Effect of hole doping on the structure and magnetic properties of hexagonal Zr$_{0.2}$Lu$_{0.8}$FeO$_3$ ceramics

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Effect of hole doping on the structure and magnetic properties of hexagonal Zr$_{0.2}$Lu$_{0.8}$FeO$_3$ ceramics

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Abstract. Zr$^{4+}$ doped multiferroic LuFeO$_3$ (LFO) samples were prepared by a sol-gel reaction method and the effect of doping on structural, electric and magnetic properties are evaluated and compared with pure LFO. X-ray diffraction and Rietveld refinement confirm that the pure and Zr doped LFO exists in the hexagonal crystal structure with space group P6$_3$cm. The unit cell parameters and the volume of Zr$_{0.2}$Lu$_{0.8}$FeO$_3$ (ZLFO) are greater than that of the undoped LFO. Magnetic measurements for ZLFO sample show a weak ferromagnetic-like behaviour at room temperature with $M_r \sim 0.013$ emu/g and finite coercivity. Hence, the paramagnetic LFO transformed to the weak ferromagnetic at room temperature upon Zr doping.

1. Introduction

Room temperature multiferroics are very important and quite interesting as they have the applications in spintronics and memory devices [1]. But not many multiferroics compounds have been introduced that can showcase coupling effect between ferroelectricity and magnetic properties at room temperature till date. This coupling effect is called Magneto-electric (ME) effect. In this, the charge can be controlled by the applied magnetic field and the spin with the applied electric field. In order to achieve the magneto-electric effect, magnetization and polarization in the material should be high enough. Also, this coupling must exist at room temperature (RT) since the majority of devices are used at room temperature. BiFeO$_3$ is the only RT multiferroic till date that shows coupling between spin and electric charges, but even in BiFeO$_3$, the magneto-electric effect is very weak due to its cycloid spin structure [1, 2].

LuFeO$_3$ is an important compound which can exist in hexagonal and orthorhombic structures. In its orthorhombic state, it shows antiferromagnetic properties at RT, but the polarization induced is too small. In the metastable hexagonal state, even though the presence of a strong magneto elastic coupling at $T_N$ exists and polarization induced is higher because of the asymmetry caused in the unit cell, the magnetic ordering limited only to a lower temperature, i.e. $\sim 130$ K [3]. Therefore, in LuFeO$_3$, the magneto-electric effect cannot be utilised at room temperature in any of the phases. In order to have the magnetic ordering of LuFeO$_3$ at RT in the hexagonal phase, such that the multiferroic properties can be utilised in practical circumstances, one method that can be adopted is doping the LuFeO$_3$ by cations like Zr$^{4+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ in place of Lu$^{3+}$. In our previous studies, an enhancement in the magnetization is observed at RT when Ni is doped in place of Fe of LFO [4]. In this paper, we

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substitute Lu$^{3+}$ with Zr$^{4+}$. The ions, Zr$^{4+}$ (72 pm) and Lu$^{3+}$ (86 pm) are of comparable size but have different valences due to which it brings about a change in the net charge on the compound. In order to neutralize the charge, either Fe$^{3+}$ shifts its valence to Fe$^{2+}$, or oxygen richness may be created in the system. The fluctuating valence of Fe cation causes the compound to have Fe$^{3+}$ and Fe$^{2+}$ ions. The Fe$^{3+}$-Fe$^{3+}$ interaction is now accompanied by Fe$^{3+}$-Fe$^{2+}$ and Fe$^{2+}$-Fe$^{2+}$ interaction. This brings a spin frustration in the unit cell. This doping by aliovalent cations has shown to be quite contributory in modifying the ferroelectric and magnetic characteristics in LuFeO$_3$.

2. Experimental Details

The method adopted for the synthesis of Zr$_x$Lu$_{1-x}$FeO$_3$, $x = 0.2$, is sol-gel method. For the preparation of ZLFO powder, precursors Fe(NO$_3$)$_3$.9H$_2$O (99.9%, Alfa Make), Lu(NO$_3$)$_3$.9H$_2$O (99.9%, Alfa Make), ZrO(NO$_3$)$_3$.xH$_2$O (99.9% Alfa Make) are measured in appropriate stoichiometric ratios. All the three precursors are dissolved in distilled water separately. Once the individual solutions become completely transparent, they are then mixed together and citric acid is added to the mixed solution. This mixture is heated while constant stirring at 250° C in air. The brown coloured fumes evolve from the solution, and at the end of the reaction, the formation of the gel is observed. The brown residue is then ground and calcinated in a furnace, to get the crystal structure, for 10 hours at 750° C. This mixture is then pelletized using a hydraulic press into pellets of 10 mm diameter and annealed for the densification. These densified samples were used for the characterization.

The purity and phase of the constituent phase of the nanocomposite were analysed by X-Ray Diffractometer with Cu-K$_\alpha$ source ($\lambda=1.5418$ Å). For electrical measurements, silver electrodes were made on both sides of the sample disc to make capacitor geometry. Pellets (diameter of 10 mm and thickness of 1 mm) with Ag paste on both sides were prepared after heating at 200 °C for 30 minutes and used for ferroelectric study using Radiant’s precision premier II. Field dependent magnetic measurements were performed using Quantum Design- PPMS VSM.

3. Results and Discussion

3.1. Structural Analysis

Figure 1. shows the XRD pattern of LuFeO$_3$ and Zr$_{0.2}$Lu$_{0.8}$FeO$_3$ samples at room temperature. It can be seen that the XRD reflections in both the diffraction patterns are exactly lined up according to the standard hexagonal LuFeO$_3$ phase (ICSD#:183152) which indicates that the hexagonal structure is stable for the doped multiferroic (ZLFO). The zoomed-in XRD pattern for the same for 2θ from 28° to 37° is shown in the inset of figure 1. It can be observed that the peak positions are shifting to the left i.e. low diffraction angles from undoped to doped sample, which indicates the increase in the lattice parameters with the doping of 20% Zr in LuFeO$_3$ as can be seen in table 1. It is either due to the fact that the ionic radius of Zr$^{4+}$ ion (radius = 72 pm) is smaller than that of Lu$^{3+}$ ion (radius = 86 pm) or maybe because of the increase in the concentration of oxygen vacancies, which is expected for the charge neutrality. For further understanding, XRD patterns are refined using FullProf program, and it is noticed that pure and Zr-doped LFO data fitted well with hexagonal $P6_3/cm$ space group. The refined XRD graph is shown in Figure 2.

A schematic representation of the hexagonal crystal structures is shown in Figure 3. The schematics were prepared using VESTA software. As can be seen in the figure, the ZLFO sample is composed of a layered structure, with Fe layer and Lu layer placed alternatively. Fe atom is surrounded by 5 oxygen atoms forming a FeO$_5$ structure. The Fe-O-Fe super exchange along the $ab$ plane and Fe-O-O-Fe super-super exchange along the $c$-axis causes the magnetism in the structure. The asymmetric arrangement of the Lu atoms in the unit cell responsible for the existing polarization in the sample [3-6].
Figure 1. XRD of Zr\textsubscript{x}Lu\textsubscript{1-x}FeO\textsubscript{3} (x = 0, 0.2) samples at RT.

Figure 2. Rietveld Refinement of Zr\textsubscript{0.2}Lu\textsubscript{0.8}FeO\textsubscript{3}. The observed and calculated patterns are shown by circles and lines, respectively. The difference between the observed and calculated patterns is shown by the blue line at the bottom of each panel. The vertical bars represent the Bragg peak positions.
Figure 3. The unit cell of $\text{Zr}_{0.2}\text{Lu}_{0.8}\text{FeO}_3$ shown with FeO$_5$ polyhedra cages

Table 1. Cell Parameters for $\text{Zr}_x\text{Lu}_{1-x}\text{FeO}_3$

| $x$  | $a$  (Å) | $b$  (Å) | $c$  (Å) | $V$  (Å$^3$) |
|------|---------|---------|---------|------------|
| 0    | 5.941   | 11.731  | 358.57  |
| 0.2  | 5.959   | 11.688  | 359.43  |

3.2. Magnetic Properties

The field dependence of the magnetization ($M$-$H$) of the ZLFO is measured at 400 K by sweeping the field from +9T to -9T and depicted in Figure 4. The $M$-$H$ loop of the pure LFO is shown in the inset of figure 4. The linear behaviour of the pure LFO without any opening in the loop indicate its paramagnetic nature at 400 K. Compared to the LFO, Zr-doped samples show an enhancement in the magnetization values. In addition, it is already established that undoped LFO show antiferromagnetic nature below ~130 K [3, 5]. On the other hand, the doped sample shows a non-linear increase in magnetization with a loop opening, as seen in the inset of figure 4, which indicates a weak ferromagnetic behaviour. From the figure, ZLFO sample shows the magnetic remanence ($M_r$) ~ 0.013 emu/g; magnetization at 9 T ($M_{9T}$) ~ 1.16 $\mu_B$/f.u and magnetic coercive field ($H_C$) ~ 135 Oe. Thus, the paramagnetic LFO exhibits weak ferromagnetic-like behaviour at RT when doping with 20% Zr in LFO. The enhancement in the magnetic properties may be due to the modification of the Fe-O-Fe exchange interaction upon Zr doping.
Figure 4. $M-H$ loops of ZLFO sample at 400 K.

4. Conclusion
The Zr-doped LFO sample was successfully synthesized in the hexagonal form using the sol-gel technique. Enhanced magnetic properties are observed in the 20% Zr-doped LFO sample. It is evident that the local lattice distortion caused by the Zr substitution is effective in improving the magnetic properties, by modifying the Fe-O-Fe bond angle and Fe-O bond length. The enhanced properties of Zr-doped LFO makes it a very good promising candidate for applications as a RT multiferroic material.

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