Structural and Magnetic properties of Room Temperature Multiferroic $Lu_{0.9}Ho_{0.1}FeO_3$

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Abstract

In recent times, $LuFeO_3$ is found to be an interesting material exhibiting room temperature multiferroic properties both in its stable orthorhombic and meta-stable hexagonal phase [1, 2]. To stabilize the single phase and also to enhance the magnetic and ferroelectric properties rare earth doping is a possibility [3, 4]. In this work, magnetic rare earth atom, Holmium is doped in place of Lu, the structural, magnetic and ferroelectric properties are investigated. Bulk nanocrystalline$Lu_{0.9}Ho_{0.1}FeO_3$ compound is synthesized by hydrothermal method. Doping with ionic radius larger than Lu, helps to stabilize the structure in a stable orthorhombic- Pnma phase. Rietveld refinement of structural data is carried out on the synthesized sample and the lattice parameters are found to be increasing as expected. Also, Ho being an element with a large magnetic moment, the effect of doping on magnetic properties is investigated. M-H isotherms didn't saturate even at magnetic field, H= 9T reflecting a strong antiferromagnetic interaction that arises from the super exchange Fe^{3+}-O-Fe^{3+} interactions. Finite remnant and coercivity values obtained from the M-H loop measured at 300 K confirms that the T_N lies above room temperature (RT). Observation of P-E loop at 300 K confirms ferroelectric ordering at RT.

Keywords: *$LuFeO_3$, Multiferroics, Single phase, P-E Hysteresis, M-H Hysteresis*

1. Introduction

Multiferroics are an interesting class of materials that exhibit both magnetic and ferroelectric properties simultaneously. These materials have potential applications in spintronic devices and memory devices [1, 2]. The prime interest is to have materials that exhibit multiferroic property at room temperature (RT) in a single phase. $BiFeO_3$ is a widely studied multiferroic system (T_c ~ 1100 K, T_N~ 643 K) [3, 4]. However, due to the weak coupling between the magnetic and ferroelectric order parameters and high leakage current, there is still room for new single-phase room temperature multiferroics. To this end, $LuFeO_3$ (LFO) is an interesting material which stabilizes into two crystallographic structures, stable-orthorhombic (O-LFO) and metastable- hexagonal (H-LFO) phases. O-LFO is reported to exhibit multiferroic property at RT (T_C ~ 1000 K, T_N~ 630 K) in spite of its non-polar nature and also exhibits small net magnetization along c- axis [5]. Hexagonal phase exhibits finite polarization due to its polar nature but the T_N of the system is still debatable [6]. Rare-earth doping is an established route to stabilize the single phase [7]. In this work, rare earth atom Ho is doped in place of Lu to stabilize the structure in the orthorhombic phase. Also, Ho being an element with a large magnetic moment, the effect of doping on magnetic properties is investigated.

2. Experimental Details

Bulk nanocrystalline compound $Lu_{0.9}Ho_{0.1}FeO_3$ is synthesized by hydrothermal method. The precursors used are $Lu(NO_3)_3 \cdot H_2O$, $Ho(NO_3)_3 \cdot H_2O$, $Fe(Cl_3)_3 \cdot H_2O$ and citric acid ($C_6H_8O_7$). The precursorsare added in distilled water in stoichiometric ratio and mixed thoroughly to get a uniform mixture. The pH of the solution is maintained at 8 by adding NH_3. The solution is then transferred to an autoclave and treated thermally at 200°C for 24 hours. After the autoclave cools down to room temperature, the solution is washed several times by distilled water and ethanol using a centrifuge at 13,000 rpm. The collected sediment is dried in a hot air oven for 6 hours at 70°C. The dried powder is grinded uniformly and annealed at 750°C for 8 hours. The annealed powder is pressed into a pellet and sintered. X-ray diffraction (XRD) measurements were performed using PANalytical X'pert Pro X-ray diffractometer at ambient conditions in the Bragg-Brentano geometry.The magnetic measurements were carried out using a Quantum Design PPMS with Vibrating Sample Magnetometer. The pellets were coated with silver paint on both sides to create an electrode- sample- electrode configuration. Next, the pellet is treated thermally at 200°C for 2 hours to increase the adhesion between the sample and electrode. To investigate the ferroelectric properties P-E loop measurements were carried out on these samples using Materials

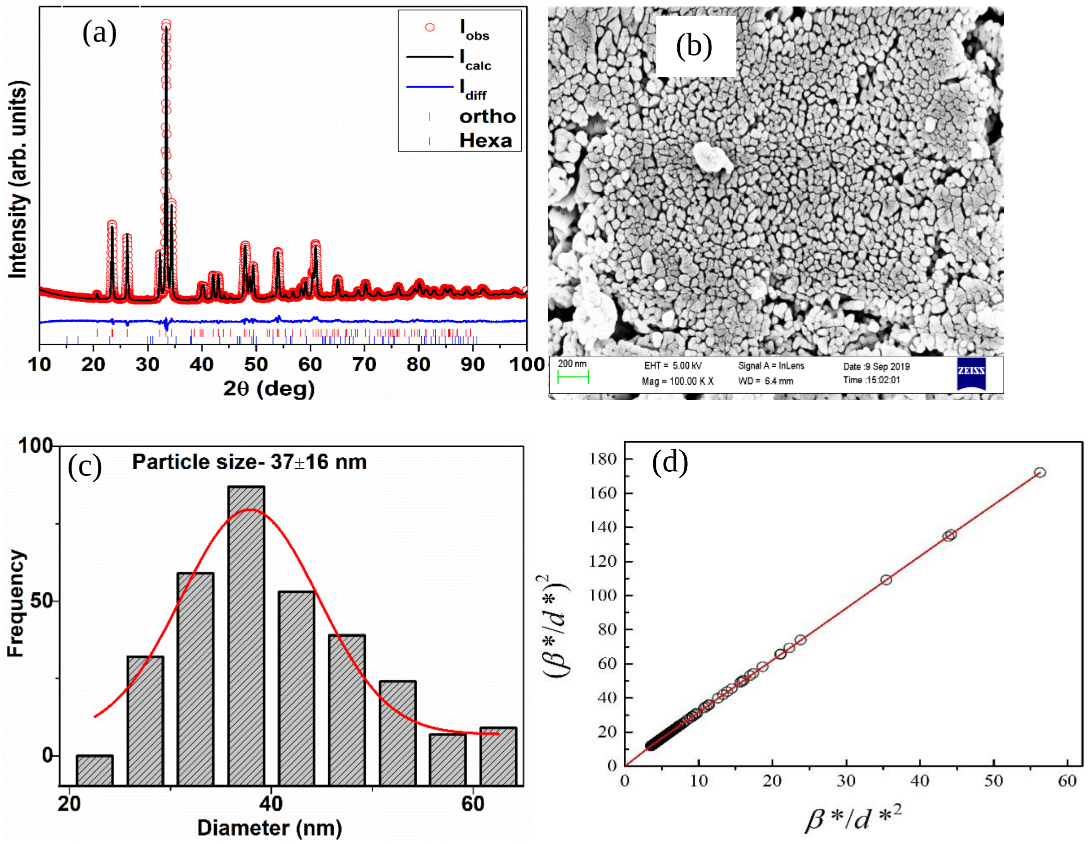

FIG 1: (a) Rietveld refinement of the room temperature XRD pattern of the synthesized $Lu_{0.9}Ho_{01}FeO_3$ powder; (b) Microstructure of the synthesized sample. (c)Histogram of the particle size distribution observed from FESEM. (d) Halder-Wagner approximation plot.

analyzer, Radiant technology.

3. Results and Discussion

3.1 Structural Studies

X-ray diffraction pattern (open circles) of the synthesized $Lu_{0.9}Ho_{0.1}FeO_3$ sample is shown in figure 1 along with Rietveld refinement (solid lines) based on the orthorhombic (Pnma) phase. It is evident from the figure that the Ho concentration of 10% stabilizes the structure into the orthorhombic phase presumably due to the bigger ionic size of Ho. The ionic sizes of the atoms influence the tolerance factor (t) strongly. Stability of the perovskite system depends on the tolerance factor which can be calculated by ($t = (r_A + r_O)/ \sqrt{2}\ (r_B + r_O)$) where r_A, r_B, r_O are ionic radii of A, B and O, respectively. Doping a bigger atom in place of Lu increases‘t’[8]. In the case of $LuFeO_3$, the calculated t is 0.90284 and with 10 % of Ho doping, t increases to 0.90344. In order to quantify the phases and also to extract the lattice parameters, Rietveld refinement is carried out using Highscore Plus software. The extracted parameters are given in table 1. The lattice parameter values extracted from refinement are larger than the values reported in the literature for pure O-$LuFeO_3$ [5]. The increase in lattice parameters by doping Ho is due to the bigger ionic radius of Ho (1.217 Å) compared to the ionic radius of Lu (1.2Å). The particle size (fig 1 b & c) of the synthesized sample is measured using FESEM (Field emission scanning electron microscope) and it was found out to be 37 ±16 nm. The average crystallite size is also calculated using Halder – Wagner approximation plot which indeed shows that crystallite size is 30.8 ±3 nm.

Table 1. Rietveld refinement parameters of the synthesized sample

Ho conc	**χ^2**	**R_{wp}**	**% of phases**		**Lattice parameters (Å) of Ortho**		
			Ortho	**Hexa**	**a**	**b**	**c**
0.1	2.7	1.8	100	0	5.548	7.571	5.219

3.2 Magnetic Properties

The magnetic measurements were carried out on the synthesized samples. The M-H isotherms taken in the field range -9T to 9T at 3K, 50 K, 100 K, 200 K, and 300 K are shown in figure 2(a). Ordering of Ho^{3+} spins at low temperatures resulted in the observation of a large magnetization of ~ 20 emu/g. Magnetization is decreasing with increase in temperature as expected. Rare-earth orthoferrites, in general, possess a canted G-type antiferromagnetic alignment (AFM). M-H loop at 3 K fails to saturate even at H= 9 T, indicating strong antiferromagnetic ordering. Even though it appears that the M-H behaviour at 300 K is linear, there is still a finite Coercive field (Hc=1518 Oe ± 25 Oe) and remnant magnetization (Mr= 0.06365 ± 8.5E-4 emu/g) as noticed in the inset of fig 2(a) asserting that T_N lies well above RT. The M-T measurements were carried out from 3K to 360 K in the presence of the magnetic field of H=100 Oe, both in the ‘zero-field-cooled’ (ZFC) and ‘field-cooled’ (FC) modes. M-T plots are shown in figure 2b. In the FC mode, magnetization increases steeply below T~ 20 K due to the ordering of Ho moments. From the M-T curves, finite magnetization persists even up to 360 K because Fe^{3+} moments orders at high temperatures due to Fe^{3+}-O-Fe^{3+} super- exchange interaction. Rare-earth orthoferrites also exhibit spin reorientation (SR) transition [9] due to the competition between various complex magnetic interactions which is observed at 16.7 K. Such SR transition leads to a change in the magnetic structure from $G_xA_yF_z$ (Γ_4) to $F_xC_yG_z$ (Γ_2), where G_x, A_y, and F_z stand for the spin component along x,y, and z-axis respectively. The minimum in M-T measured in the ZFC mode (inset of 2 (b)) arises from the partial compensation of the Ho and Fe sublattice magnetization [10].

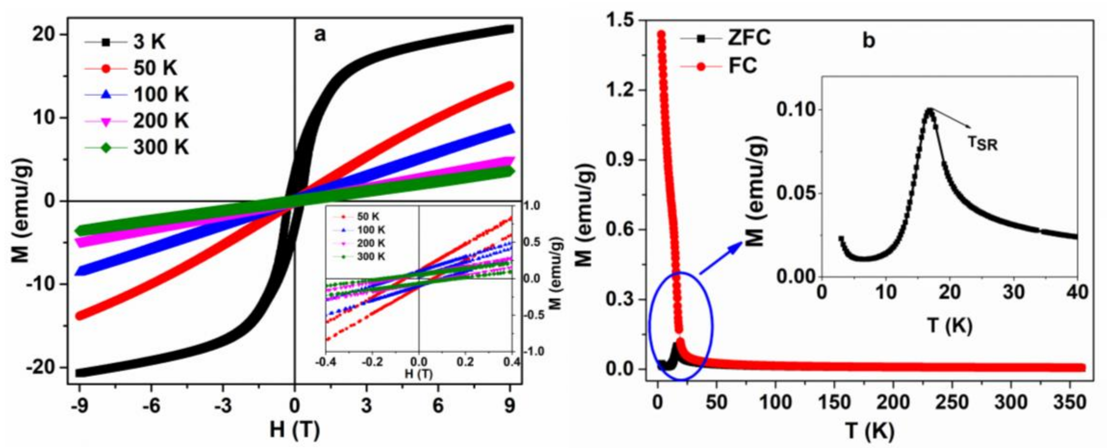

FIG 2. a) Magnetization Vs Magnetic field plots measured at different temperatures for $Lu_{0.9}Ho_{0.1}FeO_3$; b) M-T plot for $Lu_{0.9}Ho_{0.1}FeO_3$ measured from 3 K to 360 K at 100 Oe in the ZFC and FC modes

3.3 Ferroelectric Properties

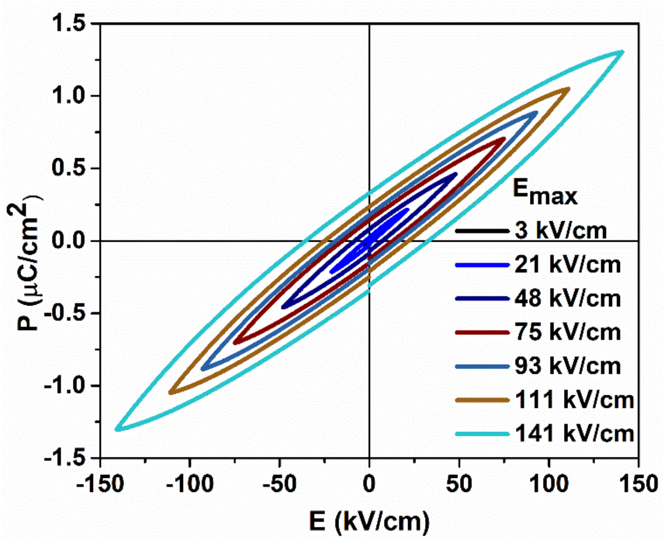

FIG 3. Room temperature P-E loops of $Lu_{0.9}Ho_{0.1}FeO_3$ measured at various fields for $-E_{mzx} \leq E \leq E_{max}$

Standard P-E loops measured at a frequency of 50 Hz at RT are shown in figure 3. The maximum polarization measured at 141 kV/cm is 1.3036 $\mu C/cm^2$. The remnant polarization (P_r) and coercivity (E_c) obtained from for this P-E loop are 0.3314 $\mu C/cm^2$ and 34.4 kV/cm, respectively. P-E loops do not saturate even at the highest fields, an observation commonly made in oxides. This is due to the contributions from non-remnant polarization, resistive and capacitive components. To filter these contributions, the measurements should be carried out in either PUND mode or remnant polarization mode. The presence of P-E loops at room temperature asserts that the sample is ferroelectric at room temperature.

4. Conclusion

$Lu_{0.9}Ho_{0.1}FeO_3$ is synthesized in the powder form using the hydrothermal method. The XRD pattern recorded on the sample confirmed that the system has stabilized into the orthorhombic structure with Pnma space group. Rietveld refinement is carried out to extract the lattice parameters. Failure of M-H isotherms to saturate even at H= 9T reflects a strong antiferromagnetic interaction that arises from the super exchange Fe^{3+}-O-Fe^{3+} interactions. Finite remnant and coercivity values obtained from the M-H loop measured at 300 K confirms that the T_N lies above RT. Observation of P-E loop at RT indicates that the sample is ferroelectric at RT. Dielectric measurements with and without magnetic field will be carried out to establish the magneto-electric coupling and multiferroic nature of this system.

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