Structure and magnetic properties of BaCoTiFe$_{10}$O$_{19}$ thin films with an easy-axis in-plane orientation

B. X. GU
Department of Physics, Nanjing University, Nanjing 210093, China

BaCoTiFe$_{10}$O$_{19}$ hexaferrite thin films with an easy-axis in-plane orientation were prepared by crystallization of amorphous films deposited by rf magnetron sputtering. The structure and magnetic properties were investigated. It is shown that CoTi-doping leads to a reduction of spontaneous magnetization and magnetic moment, which is caused by non-collinear magnetic structure and surface spin canting of small particles. The substitution of CoTi for Fe can adjust coercivity and Curie temperature over a very wide range, while still maintaining the room temperature magnetization. It is found that BaCoTiFe$_{10}$O$_{19}$ films exhibit a large squareness of hysteresis loop, $S_q = 0.68$. Thus, this film is desirable for high-density longitudinal recording systems. © *1998 Kluwer Academic Publishers*

1. Introduction

Barium ferrite has recently attracted much attention as a new thin film medium for high density longitudinal magnetic recording and magneto-optical recording, because of its large uniaxial magnetic anisotropy, large magneto-optical Faraday rotation, excellent chemical stability, high hardness and durability [1, 2]. It has been found in the BaFe$_{12}$O$_{19}$ hexaferrites that the substitution of Co for Fe can enhance the Faraday rotation and reduce the coercivity and Curie temperature to the values suitable for magnetic and magneto-optical recording [3–5]. Recently, we prepared CoTi-doped M-type hexaferrite thin films by rf magnetron sputtering. The structure, magnetic and magneto-optical properties were investigated. In the previous paper we reported the structure, magnetic properties and crystallization process of amorphous films [6]. In this paper the structure and magnetic properties of crystalline films are reported.

2. Experimental

The films were prepared by rf magnetron sputtering in an argon atmosphere, without addition reactional oxygen gas. A sintered polycrystalline target with the stoichiometric composition BaCoTiFe$_{10}$O$_{19}$ was prepared by standard ceramic technique from the high-purity oxides BaCO$_3$, CoO, TiO$_2$, and Fe$_2$O$_3$. Quartz glass was used as the substrate. The target and substrate were cooled with water. The base pressure of the chamber before introducing argon gas was better than 1.3×10^{-7} kPa. The pressure of the sputtering gas, argon, was 2.67 Pa. The deposition rate was about 1 μm/h. The film thickness was about 1.1 μm. The films exhibit a deep-red colour and transparency. The surface of the films is shiny and homogeneous. The structure of the films was analyzed by X-ray diffraction with CuK$_\alpha$ radiation. The room temperature hysteresis loops were measured by a vibrating sample magnetometer with applied field up to 1600 kA/m. The low temperature magnetization curve was measured with an extracting sample magnetometer with a magnetic field up to 5200 kA/m.

3. Results and discussion

X-ray diffraction analysis shows that as-sputtered films are amorphous. They were crystallized to single M-type hexaferrite by annealing in a tube furnace at 800 °C for one hour in an oxygen atmosphere. It is found that annealing atmosphere has an important influence on the structure of annealed films. When the as-sputtered films are annealed in air, the M-type hexaferrite can not be obtained. Fig. 1 shows the X-ray diffraction pattern of an annealed film. For comparison the X-ray diffraction pattern of the sintered polycrystalline target with the same composition is also given in Fig. 1. The pattern of the target is the same as the standard X-ray powder diffraction pattern of M-type hexaferrite. (1 0 7) is the strongest peak, (1 1 4) is the second. However, the pattern of the film shows that (1 1 0) is the strongest, (2 2 0) is the second. (1 0 7) peak disappears, whilst (0 0 6), (0 0 8), and (0 0 14) peaks normally seen in c-axis perpendicularly oriented films are almost indiscernible. This indicates that the c-axis has in-plane orientation. A clear broadening in both (1 1 0) and (2 2 0) peaks is also observed. This suggests that the grain size is probably reduced. The average particle diameter was calculated to be 65 nm using the Scherrer formula.
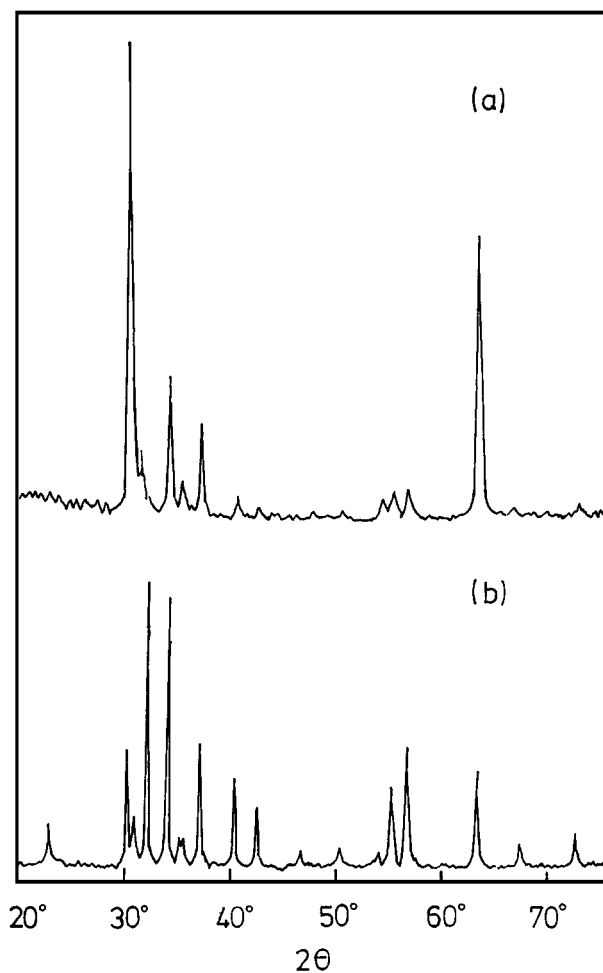
Figure 1 X-ray diffraction patterns for (a) $BaCoTiFe_{10}O_{19}$ film and $BaCoTiFe_{10}O_{19}$ polycrystalline target.

Figure 2 Magnetization curve of $BaCoTiFe_{10}O_{19}$ film measured at 1.5 K.

It is noted that M-type hexaferrite film with the easy direction of magnetization in-plane can be prepared by crystallization of amorphous films deposited with rf sputtering technique. The formation of the films with (1 1 0) texture is related to the structure of as-sputtered amorphous films. The as-sputtered films are not, however, completely disordered. The studies of Raman spectra and infrared spectra show that there are tetrahedral structures in amorphous oxide films [7]. The local structure around the Fe ions is anisotropic and is similar to that in crystalline M-type hexaferrite with (1 1 0) texture. The local structure could be the determining factor for crystallization and texturing, the directions of fastest growth forming along the preexisting directions of more crystalline-like order.

Fig. 2 shows the magnetization curve measured at 1.5 K. The spontaneous magnetization $M_s = 3.65 \times 10^5$ A/m was obtained by extrapolating the linear portion of the magnetization curve to $H = 0$. The magnetic moment μ per unit formula of the $BaCoTiFe_{10}O_{19}$ films can be calculated using both mean field theory and 1.5 K magnetization M_s with the equation

$$\mu = \frac{M_s W}{N A \mu_B} \tag{1}$$

where W is the molecular weight, N is Avogadro's number, μ_B is the Bohr magneton, and A is density.
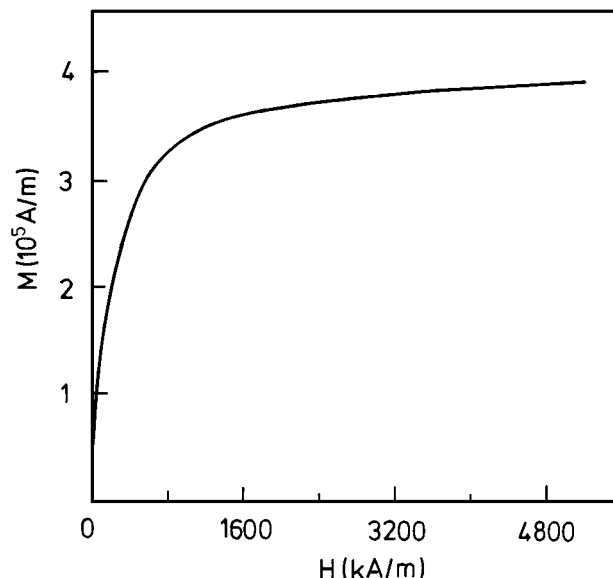
$\mu = 13.7\,\mu_B$/f.u. is obtained. This value is much smaller than 20 μ_B/f.u. for the $BaFe_{12}O_{19}$ compound and is smaller than 14.3 μ_B/f.u. for the bulk $BaCoTiFe_{10}O_{19}$ compound. Neutron diffraction and NMR studies have shows that the Ti^{4+} ions are mainly distributed within $4f_{VI}$ and 12k sites, whilst Co^{2+} ions occupy mainly $4f_{IV}$ and 12k sites [8, 9]. Using the distribution amount of Co^{2+} and Ti^{4+} ions in the 12k, $4f_{IV}$ and $4f_{VI}$ sites obtained by neutron diffraction and NMR, a larger magnetic moment μ than 14.3 μ_B/f.u. can be obtained according to the Gorter collinear magnetic structure and taking $\mu(Fe^{3+}) = 5\,\mu_B$, $\mu(Co^{2+}) = 3\,\mu_B$, and $\mu(Ti^{4+}) = 0\,\mu_B$. Additionally, from the magnetization curve we obtained a high field susceptibility as large as 1.9×10^{-4} which is much larger than 2.5×10^{-5} for the $BaFe_{12}O_{19}$ hexaferrite and 1.4×10^{-4} for bulk $BaCoTiFe_{10}O_{19}$ hexaferrite. The high field susceptibility denotes the existence of non-collinear spins in the magnetic structure [10]. Thus the decrease of the magnetic moment originates from the non-collinear magnetic structure.

The origin of the non-collinear magnetic structure is presumably related to the exchange interaction. Fig. 3
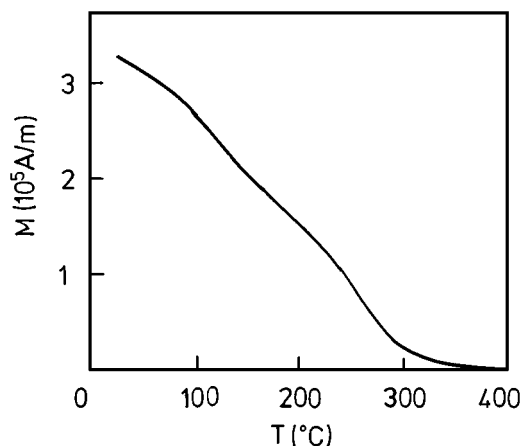

Figure 3 The temperature dependence of magnetization of $BaCoTiFe_{10}O_{19}$ film.

shows the temperature dependence of the magnetization. It can be seen that the $BaCoToFe_{10}O_{19}$ hexaferrite film has a Curie temperature $T_c = 283\,°C$, which is much lower than $450\,°C$ for the $BaFe_{12}O_{19}$ hexaferrite. The strong decrease of T_c demonstrates that some intersublattice exchange interaction are strongly diminished. From the fact that the experimental value of magnetization at 1.5 K is much smaller than the theoretical value obtained by the Gorter collinear spin model, it can be seen that the spin non-collinearity appears mostly in the spin-up sublattices, especially, the 12k sublattice which has a higher degree of frustration being in this way strongly affected by the decrease of the 12k-4f$_I$ interaction [11]. A mean-field analysis of the exchange interaction in M-type hexaferrites has been carried out by Isalgue *et al*. [12]. The result shows that the Fe(12k) sublattice, making the link among R and S structural block, is subjected to very strong competitive exchange interaction. So when the Fe^{3+} ions in the 12k sublattice are substituted by the non-magnetic Ti^{4+} ions, weakening of the superexchange interaction between magnetic ions results in a strongly canted ferrimagnetism.

Additionally, the magnetic surface effects of fine magnetic particles may also cause reduction of the magnetization of $BaCoTiFe_{10}O_{19}$ films. X-ray diffraction analysis shows that the $BaCoTiFe_{10}O_{19}$ films have a small particle size. The smaller the particle, the larger important is the surface area with respect to the volume. Because of the suppression of some superexchange interaction in the particle surface, the surface spins exhibit the non-collinearity. It causes the decrease of the saturation magnetization.

The hysteresis loops of the film measured in the direction parallel (∥) and perpendicular (⊥) to film plane at room temperature are shown in Fig. 4. The values of coercivity H_c, saturation magnetization M_s, and squareness of hysteresis loop $S_q = M_r/M_s$ are given in Table I. It is seen that the substitution of CoTi causes a slight decrease of the saturation magnetization, but it causes a dramatic decrease of the coercivity. This demonstrates
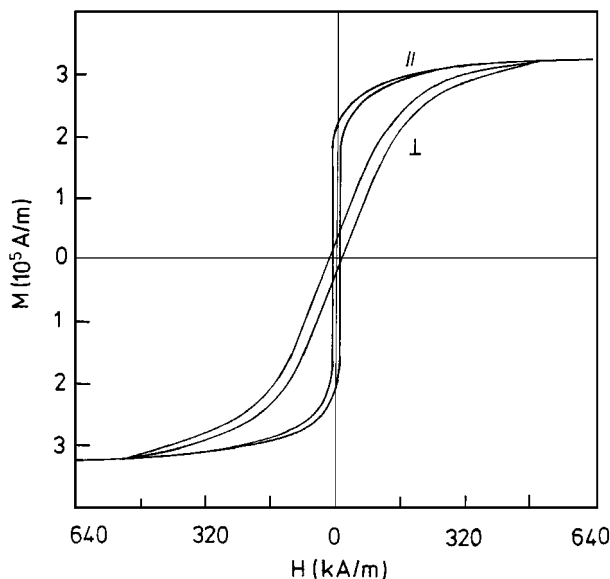
TABLE I The values of coercivity H_c, saturation magnetization M_s and squareness of hysteresis loop S_q for $BaCoTiFe_{10}O_{19}$ film measured in the direction parallel (∥) and perpendicular (⊥) to the film plane

	H_c (kA/m)	M_s (kA/m)	S_q
∥	7.96	326	0.68
⊥	12.74	326	0.10

Figure 5 FMR spectra of $BaCoTiFe_{10}O_{19}$ film measured in the direction parallel (∥) and perpendicular (⊥) to the film plane.
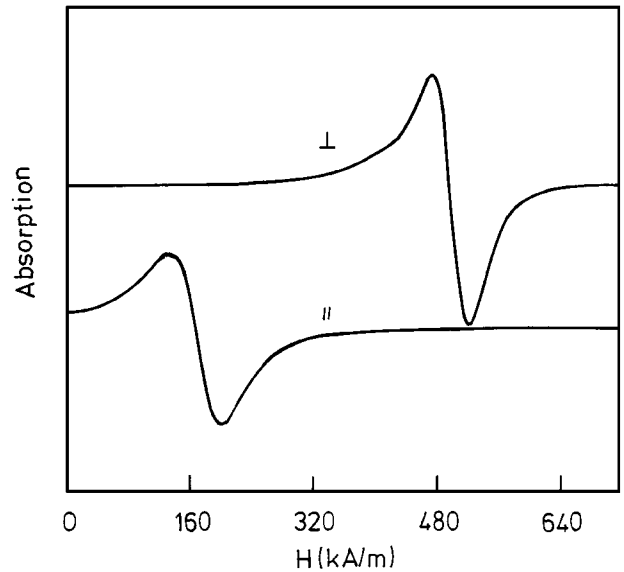

Figure 4 Hysteresis loops of $BaCoTiFe_{10}O_{19}$ film measured in the direction parallel (∥) and perpendicular (⊥) to the film plane.

that the coercivity of barium ferrite thin films can be adjusted over a very wide range by an appropriate amount of CoTi-doping, while still maintaining the saturation magnetization. It is noted that the $BaCoTiFe_{10}O_{19}$ films exhibit a large in-plane squareness. In general, larger in-plane s_q results in larger read-back signals and is therefore desirable in longitudinal recording systems.

Ferromagnetic resonance (FMR) spectra of the $BaCoTiFe_{10}O_{19}$ films were measured with a commercial EPR spectrum meter at X-band (9.778 GHz) at room temperature. The external magnetic field was applied in the direction parallel (∥) and perpendicular (⊥) to film plane. Fig. 5 shows the FMR spectra of the film. From Fig. 5 we obtained that the resonance field $H_∥ = 1.69 \times 10^5$ A/m, $H_⊥ = 4.96 \times 10^5$ A/m, and the linewidth $\Delta H_∥ = 5.65 \times 10^4$ A/m, $\Delta H_⊥ = 4.14 \times 10^4$ A/m. It is noted that the linewidth of $BaCoTiFe_{10}O_{19}$ film is smaller than 9.55×10^4 A/m for $BaFe_{12}O_{19}$ single crystals [13]. This result demonstrates that CoTi-doping can decrease the linewidth of barium ferrite.

According to FMR theory for the resonance condition, for the case of external field in the film plane (∥) and perpendicular (⊥) to the film plane we have

$$\left(\frac{w}{r}\right)^2 = H_∥(H_∥ + M_{eff}) \qquad (2)$$

$$\frac{w}{r} = H_⊥ + M_{eff} \qquad (3)$$

where $M_{eff} = M_s - H_{Aeff}$, M_{eff} is the effective magnetization, H_{Aeff} is the effective anisotropy field, $r = g\mu_0 e/2m$ is the gyromagnetic ratio, and g is g-factor. Using the values of $H_{\parallel}$ and $H_{\perp}$ measured by FMR and the value of M_s measured by VSM, we can calculate the values of M_{eff}, g, and H_{Aeff}. They are 2.4×10^5 A/m, 2.18, and 86 kA/m, respectively. Compared with $g = 1.98$ [14] and $H_{Aeff} = 1.47 \times 10^3$ kA/m [15] for single crystal of barium ferrite, it can be seen that CoTi-doping causes an increase of g-factor and a large decrease of H_{Aeff}.

4. Summary
BaCoTiFe$_{10}$O$_{19}$ hexaferrite thin films have been prepared by crystallization of amorphous films deposited by rf magnetron sputtering. The structure and magnetic properties have been studied. The obtained results are summarized below.

1. The transparent sputtered 1.1 μm thick films are polycrystalline with a fine grain size (65 nm).

2. The magnetocrystalline (c) easy axis is co-linear with the shape anisotropy.

3. The non-collinear magnetic structure was observed from the decrease of the spontaneous magnetization and the increase of high field susceptibility. Its origin is the reduction of the exchange interaction due to the substitution of Ti ions for Fe ions in the 12k sublattice and the magnetic surface effects of fine magnetic particles.

4. Ferromagnetic resonance study shows that BaCoTiFe$_{10}$O$_{19}$ films have a smaller effective anisotropy field and a larger g-factor than the bulk samples.

5. BaCoTiFe$_{10}$O$_{19}$ films exhibit a large squareness ($s_q = 0.68$) at room temperature. The coercivity and Curie temperature are controllable in a very wide range by replacing some of the Fe ions by Co and Ti ions.

Therefore these films are suitable for high-density longitudinal recording systems.

References
1. T. L. HYLTON, M. A. PARKER, M.-ULLAH, K. R. COFFEY, R. UMPHRESS and J. K. HOWARD, *J. Appl. Phys.* **75** (1994) 5960.
2. T. FUJIWARA, *IEEE Trans. Magn.* **MAG-21** (1985) 1480.
3. Y. KANEKO, Y. SAWADA, F. OHMI, M. MIYAMOTO and A. WATADA, *Jap. J. Appl. Phys.* **26s** (1987) 23.
4. H. MACHIDA, F. OHMI, Y. SAWADA, Y. KANEKO, A. WATADA and H. NAKAMURA, *J. Magn. Magn. Mater.* **54–57** (1986) 1399.
5. N. HRATSAKA, M. FUJITA and M. SUGIMOTO, *J. Magn. Soc. Jap.* **15** suppl (1991) 239.
6. B. X. GU, H. Y. ZHANG, H. R. ZHAI, M. LU and Y. Z. MIAO, *J. Phys.: Condens, Matter* **6** (1994) 1047.
7. B. X. GU, S. Y. ZHANG, H. Y. ZHANG, X. B. ZHU and H. R. ZHAI, *J. Appl. Phys.* **79** (1996) 7075.
8. L. KALVODA, M. DLOUHA and S. VRATISLAV, *J. Magn. Magn. Mater.* **87** (1990) 243.
9. H. STEPANKOVA, J. KOHOUT and Z. SIMSA, *ibid.* **104–107** (1992) 411.
10. R. GROSSINGER, *Phys. Stat. Sol. (a)* **66** (1981) 665.
11. G. ALBANESE, A. DERIU, E. LUCCHINI and G. SLOKAR, *Appl. Phys.* **A26** (1981) 45.
12. A. ISALGUE, A. LABARTA, J. TEJADA and X. OBRADORS, *ibid.* **A39** (1986) 221.
13. I. BADY, *Proc. IRE* **48** (1960) 2033.
14. J. SMIT and H. G. BELJERS, *Philips. Res. Repts.* **10** (1955) 113.
15. Y. F. WANG, K. ISHIL and J. TSUI, *J. Appl. Phys.* **32** (1961) 1621.