Structural, Magnetic, and Microwave Properties of BaFe\(_{10.5}\)Mn\(_{1.5}\)O\(_{19}\) Thin Films

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Epitaxial manganese substituted M-type barium ferrite thin films are deposited by alternating target laser ablation deposition (ATLAD) of BaFe\(_2\)O\(_4\), Fe\(_2\)O\(_3\), and MnFe\(_2\)O\(_4\) targets. The crystal structure and the epitaxy of the films are investigated by X-ray diffraction. Surface morphology is studied by atomic force microscopy. Magnetic properties of the films are characterized by vibrating sample magnetometry and magnetization as a function of temperature measurements. Ferromagnetic resonance (FMR) measurements are utilized to study the dynamic properties of the films. Possible mechanisms for main FMR linewidth broadening as a result of Mn substitution, such as increased conductivity and the presence of Jahn-Teller effect associated with octahedrally coordinated Mn\(^{3+}\) cations, are briefly discussed. Extended absorption X-ray fine structure measurements are performed to determine the cation distribution in the hexagonal unit cell. The observed 15–20% increase in saturation magnetization at 4 K and 50 K increase in the Néel temperature in comparison to bulk reference values are attributed to differences in cation distribution as a result of atomic scale deposition by the ATLAD technique.

Index Terms—Cation substitution, ferromagnetic resonance, hexagonal ferrite, laser ablation deposition.

I. INTRODUCTION

The unique electrical and magnetic properties of hexagonal ferrites, such as low conductivity, moderate magnetic moment, and high magnetocrystalline anisotropy, have contributed to their adaptation in a variety of practical applications. These materials are utilized as magnetic recording media, permanent magnets, and in high frequency non-reciprocal devices [1]–[3]. One of the most frequently utilized hexagonal ferrites in today’s demanding technologies is the M-type barium ferrite. The M-type structure can be described as intergrowth of cubic (S) and hexagonal (R) blocks formed with close packed oxygen layers [4]. The unit cell of M-type barium ferrite contains two unit formulas (BaFe\(_{12}\)O\(_{19}\)) that can be represented by the sequence of blocks RSR*SR* where the asterisk implies rotation of 180\(^\circ\) around the c-axis of the lattice.

The Fe\(^{3+}\) cations in the hexagonal unit cell are distributed among three octahedral (12k, 2a, 4f\(_{12}\)), one tetrahedral (4f\(_{IV}\)), and one pseudo-tetrahedral (4e(1/2)) sublattices [5]. The ferromagnetic arrangement of Fe\(^{3+}\) ions in the hexagonal unit cell results in a total magnetic moment of 20 \(\mu_H\) [6]. The substitution of the Fe\(^{3+}\) cations to gain control over the magnetic properties of this technologically important class of magnetic oxides has been studied by many researchers in the past [1], [6]. Several detailed studies of bulk hexagonal ferrites substituted with paramagnetic cations, such as Cr\(^{3+}\) [7] and Mn\(^{3+}\) [8], [9] have been undertaken to understand the cation distribution among the various interstitial sites in the hexagonal unit cell and the resulting magnetic properties.

In this paper we report on the deposition of epitaxial manganese substituted barium ferrite thin films by alternating target laser ablation deposition (ATLAD). Growth of high quality hexagonal ferrites by the ATLAD technique has been demonstrated recently [10]. By depositing complex crystal structures at the atomic scale through sequential ablation of multiple targets, the ATLAD technique provides unique opportunities to control the cation distribution in the unit cell. We took advantage of this unique capability to deposit epitaxial BaFe\(_{10.5}\)Mn\(_{1.5}\)O\(_{19}\) thin films.

In the following sections the structural and magnetic properties of the BaFe\(_{10.5}\)Mn\(_{1.5}\)O\(_{19}\) films are characterized and compared to bulk reference values. The preliminary results of cation distribution studies are also presented. The microwave properties of the films are investigated through ferromagnetic resonance measurements and the possible resonance linewidth broadening mechanisms in manganese substituted barium ferrite are discussed. Finally, some conclusions and directions for future work are presented.

II. THIN FILM GROWTH TECHNIQUE

Epitaxial BaFe\(_{10.5}\)Mn\(_{1.5}\)O\(_{19}\) thin films were deposited by the ATLAD technique on c-plane sapphire (Al\(_2\)O\(_3\)) substrates. The deposition chamber was evacuated to a base pressure of 10\(^{-6}\) Torr. High purity oxygen gas was introduced and a stable partial pressure of 300 mTorr was maintained throughout the deposition. During the deposition the substrates were heated to 925\(^\circ\)C by a resistive block heater. Laser pulses from a KrF excimer laser with a wavelength of 248 nm, energy of 410 ±10 mJ/pulse, and pulse width of 25 ns full width at half maximum were optically focused on the target surface to an energy density of 10±1 J/cm\(^2\). The distance between the target and the substrate was approximately 5 cm.

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Targets utilized in the deposition were prepared by conventional ceramics processing techniques. The BaFe\(_{10.5}\)Mn\(_{1.5}\)O\(_{19}\) thin films were deposited by sequential ablation of BaFe\(_2\)O\(_4\), Fe\(_2\)O\(_3\), and MnFe\(_2\)O\(_4\) targets. The targets were mounted on a carousel synchronized with the laser trigger signal via a computer. To maximize surface usage all three targets were rastered and rotated throughout the deposition. The deposition routine consisted of 3 pulses on the BaFe\(_2\)O\(_4\), 11 pulses on the Fe\(_2\)O\(_3\), 11 pulses on the MnFe\(_2\)O\(_4\), and finally another 11 pulses on the Fe\(_2\)O\(_3\) target. The aim of the deposition routine was to deposit the hexagonal R block containing the BaO plane and rotated throughout the deposition. The deposition routine consisted of 3 pulses on the BaFe\(_2\)O\(_4\), 11 pulses on the Fe\(_2\)O\(_3\), 11 pulses on the MnFe\(_2\)O\(_4\), and finally another 11 pulses on the Fe\(_2\)O\(_3\) target. The aim of the deposition routine was to deposit the hexagonal R block containing the BaO layer by ablating BaFe\(_2\)O\(_4\) and Fe\(_2\)O\(_3\) targets, then to localize the Mn cations in the spinel S blocks by ablating the MnFe\(_2\)O\(_4\) and Fe\(_2\)O\(_3\) targets. Growth rates from BaFe\(_2\)O\(_4\), Fe\(_2\)O\(_3\), and MnFe\(_2\)O\(_4\) targets were determined to be 0.14, 0.06, and 0.04 nm/shot, respectively. Approximately 2.4 nm of the film were deposited per routine, commensurate to the height of the barium ferrite unit cell (c = 2.317 nm [6]). 250 repetitions of the deposition routine resulted in a film thickness of 0.5 \(\mu\)m, measured by a scanning stylus profilometer. Laser trigger frequency was set to 1 Hz for the first 10 repetitions of the deposition routine, 5 Hz for the subsequent 10 repetitions, and finally 10 Hz for the remaining 230 repetitions.

After the deposition the films were “flash” annealed in flowing high purity oxygen gas. A 2" tube furnace was preheated to 1323 K. Thin films were inserted into the furnace in a high purity alumina crucible and annealed for 20 minutes. Upon completion the films were quickly removed from the furnace and cooled in air. Annealing beyond the 20 minute interval resulted in the deterioration of microwave properties of the films, which was interpreted as evidence of interdiffusion at the film-substrate interface.

III. STRUCTURAL AND MAGNETIC CHARACTERIZATION

Crystal structure of the films was studied by X-ray diffraction utilizing a Cu K\(_\alpha\) source. A typical \(\theta - 2\theta\) spectrum is shown in Fig. 1. Sharp peaks corresponding to c-plane diffraction suggest that the films possess a single c-axis oriented hexagonal phase. A pole figure of the highest intensity (107) diffraction peak is shown in the inset of Fig. 1. The observed sixfold symmetry is indicative of a high degree of in-plane orientation in the films.

Surface morphology of the films was studied by atomic force microscopy (AFM). A typical surface micrograph is shown in Fig. 2. The edges of stacked hexagonal platelets, 300-500 nm in diameter, are clearly visible in the figure suggesting two-dimensional step-flow growth. Average surface roughness was measured to be approximately 1.26 nm. The alignment of hexagonal platelets with their surface normal perpendicular to the film plane is consistent with the results of the rocking curve measurement of the (008) diffraction peak in the inset of Fig. 2. Full width at half maximum value of \(\Delta\omega\) was measured to be 0.25\(^\circ\), indicative of a narrow c-axis dispersion in the films.

Magnetic properties of the films were studied by vibrating sample magnetometry. Typical hysteresis loops with the magnetic field applied perpendicular and parallel to the film plane are shown in Fig. 3. Hysteresis loops indicate a uniaxial magnetic structure, consistent with the high degree of c-plane orientation of the films observed in X-ray diffraction results. Saturation magnetization value of \(4\pi M_S = 4.3 \pm 0.2\) kG was measured for the BaFe\(_{10.5}\)Mn\(_{1.5}\)O\(_{19}\) films, compared to \(4\pi M_S = 4.6 \pm 0.2\) kG previously reported for intrinsic barium ferrite films deposited by a similar technique [10]. Lower magnetic moment as a result of manganese substitution was previously reported in bulk Mn-substituted barium ferrite [8]. A uniaxial magnetocrystalline anisotropy field \(H_A = 2K_1/M_S\), of 17.0 \(\pm\) 0.2 kOe was measured for the BaFe\(_{10.5}\)Mn\(_{1.5}\)O\(_{19}\) films. This result suggests that the anisotropy constant \(K_1\) remains largely unaffected by the substitution of manganese. The increase in \(H_A\) is therefore a result of lower magnetic moment in the films. This result is consistent with prior findings in bulk manganese substituted barium ferrite [8]. A low coercive field of \(H_C = 150 \pm 50\) Oe, acquired with the magnetic field applied along the easy direction, is indicative of high crystalline quality of the films. Magnetization as a function of temperature curve is shown as the inset of Fig. 3. A saturation magnetization, \(4\pi M_S = 7.1 \pm 0.3\) kG, was measured at 4 K. The Néel temperature was measured to be \(T_N = 683\) K. The saturation magnetization at 4 K was 15–20%
Fig. 3. Room temperature hysteresis loops of the BaFe$_{10.5}$Mn$_{1.5}$O$_{19}$ thin film with the magnetic field applied perpendicular (easy) and parallel (hard) to the film plane. Saturation magnetization as a function of temperature (inset).

Fig. 4. Main resonance line for the BaFe$_{10.2}$Mn$_{1.3}$O$_{19}$ thin film. FMR frequency as a function of applied field (inset a). Main resonance linewidth as a function of frequency (inset b).

Extended X-ray absorption fine structure (EXAFS) analysis was carried out to explore the short range order and the cation distribution of film samples. Mn and Fe K edge absorption data were collected at the beamline X23B in the National Synchrotron Light Source in fluorescence yield mode. For comparison, Fe K edge absorption data for ATLAD grown BaFe$_{12}$O$_{19}$ films were also collected. Mn edge scans ranged from 200 eV below the absorption edge to 12 photoelectron wave numbers (k) above due to the onset of the Fe K edge at 7112 eV. Fe edge scans ranged from 50 eV below the absorption edge to 14 k above. The measured intensity was first converted to absorption coefficient $\mu(E)$. After a smooth pre-edge function subtraction, the data was normalized and converted to k-space and Fourier transformed (FT) to radial coordinate space. The FT can be used to isolate and identify different coordination spheres around the specific absorbing atom. It is noted that a scattering phase-shift (typically a few tenths of an Angstrom) is calculated and added later to the FT data.

Fourier-transformed Fe and Mn K edge EXAFS of ATLAD grown BaFe$_{12}$O$_{19}$ and BaFe$_{10.5}$Mn$_{1.5}$O$_{19}$ films are plotted in Fig. 5. The first FT peak at $r \sim 1.5$ Å represents the interaction between the absorbing atom and its nearest oxygen neighbor. The split peak feature at radial coordinate near 2–3.5 Å indicates that the absorbing atom has both tetrahedral and octahedral coordination in the ferrite structure [13], [14]. The octahedral (B) site occupancy (2a, 4f$_V$, and 12 k) contributes to the first peak amplitude in the range of 2–3.5 Å. The tetrahedral (A) site occupancy (4e(1/2) and 4f$_V$) partially contributes to the second peak. Comparative heights of the two peaks are indicative of the comparative occupancy of the absorbing atom between the two types of sites (although amplitude variation may arise from atomic disorder). FT Fe spectra of BaFe$_{10.5}$Mn$_{1.5}$O$_{19}$ has a higher amplitude in the second peak than that of BaFe$_{12}$O$_{19}$, which suggests a higher occupancy of Fe at A site (4e(1/2) and 4f$_V$). In other words, substituted Mn ions preferentially replace Fe in B sites. This observation is further evidenced by the higher amplitude of the B site peak in the split-peak region than the A site one in the Mn edge FT spectra and the FEFF fitting results to be reported elsewhere.

Fig. 5. FT spectra of the BaFe$_{10.5}$Mn$_{1.5}$O$_{19}$ films shifted to a lower R value compared with the BaFe$_{12}$O$_{19}$ films.
spectra. This is particularly evident in the Mn FT spectrum, and can be interpreted as a sign of distortion in the BaFe_{10.5}Mn_{1.5}O_{19} structure induced by Mn substitution. This observation can be explained in part by the differences in Fe^{3+} and Mn-O FT peak at ∼1.5 Å indicates larger number of oxygen near neighbors and less thermal and structural disorder around the Mn ions.

IV. DISCUSSION AND CONCLUSIONS

Based on the structural, magnetic, and microwave characterization results presented above we conclude that high quality BaFe_{10.5}Mn_{1.5}O_{19} thin films were deposited at the atomic scale from BaFe_{2}O_{4}, Fe_{2}O_{3}, and MnFe_{2}O_{4} targets. By separating the sources of different species of ions the ATLD technique provides unique opportunities to grow complex crystals while allowing controlled cation substitution in the unit cell. X-ray diffraction results confirm that even though three separate targets are utilized during film growth the epitaxy and the integrity of the unit cell are maintained. While in this paper we’ve focused our attention on hexagonal ferrites this technique is applicable to a wide variety of materials. Based on preliminary cation distribution studies we believe that the 50 K increase in Néel temperature and the enhanced magnetic moment at 4 K compared to bulk values are a direct result of the localization of Mn cations in the spinel (S) blocks of the hexagonal unit cell. Detailed cation distribution studies in the ATLD deposited BaFe_{10.5}Mn_{1.5}O_{19} films are currently underway and will be published at a later date.

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