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Switching field distributions and magnetocrystalline anisotropy fields in Zn-Ti and Co-Ti equally co-substituted BaM ferrites

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M-type hexagonal barium ferrites $\text{Ba}(\text{M}_x\text{Ti}_x)\text{Fe}_{12-2x}\text{O}_{19}$ (M=Co or Ti, $x=0-0.5$) are synthesized by chemical route. Experimental values of the anisotropy fields H_K are extracted from microwave measurements. It is shown that H_K values are very close to the higher switching field. Results show that the shift through lower values both for H_K and the switching field distributions are the largest for CoTi substitutions. A qualitative analysis based on the cations occupation sites is proposed.

Index Terms— substituted hexaferrites, magnetocrystalline anisotropy field, Switching Field Distributions, ions site occupancy

I. INTRODUCTION

IN REASON of its high saturated magnetization M_S , high reduced remanent magnetization m_R ($m_R=M_R/M_S$), and strong uniaxial crystalline anisotropy field H_K , M-type barium hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ (BaM) has common applications in the fields of permanent magnets, magnetic recording and data storage materials, as well as components in electrical devices operating at microwave frequencies [1]. Its use in microwave and millimeter wave (MMW) devices applications, such as circulators [2], [3], meet a reduction in the value of H_K while maintaining a value of m_R close to 0.8 [4]. It is well established that when substituting Fe^{3+} ions by other metal trivalent cations or equiatomic divalent-tetravalent cation combinations, H_K can be diminished [1]. This paper work reports on the consequences of Co^{2+} - Ti^{4+} and Zn^{2+} - Ti^{4+} equiatomic co-substitution for Fe^{3+} on BaM on the switching field distribution and on the magnetocrystalline anisotropy field, the latter being determined by microwave measurements. The switching field distribution (SFD) $f(H)$ is the probability density for a given switching field H . Samples of compositions $\text{Ba}(\text{M}_x\text{Ti}_x)\text{Fe}_{12-2x}\text{O}_{19}$ (M=Co or Ti, $x=0-0.5$) were prepared by chemical route. Our objective is to determine the anisotropy field H_K and the SFD of each of these compositions.

II. DETAILS ON MATERIALS AND EXPERIMENTS

Ceramic samples with compositions $\text{BaFe}_{12-2x}\text{M}_x\text{Ti}_x\text{O}_{19}$, where M represents Co or Zn, and with $x=0-0.5$, were prepared by ceramic processing (firing temperature of 1040°C), powders being synthesized beforehand by chemical route. Samples were cylindrical in shape (height 1.6 mm and diameter 6.8 mm). X-ray diffraction analysis were carried out on a Panalytical Empyrean (Cu $K\alpha$ radiation). Rietveld refinements revealed that the insertion of the dopants into the BaM crystal structure is effective to within about 10%. Magnetic measurements were performed using a Vibrating Sample Magnetometer EZ9 from MicroSense, with a maximum applied field intensity of 1500kA/m. Hysteresis loops were measured in the parallel and perpendicular directions of their basal plane. For each sample these loops

were completely identical, with $m_R=0.5$, which shown the isotropy of the materials [5]. SFD can be obtained by differentiating the reduced Isothermal Remanent Magnetization (IRM) curve $m_R(H)$ [6]: $f(H)=[dm_R/dH]_{H=H_K/2}$. The frequency evolution of the imaginary part of the magnetic permeability was extracted using a Rohde & Schwarz ZVA67 vector network analyser in the frequency band [10GHz-60GHz]. For each composition the values of H_K were measured. In this goal, the anisotropy field H_K of each sample was deduced from its resonant frequency f_R determined by the maximum of the imaginary part μ'' of the intrinsic permeability. Actually, the relationship between H_K and f_R writes $f_R=\gamma H_K$, γ being the gyromagnetic ratio ($\gamma=1.7608 \cdot 10^{11} \text{ s}^{-1}\text{T}^{-1}$).

III. THE SWITCHING FIELD DISTRIBUTIONS

We determined the switching field distribution (SFD) for each sample examined in this study, after correction for the demagnetizing field (Fig. 1). The values of the anisotropy fields H_K measured with microwave experiments are also reported in Fig.1. H_K is always slightly lower than the higher switching field, although this is less true for CoTi than for ZnTi. A reason for this is may lie in complex switching mechanisms like dipolar interactions, that surely influence SFD measurements [ref= publi Martinez JAP 2012]. The value of the most probable switching field (MPSF: located by the maximum of $f(H)$) and that of the anisotropy field H_K are presented Table 1. When x increased, H_K decreased more strongly for BaM-CoTi than for BaM-ZnTi samples. As early as $x=0.1$, for both compositions, the MPSF was shifted by about 91 kA/m towards the weak fields, compared to pure BaM (Fig.1). It can be also observed that, for the two compositions with $x=0.1$, the SFD were identical in the low field region (ie at lower value than the MPSF. However, they are clearly different in the high fields region (ie at higher value than the MPSF), where higher fields were more probable for BaM-TiZn than for BaM-CoTi samples. This finding was also be made for $x=0.5$ (here the MPSF shifted by 308 kA/m for BaM-CoTi and 265 kA/m for BaM-ZnTi, with regard to $x=0.1$).

IV. DISCUSSION

The magnetic anisotropy in BaM ferrite is influenced by the Fe^{3+} ions distribution in five crystallographic sites: three octahedral sites 12k ($\uparrow, -0.18$), 2a ($\uparrow, 0.23$) and 4f2 ($\downarrow, 0.51$), one tetrahedral site 4f1 ($\downarrow, 0.18$), and one bipyramidal site 2b ($\uparrow, 1.4$) (the arrows indicate upward and downward spins configuration, the following value is that of the Fe^{3+} contribution to the first anisotropy constant K_1 , expressed in $\text{cm}^{-1}/\text{ion}$ units [7].)

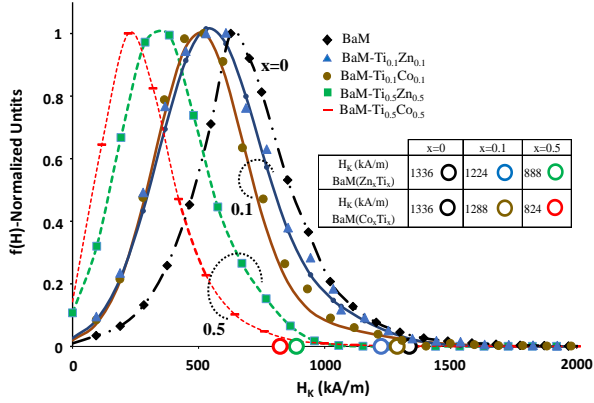


Fig. 1. SFD and magnetocrystalline fields values H_K (inset). The later are also represented by the large open circles in the figure **sur axe des abscisses**. H_K values were obtained from microwave measurements. The values for x are also indicated (dashed circles). For a sake of clarity, only results for x=0, 0.1 and 0.5 are shown.

TABLE I
DATA FROM SFD AND MICROWAVE MEASUREMENTS (H_K)

| | | x=0 | x=0.1 | x=0.2 | x=0.3 | x=0.4 | x=0.5 |
|--------------------------------------|-------------------------------------|------|-------|-------|-------|-------|-------|
| Most probable switching field (kA/m) | BaM-Zn _x Ti _x | 630 | 520 | 434 | 420 | 347 | 330 |
| | BaM-Co _x Ti _x | 630 | 530 | 440 | 405 | 310 | 220 |
| Anisotropy field H_K (kA/m) | BaM-Zn _x Ti _x | 1336 | 1224 | 1112 | 1048 | 968 | 888 |
| | BaM-Co _x Ti _x | 1336 | 1288 | 1208 | 1088 | 928 | 824 |

Then the major positive contribution to the magnetic anisotropy constant K_1 comes from iron ions at 4f2 and 2b sites, whereas 4f1 and 2a sites occupation have limited influence on the value of K_1 . According to [8], two criteria influence the actual doping ions site occupancy. First, according to Ligand theory, ions with d^1 , d^2 , d^3 and d^4 electrons prefer tetrahedral site, ions with d^6 , d^7 , d^8 and d^9 electrons prefer octahedral site, and ions with d^0 , d^5 and have no preference [1]. As the second criterion, ions of higher electro-negativity have higher tendencies for octahedral sites. Consequently, considering Co-Ti co-substitution first, Co^{2+} ions preferentially occupy the 2b and 2a sites while Ti^{4+} ions occupy 2a and 4f2 sites. Therefore, the presence of Co^{2+} is expected primarily in 2a and 2b, whereas the site distribution of Ti^{4+} would be uniform. However, it was also reported [9] that at low doping levels ($x < 1$) Ti^{4+} first occupy 2a and 4f2 sites, then pushing Co^{2+} to 2b sites. Finally, Co^{2+} would occupied foremost 2b, and also 2a sites, whereas Ti^{4+} occupy 2a and 4f2. For ZnTi co-substitutions, the literature is less extensive: Ti^{4+} ions may mainly occupy 4f2 and 12k, whatever

its partner cation, the non-magnetic Zn^{2+} ions replace Fe^{3+} at 4f1 only [10], [11], the contribution of which to the anisotropy ($0.18 \text{ cm}^{-1}/\text{ion}$) being negligible. Moreover, the single-ion model showed that the total anisotropy constants are closely related to the occupancies of the Fe^{3+} ions and that Fe^{3+} ions on the 2b site provide the largest positive contribution to the magnetocrystalline anisotropy. Then, since the nonmagnetic Zn^{2+} and Ti^{4+} ions have no contribution to magnetocrystalline anisotropy, and making the hypothesis that they occupy 4f2, 12k and 4f1, it is expected that the total anisotropy in BaM-ZnTi materials would strongly decrease with the substitution level, since Fe^{3+} ions are the main contributors. Whereas, for BaM-CoTi materials, the presence of Ti^{4+} in the 2a and 4f2 sites weakened the uniaxial magnetocrystalline anisotropy, while magnetic Co^{2+} in 2b sites, on the contrary, would contribute to maintain a higher value of the anisotropy. This helps to understand why the probability density for the higher switching fields region is lower for BaM-ZnTi than for BaM-CoTi.

To conclude, these results established firstly that the higher switching field can be identified as the anisotropy field. The experiments also shown that CoTi substitution is more effective in order to lower the magnetocrystalline anisotropy than substitution by ZnTi. Although the presented interpretation would require to be supported by other experiments (hysteresis loops, Mössbauer spectroscopy), our qualitative analysis based on a commonly admitted cations site occupation and the single-ion model of anisotropy enabled to explain the distinctive SFD between $\text{BaFe}_{12-2x}\text{Co}_x\text{Ti}_x\text{O}_{19}$ and $\text{BaFe}_{12-2x}\text{Zn}_x\text{Ti}_x\text{O}_{19}$.

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