

Suppression of ferroelectric polarization and hence room temperature multiferroicity of LuFeO₃ on Cu and Mn doping

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Abstract

Room temperature multiferroicity has been in the centre of interest for last few years due to its enormous potential to be applied as real multifunctional device. LuFeO₃ is a potential candidate as room temperature multiferroic¹, which offers strong multiferroic coupling at room temperature [1]. Presence of ferroelectric polarization is observed in Mn-doped LuFeO₃ also. The main area of restriction is its low polarization, which is to be improved before it can be applied in real devices. In order to do that proper understanding of the mechanism of generation of ferroelectricity is needed. In order to do that we observed that, the ferroelectric and multiferroic properties at room temperature, in orthorhombic distorted perovskite LuFeO₃ are greatly affected by Cu or Mn doping. If we replace Fe⁺³ ion (Ionic Radius=126) with some amount another ion of increasing ionic radius Mn⁺² (Ionic Radius=127) and Cu⁺² (Ionic Radius = 128) the ferroelectric properties are greatly affected as evidenced by the P-E Hysteresis loop measurements. The appearance of ferroelectricity in LuFeO₃ could be attributed to the spin current based model as proposed by Katsura *et al.* [3]. The effect of Cu and Mn doping also can be explained with the Spin current based model [3]. Copyright © 2017 VBRI Press.

Keywords: Improper ferroelectricity, type-II multiferroics, magnetism, spin current model, remanent polarization.

Introduction

Room temperature multiferroics are potential candidate to be applied as real multifunctional devices, Such as smart four state memory, spintronic applications, magnetodielectric sensor, magneto resistive magnetic field sensor etc. Some improper ferroelectrics, such as geometric ferroelectric (YMnO₃), magnetic ferroelectric (TbMnO₃, DyMnO₃) and electronic ferroelectric (Pr_{1-x}Ca_xMnO₃,) shows appreciable multiferroic coupling but at very low temperature, not suitable to be used in real devices. We have reported in our previous paper [1] that LuFeO₃ shows strong multiferroic coupling even at room temperature in a canted antiferromagnetic ordered state, which is not otherwise known to be a ferroelectric material. But its ferroelectric polarization is too low to be applied in real memory devices. In order to tailor-made polarization, we need to understand the underlying mechanism behind the generation of ferroelectric polarization in this compound. Ferroelectric polarization is also observed in Mn-doped LuFeO₃ earlier [2]. This type of improper like polarization in a centrosymmetric structure having a noncollinear spin structure can be explained with the help of spin-current induction model [3] where spin-orbit-coupling-driven reverse

Dzyaloshinskii - Moriya interaction dominates over exchange striction. The simultaneous occurrence of magnetic and ferroelectric transition temperature identifies this material as a multiferroic material of type-II variety, where the ferroelectricity is being originated from canted magnetic order. In this paper, we have investigated the effect of doping of Mn and Cu to the ferroelectric properties, multiferroic coupling and magnetic order of LuFeO₃. In LuFeO₃ it is found that the Fe³⁺-Fe³⁺ superexchange interaction is exceptionally strong⁴, which results in high transition temperature T_N (~627K) from paramagnetic phase (PM) to antiferromagnetic phase (AFM) [4]. In LuFeO₃ there are no Fe³⁺-Lu³⁺ or Lu³⁺-Lu³⁺ interactions because Lu³⁺ has no localized magnetic moment. Because of observation of ferroelectric polarization in an antiferromagnetic ordered state, multiferroicity is highly expected in this material [2]. We studied the mechanism of origin of ferroelectricity and multiferric coupling in this material by willfully disturbing the magnetic order at room temperature. As these systems are low resistive improper ferroelectric, we adopted widely accepted pulse based polarization measurement protocol known as PUND and another fourteenpulse measurement protocol extracting

the actual ferroelectric component from the overall polarization [4]. Our main objective of this work is to understand the mechanism of generation of ferroelectricity in LuFeO_3 , in order to tailor-made its ferroelectric properties to apply this novel ferroelectric material in real multifunctional memory devices [5].

Experimental

Materials used

Pure single phase LuFeO_3 , Mn-doped (20%) LuFeO_3 and Cu-Doped (20%) LuFeO_3 ceramics were synthesized by standard solid-state reaction using Lu_2O_3 (99.99%), Fe_2O_3 (99.9%), CuSO_4 (99.9%) and MnSO_4 (99.9%) purchased from Sigma-Aldrich manufactured in Germany, as precursor.

Methods

The raw powders with the stoichiometric ratio were mixed with the help of high energy ball mill with zirconia in deionized water for 24 hr. The mixtures were calcined at 1373K in air for 4 hr. Then the powder is again ball milled for 12hrs. Then 5 Wt% organic binders (PVA) were mixed with the sample and pressed under uniaxial pressure of 80 MPa into pallets. Then those pallets were sintered at 1473K for 10 hrs to obtain dense ceramic. Silver paste was used as electrodes. Magnetic Properties of the ceramics were measured with the help of a Vibrating Sample Magnetometer (VSM) (Lakeshore Cryotronics Model No: -7400) The P-E loop measurements were carried out with the help of a Precision Material Analyzer (Radiant Technologies).

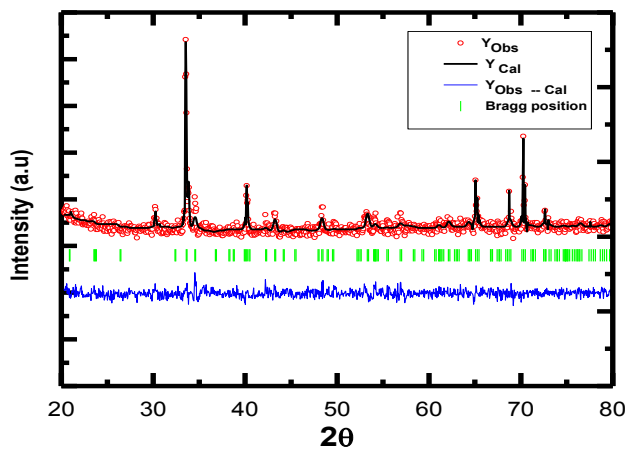


Fig. 1. XRD pattern of as prepared LuFeO_3 sample at room temperature.

Results and discussion

Fig. 1 shows the XRD pattern of as prepared LuFeO_3 sample at room temperature. The results of Rietveld analysis indicate single phase structure of space group Pbnm . The lattice parameters of the pure as well as Mn and Cu doped LuFeO_3 sample are calculated from the powder XRD pattern performing Rietveld refinement

using Full prof software. The lattice parameters indicate the distortion of the lattice structure of the pure LuFeO_3 . Fig. 2 shows FESEM micrograph of as prepared LuFeO_3 sample, showing an average grain size of about $10\mu\text{m}$. Fig. 3(a) shows the P-E hysteresis loop of pure LuFeO_3 sample, With $P_s \sim 6\text{nC}/\text{cm}^2$. The samples are having high loss, and we have applied a specific pulse protocol to obtain remanent polarization in these samples, eliminating the large leakage component present in the aforesaid samples.

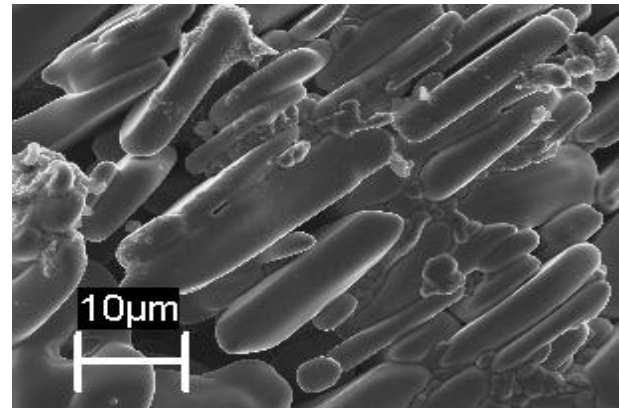


Fig. 2. FESEM micrograph of as prepared LuFeO_3 sample.

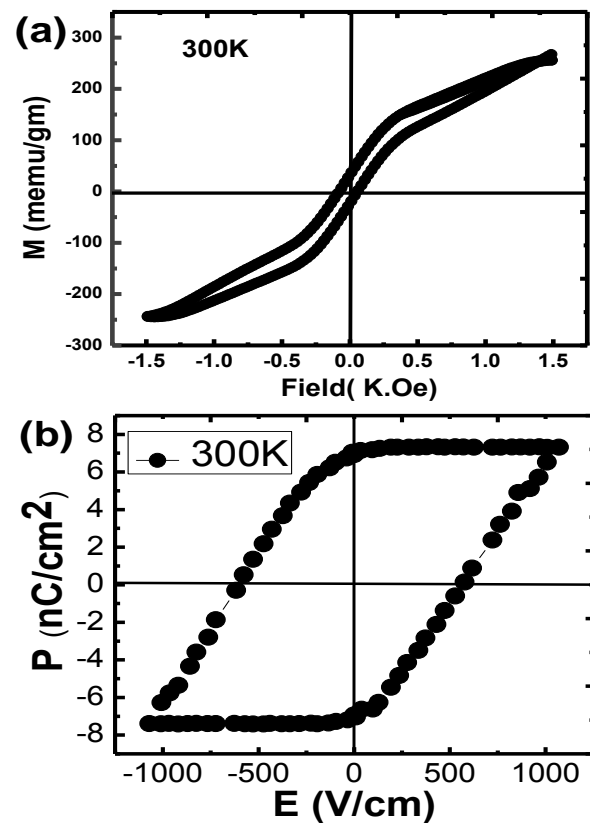


Fig. 3(b) shows the P-E hysteresis loop of pure LuFeO_3 sample, With $P_s \sim 6\text{nC}/\text{cm}^2$ (a)shows the magnetic hysteresis loop (M-H) of the un-doped LuFeO_3 sample.

Whereas in Fig. 3(b) we show the magnetic hysteresis loop (M-H) of the un-doped LuFeO_3 sample. The M-H

loop indicates presence of antiferromagnetic type of magnetic order in the aforesaid sample at room temperature.

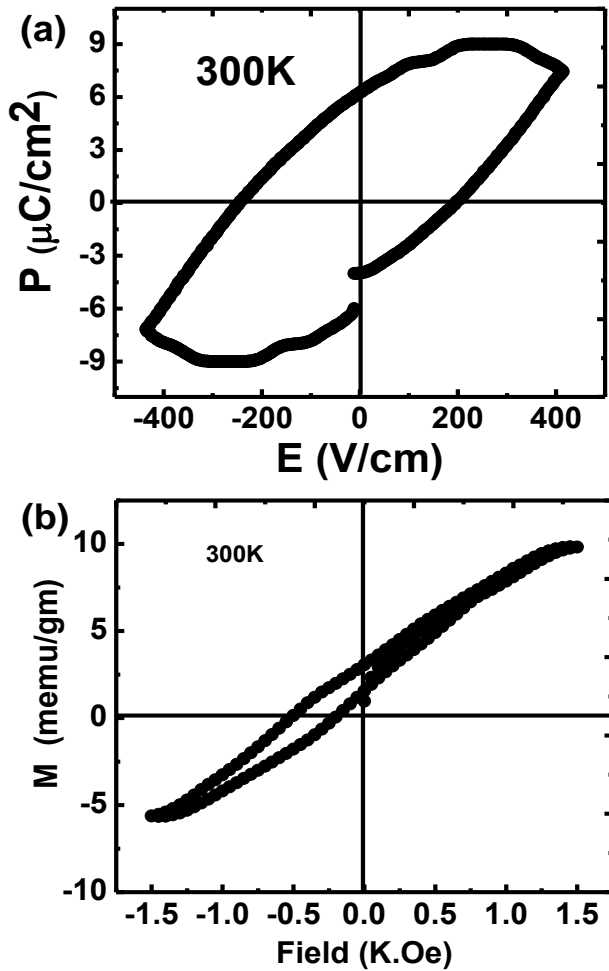


Fig. 4(a) Shows P-E hysteresis loop in case of Mn- doped (20%)-LuFeO₃ sample. (b) Shows the M-H loop of pure (undoped)-LuFeO₃ sample is suppressed due to Mn-doping.

Shows P-E hysteresis loop in case of Mn- doped (20%)-LuFeO₃ sample. Here from the cigar shaped P-E loop, we can observe that the ferroelectricity present of the pure (undoped)-LuFeO₃ sample is suppressed due to Mn-doping. The leakage and other non-ferroelectric contribution have increased at the cost of intrinsic ferroelectric polarization present in the sample. Fig. 5(b) shows the magnetic (M-H) hysteresis loop as obtained for Mn-doped LuFeO₃ sample at room temperature. Here we can observe that the antiferromagnetic order present in the pure LuFeO₃ sample is affected by Mn-doping but has not destroyed. Total contribution of ferroelectric polarization in these types of lossy ferroelectrics is intrinsic ferroelectric polarization, diode effect, non-ferroelectric contribution, resistive leakage etc. To eliminate the contributions, we have applied a specific fourteen pulse based protocol to modified sawyer tower circuit, the details of this technique can be found elsewhere [4].

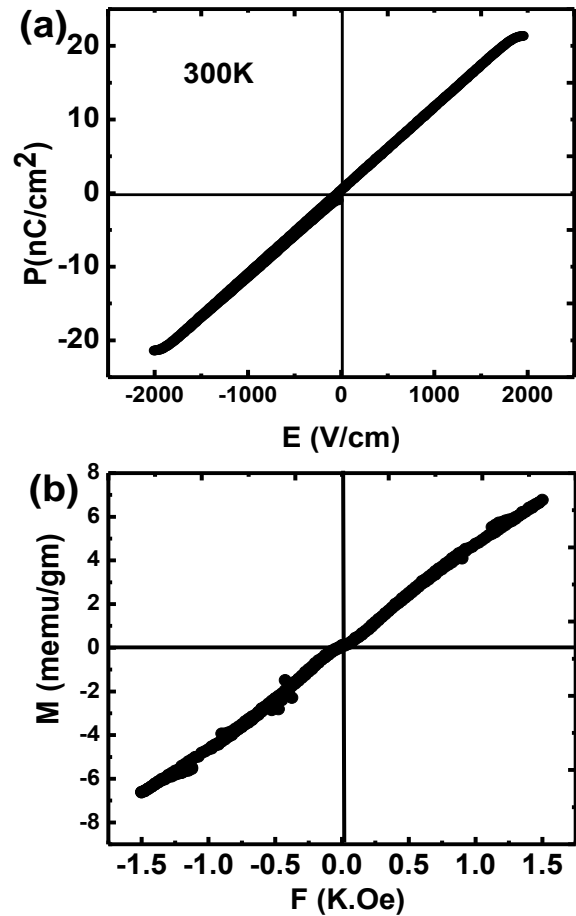


Fig. 5. (a) shows the P-E loop of Cu –doped LuFeO₃ sample (b) shows the magnetic (M-H) hysteresis loop as obtained for Cu-doped LuFeO₃ sample at room temperature.

Now we try to investigate the origin of ferroelectricity in orthorhombic LuFeO₃ sample. We have calculated the ionic displacement in the above-mentioned sample, which shows that the total average displacement of the ions over a unit cell comes out to be zero, thus can't contribute to the ferroelectric polarization present in the sample. Thus ferroelectricity present in the aforesaid sample may be originating from some secondary order, as in case of "improper" type-II ferroelectrics, most probably from the (antiferro) magnetic order. We have shown in one of our previous paper [1] that the ferroelectric and magnetic transition of the pure LuFeO₃ sample falls in the same temperature regime, which also indicate that the ferroelectric polarization present in the LuFeO₃ sample is originating from the magnetic order. The strong multiferroic coupling present in the aforesaid sample [1] also indicates the presence of strong correlation between these two orders. To further investigate the origin of ferroelectric polarization in this material, we have willfully disturbed the magnetic order present in the sample by doping with Mn and Cu [2]. We observed that the ferroelectric order is also get disturbed. In the Mn substituted sample the magnetic order is partially disturbed, as a result the ferroelectricity is also

partially suppressed. Where as in case of Cu- doped sample the magnetic order is completely destroyed with the help of doping, and the ferroelectric polar order is also completely destroyed in this sample.

Conclusion

Thus, we conclude that the ferroelectricity present in the orthorhombic LuFeO₃ sample has its origin in its magnetic order. This is the central result of this paper. The origin of ferroelectricity in this sample can be explained with the help of spin current based model as proposed by Katsura *et al.* [3]. There is huge possibility to enhance the ferroelectric polarization and hence the multiferroic coupling present in pure orthorhombic LuFeO₃ sample by tailoring its magnetic order in order to achieve higher polarization and strong multiferroic coupling in this material, even at room temperature, which will be very much useful to be used in real multifunctional devices.

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Author's contributions

This work is conceived, performed, planned and presented by Ujjal Chowdhury.

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