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A. L. Geiler
Northeastern University

Y. He
Northeastern University

S. D. Yoon
Northeastern University

A. Yang
Northeastern University

Y. Chen
Northeastern University

See next page for additional authors

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Author(s)

A. L. Geiler, Y. He, S. D. Yoon, A. Yang, Y. Chen, V. G. Harris, and C. Vittoria



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Epitaxial growth of $\text{PbFe}_{12}\text{O}_{19}$ thin films by alternating target laser ablation deposition of Fe_2O_3 and PbO

A. L. Geiler,^{a)} Y. He, S. D. Yoon, A. Yang, Y. Chen, V. G. Harris, and C. Vittoria
Center for Microwave Magnetic Materials and Integrated Circuits, Northeastern University, Boston, Massachusetts 02115 and Electrical and Computer Engineering Department, Northeastern University, Boston, Massachusetts 02115

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Oriented *M*-type hexaferrite thin films are deposited using the alternating target laser ablation deposition (ATLAD) technique utilizing PbO and Fe_2O_3 targets. Crystallographic, dc magnetic, and microwave characterization results confirming the presence of a hexagonal $\text{PbFe}_{12}\text{O}_{19}$ phase are presented. We conclude that the ATLAD technique holds great promise for layer by layer deposition of various hexaferrite materials, the properties of which can be adjusted by varying the composition of the targets as well as the number of laser shots from each target during the deposition process. This would provide control over the uniaxial anisotropy fields and saturation magnetization values that was not possible in the conventional single target LAD technique. © 2007 American Institute of Physics. [DOI: 10.1063/1.2710222]

INTRODUCTION

Hexagonal *M*-type ferrites $\text{MeO} \cdot 6\text{Fe}_2\text{O}_3$ (Me = Ba, Pb, Sr) are an important family of materials possessing high uniaxial anisotropy and saturation magnetization. Such properties make these materials highly practical in many high frequency microwave¹ as well as permanent magnet applications. The pulsed laser ablation deposition (LAD) technique has proven to be very effective in the growth of epitaxial *M*-type hexaferrite films.²⁻⁴ The ability to alternate the targets during the deposition process allows for the growth of complex magnetic structures tailored for specific requirements in terms of magnetization and anisotropy fields. Such specialized properties may not be realized by natural growth processes. The ability to build the unit cell structure layer by layer provides unique opportunities to affect the cation distribution resulting in normal or inverse spinel structures.^{5,6} We have referred to this technique in the past as “alternating target LAD” technique or ATLAD.⁷

Film growth utilizing multiple targets is not a new idea. What is different in this work is the extension of the ATLAD technique to more complex magnetic structures than previously thought possible. These structures include ferrites of hexagonal crystal structure in which, similar to spinels, magnetic ions exist in layers. Clearly, a great number of possible magnetic structures are allowed. However, as in any scientific endeavor we need a frame of reference or a calibration standard for our results. The ideal standard would have been $\text{BaFe}_{12}\text{O}_{19}$ since much is known about this material. However, BaO targets are difficult to prepare and utilize due to their instability in ambient atmosphere. We have opted for a standard of $\text{PbFe}_{12}\text{O}_{19}$.

In this paper we describe the attempt to deposit *M*-type hexaferrites using the ATLAD technique. We chose to deposit *Pb M*-type hexaferrite ($\text{PbFe}_{12}\text{O}_{19}$) on $\langle 111 \rangle$ MgO sub-

strates as the component targets for the ATLAD process (PbO and Fe_2O_3) were readily available. Additionally, a lower anisotropy field makes this material more attractive than other *M*-type hexaferrites for lower microwave frequency applications.

Films deposited using the ATLAD technique were characterized in terms of composition, crystal structure, dc magnetic properties, and microwave properties. While the results suggest the presence of a secondary cubic phase in the films, it is evident that the films' principal component is a hexagonal $\text{PbFe}_{12}\text{O}_{19}$ (*PbM*) structure and their properties are in good agreement with the previously published results. Therefore, the artificial hexaferrite films were obtained using the ATLAD technique.

GROWTH TECHNIQUE

Two commercially available targets were used in the deposition process, lead oxide (PbO) and iron oxide (Fe_2O_3). Targets were mounted on a rotating holder the motion of which was synchronized with the laser trigger signal. Laser output power was set to 400 mJ and the trigger frequency to 10 Hz. Best results were obtained with the number of shots from PbO and Fe_2O_3 targets sets to 3 and 33, respectively, in each laser cycle. The ratio of shots is thereby determined to approximately follow the atomic ratio of Pb^{2+} and Fe^{3+} ions in the unit cell. The total number of shots in each cycle was selected to construct one-half of the $\text{PbFe}_{12}\text{O}_{19}$ unit cell or $23.06 \text{ \AA}/2 = 11.53 \text{ \AA}$. The routine was executed 500 times to result in $500 \times 11.53 \text{ \AA} = 0.576 \text{ \mu m}$ overall film thickness. Each deposition took approximately 1 h.

Prior to deposition the chamber was evacuated to 2.0×10^{-5} Torr. Oxygen was then introduced to the chamber until a stable partial pressure of 300 mTorr was established. The substrate was heated to 700 °C during the deposition. To obtain the optimum lattice match between the substrate and the film, $\langle 111 \rangle$ MgO with $\sqrt{2}a = 5.96 \text{ \AA}$ was selected. The

^{a)}Electronic mail: ageiler@ece.neu.edu

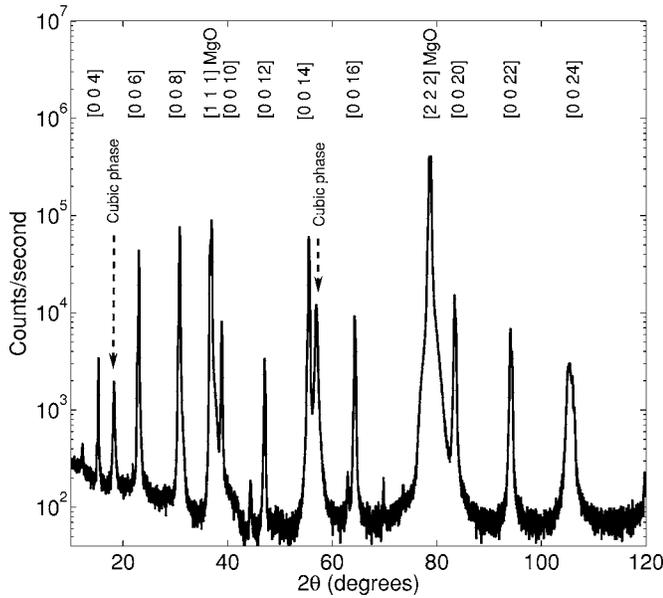


FIG. 1. X-ray diffraction spectrum of ATLAS deposited $\text{PbFe}_{12}\text{O}_{19}$ film (Cu $K\alpha$ radiation).

lattice constant of the a axis in PbM is 5.88 \AA resulting in a mismatch of 1.36%. Optimal growth conditions were found to be consistent with previously published work on single target LAD growth of epitaxial PbM.^{2,3}

EXPERIMENTAL RESULTS

The crystal structure of the artificial PbM films was studied by θ - 2θ x-ray diffractometry using a Cu $K\alpha$ source. A typical x-ray diffraction (XRD) spectrum for a film deposited under the conditions described above is shown in Fig. 1. The spectrum shows a c -axis oriented PbM (Ref. 8) structure with a secondary phase most notably represented by the peaks at $2\theta=18.30^\circ$ and 56.90° . After a careful analysis of the lattice constants of the substrate and various $\text{PbO}-\text{Fe}_2\text{O}_3$ phases we conclude that the second phase is likely to be a cubic PbFe_2O_4 phase with a lattice constant of 7.83 \AA . This conclusion is further supported by the dc magnetic characterization results to be discussed shortly. Composition of the films was further verified by energy dispersive x-ray microanalysis (EDAX) showing atomic percentage ratio between Pb^{2+} and Fe^{3+} ions to be approximately 1:11 which is in reasonable agreement with the 1:12 ratio in the formula unit.

Dc magnetic properties of the films were determined by vibrating sample magnetometry (VSM). Typical hysteresis loops are shown in Fig. 2 for magnetic field applied perpendicular and parallel to the film plane. Film thickness was measured to be approximately $0.5 \mu\text{m}$ by a stylus surface profilometer. These results confirm the presence of an easy magnetization direction perpendicular to the film plane. From the intersection of the in-plane and out-of-plane magnetization curves the anisotropy field was estimated to be 12.5 kOe. This is in reasonable agreement with the bulk value of 13.5 kOe reported in the literature.⁹ The $4\pi M_S$ value was found to be 1.8 kG from VSM measurements, significantly lower than the bulk value of 4.0 kG.⁹ It is con-

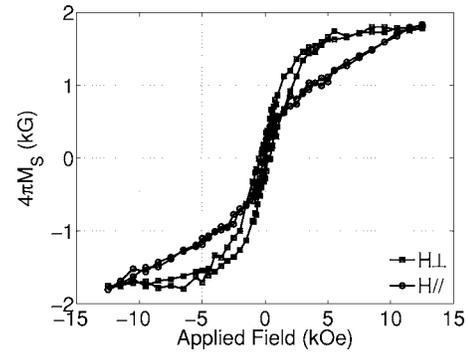


FIG. 2. Hysteresis loops of ATLAS deposited $\text{PbFe}_{12}\text{O}_{19}$ film annealed in ambient oxygen environment for 1 h.

sistent, however, with the $4\pi M_S$ value of approximately 2.0 kG measured for single target LAD deposited films.² The in-plane and out-of-plane coercive fields in the as-deposited films were measured to be 0.2 and 1.5 kOe, respectively. We found that postdeposition annealing of the films at 900°C in ambient oxygen environment for about an hour resulted in reduction of the in-plane and out-of-plane coercive fields to 0.18 and 0.28 kOe, respectively, as shown in Fig. 2. The presence of a cubic phase exhibited itself in the low field behavior of the hysteresis curves. This behavior was also observed in the films that were annealed at 900°C .

Ferromagnetic resonance (FMR) was observed in the films by a broadband measurement technique based on a planar device.^{10,11} Films were placed within a junction formed by shorted slotline and coplanar waveguide lines. The propagation of the fixed frequency microwave signal in this device was restricted to the magnetic sample. Hence, the transmitted signal tracked permeability changes in the material as it went through FMR in an externally applied field. Sample FMR spectra for several measurement frequencies are shown in Fig. 3. Typical resonance linewidths of approximately 1.1–1.3 kOe were measured in the 26–35 GHz frequency range. From a linear fit of the resonance frequency versus applied field an anisotropy field of approximately

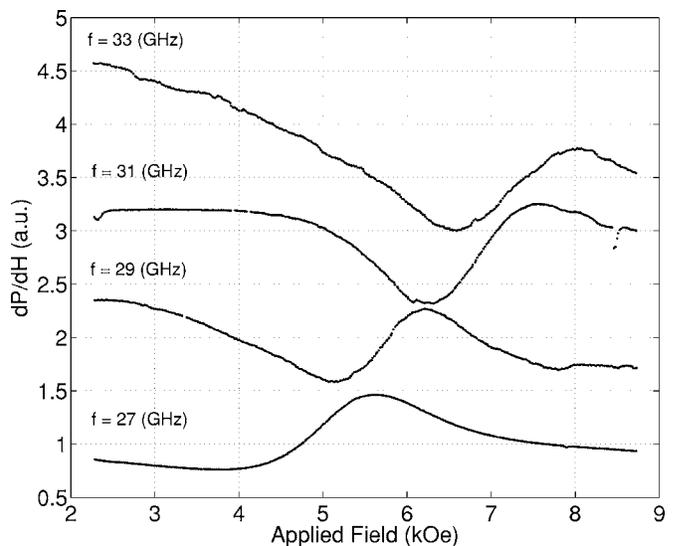


FIG. 3. Ferromagnetic resonance spectra obtained from ATLAS $\text{PbFe}_{12}\text{O}_{19}$ films by a broadband measurement technique.

9 kG and a gyromagnetic ratio of 1.6–1.65 were deduced. There is an apparent discrepancy between the VSM and FMR data. According to the VSM data the anisotropy field is approximately 12.5 kOe whereas the FMR results imply a value of approximately 9 kOe. Also, the measured gyromagnetic ratio of 1.6–1.65 is lower than the bulk value of 2. We believe that this may be due in part to the diffusion at the film-substrate interface during high temperature (900 °C) postdeposition annealing. The effect of the diffusion layer can be significant with a film thickness of approximately 0.5 μm .

DISCUSSION AND CONCLUSIONS

We have deposited *M*-type hexaferrite thin films utilizing the ATLAD technique. The major phase in the films is the *c*-axis oriented hexagonal phase with a cubic phase present as a secondary phase. Since the cubic phase is not present in the targets we believe that it can be eliminated from the films completely through a careful optimization of growth conditions, such as substrate temperature and partial oxygen pressure. The films show a preferred magnetization direction perpendicular to the film plane and a uniaxial magnetic anisotropy field component in the VSM measurements. Ferromagnetic resonance with a broad linewidth (1.1–1.3 kOe) was observed in the films at several frequencies. The linewidth is broad compared to an intrinsic linewidth of 30 Oe in $\text{BaFe}_{12}\text{O}_{19}$. It is not surprising in view of the presence of a secondary phase in the films. Postdeposition annealing in ambient oxygen environment was found to reduce the in-plane and out-of-plane coercive fields, most likely through the reduction of the number of defects in the films and the reduction of the cubic phase.

A close examination of the *M*-type hexaferrite crystal structure, in this case $\text{PbFe}_{12}\text{O}_{19}$, shows that while the spinel blocks of the unit cell contain only Fe^{3+} and O^{2-} ions, the Me layer, in this case $\text{Me}=\text{Pb}$, contains Fe^{3+} and O^{2-} in addition to Pb^{2+} ions within the same plane. Since in our deposition routine the Pb^{2+} ions are introduced by laser shots from the PbO target and Fe^{3+} ions are introduced from the Fe_2O_3 target, Pb^{2+} and Fe^{3+} ions cannot occur in the same plane. Nevertheless, XRD data suggest that the films possess an *M*-type hexagonal structure with a *c*-axis lattice constant of 23.06 Å which is consistent with reference data on bulk⁹ and thin film^{2,3} $\text{PbFe}_{12}\text{O}_{19}$. Therefore, we believe that these films may possess an unusual phase of $\text{PbFe}_{12}\text{O}_{19}$; one where Pb^{2+} and Fe^{3+} ions are not within the same crystal plane. This observation may help explain the low saturation magnetization value of approximately 1.8 kG compared to 4.0 kG in the bulk case.

The implications of layer by layer deposition of *M*-type hexaferrites are immense. This technique may allow the tailoring of the anisotropy field of the material for specific applications. Various ions that affect the anisotropy field of the *M*-type hexaferrites, such as scandium, indium, aluminum, etc.,¹ can be introduced in various locations of the unit cell by incorporating corresponding targets in the deposition rou-

time. The saturation magnetization of the *M*-type hexaferrites may also be possible to control in a similar manner by replacing the Fe^{3+} ions in various locations within the unit cell by other ions. Since lead oxides are highly volatile, in the case of $\text{PbFe}_{12}\text{O}_{19}$ the ATLAD technique has the added advantage of being able to compensate for the amount of Pb^{2+} lost to evaporation during the deposition by simply adjusting the number and energy of shots from the respective target. Such an operation is not possible in the conventional single target LAD technique since the stoichiometry of the target ultimately determines the ratios of the ions in the resulting films.

A number of issues with the ATLAD of $\text{PbFe}_{12}\text{O}_{19}$ still need to be addressed. Most importantly the presence of a secondary cubic phase in the films needs to be eliminated. We expect to be able to accomplish this by a careful optimization of growth conditions, such as substrate temperature and partial oxygen pressure. Prior work in single target deposition^{2,3} of $\text{PbFe}_{12}\text{O}_{19}$ suggests that 700 °C substrate temperature, which was utilized in our process as well, is the optimum crystallization temperature that prevents evaporation of lead oxides during deposition. Reported partial oxygen pressure conditions vary significantly, however, with values as low as 50 mTorr (Ref. 3) and as high as 2.25 Torr.² The value of 300 mTorr used in our process falls within this range and it is possible that the secondary cubic phase can be eliminated through further partial oxygen pressure optimization. As mentioned previously, in the artificial $\text{PbFe}_{12}\text{O}_{19}$ films we deposited, Pb^{2+} and Fe^{3+} ions may not be located on the same crystal plane. Further investigation is necessary to determine whether this is a new stable $\text{PbFe}_{12}\text{O}_{19}$ phase and whether this structure results in low saturation magnetization value compared to values typically reported for conventional bulk material. If this is indeed the case it would be an interesting area for further research as this material would possess high uniaxial anisotropy and low saturation magnetization.

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