

Barium Hexaferrite Thin Films Prepared by the Sol-Gel Method

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Nano-crystalline hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ (BaM) thin films have been prepared by the sol-gel method. A solution of Ba-nitrate and Fe-nitrates was dissolved in solvent with the stoichiometric ratio Ba/Fe=1/10. Films were spin-coated onto SiO_2/Si substrates, dried and then heated in air at various temperatures. In films prepared at a drying temperature $T_d=250$ °C and a crystallizing temperature 650 °C, single-phase BaM was obtained. High coercivities were obtained in these nano-crystalline thin films, 4~5.5 kOe for hexaferrite. Polycrystalline BaM/ $\text{SiO}_2/\text{Si}(100)$ thin films were characterized by Rutherford backscattering (RBS), thermogravimetry (TGA), differential thermal analysis (DTA), x-ray diffraction (XRD), and vibrating sample magnetometry (VSM), as well as Fourier transform infrared spectroscopy (FTIR). The perpendicular coercivity $H_{C\perp}$ and in-plane coercivity $H_{C\parallel}$ after annealing at 650 °C for 2 hours were 4766 Oe and 4480 Oe, respectively, at room temperature, under a maximum applied field of 10 kOe.

1. Introduction

M-type hexagonal barium ferrite (BaM) is well established as a permanent magnetic material. It has excellent chemical stability and is relatively cheap to produce. Barium ferrite magnetic materials with high coercivity also have applications as magnetic recording media, and in microwave devices. [1] Various preparation methods have been developed, including sputtering [2], pulsed laser deposition [3], metallorganic chemical vapor deposition [4], and the sol-gel method [5].

The sol-gel technique has emerged in recent years as a versatile method for synthesizing inorganic materials. Apart from the advantage of low temperature processing, a sol-gel route makes it possible to obtain nano-particle materials [1]. Though the sol-gel process has made an impact on materials technology, the high cost of alkoxides appears to be a hindrance to its large scale use in preparing conventional materials. In this work, thin films of barium hexaferrite (BaM) layers on thermally oxidized silicon wafers were fabricated by the sol-gel method. We have avoided using alkoxides, thereby ensuring that the preparation cost is not high. Polycrystalline barium hexaferrite thin films were characterized with RBS, XRD, VSM, TGA-DTA, and FTIR.

2. Experimental Procedures

A block diagram outlining the preparation process is

shown in Fig. 1. Barium nitrate [$\text{Ba}(\text{NO}_3)_2$] and iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] were used as starting materials, and were combined so that the composition ratio Ba/Fe=1/10. These were dissolved in methanol and distilled water. The solution was refluxed at 80 °C for 24 h. The resulting precursor solutions were made 0.2 M. The films were spin-coated onto thermally oxidized silicon substrates (10×10 mm), dried, and then heated in air at various temperatures. The crystal structures and stoichiometries were investigated by x-ray diffraction using CuK α radiation and Rutherford back-scattering spectroscopy. Thermal analysis by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on the dried powder obtained from the $\text{BaFe}_{12}\text{O}_{19}$ precursor solution. The FTIR studies were done using a FTIR spectrophotometer (Mattson) on films coated onto KBr single-crystal substrates. Magnetic properties were measured using a vibrating sample magnetometer at a maximum applied field of 10 kOe.

3. Results and Discussion

The thermal decomposition characteristic of the gel system with temperature was studied by DTA and TGA, as shown in Fig. 2. In this study, the $\text{BaFe}_{12}\text{O}_{19}$ (BaM) was pre-dried at 120 °C for 12 hours and the thermolysis behavior was analyzed using a heating rate of 5 °C/min. TGA analysis indicated a major weight loss at 260~600 °C. It can be seen that the gel exhibited approximately 68 % weight loss up to 600 °C. While the rapid weight decrease was due to evaporation of the solution and thermal decom-

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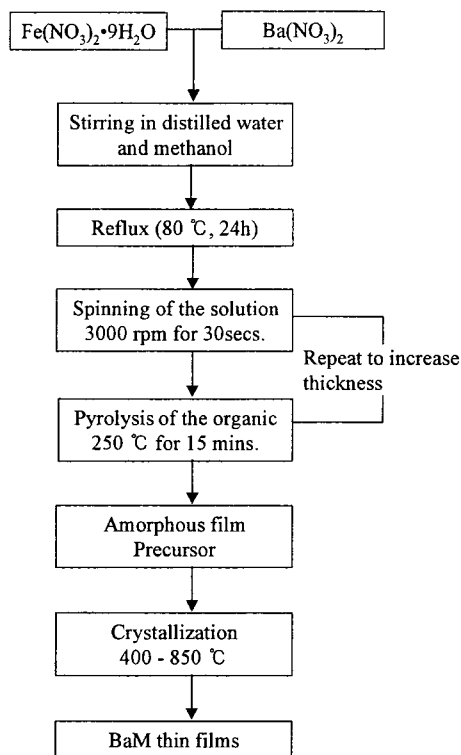


Fig. 1. Preparation process for BaFe₁₂O₁₉ thin films.

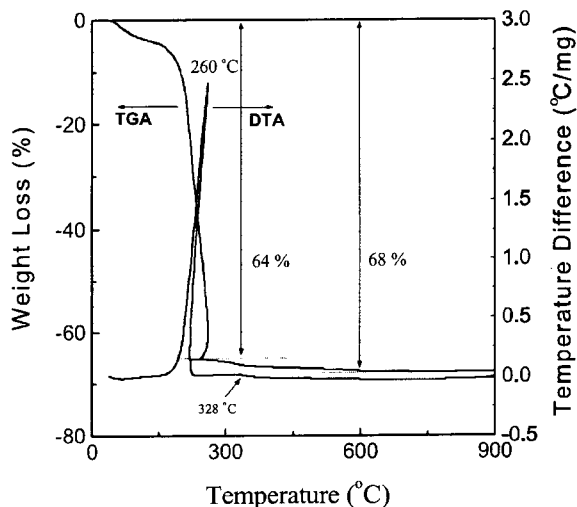


Fig. 2. TGA/DTA curves of BaFe₁₂O₁₉ gel powder.

position of organic components, the gradual decrease in the weight is thought to be caused by the thermal decomposition of organic groups bonded to the oxide network. DTA analysis indicated an exothermic peak. The peak at 260 °C is associated with the organic weight losses. However, the final peak appears at about 328 °C. No additional peak was observed above 328 °C, indicating that complete thermal decomposition and crystallization of BaFe₁₂O₁₉ occur simultaneously. Figure 3 shows x-ray diffraction (XRD) patterns for the barium ferrite films prepared by sol-gel method. No diffraction lines are observed in Fig. 3(a) for an as-deposited film. This indicates that the film is amorphous. M-type single phase is observed in the sample annealed at

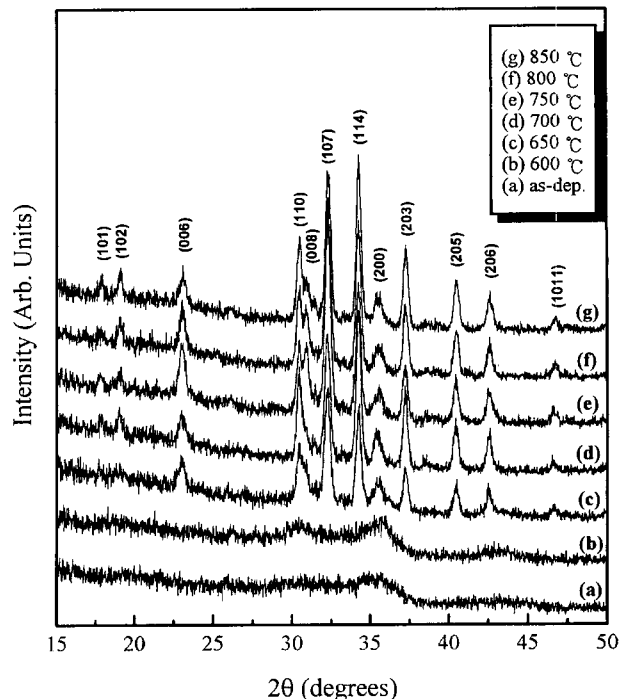


Fig. 3. X-ray diffraction patterns of thin films annealed at various temperatures.

temperatures above 650 °C. It should be noted that no α -Fe₂O₃ phase is detectable. The stoichiometric Ba/Fe ratio was confirmed by RBS. The average size of the crystallites can be estimated from the full-width at half-maximum (FWHM) of the peaks using the Scherrer equation [6], and the results are listed in Table 1.

FTIR structure investigations are mostly used to characterize the synthesis reactions, and to identify the effect of structure of the solution on the formation of the film. Fig. 4(a) shows the spectrum of the barium ferrite precursor prepared from barium nitrate reacted with the solvent mixture system. The band at 3430 cm⁻¹ is due to O-H species in the precursor and those at 2800~3000 cm⁻¹ are due to C-H stretching frequencies. The band seen at 1500~1600 cm⁻¹ is due to C=O, arising due to the bridging type metal-acetate bonding (M-OCOO-M), and a set of bands at 1480 and 1360 cm⁻¹ can be assigned to the NO₂ stretching vibrations of the nitrate group. In addition, it is noted that a M-OR stretching peak, which should be observed before the formation of metal-oxygen bond, was visible near 650 cm⁻¹ [8]. This might be attributable to a metal-oxygen stretching peak of the M-O-M bond, and the presence of the M-O-M

Table 1. Particle size D, in-plane coercivity $H_{c||}$, perpendicular coercivity $H_{c\perp}$, lattice parameters a_0 and c_0 of BaFe₁₂O₁₉.

Annealed Temperature (°C)	D (nm)	$H_{c }$ (Oe)	$H_{c\perp}$ (Oe)	a_0 (Å)	c_0 (Å)
650	41	4480	4766	5.871	23.269
750	46	4656	4872	5.873	23.273
850	58	5180	5229	5.878	23.271

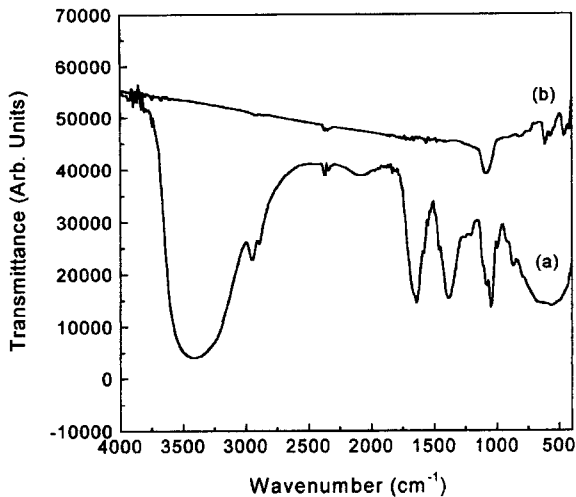


Fig. 4. FTIR spectra of BaFe₁₂O₁₉ (a) precursor dissolved in mixture solvent system and (b) thin film pyrolysed at 750 °C for 2h.

peak can verify a gelation at a Ba-Fe precursor synthesis step.

Next, the structural change of the film on heating will be discussed. Fig. 4(b) shows the spectrum of a barium ferrite thin film annealed at 750 °C, which shows absence of absorption bands corresponding to organics and hydroxyls indicating complete removal of organics and hydroxyls. In Figure 4(b), the band at 1000~1200 cm⁻¹ is clearly observed in the thin film. These peaks can be assigned to carboxylate groups. However, the metal oxygen stretching peak of the M-O-M bond (600 cm⁻¹) was still observed. It is noteworthy that the M-O-M peak is shifted to higher frequency by heat treatment. This can be interpreted to mean that the metal-oxygen bond became stronger as the gel evolved to a hexagonal structure. With these results, it can be inferred that on heat treatment of barium ferrite gel, the polymer was desorbed and the by products (ester, alcohols) or solvent was evaporated by the heat treatment. The elimination of organics may affect the crystallization behavior, such that crystallization occurs at a lower temperature, where the barium ferrite phase forms more readily into a homogeneous dense microstructure.

Figure 5 shows a magnetic hysteresis loop of the sample annealed at 650 °C for 2 h. The perpendicular coercivity H_{CL} and in-plan coercivity $H_{C||}$ were 4766 Oe and 4480 Oe, respectively, at room temperature at a maximum applied field of 10 kOe. This shows that the film has isotropic properties [7]. The perpendicular coercivity squareness $S^* = 1 - (M_r/H_c)/(dM/dH)$, a measure of the slope of the loop at H_c , is 0.65. The orientation coefficients $S = M_r/M_s$ in both the parallel and perpendicular directions are plotted in Fig. 6 as a function of annealing temperature for the samples heated in air. Above 650 °C insignificant differences are observed and the corresponding values lie around 0.5, revealing that thin films are magnetically isotropic.

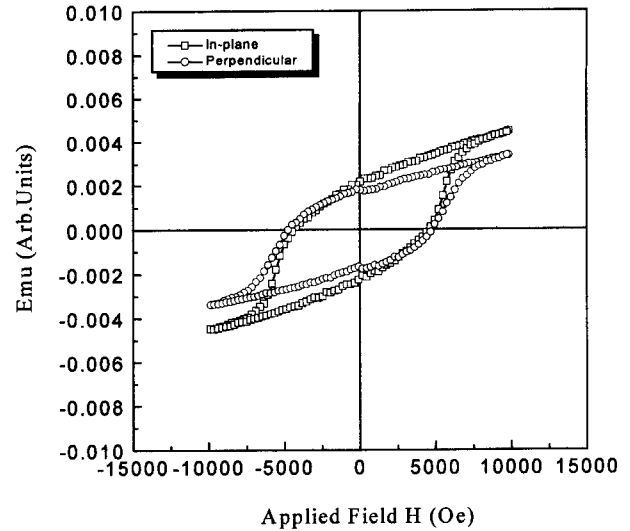


Fig. 5. In-plane and perpendicular hysteresis loops of the film annealed at 650 °C for 2h.

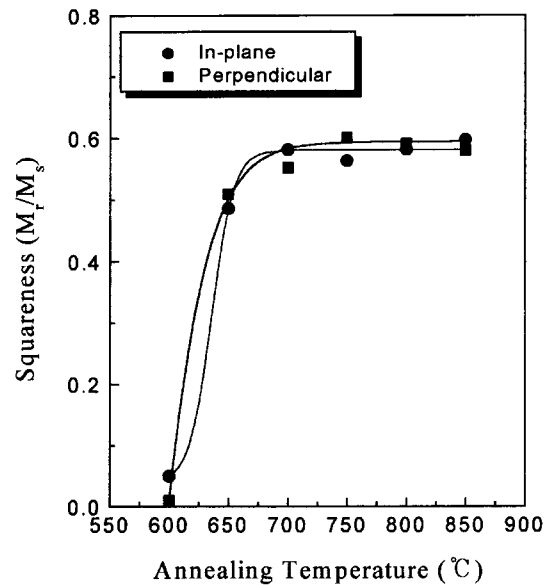


Fig. 6. Dependence of squareness both in-plane and perpendicular directions on annealing temperatures for Ba ferrite thin films.

4. Conclusion

High-coercivity polycrystalline BaFe₁₂O₁₉ thin films were successfully grown by the sol-gel method. Ba ferrite films can be obtained by choosing a starting composition ratio of Ba/Fe = 1/10, a drying temperature of 250 °C and a crystallizing temperature of 650 °C. The crystallization temperature is at least 100 °C lower than the values previously reported for the other preparative methods [9].

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