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Properties of pulsed laser deposited scandium-doped barium hexaferrite films

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The properties of thin films of $BaSc_xFe_{12-x}O_{19}$ ($x=0.4$) were determined by structural and magnetic measurements. Films were deposited by pulsed laser ablation deposition onto c-plane sapphire at oxygen pressures between 10 and 100 mTorr. X-ray diffraction measurements showed all films to be single-phase c-axis oriented hexaferrites with expanded c-axis lattice constants compared to $x=0$ films. Magnetometry measurements showed that all films had the easy axis (c-axis) normal to the film plane, with a mean saturation magnetization value of 3.8 kG. The mean uniaxial anisotropy field value was 10.6 kOe. This ability to adjust the uniaxial anisotropy field in hexaferrite films through selective substitution will be important for future planar microwave devices. © *1999 American Institute of Physics.* [S0021-8979(99)42208-X]

Hexagonal ferrites are gaining importance as technological materials because of their strong internal anisotropy fields that can provide for either uniaxial or planar magnetic self-biasing.

One parameter of primary importance for the use of M-phase hexaferrites $MeO \cdot 6Fe_2O_3$ (Me=Sr, Ba) in millimeter wavelength devices such as circulators is the intensity of the uniaxial anisotropy field (H_A).[1] The existence of a substantial H_A yields a ferrimagnetic resonance (FMR) at millimeter wavelengths without an external magnet if the oriented hexaferrite is self-biased by a high magnetic remanence, or with relatively small external magnets to overcome the demagnetizing field for the case of c-axis oriented single crystal films having small coercive fields. In either case, the size and strength of the external magnet needed will be significantly less than those required for analogous devices made from standard microwave spinel ferrites or garnets operating at the same frequency.[2,3] Predictions for the values of H_A needed to build circulators operating at particular frequencies can be made based on standard circulator models. In particular, it has been indicated that for film-based circulator designs operating in the important frequency range near 35 GHz the hexaferrite H_A values should be about 11 kOe.[2] Unfortunately, the H_A values for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ are, respectively, 17 and 19 kOe,[4] and are thus too high for efficient circulator operation in this frequency band. Hence, new hexaferrite materials must be developed.

Research by Perekalina and Cheparin on the partial substitution of Fe_2O_3 by Sc_2O_3 in M-phase hexaferrites has shown that the replacement of iron cations by trivalent scandium causes a faster decrease in the magnetocrystalline anisotropy than in the magnetization, leading to hexaferrites having H_A values below 10 kOe while still keeping saturation magnetization values ($4\pi M_s$) above 4.0 kG.[5] Further research has extended the knowledge of the magnetic properties of the solid solution $BaSc_xFe_{12-x}O_{19}$ over scandium atomic fractions (x) of from $0 \leq x \leq 1.8$, yielding hexaferrites having H_A values of from 17.7 to 0 kOe.[6] The usefulness of these hexaferrites has been demonstrated by their application in K-band filter applications.[6]

In order to further explore the properties of solid solutions of $BaSc_xFe_{12-x}O_{19}$, and to develop the ability to adjust the uniaxial anisotropy field intensity for millimeter wavelength circulator applications, a series of $BaSc_{0.4}Fe_{11.6}O_{19}$ films were grown at varying oxygen pressures of from 10 to 100 mTorr, as previous research on films of pure barium hexaferrite had determined that the film crystallographic properties varied with the oxygen pressure during growth.[7] Here, we report on the crystallographic and magnetic properties of the $BaSc_{0.4}Fe_{11.6}O_{19}$ films.

The scandium-doped barium hexaferrite films were deposited onto c-plane sapphire substrates by pulsed laser ablation deposition (PLD). The light source was a Lambda-Physik Compex 205 excimer laser (248 nm) operating at a pulse rate of 50 Hz. The laser beam was focused onto the ablation target to yield an energy density of greater than 4 J/cm^2. Films were deposited in a Neocera PLD chamber, which was evacuated to a base pressure below 2×10^{-6} Torr before the introduction of high purity (99.996%) oxygen gas. Four films were deposited at oxygen background gas pressures of from 10 to 100 mTorr. The substrate heater temperature was fixed at 900 °C for all samples, as previous work has shown that temperatures of 900 °C or above yield the best quality hexaferrite films.[8] Each film was deposited over a 20 min period. The resulting films had thicknesses of approximately 200 nm, and they were characterized without post-processing.

The ablation target consisted of a pressed and sintered ceramic disk of scandium-doped barium hexaferrite. It

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TABLE I. Film crystallographic and magnetic parameters.

P (mTorr O_2)	x	$d_{(00n)}$ (Å)	(008) FWHM (deg)	$4\pi M_s$ (kG)	H_c (kOe)	H_A (kOe)
10	0.4	23.286	0.671	3.8	0.72	11.0
20	0.3	23.287	0.816	4.0	0.92	10.1
50	0.4	23.252	0.638	3.9	0.60	11.4
100	0.3	23.288	0.576	3.5	0.52	9.9

proved very difficult to obtain pressed substituted-hexaferrite disks having densities near 5 g/cm^3 without incorporating binders that would contaminate the deposited films. Here, the density of the disk was 4.1 g/cm^3. The fraction of scandium cations in the target was determined from energy dispersive x-ray spectroscopy (EDS) measurements as $BaSc_xFe_{12-x}O_{19}$ ($x = 0.4 \pm 0.1$). No peaks corresponding to other elements were observed in the EDS data. This target was mounted 6 cm from the substrate, and was rotated and rastered so as to provide maximum surface area to the incident laser beam during deposition.

Crystallographic data was obtained on the films from reflection x-ray diffraction (XRD) measurements taken on a Rigaku 300 XRD system. EDS measurements were taken on all films, and also on a high-purity single crystal platelet of $BaFe_{12}O_{19}$ and a single crystal platelet of $BaSc_{0.9}Fe_{11.1}O_{19}$[3] for instrument calibration. Thin film corrections were used in determining the compositions of the films since the x-ray penetration depths were greater than the film thickness.[9] The atomic fraction of scandium per formula unit is shown for each film in Table I, and is seen to be consistent with the value measured for the target.

The magnetic properties of each film were obtained using a Digital Measurement System vibrating sample magnetometer/torque magnetometer. Magnetization and torque measurements were taken with the 14 kOe applied magnetic field both in the sample plane and rotated normal to the film plane.

An examination of the XRD patterns indicated that all films were highly phase-pure and c-axis oriented. Figure 1 shows a Θ–2Θ XRD pattern for the film grown at an oxygen
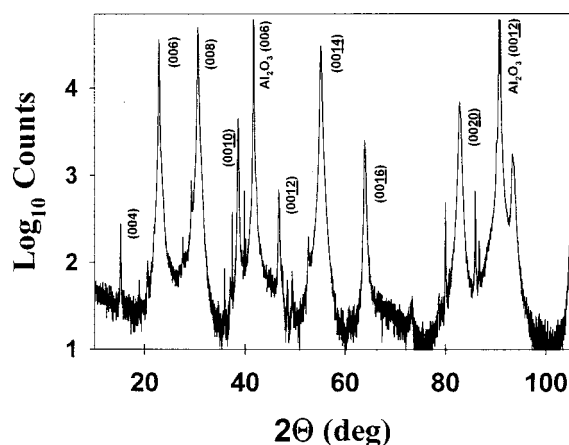

FIG. 1. A Θ–2Θ diffraction pattern is shown for the 10 mTorr film. Miller indices are labeled for both sapphire and film peaks.

background pressure of 10 mTorr, where the logarithm of the intensity data has been plotted to reveal the low-intensity diffraction peaks. Here, Miller lattice indices have been labeled for the observed hexaferrite and the sapphire substrate diffraction peaks, where the indices for the scandium-doped barium hexaferrite have been indexed to barium hexaferrite from standard databases.[10] All of the significant diffraction peaks not corresponding to sapphire arise from reflections from the $(00n)$ hexaferrite planes. Indeed, all of the reflections from $(00n)$ planes listed in standard International Center for Diffraction Data databases are clearly observed in Fig. 1,[10] as well as a reflection for the (004) line not listed in the database. These results indicate the films have a high degree of c-axis orientation. Nearly identical results are obtained for the remaining three films.

Values for the c-axis lattice constants ($d_{(00n)}$) were obtained through least-squares fits of the centroids of the four most intense $(00n)$ diffraction peaks to the Bragg diffraction law, and are listed in Table I. Curiously, these results do not follow the distinct trend in c-lattice parameter found previously in measurements on PLD grown $BaFe_{12}O_{19}$ films where $d_{(00n)}$ was found to decrease with increasing oxygen background gas pressure.[7] Here, three films show values near 23.287 Å, while the 50 mTorr film shows a lower value for $d_{(00n)}$ of 23.252 Å. It is unclear why this set of films does not show the same trend as the $x = 0$ films of Ref. 7, although it may be the consequence of a limited data set. For comparison, typical values of $d_{(00n)}$ for bulk $BaFe_{12}O_{19}$ range between 23.17 and 23.22 Å,[4,10] while previous results on $BaSc_xFe_{12-x}O_{19}$ solid solutions show an expansion of lattice parameters with increasing x.[5] Assuming that the lattice parameters expand linearly with increasing scandium doping, and that the films are not strained, the value of x for each film can be inferred from the lattice parameters listed for Ref. 5. This yields $x = 0.28$ for the 50 mTorr film, and $x = 0.42$ for the remaining films in good agreement with the EDS results.

Asymmetric diffraction measurements were taken to determine the crystallographic quality of the films. Using the rocking curve result for the (008) diffraction peak. The full-width-half maximum (FWHM) peak width results for the films are listed in Table I. All of these values are comparable to results obtained previously for high quality PLD grown $BaFe_{12}O_{19}$ films.[7,8]

Values for the volume saturation magnetization and the uniaxial anisotropy field were obtained from magnetization curves taken with the applied field (H) either along the film normal, or in the film plane. Figure 2 shows the results for both orientations for the film deposited at 10 mTorr. Measurements along the easy axis (film normal) yield square loop magnetization curves canted from vertical because of the film demagnetizing field. A volume independent method was used to estimate $4\pi M_s$ by determining the demagnetizing field for each film through the low field intercept to saturation. Table I lists the deduced $4\pi M_s$ values for all films, along with coercive field (H_c) values along the easy axis. For comparison, the results on single crystals from Ref. 6 yields a $4\pi M_s$ value near 4.2 kG when $x = 0.4$. Hence, the
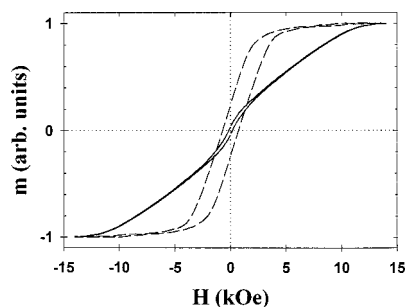
FIG. 2. Magnetization curves for the 10 mTorr film are shown when H lies along the film normal, i.e., easy axis (dashed lines), and in the film plane (solid lines).
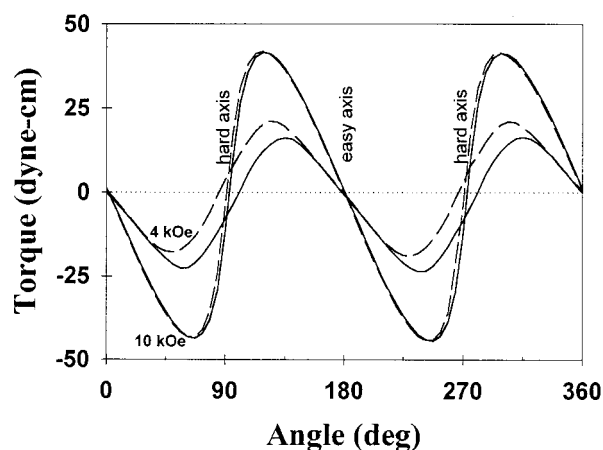

FIG. 3. Magnetic torque vs rotation angle results are presented for a 100 mTorr film for $H=4$ and $H=10$ kOe for both cw (solid lines) and ccw (dashed lines) rotations. The rotation is about an axis in the film plane.

$4\pi M_s$ are lower than that measured for bulk materials, a result that appears to be typical for films of barium hexaferrite.[2,7,8,11]

The magnitude of H_A for each film was obtained from magnetization curves taken with H in the film plane. As shown in Fig. 2, the magnitude in the hard plane has three distinct regions: a low field and medium field region having different linear slopes, and a high field region above a knee where the magnetization asymptotically approaches saturation. This behavior is in contrast to measurements on single crystal hexaferrite platelets where the approach to saturation is linear until the knee at H_A is reached, indicating that the behavior is governed by coherent rotation for the platelets. Instead, the magnetization behavior for the films implies that a range of H_A values are present in the film. Estimates for H_A were taken as the magnetic field value where the extension of the linear slope in the medium field region intercepted the saturation moment. These values are listed in Table I, and are found to be somewhat lower than the H_A value of 12 kOe obtained for the single crystal materials in Ref. 6.

Torque magnetometry measurements were taken to further examine the uniaxial anisotropy orientation in the films. Figure 3 shows torque results when the film is rotated about an axis in the film plane for both clockwise (cw) and counterclockwise (ccw) directions for $H=4.0$ and $H=10.0$ kOe. Angular positions of the film easy and hard axes are also labeled on the plot. The torque data indicates that the easy axis of uniaxial anisotropy lies along the film normal, in agreement with the crystallographic data. In addition, an evaluation of the magnetic field dependence of the rotational hysteresis loss shows that a nonzero loss is still present at 14 kOe, further indicating that a distribution of anisotropy field values may be present in the film.

If a range of H_A values are present in these films, they may arise from magnetostriction induced changes in the uniaxial anisotropy of different layers within each film caused by the large biaxial stresses remaining from the growth process. This tensile stress will arise during the cooling of each film from the growth temperature because of the large thermal expansion mismatch between film and substrate, and is sufficiently large in magnitude to cause peeling of thicker films from the sapphire substrate.[8]

Overall, the scandium-substituted barium hexaferrite films examined here show good crystallographic and magnetic properties, and demonstrate that the uniaxial anisotropy field value can be adjusted in PLD hexaferrite films by using solid solutions. Future research will include evaluating films having different scandium compositions, analyzing the effects of stress on the uniaxial anisotropy field and magnetization value in hexaferrite films, and on depositing the thick films required for millimeter wavelength devices.

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