

## BaFe<sub>12</sub>O<sub>19</sub> thin films grown at the atomic scale from BaFe<sub>2</sub>O<sub>4</sub> and $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> targets

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Hexagonal barium ferrite (BaFe<sub>12</sub>O<sub>19</sub>) thin films were grown at the atomic scale by alternating target laser ablation deposition (ATLAD) of orthorhombic BaFe<sub>2</sub>O<sub>4</sub> and rhombohedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on (001) Al<sub>2</sub>O<sub>3</sub> substrates. Crystallographic, magnetic, and microwave properties of the ATLAD films were determined to be comparable with single crystal quality bulk and films of BaFe<sub>12</sub>O<sub>19</sub> produced by other techniques. The ability to deposit high quality hexagonal ferrite thin films by utilizing multiple targets of different chemical compositions in the deposition routine provides unique opportunities to control the ionic distribution in the unit cell of this important class of ferrite materials.

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Laser ablation deposition (LAD) has long been established as an effective technique for the growth of thin films of various materials, including ferrites of spinel, garnet, and hexagonal crystal structures. Various process parameters, including substrate temperature, pressure, ablation yields, and deposition rate, influence the chemical composition and the crystal structure of the deposited films. The composition and the structure of the films are also highly dependent on the composition, structure, and ionic distribution of the target. Epitaxial growth imposes an additional requirement that the lattice constant and the thermal expansion coefficient mismatches be minimal.

It has been previously demonstrated that high quality hexagonal barium ferrite films can be deposited by the single target LAD technique. The fundamental question raised in this paper is the following: Is it possible to grow high quality hexagonal ferrite films with good crystallographic, magnetic, and microwave properties while relaxing the restrictions imposed on these properties by the chemical composition and the ionic distribution of a single target? To address this question, we have developed a deposition process that utilizes multiple targets of different compositions and ionic distributions to grow hexagonal ferrites. As a result, this process allowed specific ions to be introduced in any order and at any time during film growth while maintaining the crystal structure coordination within the unit cell. We have referred to this deposition method as alternating target laser ablation deposition (ATLAD).<sup>1</sup>

In the past, the ATLAD technique was applied in the growth of spinel ferrites enabling control over the inversion parameters of the resulting films.<sup>1,2</sup> We have also reported on the deposition of hexagonal *M*-type lead ferrite (PbFe<sub>12</sub>O<sub>19</sub>) from PbO and Fe<sub>2</sub>O<sub>3</sub> targets.<sup>3</sup> While this method resulted in a hexagonal crystal structure, there was an uncertainty regarding the local ion distribution in the Pb<sup>2+</sup> basal plane. The uncertainty emerged from the fact that the layers of PbO and Fe<sub>2</sub>O<sub>3</sub> were deposited sequentially rather than simultaneously, while within the intrinsic *M*-type lead ferrite structure, Pb<sup>2+</sup> and Fe<sup>3+</sup> ions coexist within the same basal plane.<sup>4</sup>

We have alleviated this uncertainty by utilizing BaFe<sub>2</sub>O<sub>4</sub> target instead of PbO or BaO to deposit hexagonal *M*-type barium ferrite (BaFe<sub>12</sub>O<sub>19</sub>) thin films resulting in a significant improvement in the crystallographic, magnetic, and microwave properties.

BaFe<sub>12</sub>O<sub>19</sub> films were deposited on the *c*-axis oriented sapphire (Al<sub>2</sub>O<sub>3</sub>) substrates. Comparing the areas of the oxygen planes in both crystals, a lattice mismatch of 7% was deduced.<sup>5</sup> Thermal expansion coefficient of the substrate was  $7.8 \times 10^{-6}$  ppm/°C,<sup>6</sup> while for the hexagonal barium ferrite, the accepted value was  $10 \times 10^{-6}$  ppm/°C.<sup>7</sup> The deposition chamber was evacuated to a base pressure of  $10^{-6}$  Torr. The substrate was heated to 925 °C by a resistive block heater. Films were grown in a high purity (99.999%) oxygen environment of 300 mTorr. A KrF excimer laser with a wavelength of 248 nm, energy of  $410 \pm 10$  mJ/pulse, and 25 ns full width at half maximum pulse width were focused to an energy density of  $10 \pm 1$  J/cm<sup>2</sup> on the target surface. The substrate was positioned at a distance of approximately 5 cm from the target. The target carousel was synchronized with the laser trigger signal and allowed for target rastering to maximize surface usage.

The deposition routine was designed to construct the BaFe<sub>12</sub>O<sub>19</sub> unit cell. For this purpose, 3 shots on the BaFe<sub>2</sub>O<sub>4</sub> target and 33 shots on the Fe<sub>2</sub>O<sub>3</sub> target were utilized. Laser frequency was set to 1 Hz for the first 10 repetitions of the deposition routine, 5 Hz for the subsequent 10 repetitions, and finally to 10 Hz for the remaining 280 repetitions. A total of 300 repetitions resulted in an average film thickness of  $6500 \pm 500$  Å, as measured by a scanning surface profilometer.

All films deposited under the above conditions were annealed in a tube furnace in flowing oxygen. To minimize the diffusion at the film-substrate interface “flash” annealing was performed. The furnace was first preheated to a temperature of 1050 °C. The films were quickly inserted into the furnace, annealed for 20 min, and immediately removed from the furnace. Annealing of the films for time intervals longer than 20 min resulted in a rapid deterioration of the magnetic properties that was interpreted as evidence of diffusion.

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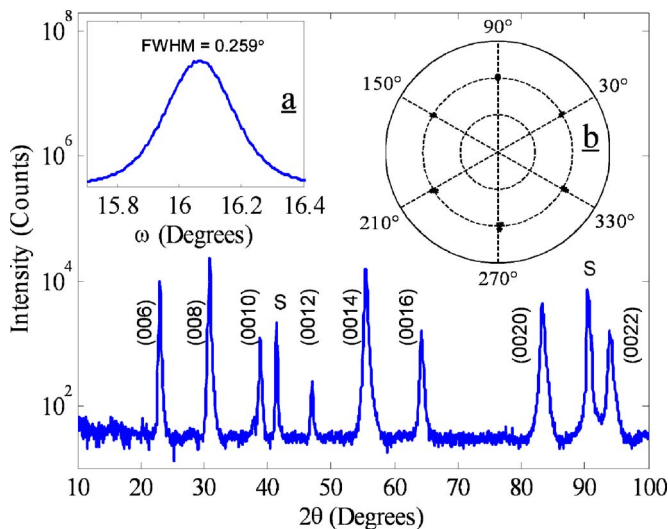


FIG. 1. (Color online)  $\theta$ - $2\theta$  x-ray diffraction spectrum. Rocking curve of the  $\langle 008 \rangle$  barium ferrite peak (inset a) and pole figure of the  $\langle 107 \rangle$  barium ferrite peaks (inset b).

The crystal structure of the films was characterized by  $\theta$ - $2\theta$  x-ray diffractometry (XRD) using a  $\text{Cu K}\alpha$  source. A typical XRD spectrum is shown in Fig. 1. With the exception of two substrate peaks, only sharp  $\langle 002n \rangle$  hexagonal barium ferrite peaks are present in the spectrum suggesting a single phase growth with good  $c$ -axis orientation. A lattice constant of  $c = 23.17 \pm 0.02 \text{ \AA}$  was deduced, which compares well with the value of  $c = 23.22 \text{ \AA}$  reported in the literature for bulk barium ferrite.<sup>8</sup> Rocking curve measurements of the  $\langle 008 \rangle$  barium ferrite peak suggest a narrow  $c$ -axis dispersion as indicated in the inset (a) of Fig. 1 and by the full width at half maximum value of  $\Delta\omega \approx 0.26^\circ$ . This value should be compared with the values of  $0.15^\circ$  and  $0.08^\circ$  for high quality barium ferrite films prepared by the single target LAD (Ref. 9) and liquid phase epitaxy<sup>10</sup> (LPE) techniques, respectively. Crystallographic texture of the films was determined by the pole figure measurements of the highest intensity  $\langle 107 \rangle$  barium ferrite peak. Scattered x-rays were detected over the range of  $60^\circ$  of the tilt angle  $\chi$  by a general area detector diffraction system as a function of the in-plane rotation angle  $\varphi$  between  $0^\circ$  and  $360^\circ$ . As shown in the polar diagram in the inset (b) of Fig. 1,  $\langle 107 \rangle$  barium ferrite diffraction peaks exhibit a sixfold symmetry and no other peaks are visible in the given range of tilt and rotation angles. This suggests that the films are highly oriented in the plane.

Magnetic properties were determined by vibrating sample magnetometer (VSM) measurements with the magnetic field applied perpendicular and parallel to the film plane and ferromagnetic resonance (FMR) measurements with the dc magnetic field applied perpendicular to the film plane. Typical VSM hysteresis loops are shown in Fig. 2. The hysteresis loop with the field applied perpendicular to the film plane exhibited a coercive field of  $154 \pm 10 \text{ Oe}$ . This should be compared with the coercive field of  $250 \text{ Oe}$  for high quality barium ferrite grown by single target LAD,<sup>9</sup> and  $< 10 \text{ Oe}$  for films grown by LPE.<sup>11</sup> Taking into account the volume of the film, the saturation magnetization ( $4\pi M_S$ ) was deduced to be  $4.6 \pm 0.2 \text{ kG}$ . A uniaxial anisotropy field of  $16.5 \pm 0.2 \text{ kOe}$  was determined directly from the saturation field of the hysteresis loop with the field applied parallel to the film plane. These parameters were consistent with refer-

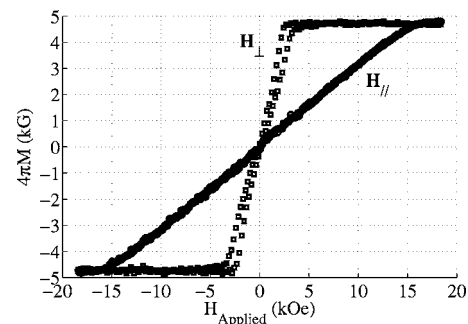


FIG. 2. Hysteresis loops with magnetic field applied perpendicular and parallel to the film plane.

ence values of  $4\pi M_S = 4.7 \text{ kG}$  and  $H_A = 16.3 \text{ kOe}$  for bulk single crystal barium ferrite.<sup>4,12,13</sup>

The temperature dependence of the magnetization of the films was studied by VSM utilizing a high temperature attachment that allowed the magnetic moment to be measured as a function of temperature between  $26$  and  $800^\circ \text{C}$ . Measurements were performed in a magnetic field of  $8 \text{ kOe}$  applied perpendicular to the film plane to ensure magnetic saturation of the samples. The Néel temperature for the films was determined to be  $465 \pm 10^\circ \text{C}$  ( $738 \pm 10 \text{ K}$ ) which was in close agreement with the previously published value of  $450^\circ \text{C}$  ( $723 \text{ K}$ ) for bulk single crystal barium ferrite.<sup>4,13</sup>

Microwave properties of the films were investigated by FMR measurements using a shorted waveguide technique with magnetic field applied perpendicular to the film plane between  $40$  and  $60 \text{ GHz}$ . A peak-to-peak resonance linewidth of  $42 \text{ Oe}$  was measured at  $52 \text{ GHz}$ , as shown in the inset of Fig. 3. This should be compared with the peak-to-peak FMR linewidth of  $23 \text{ Oe}$  for high quality barium ferrite grown by single target LAD,<sup>14</sup>  $27 \text{ Oe}$  for films grown by LPE,<sup>10</sup> and  $25 \text{ Oe}$  for single crystal platelets fabricated by the flux-melt growth method.<sup>12</sup> Also shown in the inset is the theoretical fit to the experimental data based on the derivative of the Lorentzian power absorption profile. A good fit was obtained with the exception of small deviations at the low and high field limits relative to the FMR field. The deviation on the low field side of the main FMR mode was due to spin wave mode excitation to be discussed shortly. The deviation at high field side may be due to a surface mode excitation or an interfacial mode excitation as a result of variation in the internal field at the film-substrate interface.

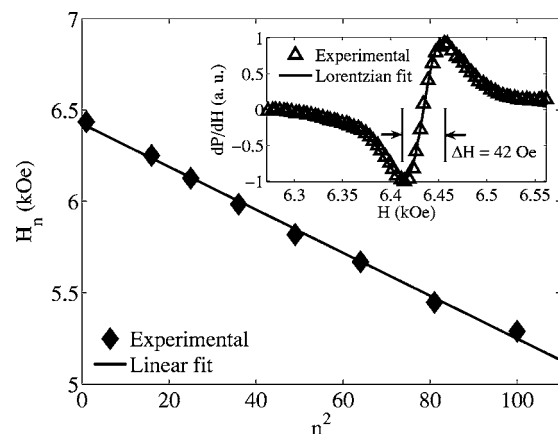


FIG. 3. Spinwave mode resonance field vs mode index squared. Main resonance mode fitted by derivative Lorentzian power absorption profile (inset).

TABLE I. Comparison of properties of barium ferrite thin films deposited by different techniques.

Technique	$\Delta\omega$ (deg)	$4\pi M_S$ (kG)	$H_A$ (kOe)	$H_{C,perp}$ (Oe)	$\Delta H$ (Oe)	$A$ (erg/cm)	$g$
ATLAD	0.259	$4.6\pm 0.2$	$16.5\pm 0.2$	$154\pm 10$	42	$0.6\pm 0.1\times 10^{-6}$	1.996
LAD <sup>a</sup>	0.15	$4.2\pm 0.12$	$16.4\pm 1.0$	250	23	$0.64\times 10^{-6}$	2
LPE <sup>b</sup>	0.08	4.4	16.4	<10	27	...	1.991
Flux melt <sup>c</sup>	...	4.7	16.3	...	25	...	2.01

<sup>a</sup>After Refs. 9 and 14.<sup>b</sup>After Ref. 10.<sup>c</sup>After Ref. 12.

Up to eight spin wave modes were observed in the spin wave resonance (SWR) spectra of the films. The spin wave modes obey the following dispersion relation for the radial frequency  $\omega$  as a function of the spin wave order number  $n$ :

$$\omega = \gamma \left[ H_n + H_A - 4\pi M_S + \frac{2A}{M_S} \left( \frac{\pi}{t} \right)^2 n^2 \right], \quad (1)$$

where  $\gamma$  is the gyromagnetic ratio,  $H_A$  is the uniaxial magnetic anisotropy field,  $M_S$  is the saturation magnetization,  $H_n$  is the  $n$ th mode resonance field,  $t$  is the thickness of the film, and  $A$  is the exchange stiffness constant.<sup>15</sup> By plotting the measured FMR field [ $n=0$  in Eq. (1)] as a function of frequency between 42 and 60 GHz the gyromagnetic ratio  $\gamma$  was determined to be  $2\pi \times 2.794$  MHz/Oe corresponding to a  $g$  factor of 1.996. Spin wave order numbers  $n$  were indexed and the SWR field values  $H_n$  were plotted as a function  $n^2$  to provide a linear fit according to Eq. (1), as shown in Fig. 3. From the slope of the linear fit,  $A$  was determined to be  $0.6\pm 0.1\times 10^{-6}$  erg/cm, which is consistent with the previously published calculated<sup>16</sup> and measured values.<sup>9,14,15</sup>

In Table I, a comparison of magnetic and microwave properties of high quality barium ferrite thin films and single crystals prepared by different techniques is presented. It is evident that the properties of the films deposited by the ATLAD technique are comparable with those prepared by single target LAD, LPE, and flux-melt growth methods. From this comparison, we conclude that the ATLAD technique is capable of producing high quality hexagonal barium ferrite thin films as indicated by the low coercive field, narrow main mode linewidth, and multiple spin wave mode excitations in the SWR spectra.

We further conclude that significant improvements in the crystallographic, magnetic, and microwave properties of the hexagonal ferrite films were obtained as one of the component targets used in the ATLAD routine was changed from PbO to BaFe<sub>2</sub>O<sub>4</sub>. We believe that these improvements are due in part to the availability of the Fe<sup>3+</sup> ions in the BaFe<sub>2</sub>O<sub>4</sub> target to occupy the corresponding sites in the basal plane containing the Ba<sup>2+</sup> ion in the hexagonal unit cell. The Fe<sup>3+</sup> ions were not present in the PbO target, and therefore, the occupation of the corresponding sites in the Pb<sup>2+</sup> plane of lead ferrite was uncertain. Evidently, selection of the targets and the deposition routine affects the occupation of various lattice sites within the unit cell.

Having developed the ATLAD technique for the growth of hexagonal ferrites, we are now well positioned to explore the unique possibilities that the technique offers to study the effects of various lattice substitutions on the resulting magnetic and microwave properties of this important class of

ferrite materials. ATLAD allows different magnetic and non-magnetic ions to be substituted into the hexagonal crystal structure by simply incorporating additional targets in the deposition routine. The substitution amount and distribution in the unit cell can be adjusted by varying the number and the timing of shots from the corresponding target in the deposition routine, as opposed to being largely predetermined by the chemical composition of a single target. Therefore, while the ATLAD technique is capable of producing high quality hexagonal ferrites, it offers unique possibilities to control the ionic distribution within the lattice structure of the films that may translate into a systematic way to adjust the magnetic properties, such as the uniaxial anisotropy field and the saturation magnetization, as required for specific microwave applications.

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