Magnetism, Structure, and Cation Distribution in $MnFe_2O_4$ Films Processed by Conventional and Alternating Target Laser Ablation Deposition

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A series of manganese ferrite thin film samples were prepared by alternating target laser ablation deposition and conventional pulsed laser deposition techniques on (111) MgO substrates. By extended X-ray absorption fine structure (EXAFS) analysis, we have discovered that the cation distribution was sensitive to the processing oxygen pressure and the preparation technique. Correspondingly, the saturation magnetization and uniaxial anisotropy fields change. Saturation magnetization was found to decrease while the percentage of Mn ions on the octahedral site increased, as a function of oxygen processing pressure. The highest magnetization (~4.5 kG) and anisotropy field (~0.5 kOe) corresponded to the sample grown at the lowest oxygen pressure.

***Index Terms*—EXAFS, ferrite films, pulsed laser deposition.**

I. INTRODUCTION

SPINEL ferrites are unique candidates for many microwave applications owing to their high permeability and low loss at high frequencies. In the spinel ferrite structure, oxygen atoms form a closed packed lattice with transition metal ions residing at the interstitial tetrahedral (A) sites and the octahedral (B) sites. The type, valence, and distribution of metal cations determine to a large degree the magnetic and electronic properties of the material. The ability to tune the cation distribution may prove useful in tailoring the electronic and magnetic properties of spinel ferrites for specific applications. This has been shown to be the case in Mn-ferrite grown on (100) MgO [1].

$MnFe_2O_4$ in bulk form is a mixed spinel ferrite, in which 20% of the Mn ions occupy the B sites [2] and 80% of the manganese ions are on the A sites. The Fe ions distribute on the remainder of the A and B sites. In hopes of controlling and tailoring the cation redistribution in Mn-ferrite grown on (111) MgO, we have explored a variant of pulsed laser deposition that we describe as alternating target laser ablation deposition or AT-LAD. The goal of this processing scheme is to control the growth of the ferrite at the atomic scale. If one views the spinel structure along the $\langle 111 \rangle$ direction, the structure can be described as a layer-by-layer packing of planes containing only A or B site cations. Because of this, it may be possible to artificially construct a spinel ferrite by layer-by-layer deposition. In AT-LAD, a pulsed laser beam is sequentially incident upon two binary oxide targets, in our case MnO and Fe_2O_3. In this manner, MnO and Fe_2O_3 layers are deposited at thicknesses well below the unit cell dimension. The successful growth of $MnFe_2O_4$ on (100) MgO using the AT-LAD technique has been demonstrated [1]. In this paper, we compare the magnetic, structural, and atomic structure properties of Mn-ferrite films grown on (111) MgO substrates by AT-LAD and conventional PLD. The films are grown as a function of oxygen background pressure which has also been shown to strongly affect the cation distribution.

II. RESULTS AND DISCUSSION

A. Magnetic Properties

Two series of $MnFe_2O_4$ films were deposited by AT-LAD and conventional laser ablation deposition technique under varying oxygen pressures on MgO (111) substrates. The substrate temperature was fixed at 700 °C. The films' thickness are ranged from 0.65 to 0.85 μm. It is revealed by X-ray diffraction (XRD) data that the films grown on (111) oriented MgO substrates have peaks indexed to (n,n,n) suggesting epitaxial growth. The saturation magnetization and anisotropy field are plotted for all films as a function of processing oxygen pressure in Fig. 1. The saturation magnetization $(4\pi \mathrm{M_s})$ for films grown using both techniques is measured to decrease as the oxygen pressure increased from 1 to 50 mT. The AT-LAD films consistently had higher magnetization with the highest approaching the bulk value of 4.5 kG for Mn-ferrite for the film grown near 1 mTorr. The highest value for conventional growth was ~3.3 kG at the same pressure. The magnetic anisotropy field, H_a, was measured by perpendicular ferromagnetic resonance (FMR) at room temperature. The FMR condition is $\omega/\gamma = H - H_a - 4\pi M_s$, where ω is the radial frequency, γ is the gyromagnetic coefficient, H is the external magnetic field, H_a is the total magnetic anisotropy field, and M_s is the saturation magnetization which was measured by vibrating sample magnetometry (VSM) [1]. The anisotropy field, H_a, for the conventional growth ranged from 200 Oe at low pressures ($\sim$ 1 mTorr) to $\sim$ 1000 Oe for $p_\mathrm{ox} > 1$ mTorr. In comparison, the AT-LAD films had consistently low values of H_a near zero. Overall, it is clear that the AT-LAD technique allows for growth of samples with improved magnetic properties. We

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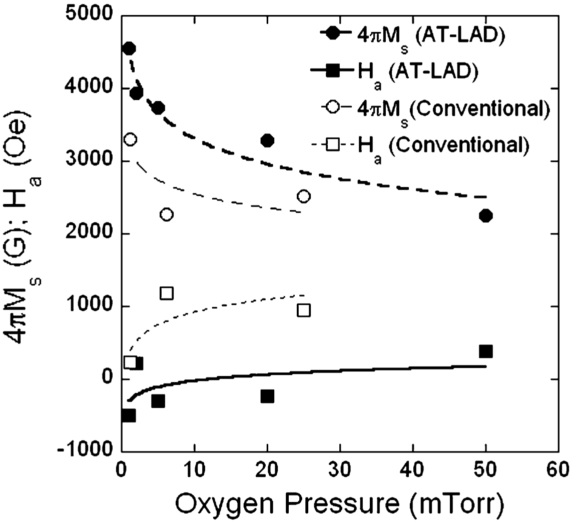

Fig. 1. Magnetization (as $4\pi M_s$) and anisotropy field (H_a) for films grown using both AT-LAD and conventional PLD as a function of oxygen processing pressure.

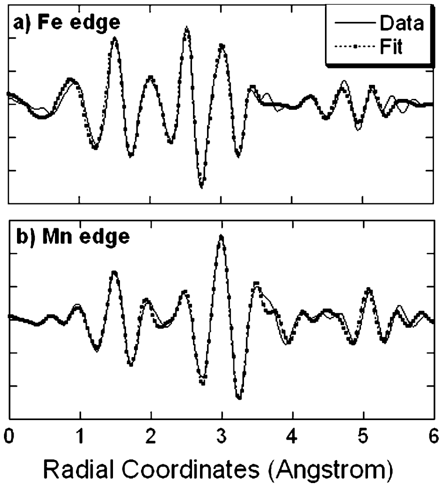

Fig. 2. Real part of the Fourier transform amplitude of EXAFS data with the best fit from Fe (a) and Mn (b) K-edge absorption for a manganese ferrite AT-LAD deposited thin films on a (111) MgO substrate at an oxygen pressure of 5 mTorr.

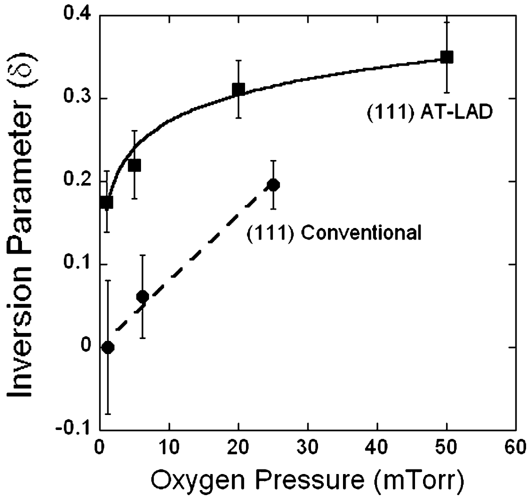

Fig. 3. Inversion parameter, δ, as a function of oxygen pressure for both processing techniques. Lines in the figure are intended as a guide to the eye.

believe the origins of these dependencies may lie in the cation disorder. The difference in the cation inversion parameter in our samples and the bulk value is a measure of cation disorder. The measurement of cation inversion and its subsequent relationship to the magnetic properties will be discussed in the next section.

B. Extended X-Ray Absorption Fine Structure (EXAFS) Analysis

X-ray absorption spectra were collected in fluorescence yield at room temperature under standard conditions using beamline X23B in the National Synchrotron Light Source (NSLS).[1] EXAFS analysis of cation distribution was first performed by Harris *et al.* in 1996 [3]. Calvin extended this approach in 2002 having performed the first multi-edge refinement of the spinel structure [4]. Both Harris *et al.* and Calvin *et al.* made use of theoretical standards generated by FEFF codes of Rehr *et al.* [5] together with the refinement procedures outlined by Sayers and Bunker [6]. In this paper, the data analysis codes, Athena and Artemis, developed by Ravel and Newville [7], were used to analyze the distribution of cations in samples prepared under varying processing conditions and techniques. The Fourier transform of the EXAFS data provides a real space radial structure function of the environment of the absorbing ion where the absolute amplitude of the function corresponds with the coordination and atomic order of atoms present at the radial distance. In these data, the radial distance corresponds to bond distances that have been shifted in space by a unique electron phase shift which must be calculated from (quasi) first principles and fit the experimental data. The real part of the Fourier transform of the Fe and Mn EXAFS data for 5 mTorr AT-LAD grown sample and the best fits are shown in Fig. 2. These data are representative of the fitting quality. The fit results allow for the determination of lattice parameter, oxygen displacement vector, and cation distribution.

It is shown in Fig. 3 that the site preference of Mn ions depends strongly upon the oxygen pressure and the growth technique. Generally, as the oxygen processing pressure was increased, more Mn ions are measured to occupy B sites, i.e., increasing the inversion parameter, δ (where δ is defined as $(Mn_{1-\delta}Fe_{\delta})^{tet}[Mn_{\delta}Fe_{2-\delta}]^{oct}O_4$). This is true for both processing techniques. At low oxygen pressures, the AT-LAD sample has an inversion parameter of 0.17 ± 0.04. This is very near to the bulk value of 0.2. The magnetic properties of this sample depicted in Fig. 1 are also bulk-like. This is evidence that in fact, ATLAD can indeed create a near bulk like thin film by a layer-by-layer approach. It is less clear why the conventional PLD grown sample under the same conditions is a normal spinel (i.e., 100% Mn is on the A-site). As the pressure is increased, the inversion parameter for the AT-LAD samples

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[1] Data collection was performed using a fluorescence yield technique at beamline X23B at the National Synchotron Light Source (Brookhaven National Laboratory, Upton, NY). At the time data were collected the storage ring energy was 2.54 GeV and the ring current ranged from 180 to 250 mA.

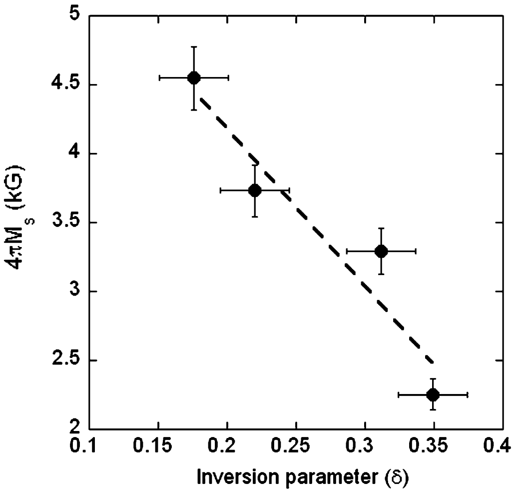

Fig. 4. Variation of saturation magnetization as a function of inversion coefficient, δ for AT-LAD prepared samples.

reaches 0.35. In Fig. 4, the inversion parameter is compared with the magnetization. Here, one sees a clear near linear trend of decreasing magnetization with increasing inversion parameter. This trend in fact agrees with that measured in the Cu-ferrite system [8].

Under high oxygen pressure, collisions between oxygen molecules and Mn cations increase, thus reducing the kinetic energy (KE) of the ions arriving at the substrate. This reduced KE leads to low surface mobility of the ions and the "freezing in" of cation disorder. In addition, the increase in collisions would lead to an increase in Mn^{3+} ions. Since Mn^{3+} ions strongly prefer B sites, this too will result in a high degree of cation inversion. Since Mn^{3+} ions have 4 μ_B compared with 5 μ_B of Mn^{2+} ions, it is expected that the magnetization will decrease with an increase in cation inversion. Local structural distortions and defects, and the subsequent valence changes associated with them, may also play an important role in the strength of the exchange constants and the sample's magnetization.

The increase in δ in AT-LAD samples compared with that measured in PLD samples can be attributed to the nature of the layer-by-layer growth scheme. In this approach, we had aimed at artificially creating an inverted spinel. Although we failed to completely invert the spinel, we did succeed in the partial inversion.

III. CONCLUSION

A series of manganese ferrite thin film samples were prepared by alternating target laser ablation deposition and conventional pulsed laser deposition techniques on (111) MgO substrates. By extended X-ray absorption fine structure analysis, we measured a strong negative and near linear correlation between cation inversion and magnetization. At low pressures, AT-LAD provided near bulk like cation inversion as well as magnetism and magnetic anisotropy. Conventional PLD under similar conditions resulted in reduced inversion, low magnetization, and high anisotropy fields. At low oxygen pressures, the conventional PLD film had a normal cation distribution. We attribute high inversion with high processing pressure at higher pressures the frequency of ablated ion collisions within the oxygen plasma resulting in the loss of ion kinetic energy and a subsequent reduction in adatom mobility.

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