

ANNEALING INDUCED STRUCTURAL PHASE CHANGE OF HEXAGONAL-LuFeO₃ THIN FILMS

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ABSTRACT

We present structural, optical, and magnetic properties of multiferroic LuFeO₃ thin films, deposited on single crystal sapphire and YSZ substrates by an RF magnetron sputtering system. Growth temperature and annealing are found to be critical to stabilize hexagonal LuFeO₃ thin films. We found that annealing hexagonal LuFeO₃/Sap thin films above 950 °C change the crystal structure of LuFeO₃ from a metastable hexagonal to the bulk orthorhombic structure. However, h-LuFeO₃/YSZ thin films remained mostly unaffected by annealing up to 1200 °C. The electronic excitations of the LuFeO₃ thin films are dominated by Fe³⁺ d to d on-site electronic excitations as well as O 2p to Fe 3d, Lu 6s, and 5d charge-transfer excitations. We observed that the electronic excitations for hexagonal LuFeO₃ and orthorhombic LuFeO₃ thin films are distinctly different, consistent with the excitations expected from the FeO₅ and FeO₆ building blocks for hexagonal and orthorhombic LuFeO₃, respectively. Furthermore, the electronic excitations exhibit strong temperature dependence at the magnetic transition temperature, indicating the spin-charge coupling.

INTRODUCTION

Rare earth orthoferrites RFeO₃ (R = Dy - Yb) having an orthorhombic structure are magnetic but non-polar oxides. These orthoferrites have been successfully stabilized in a metastable hexagonal structure (P6₃cm) in a thin film form by depositing these oxides onto hexagonal substrate templates.^{1,2-5} Interestingly, the hexagonal RFeO₃ thin films have different physical properties than their bulk counterparts. In particular, the hexagonal ferrite thin films undergo a magnetic transition from a paramagnetic state to an antiferromagnetic state in the temperature range ~130-150 K.^{4,6,7} Furthermore, the antiferromagnetic structure in a triangular lattice in the hexagonal ferrites are a canted spin-type, resulting in a weak ferromagnetic state. Although the bulk orthoferrites are non-polar, these hexagonal ferrite thin films are polar due to a structural distortion that occurs at a high temperature >500 K.^{4,7} Therefore, the hexagonal RFeO₃ thin films possess ferroelectric and ferromagnetic properties, known as the multiferroic properties. Of this RFeO₃ family, hexagonal LuFeO₃ (in short h-LuFeO₃) has been widely studied and shows a strong multiferroic property.^{5,8,9,10,11}

The metastable h-LuFeO₃/Al₂O₃ thin films have been found to undergo a structural phase transition during the annealing process above 1000 °C.¹² The lattice mismatch between h-LuFeO₃ film and Al₂O₃ substrate is significant, and thus the h-LuFeO₃ thin films are highly strained. The strain in the thin film couple with the physical conditions are the possible reasons for the observed annealing-induced phase change. While most of h-LuFeO₃ thin films investigated so far have been deposited either by Pulse Laser Deposition or by Metal-Organic Chemical Vapor Deposition,^{3,7,11-14} these deposition methods are very expensive and not desirable for preparing thicker films. On the other hand, Radio-Frequency (RF) Magnetron Sputtering is relatively cost effective and one of the most commonly used methods for the deposition of oxides. Furthermore, an RF Magnetron Sputtering offers flexibility in terms of controlling the growth conditions, maintaining the stoichiometry, and a higher deposition rate. The optical properties and the electronic excitations of the h-LuFeO₃ thin films have not been thoroughly investigated. Optical Spectroscopy is a novel

tool which can probe the electronic excitations that are connected to the building block of the compound and also probe the coupling among the spin charge, and lattice degrees of freedom.

In this letter, we report on structural, optical, and magnetic properties of multiferroic h-LuFeO₃ thin films, deposited on (0001) sapphire and (111) YSZ substrates by an RF magnetron sputtering system. We studied the effect of the growth temperature and annealing on the structure of h-LuFeO₃ thin films. Based on the X-ray diffraction and optical spectra, annealing above 950 °C has been found to change the crystal structure of h-LuFeO₃/Al₂O₃ from a metastable hexagonal structure to an orthorhombic structure. Optical spectroscopy in the 0.5-6.5 eV range has been used to study the optical and electronic excitations of the thin films. The electronic excitations of h-LuFeO₃ thin films mainly originate from Fe³⁺ d to d on-site, O 2p to Fe 3d charge transfer, and 2p to Lu 5d and 6s charge transfer excitations. Since the building blocks of h-LuFeO₃ and o-LuFeO₃ are FeO₅ and FeO₆ respectively, the electronic excitation signatures, therefore, are expected to be different for these two phases of LuFeO₃. We also report the temperature dependence of the energy band gap at ~2.0 eV and a stronger upper band edge at ~3.5 eV which supports the spin-charge coupling effect in the h-LuFeO₃ thin film.

EXPERIMENTAL

LuFeO₃ was prepared by a conventional solid state reaction. A stoichiometric ratio of Lu₂O₃ and Fe₂O₃ powder samples were thoroughly mixed in a ball-mill and then in mortar and pestle. The mixture was then pressed into pellets and sintered at 1200 °C for 12 hours. After sintering, the process was repeated one more time. The sintered pellets were used as a target material to deposit LuFeO₃ thin films using RF Magnetron Sputtering System. Single crystal substrates of (0001) sapphire and (111) YSZ were ultrasonically cleaned in acetone and ethanol bath in sequence. Before thin film deposition, we preheated substrates at 600 °C for 30 min and slowly increased the substrate temperature to the final temperature between 700 and 850 °C. The sputtering power was slowly increased to strike the plasma and then to maintain the desired deposition rate. The chamber was pumped out to the base pressure of 2×10^{-6} Torr. For most of the deposition runs, we used oxygen partial pressure between 1 and 10 mTorr and the deposition pressure between 5 and 25 mTorr. The substrate stage was rotated at 20 rpm to improve the uniformity of the sample thickness, deposited in the range of 50 - 100 nm. All as-grown films were post-deposition annealed at temperatures between 800 °C and 1200 °C for about 3 hours.

X-ray diffraction (XRD) and atomic force microscopy (AFM) have been employed to characterize the surface morphology and structural properties of the thin films. We measured variable-temperature (10 - 400 K) transmittance in the wavelength range of 190 - 3000 nm, with a spectral resolution of 1 nm, using Lambda 950 spectrophotometer coupled with a continuous flow helium cryostat and a fiber optic spectrometer coupled with a closed-cycle helium refrigeration system. The magnetic data were measured using the Vibrating Sample Magnetometer option of a Physical Property Measurement System (Quantum Design).

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction (XRD) patterns of ~80 nm h-LuFeO₃ thin films, deposited on (0001) Al₂O₃ and (111) YSZ at 800 °C and annealed at 850 °C. The oxygen partial pressure, argon partial pressure, and deposition pressures were 2 mTorr, 4.5 mTorr, and 6.5 mTorr, respectively. As seen, only peaks corresponding to the (002), (004), and (008) planes of h-LuFeO₃ are observed. No other phases are visible in the xrd pattern. Note that the smaller sharp peaks at ~21° for h-LuFeO₃/Al₂O₃ and at ~27° and 56° for h-LuFeO₃/YSZ are associated with Al₂O₃ and

YSZ substrates, respectively. Based on the xrd patterns, we confirm that h-LuFeO₃ thin films are of a very high quality and single crystalline.

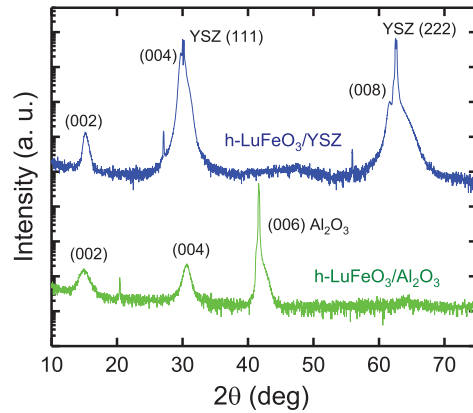


Figure 1: XRD patterns of 80 nm h-LuFeO₃ thin films, deposited on (bottom) (0001) Al₂O₃ and (top) (111) YSZ at 800 °C and annealed at 850 °C. Only (00l) planes are observed, indicating the single crystalline quality of the thin films.

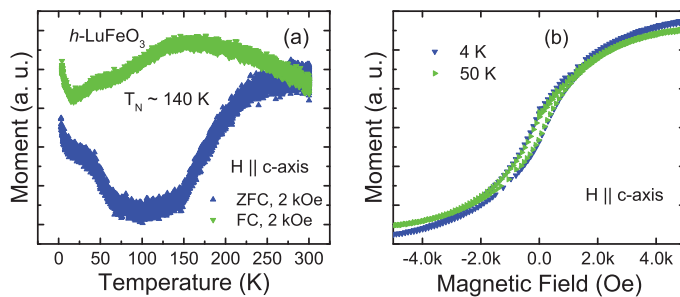


Figure 2: (a) ZFC and FC magnetic moment of a 80 nm h-LuFeO₃/Al₂O₃ thin film as a function of temperature for the out-of-plane ($H \parallel c$ -axis), showing a magnetic transition temperature $T_N \sim 140$ K. (b) M-H hysteresis loops measured at 4 K and 50 K for the h-LuFeO₃/Al₂O₃ thin film. The observation of smaller M-H loops is consistent with a canted antiferromagnetic state below T_N .

We measured the out-of-plane magnetic moment of the sample as a function of temperature and the magnetic field in order to study the magnetic property. Figure 2a shows the zero-field cooled (ZFC) and field-cooled (FC) magnetic moment of an h-LuFeO₃ thin film on (0001) Al₂O₃ as a function of temperature for $H = 2$ kOe parallel to the c-axis (the out-of-plane field). The magnetic moment shows a broad peak in the FC moment and a sharp change in the ZFC moment at the magnetic transition temperature $T_N \sim 140$ K, which is consistent with the previously reported

values for T_N .^{6,7,10} The magnetic moment increases below 50 K. The M-H hysteresis loops were measured at 4 K and 50 K, as shown in Fig.2b. The small hysteresis loops were observed below 50 K, consistent with a canted antiferromagnetic ordering T_N . Similarly, the h-LuFeO₃/YSZ thin film also shows a very similar magnetic property (not shown).

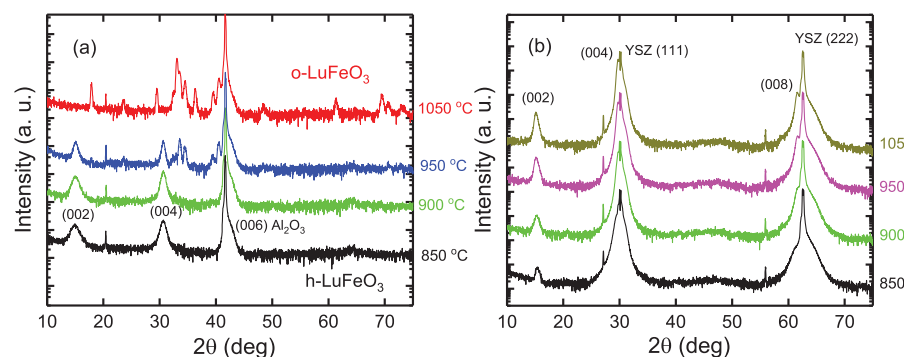


Figure 3: XRD patterns of (a) h-LuFeO₃/Al₂O₃ thin films and (b) h-LuFeO₃/YSZ thin films. Thin films were annealed at temperatures between 850–1050 °C, as labeled on the right side, before each x-ray scan. The xrd pattern for h-LuFeO₃/Al₂O₃ thin films changes at 950 °C with new peaks appearing in the $2\theta = 30\text{--}40^\circ$ range, indicating a structural phase change. In contrast, the xrd pattern for h-LuFeO₃/YSZ thin films remains unchanged after annealing in the same temperature range.

In order to study the effect of annealing on the structure and the surface morphology of the samples, we annealed h-LuFeO₃ thin films at temperatures between 850–1050 °C for 3 hours in a tube furnace, as shown in Fig. 3a. The xrd pattern starts changing for h-LuFeO₃/Al₂O₃ thin films at 950 °C with new peaks developing in the $2\theta = 30\text{--}40^\circ$ range, which is an indicative of a structural phase change. In particular, the xrd pattern appears completely different for the sample annealed at 1050 °C and the presence of the triplet peaks between 32° and 35° confirms that the structure has changed to an orthorhombic LuFeO₃ (in short, o-LuFeO₃) phase. Therefore, we conclude that annealing causes the structural and phase changes from h-LuFeO₃ to o-LuFeO₃ starting at $T_{\text{phase}} \sim 950^\circ\text{C}$. It is noted that the 950 °C thin film is in mixed phases of h-LuFeO₃ and o-LuFeO₃. Recently, Cao et al. have reported such structural phase transition of h-LuFeO₃ films at 1000 °C.¹² In contrast, as shown in Fig. 3b, the xrd pattern for the h-LuFeO₃/YSZ thin films fairly remains unchanged even after annealing in the same temperature range. In fact, the xrd of the h-LuFeO₃/YSZ thin film remains the same even after annealing up to 1250 °C (not shown here). Based on the lattice unit cell analysis, the lattice mismatch between h-LuFeO₃ ($a = 5.965 \text{ \AA}$) and (0001) Al₂O₃ ($a = 4.758 \text{ \AA}$) is $\sim 25\%$, creating a significant lattice strain in the thin film. Similarly, the lattice mismatch between (111) YSZ ($a = 5.16 \text{ \AA}$) and h-LuFeO₃ is $\sim 16\%$ which means the lattice strain in the h-LuFeO₃/YSZ thin film is smaller than it is in the h-LuFeO₃/Al₂O₃ thin film. Further, the interfacial bonding in h-LuFeO₃/YSZ is stronger than that in h-LuFeO₃/Al₂O₃ due to the better matching of the oxygen network at the interface between h-LuFeO₃ and the substrate.^{8,12} Consequently, annealing above 950 °C causes an irreversible phase change on the highly-strained h-LuFeO₃/Al₂O₃ thin film from a metastable hexagonal structure to a bulk orthorhombic structure. Therefore, h-LuFeO₃ deposited on (111) YSZ substrate is more stable and energetically favorable

than h-LuFeO₃ deposited on (0001) Al₂O₃ substrate. Further implications of this results are that the growth temperature for h-LuFeO₃/Al₂O₃ thin films must be kept below 950 °C.

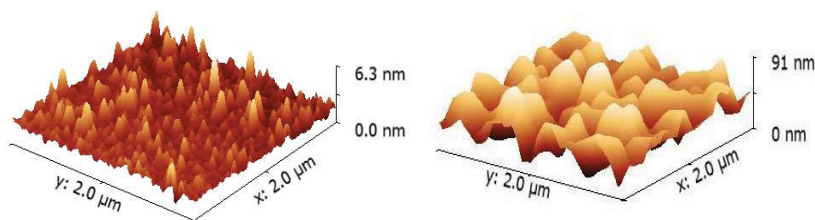


Figure 4: AFM Images of the h-LuFeO₃/Al₂O₃ thin film annealed at (left) 850 °C and (right) 1050 °C. The surface structures significantly increased after annealing the sample at 1050 °C.

Figure 4 shows AFM images of the h-LuFeO₃/Al₂O₃ thin film annealed at 850 °C and 1050 °C. The AFM images were taken at room temperature in a tapping mode. It is clear that the annealing significantly changes the surface morphology of the thin films. For example, the root-mean-squared values for the h-LuFeO₃ thin film annealed at 850 °C is ~7 nm whereas for the thin film annealed at 1050 °C is ~55 nm. During the phase change process of the h-LuFeO₃ thin film from a hexagonal structure to an orthorhombic structure due to annealing above 1050 °C, the lattice strain in the sample is expected to change from a strained film to a fully relaxed film because the film is no longer single crystalline. When the lattice strain is released due to annealing, the thin film can form bigger granular structures, as observed in the AFM image, by the nucleation process.

The optical properties and the electronic excitations of the h-LuFeO₃/Al₂O₃ thin films annealed at different temperatures have been explored using a UV-VIS-NIR spectrophotometer in the energy range 0.5 - 6.5 eV and in the temperature range 10 - 300 K. Figure 5a shows the representative 300 K absorption coefficient as a function of photon energy for the h-LuFeO₃/Al₂O₃ thin film, annealed at 900 °C and 1050 °C. The arrows indicate the four prominent electronic transitions at ~2.3, 2.9, 4.2, and 5.6 eV for the h-LuFeO₃/Al₂O₃ thin film, annealed at 900 °C. Based on the theoretical calculations and available experimental optical data,^{2,7,14-16} we assigned the electronic excitations at 2.3 eV to Fe³⁺ d to d on-site excitation, 2.9 and 4.2 eV to O 2p to Fe 3d charge transfer, and >5 eV to O 2p to Lu 5d and 6s charge transfer excitations. Note that O 2p and Fe 3d states are strongly hybridized, and thus Fe d to d excitation is not purely d to d rather it is a p-d hybridized state to a d-state excitation. As seen, the electronic excitations are distinctly different for h-LuFeO₃ thin films annealed at 900 °C and 1050 °C which is consistent with the expected spectra for a hexagonal phase at 900 °C and an orthorhombic phase at 1050 °C. We can explain the distinction between two optical spectra based on the crystal structure of these two phases. The building block for h-LuFeO₃ is a trigonal bipyramidal FeO₅ while the building block for o-LuFeO₃ is an octahedral FeO₆. Thus, the electronic excitation signatures of h-LuFeO₃ and o-LuFeO₃ are expected to be different because the crystal-field environments for FeO₅ and FeO₆ are uniquely different. In addition, the electronic excitations of o-LuFeO₃ moved to higher energies, consistent with the expected electronic excitations from o-LuFeO₃.¹⁴

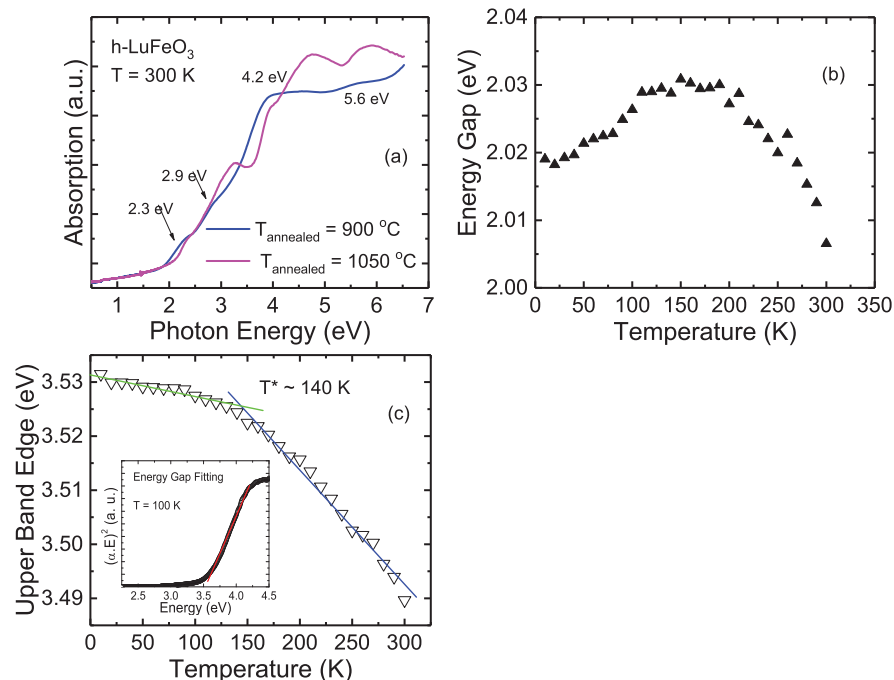


Figure 5: (a) Room temperature absorption coefficient as a function of photon energy for the h-LuFeO₃/Al₂O₃ thin film, annealed at 900 °C and 1050 °C, respectively. The arrows indicate the electronic transitions for the 900 °C annealed thin film. (b) The direct energy band gap as a function of temperature, showing a broad peak around 150 K. (c) The upper energy band edge as a function of temperature for the 900 °C annealed h-LuFeO₃/Al₂O₃ thin film. The band edge changes the slope around the magnetic transition temperature 140 K. The inset shows an example of the energy band edge fitting with the direct energy band gap model.

The energy band gap of the h-LuFeO₃/Al₂O₃ thin film has been extracted from the measured optical absorption data using the direct-type energy gap analysis. The energy gap of h-LuFeO₃ as a function of temperature is shown in Fig. 5b. The room temperature energy gap has been extracted to be $\sim 2.01 \pm 0.02$ eV, which is consistent with the published values.^{2,15} The energy gap has a peak value of ~ 2.03 eV at ~ 150 K which slightly decreases to 2.02 eV at 10 K. As discussed above, this energy gap corresponds to the gap between the hybridized O 2p and F 3d states (occupied) and the empty F 3d states. The energy gap of h-LuFeO₃ shows a strong temperature dependence with a broad peak around the magnetic transition temperature 140 K, indicating the coupling between the spin and charge degrees of freedom in the system. The fact that the magnetic property of h-LuFeO₃ arises due to the spins of Fe 3d electrons and the energy gap is associated with the electronic excitation from the Fe 3d–O 2p hybridized state to the Fe 3d state suggest that the peak at 140 K

in the temperature dependence of the energy gap is a result of the spin-charge coupling. To confirm the coupling effect, we also analyzed the upper energy band edge corresponding to the O 2p to Fe 3d charge-transfer excitation at 4.2 eV. As the 4.2 eV excitation is much stronger than the electronic excitation at 2.3 eV, the energy band edge analysis for this peak has a better resolution. The inset in Fig. 5c shows an example of the energy band edge fitting with the direct energy band gap model. As seen in Fig. 5c, the upper band edge also exhibits a strong temperature dependence. Overall, the band edge displays a linear blueshift upon cooling with a discontinuity around $T_N \sim 140$ K, supporting the spin-charge coupling. The slope of the blueshift decreases after the onset of the magnetic state.

The sensitivity of the electronic excitations to the magnetic ordering through the spin-charge coupling effect has been observed in other multiferroic LuFe_2O_4 and YFe_2O_4 thin films.¹⁷ The common structural features of the h-RFeO₃ and RFe₂O₄ oxides are that they all have a frustrated triangular lattice and hence the frustrated spin systems. The effect of annealing on the structural phase change observed in h-LuFeO₃ may not be unique. In fact, our preliminary results suggest that h-YbFeO₃ thin films also go through a very similar annealing-induced phase change (Work underway and will be published elsewhere). We anticipate that the other family members of metastable h-RFeO₃ are also likely to undergo such phase change from a metastable hexagonal to the orthorhombic bulk form if the lattice mismatch is greater than 20%. In future work, we plan to investigate the other family members of h-RFeO₃ thin films.

CONCLUSIONS

We successfully deposited single crystalline h-LuFeO₃ thin films on (0001) Al₂O₃ and (111) YSZ by RF Magnetron Sputtering. Annealing above 950 °C causes an irreversible phase change from a metastable hexagonal structure to an orthorhombic structure (bulk phase) for h-LuFeO₃/Al₂O₃ thin films. The electronic excitation spectra also support the structural and phase change of the h-LuFeO₃/Al₂O₃ thin films. In particular, the electronic excitations moved to the higher energies as the phase changes from a hexagonal phase to an orthorhombic phase. However, h-LuFeO₃/YSZ thin films remained mostly unaffected by annealing up to 1200 °C, indicating a stronger interface bonding between the h-LuFeO₃ thin film and a YSZ substrate. The energy band gap of an h-LuFeO₃/Al₂O₃ thin film is 2.01 ± 0.02 eV at 300 K. The energy gap and the upper band edge of the 4.2 eV electronic excitation in the h-LuFeO₃ thin film exhibit a strong temperature dependence with a discontinuity around the magnetic transition $T_N \sim 140$ K, indicating the spin-charge coupling in h-LuFeO₃.

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