Pulsed Laser Deposition as a Novel Growth Technique for Thin Film $LuFe_2O_4$ and Related Multiferroic Nature

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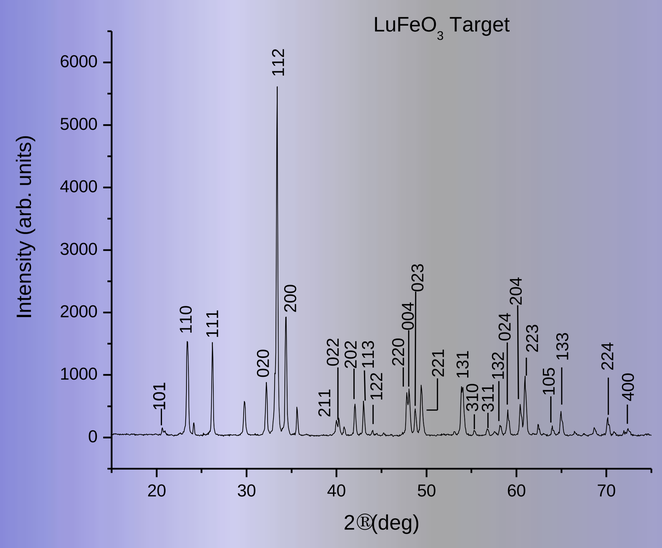
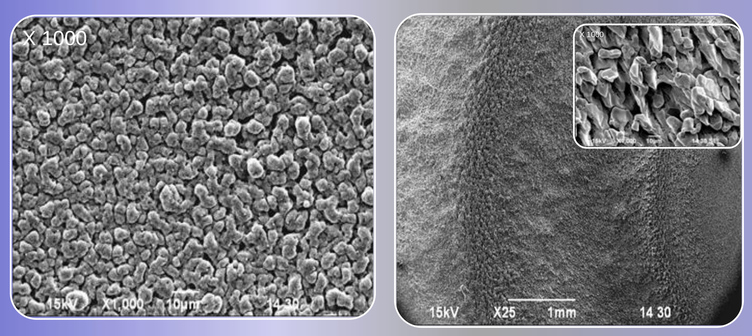
Abstract

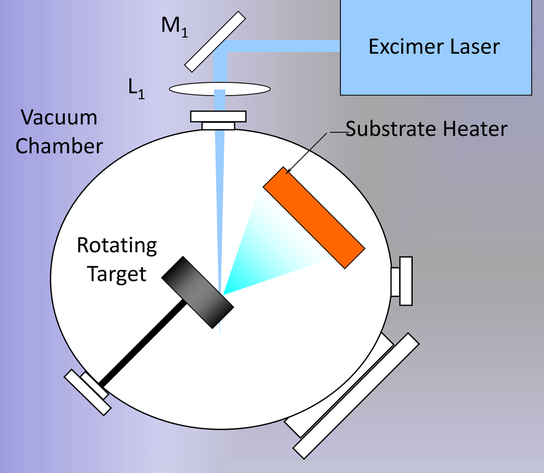
Growth of polycrystalline Lutetium Iron Oxide via pulsed laser deposition is shown herein, and the multiferroic $LuFe_2O_4$ phase is stabilized. Fluence and pressure dependent phase growth is demonstrated, along with crystalline structure in vacuum (~10^{-5} torr) conditions. Thermodynamic considerations at the laser-target interaction are investigated, as well as at the plume-substrate interface, which reveal that the necessary Gibbs free energy is available in the optimized growth environment to allow formation of the $LuFe_2O_4$ polycrystalline phase. The resulting growth rate is found to be related to the Gibbs free energy and concentration of nucleation sites on the substrate. Characterization of the multiferroic aspect of $LuFe_2O_4$ entailed direct measurement of the ferroelectricity in the thin film, as well as magnetic behavior, both at various temperatures. In particular, the ferroelectric polarization vs. voltage data yields a value of 0.61 μC/cm² at 300 K; moreover, these data are in agreement with those reported in the literature. Strong magnetization vs. applied field data shows the magnetization at 300 K to be 150 emu/cm³ and increasing to 200 emu/cm³ at 10 K.



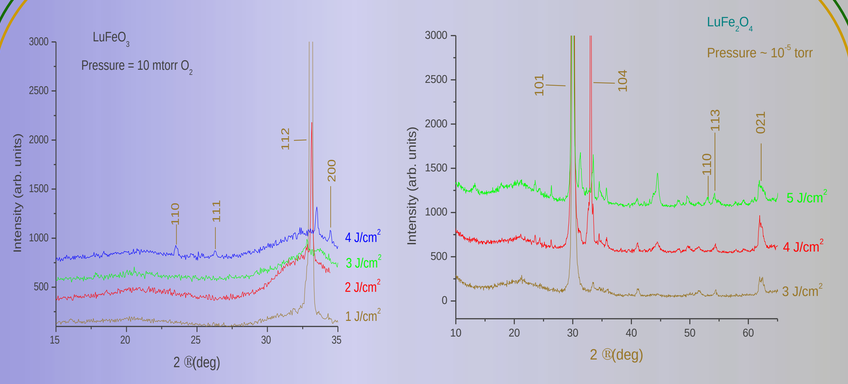
XRD analysis shows the $LuFeO_3$ phase for the stoichiometric target.



Scanning electron microscope images of (left) non-ablated central region of the target and an (right) ablated track with an inset at 1000x to illustrate the conical formations at the target surface after several hundred thousand pulses.



Schematic of the pulsed laser deposition chamber depicting the Excimer laser source with the focusing optics and rotating target holder. A heated substrate facilitates the mobility of the arriving species and nucleation of critical binding sites.



Noting that for $\Delta G^0 < 0$ a reaction is favorable by the second law of thermodynamics, the $LuFeO_3$ phase will tend to form before the $LuFe_2O_4$ phase since $\Delta G^0_{LuFeO3} < \Delta G^0_{LuFe2O4}$ [Table 1]. According to

$$\Delta G^0 \approx RT \ln P(O_2)$$

in order for the $LuFeO_3$ phase to form at a partial pressure $P(O_2)$ = 10 mtorr the required free energy is ΔG^0 = -64.68 kJ/mol, while for the $LuFe_2O_4$ phase ΔG^0 = -21.56 kJ/mol. The trend in the free energies ($\Delta G^0_{LuFeO3} < \Delta G^0_{LuFe2O4}$) continues for each increase in ambient oxygen pressure. Table 1 gives the tabulated values of the optimal partial oxygen pressures and associated Gibbs free energies for three phases found in this study.

Table 1

Tabulated [1] Gibbs free energy ΔG^0		
$LuFeO_3$ perovskite phase	$LuFe_2O_4$ hexagonal phase	$Lu_3Fe_5O_{12}$ garnet phase
-130.30 kJ	-44.64 kJ	-8.07 kJ

The thermo-chemical equations for each LFO phase and the associated Gibbs free energies used in Table 1 follow:

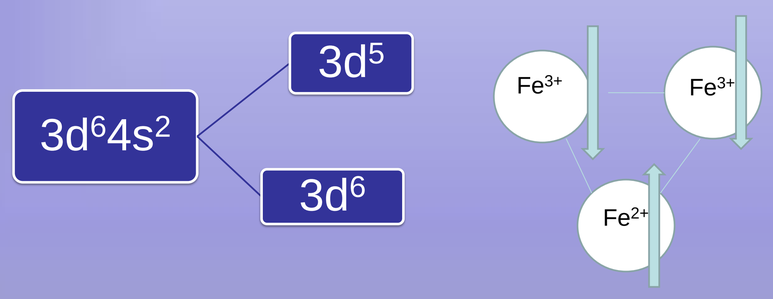
$Fe + ½\ Lu_2O_3 + ¾\ O_2 \rightarrow LuFeO_3$ with $\Delta G^0 = ¾\ RT \ln P(O_2)$

$2FeO + ½\ Lu_2O_3 + ¼\ O_2 \rightarrow LuFe_2O_4$ with $\Delta G^0 = ¼\ RT \ln P(O_2)$

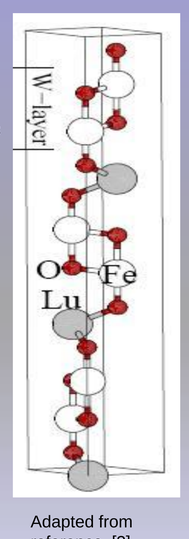
$3LuFeO_3 + 2/3\ Fe_3O_4 + 1/6\ O_2 \rightarrow Lu_3Fe_5O_{12}$ with $\Delta G^0 = 1/6\ RT \ln P(O_2)$

Magnetism and charge frustration in $Lufe_2O_4$

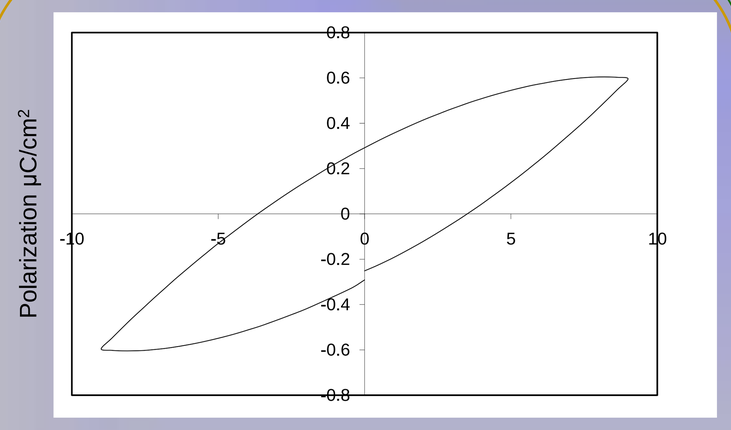
The topologically charge frustrated triangular [3] ionic arrangement of $LuFe_2O_4$. The exotic magnetic and electronic properties are due to the peculiar arrangement of ions and the d-shell electrons.



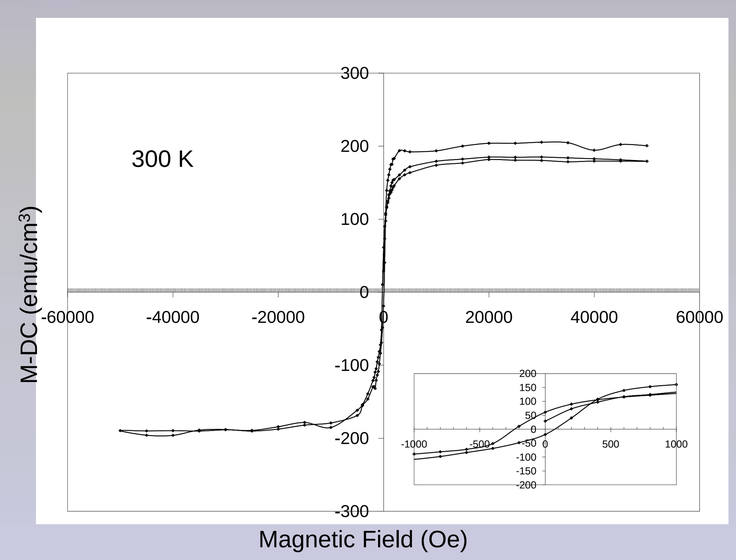
From the magnetization saturation data of M = 200 emu/cm³ the number of Bohr magnetons per unit cell is found to be 6.45 μ_B/ $LuFe_2O_4$. Structural configuration of the $LuFe_2O_4$ unit cell contains 6 Fe atoms each with an average of 1.07 μ_B per Fe site.

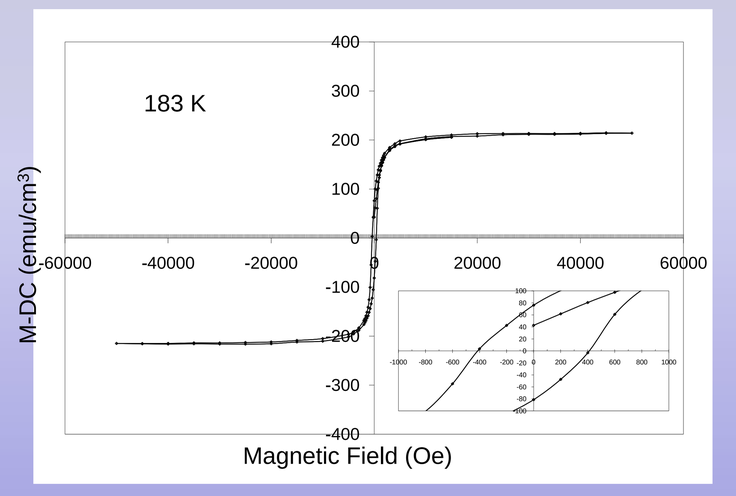


Adapted from reference [2].



Electronic polarization at room temperature yields a saturation value of 0.61 μC/cm²





Hysteretic magnetic response the $LuFe_2O_4$ thin films at 300 K and 10 K, with respective magnetization of 150 emu/cm³ and 200 emu/cm³ . Inset are the blown up regions showing the virgin curves.

CONCLUSIONS: The multiferroic $LuFe_2O_4$ phase has been stabilized from a target in the $LuFeO_3$ phase in thin film form as confirmed by XRD and Gibbs free energy considerations. In vacuum conditions and higher energies (laser fluence) the $LuFe_2O_4$ phase is stabilized. Polarization data and the large magnetization indicate the possible multiferroic nature of the quasi-2D $LuFe_2O_4$ structures.

References:

[1] Gschneider, Eyring, *Handbook on the Physics and Chemistry of Rare Earth Materials*, North-Holland Elsevier Science Publishers B.V., The Netherlands, (1990).

[2] Xiang J., Whang-Bo M.H., *Charge Order and the Origin of Giant Magnetocapacitance in $LuFe_2O_4$*, Cond. Mat., (2007).

[3] N. Ikeda *et. al., Nature* **436**, 1136-1138 (2005).

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