-1})	4.8×10^5				

TABLE II

Phases	M	Y	M + Y	M + S	S
σ_s	84	39	59	89	101
H_c ($Am^{-1} \times 10^4$)	31×10^5	6.3	4.8	10	2

given in Table I. These results are surprising compared to those of X-ray diffraction. We must take into account that the magnetic properties of powders are average properties, for example: the saturation magnetization of a mixture of ferromagnetic products is the weighted average of the magnetization of the different products. In the same way the coercive field is an average value taking into account the relative distribution of the coercive fields of the different products. The derivatives of the magnetization versus the field give this distribution and allows the detection of polyphased systems; they are shown in Fig. 1 for W, Z and Y preparations. Then: Y is pure and Z is formed by two phases: Y characterized by a narrow distribution at low fields and a compound with a large coercive field like M. We can write effectively:

$$Ba_3Fe_{24}Co_2O_{41} \rightarrow BaFe_{12}O_{19} + Ba_2Fe_{12}Co_2O_{12}$$

$$Z \rightarrow M + Y$$

The calculated magnetization of such a mixing corresponds to the experimental one:

$$\frac{\sigma_s(M) + \sigma_s(Y)}{2} = \frac{84.0 + 38.8}{2}$$

$$= 61.3 \text{ uem CGS g}^{-1}$$

At the temperatures used for the glass synthesis method it is not possible to obtain the Z phase. W has a single broad distribution which involves only one phase. Thus we can write:

$$BaFe_{16}Co_2O_{27} \leftrightarrow BaFe_{12}O_{19} + 2CoFe_2O_4$$

$$W \leftrightarrow M + 2S$$

We prepared the mixture M + 2S and compared its magnetic properties to the others products (Table III). A great variation in the coercive field, H_c, is recorded between $BaFe_{16}Co_2O_{27}$ prepared by the glass ceramic method and the mixing (M + 2S). Moreover the derivative of the magnetization of the mixing presents two peaks corresponding with two products. Thus W prepared by the glass ceramic method is also different from the single mixture of M and S. There is probably a solid solution between M and S: a part of the cobalt entering the M structure; this leads to a coalescence of the two coercive fields. At the temperature used it is also impossible to have the W phase.

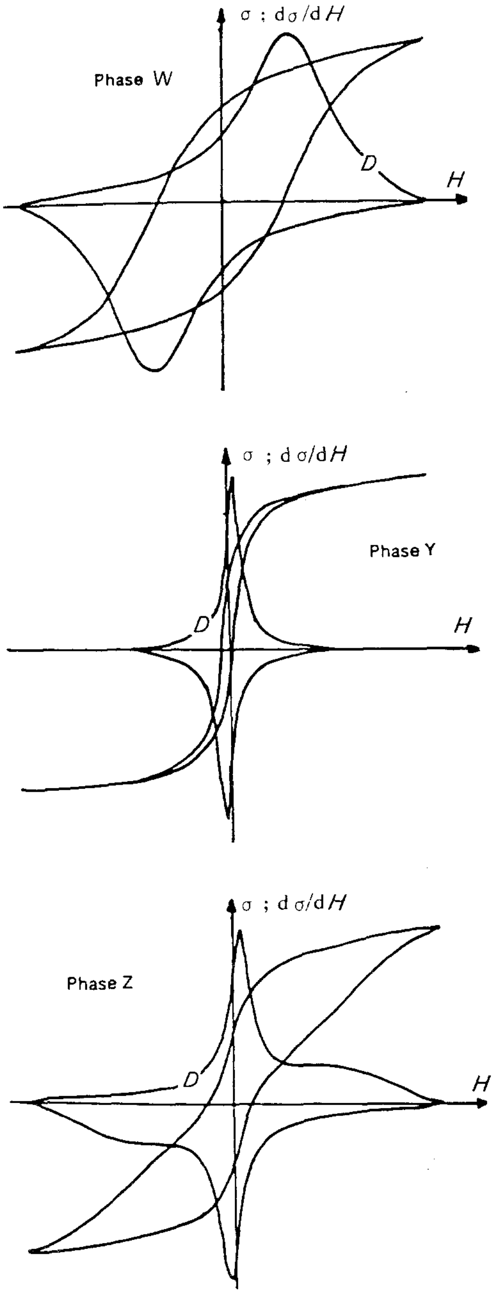

Figure 1 Hysteresis curves with their derivatives D for W, Z and Y phases ($H_{max} = 3.6 \times 10^5$ Am^{-1}).

first. In the same way the dissolution of these spinels having a low magnetization explains the increase of the magnetization with the time of dissolution. For a long time (> 5 h) the solvent also attacks the M phase.

This ferrite formation process is characteristic of the glass synthesis method which uses anhydrous boron oxide and a large amount of barium oxide. Indeed the preparation by the ceramic route ($T = 850\,^{\circ}\mathrm{C}$ for 12 h) of doped barium hexaferrite gives powders with the same macroscopic properties but TEM observations show little isolated cubic crystallites of $CoFe_2O_4$. Then we can conclude the crystallites are bi-phased and the cobalt ferrite is in the core of the platelets.

5. Conclusions

The previous study of the hexagonal barium and cobalt ferrite family has shown that only the M, S and Y phases are stable at 1050 °C. In the same conditions the Z phase is a mixture of M and Y, and W a mixture of S and M lightly doped with Co.

All the recovered products have the M structure except when the cobalt rate increases above $x = 0$ then there is formation of a spinel parasitic phase $CoFe_2O_4$. The amount of $CoFe_2O_4$ decreases when the annealing temperature increases so it crystallizes first and is situated at the core of the hexaferrite platelets. This fact is confirmed by a selective dissolution of the spinel which shows hexagonal holes in the platelets. If these pigments are used for magnetic recording it is necessary that the Co–Fe doping does not induce a bimodal distribution of the coercive fields. To dope barium hexaferrite, fluorine joint with cobalt, not like titanium, does not fix the cobalt into the crystalline network.

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