

PAPER • OPEN ACCESS

Room temperature multiferroic properties of hexagonal $\text{Lu}_{0.85}\text{Sr}_{0.15}\text{FeO}_3$ ceramics

To cite this article: K U Poojitha *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **577** 012070

View the [article online](#) for updates and enhancements.

Room temperature multiferroic properties of hexagonal $\text{Lu}_{0.85}\text{Sr}_{0.15}\text{FeO}_3$ ceramics

Poojitha K U, Pittala Suresh and P S Anil Kumar¹

Department of Physics,

Indian Institute of Science, Bangalore – 560012, Karnataka, India

E-mail: anil@iisc.ac.in

Abstract. The structural, electric and magnetic properties of bulk hexagonal $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ and 0.15) ceramics are investigated. XRD data and rietveld refinement confirm the hexagonal structure with $P6_3cm$ space group. Magnetic measurements for Sr-doped sample indicate a ferromagnetic-like behavior at the room temperature with a very high coercivity of the order of ~ 4.4 kOe. P-E hysteresis loops show an enhanced ferroelectric property with Sr doping. Hence, towards the realization of applications, the multiferroic properties of hexagonal LuFeO_3 are improved remarkably by 15% Sr substitution at Lu site.

1. Introduction

Room temperature multiferroics are very much fascinating due to the potential applications in spintronics and memory devices. These are promising due to their unique ability to control the charge with the applied magnetic field and the spin with an applied electric field [1]. This property is known as magnetoelectric (ME) effect and is used to fabricate various multifunctional devices. To achieve ME effect, the polarization and magnetization should be high enough in the material. Moreover, the ME coupling constant should be high without which the realization of practical device applications will not be possible. However, multiferroics with finite ME coupling are very scarcely available. Much of the research is dedicated in improving the ME coupling constant of the existing multiferroics and to find new materials for possible multiferroicity. The implementation of this will require coexistence of long-range magnetic and electric orders at room temperature (RT).

LuFeO_3 (LFO) is an exciting candidate that exists in orthorhombic and metastable hexagonal structure [2]. In the orthorhombic phase, it is antiferromagnetic, and the spin structure induces small polarization in the system. On the other hand, if the material transforms to a hexagonal phase, the structure promotes asymmetry in the unit cell and exhibits more polarization than its orthorhombic phase. However, the magnetic ordering shifts to the lower temperature ~ 130 K [3, 4]. Thus, LuFeO_3 in both orthorhombic and hexagonal phases is not useful for the RT multiferroic applications. However, shifting magnetic ordering of the hexagonal phase to RT makes LFO, a very promising material due to its high polarization and triangular arrangement of Fe spins, which brings spin frustration in the unit cell. Doping strategy is one way to alter the magnetic ordering by changing the local environment of Fe ions in the unit cell. In this work, we focus on achieving RT magnetism in the sample by doping Sr at Lu site of the LFO. Though Sr possesses no magnetism, it is interesting because the charge neutrality in the system is compensated either by (i) change in the valence state of Fe cation, Fe^{3+} to Fe^{4+} or (ii) by creating the oxygen vacancies in the system. The fluctuating valence of Fe cation promotes the movement of conduction electrons in the lattice [5]. Hence, in this work, we report the preparation of hexagonal $\text{Lu}_{0.85}\text{Sr}_{0.15}\text{FeO}_3$ polycrystalline samples using the sol-gel method. Also, the effect of dopant ion on achieving the room temperature electrical and magnetic properties are discussed.

¹ To whom any correspondence should be addressed.



2. Experimental details

2.1. Preparation Technique

Polycrystalline samples of $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ and 0.15) (LSFO) were prepared using sol-gel synthesis. The starting materials, $\text{Lu}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (99.9%, Alfa Make), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%, Alfa Make) and SrCO_3 (99.9%, Sigma Aldrich Make) were taken in the stoichiometric ratio for the preparation of LSFO powders. The precursors were weighed carefully using a sensitive balance and dissolved separately in dil. HNO_3 . These solutions were mixed under a magnetic stirrer to obtain a clear and transparent solution. Then, all the solutions were added together into a glass beaker, and citric acid was added as a chelating agent. This mixture was stirred for 4 hr to form a uniform solution. Finally, the solution was heated slowly using a hot plate to remove the unwanted organics such as nitrates, carbonates etc from the solution. At the end of the reaction, the xerogel powder was obtained. The end product was ground through and calcinated at 750°C to attain the required phase. The calcinated powders were made into pellets and used for further characterizations.

2.2. Characterization Techniques

The crystal structure of the pure and Sr-doped LuFeO_3 powders were examined by using X-ray diffractometer having Cu-K_α source ($\lambda=1.5418 \text{ \AA}$). The Raman modes were examined by Horiba JobinYvon, LabRAM-HR 800 micro-Raman system equipped with 514.5 nm. The samples were made into pellets and silver electrodes were applied on both sides of the samples. These pellets were cured at 300°C for 30 min to carry out the electrical measurements. Ferroelectric measurements were performed using Radiant's precision premier II at RT. Field dependent magnetic measurements were performed using Quantum Design SQUID magnetometer at RT.

3. Results and Discussion

3.1. Structural Analysis

Fig.1 shows XRD pattern of $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ and 0.15) samples at room temperature. The observed diffraction pattern for all the samples indicates the LuFeO_3 phase with no secondary phases. The XRD reflections exactly match with the standard data (ICSD # 183152) of LuFeO_3 hexagonal phase. Though the synthesis of hexagonal phase of LuFeO_3 is difficult, we could achieve it by our sol-gel synthesis method. The magnified view of the XRD from $2\theta = 28^\circ - 36^\circ$ is shown in the inset of figure 1 (a). From the figure, a systematic shift in the peak positions towards low diffraction angles are noticed, which indicates the decrease in lattice parameters as Sr doping concentration increases. To understand further, Rietveld refinement is performed on the data using FullProf program [6]. A perfect fitting is obtained with hexagonal $P6_3cm$ space group. The refined XRD graph is shown in figure 1 (b).

The schematic view of the unit cell for $x = 0.15$ is shown in figure 2. It is essential to understand the arrangements of the atoms in the unit cell to understand the changes in electric and magnetic properties. The unit cell consists of the layer structure, having three Fe layers and two Lu layers arranged alternatively. The Fe atoms are surrounded by five oxygen atoms forming FeO_5 cage, and Lu is surrounded by seven oxygen forming a LuO_7 cage. The Fe^{3+} ions are coupled through oxygen along ab-plane and lead to the magnetism in this system while the asymmetry in the Lu atoms and buckling of FeO_5 cages leads to the ferroelectricity along c -axis. It is noticed that lattice parameters, a and c , also the cell volume (V) of the hexagonal LuFeO_3 decreases with Sr doping content, $x = 0.15$. This is due to the dissimilarity in the ionic radius of Sr^{2+} ion (1.18 \AA) which is larger than that of Lu^{3+} ion (0.97 \AA) also may be due to the increase in the concentration of oxygen vacancies, which are expected for the charge neutrality.

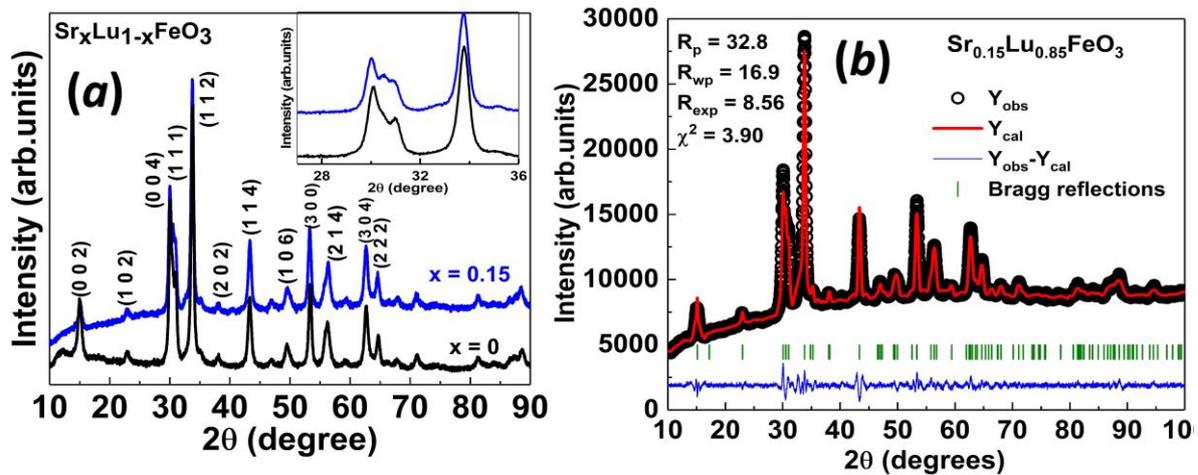


Figure 1. (a). XRD of LSFO samples at RT, (b). XRD Rietveld Refinement of $\text{Lu}_{0.85}\text{Sr}_{0.15}\text{FeO}_3$ sample.

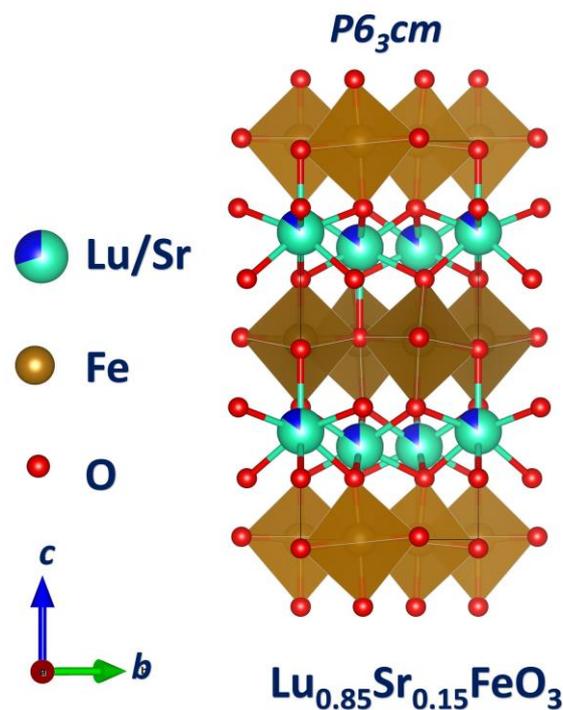


Figure 2. The unit cell of $\text{Lu}_{0.85}\text{Sr}_{0.15}\text{FeO}_3$ shown with FeO_5 polyhedra cages.

3.2. Magnetic Properties

The magnetic properties are investigated at 400 K on the pure and Sr-doped LFO sample. The M-H loops are measured by sweeping the field from 7 T to -7 T as shown in figure 3. The M-H loop of the undoped sample shows a linear dependent curve without any opening in the loop, indicating the paramagnetic nature. It is already established that undoped LFO shows antiferromagnetic nature below ~130 K. On the contrary, Sr-doped LFO shows a nonlinear increase of magnetization with a large loop opening indicating ferromagnetic nature. That means Sr doping pushes the magnetic ground state above the room temperature. The measured magnetic parameters for the Sr-doped sample are as

follows; magnetic remanence (M_r) $\sim 0.012 \mu_B/\text{f.u.}$; magnetization at 7 T (M_{7T}) $\sim 0.07 \mu_B/\text{f.u.}$ and magnetic coercive field (H_c) ~ 4450 Oe. In general, the doping of Sr leads to an increase in the number of oxygen vacancies thus changing the Fe coordination without changing the Fe valence. Also, the change in Fe valence can be expected for the charge compensation. As the coordination of the Fe changes upon doping, the lattice distortion happens and lead to the modifications in the Fe-O-Fe bond angle and Fe-O, Lu/Sr-O bond lengths. The refinement results for Sr-doped LFO clearly shows a change in the bond lengths and bond angles when compared to the pristine LFO. These changes eventually affect the exchange interaction and disturb the antiferromagnetic alignment of the Fe spins, thereby significantly enhance the magnetization values. Therefore, the structural modifications and change in Fe valence lead to the increase in magnetization on Sr substitution [7]. The high coercive field of the Sr-doped sample may be due to the large crystalline anisotropy of the sample.

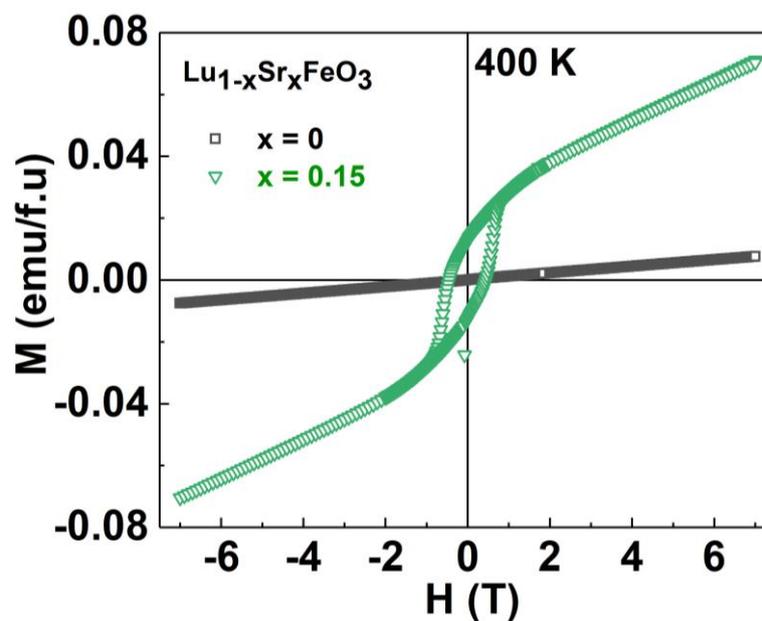


Figure 3. M-H loops of $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ and 0.15) samples at 400 K.

3.3. Electric Properties

The ferroelectric hysteresis (P-E) loops of the pure and Sr-doped LFO samples are depicted in figure 4. From the figure, it can be concluded that the loops have no tendency of saturation, revealing the lossy nature. For the pure LFO, the presence of oxygen vacancies and interfacial polarization can cause the leaky behavior; whereas an extra contribution from the charge conduction through Fe^{3+} to Fe^{4+} is presented for Sr-doped samples. Nevertheless, compared to the pure sample, Sr-doped sample show improved polarization values. The remnant polarization (P_r) increases from $0.03 \mu\text{C}/\text{cm}^2$ for $x = 0$ to $0.11 \mu\text{C}/\text{cm}^2$ for $x = 0.15$ and polarization at the maximum field (P_{max}) increases to $0.33 \mu\text{C}/\text{cm}^2$ from $0.19 \mu\text{C}/\text{cm}^2$ as x changes from 0 to 0.15 . Similarly, the coercive field (E_c) found to increase from $9.4 \text{ kV}/\text{cm}$ to $13.7 \text{ kV}/\text{cm}$ as x changes from 0 to 0.15 . The enhanced polarization of Sr-doped samples is due to the increased Lu-O bond length along the c -axis and due to the increased FeO_5 tilt [8].

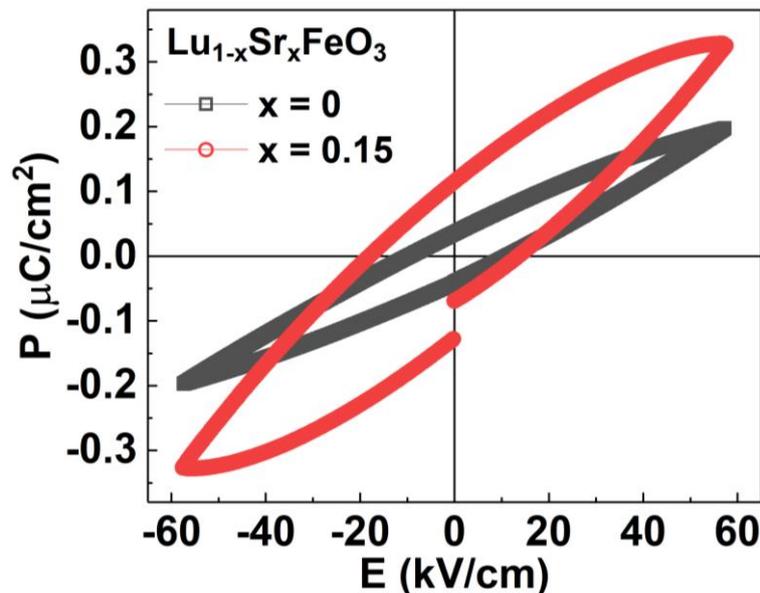


Figure 4. P-E Loops of $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ and 0.15) samples at RT.

4. Conclusions

The polycrystalline samples of hexagonal $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ and 0.15) ceramics were successfully synthesized using the sol-gel technique. The lattice parameters and the volume of the unit cell decrease with Sr doping in LFO. The Sr doped samples show a ferromagnetic behavior at the room temperature with a very high coercivity of the order of ~ 4.4 kOe. The appearance of the magnetism at room temperature is attributed to the crystal distortions and oxygen vacancies. The ferroelectric properties of LuFeO_3 are improved with Sr doping. The enhanced multiferroic properties of Sr-doped LFO are very promising to realize the room temperature spintronic and memory applications.

Acknowledgments

One of the Authors, S. P., acknowledges the financial support from the Dr. D. S. Kothari postdoctoral fellowship No.F.4-2/2006 (BSR)/PH/13-14/0085. Authors also acknowledge the help from Prof. S. Srinath, School of Physics, University of Hyderabad for electrical measurements.

References

- [1] Eerenstein W, Mathur N D and Scott J F 2006 *Nature* **442**, 759.
- [2] Song S, Han H, Jang H M, Kim Y T, Lee N-S, Park C G, Kim J R, Noh T W and Scott J F 2016 *Adv. Mater.* **28**, 7430.
- [3] Suresh P, Vijaya Laxmi K, Bera A K, Yusuf S M, Bheema Lingam Ch, Jeil Jung and Anil Kumar P S 2018 *Phys. Rev. B.* **97**, 184419.
- [4] Disseler S M, Borchers J A, Brooks C M, Mundy J A, Moyer J A, Hillsberry D A, Thies E L, Tenne D A, Heron J, Holtz M E, Clarkson J D, Stiehl G M, Schiffer P, Muller D A, Schlom D G and Ratcliff W D 2015 *Phys. Rev. Lett.* **114**, 217602.
- [5] Thakur S, Singh K and Pandey O P 2017 *Mater. Chem. Phys.* **187**, 96.
- [6] FULLPROF suite, <http://www.ill.eu/sites/fullprof/>
- [7] Hussain S, Hasanain S K, Jaffari G H, Ali N Z, Siddique M and Shah S I 2015 *J. Alloys. Comp.* **622**, 8.
- [8] Suresh P, Vijaya Laxmi K and Anil Kumar P S 2018 *J. Mag. Mag. Mater.* **448**, 117.