



Role of defects and oxygen vacancies on dielectric and magnetic properties of Pb^{2+} ion doped LaFeO_3 polycrystalline ceramics

K. Devi Chandrasekhar^{a,*}, S. Mallesh^{a,b}, J. Krishna Murthy^c, A.K. Das^a, A. Venimadhav^c

^a Department of Physics & Meteorology, Indian Institute of Technology, Kharagpur 721302, India

^b Department of Physics, Indian Institute of Technology, Madras 600036, India

^c Cryogenic Engineering Centre, Indian Institute of Technology, Kharagpur 721302, India

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ABSTRACT

We have presented the dielectric/impedance spectroscopy of $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$ ($x=0.15$ and 0.25) polycrystalline samples in a wide temperature and frequency range. They exhibited colossal dielectric permittivity and multiple relaxations. Temperature and field dependent magnetization study showed enhancement of magnetization upon Pb doping which has been ascribed to the defect driven magnetization phenomenon. Overall we have emphasized the formation of various kinds of defects and their influence on dielectric and magnetic properties in the system.

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1. Introduction

Recently, miniaturization of modern microelectronic technology demands high performance and cost effective materials. Colossal dielectric constant (CDC) materials are going to be key electronic components in modern microelectronic technology. Achieving and understanding of CDC is one ongoing problem in condensed matter physics. In this regard, perovskite transition metal oxides have been the focus of scientific interest over a decade; several materials have exhibited CDC behavior in a wide temperature/frequency range [1]. Materials with multiferroic and CDS property are highly desirable for novel spintronic devices [1–4]. In fact multiferroic behavior is demonstrated in several CDC materials [2,5,6]. However, the origin of CDC and the associated multiferroic coupling in these materials remain elusive [6–9].

Recently, much attention has been paid to LaFeO_3 which exhibits complex electrical and magnetic behavior with strong correlation among the spin, charge and orbital degrees of freedom. LaFeO_3 is an orthorhombically distorted perovskite crystal structure with strong super exchange interaction between the Fe^{3+} – Fe^{3+} via O^{2-} ion leading to an antiferromagnetic (AFM) ordering Néel temperature $T_N \sim 740$ K [10]. A small deviation in AFM arrangement of spins can develop a weak magnetic moment. Apart from magnetism, the A-site doped LaFeO_3 is a state of the art material for gas sensing, catalytic and exchange bias applications [11,12]. For example oxygen ion conduction in A-site doped

LaFeO_3 can be used to build an efficient solid state fuel cell [13]. Moreover doping the A-site with a divalent cation leads to the charge disproportionation of Fe that results in a mixed valence state of iron i.e. $\text{Fe}^{4+}/\text{Fe}^{3+}$ [14].

The occurrence of multiferroic nature in LaFeO_3 is demonstrated by Acharya et al. These authors have observed both ferroelectric and ferromagnetic behavior in LaFeO_3 without any structural transition or dielectric anomaly; however the appearance of such a ferroelectric nature is unusual [15]. Contradictory to this, Idrees et al. have observed the polaronic conduction mechanism in this system and have assigned the CDC to extrinsic effects [16]. These studies demand meticulous experiments to confirm various polarization mechanisms in CDC materials. The polarization of dipolar crystals is influenced by crystallographic defects/vacancies and formation of long range/localized motion of various charged defects and vacancies. Such defects can also modify the magnetization property [17]. In this paper, we have focused on the effect of divalent Pb^{2+} ion on the structural, dielectric and magnetic properties of $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$. We have emphasized possible defects and their role on transport and magnetic properties using impedance spectroscopy and SQUID magnetometer.

2. Experimental details

Polycrystalline $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$ ($x=0.15$ and 0.25) samples were prepared by solid state reaction method using high purity oxides of La_2O_3 , Fe_2O_3 and PbO (Aldrich 99.99% purity) as raw materials. Stoichiometric amounts were weighed and thoroughly mixed and calcined in air between 650°C and 1000°C with intermed-

* Corresponding author. Tel.: +886988873428.

E-mail address: sekhar.kakarla@gmail.com (K. Devi Chandrasekhar).

iate grindings. The final sintering was carried on pellet samples (10 mm in diameter and 1 mm thickness) at 1000 °C for 24 h. The structural and surface morphology was studied using X-Ray Diffraction (XRD) with Cu- K_{α} ($\lambda=1.5414$ Å) radiation (Philips Pan Analytical X-pert) and JEOL JSM5800 Field Emission Scanning Electron Microscopy (FESEM), respectively. Dielectric properties were investigated using Agilent 4294A impedance analyzer with an ac excitation of 500 mV in the frequency range of 40 Hz–10 MHz. Electrodes for the dielectric measurements were made by applying wet silver paste on both side of the pellets (diameter 10 mm, thickness 1 mm) and were heated at 200 °C for 5 h. All the dielectric measurements were performed on the home made Liquid Nitrogen (LN₂) based cryostat. The temperature and field dependent magnetization were performed with commercial Quantum design SQUID-VSM magnetometer.

3. Results and Discussions

3.1. XRD analysis

The room temperature XRD pattern for La_{1-x}Pb_xFeO₃ ($x=0.15$ and 0.25) samples is shown in Fig. 1(a). The structural analysis has been carried out using Rietveld refinement (solid lines in Fig. 1(a)) method. The analysis confirms the orthorhombic crystal structure with Pbnm space group. A minor amount of secondary phase (La₂O₃) is observed in La_{0.75}Pb_{0.25}FeO₃ (LPFO0.25) sample. This is due to volatile nature of Pb and it is indicated by '*' symbol in Fig. 1(a). The obtained fitting parameters for both the samples are shown in Table 1. Fig. 1(b and c) shows FESEM images of La_{0.85}Pb_{0.15}FeO₃ (LPFO0.15) and LPFO0.25 samples, respectively. Inhomogeneous grain distribution is observed in both the samples with grain size of the order of 200–500 nm. It can be noticed from

the micrographs that the size of the grains decreases while grain boundaries (GB) increase with the increase of Pb concentration.

It is well known that in oxide materials, the transport and magnetic properties are greatly influenced by the presence of various kinds of defects (oxygen vacancies, hole and electron doping and impurities) and crystallographic disorder that in turn depends on various parameters such as synthesis conditions, doping, etc. [17]. Prior information on formation of various kinds of defects would be useful to understand the transport/magnetic properties of the system. Here, we discuss the possible defect formation in the present compound. In most of the cases the formation of oxygen vacancies is inevitable during the synthesis of ceramics unless the reaction is carried out in oxygen atmosphere. During the high temperature sintering process, the thermodynamic reaction of oxidation and reduction of grain and GB happens at different reaction rates that result in oxygen deficient

Table 1

The obtained Rietveld parameters for both the samples, where the atomic position of Fe ion is $(x\ y\ z)=(0.5\ 0)$.

	LPFO0.15			LPFO0.25		
a (Å)	5.558			5.5545		
b (Å)	5.563			5.5647		
c (Å)	7.864			7.8675		
v (Å ³)	243.161			243.18		
	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
La	0.990	0.023	0.250	0.987	0.0249	0.250
O1	0.012	0.490	0.250	0.028	0.516	0.250
O2	0.749	0.196	-0.025	0.728	0.183	-0.021
$\langle \text{Fe-O} \rangle$ (Å)	1.9319			1.762		
$\langle \text{Fe-O-Fe} \rangle$ (°)	159.42			157.22		
χ^2	2.81			4.23		

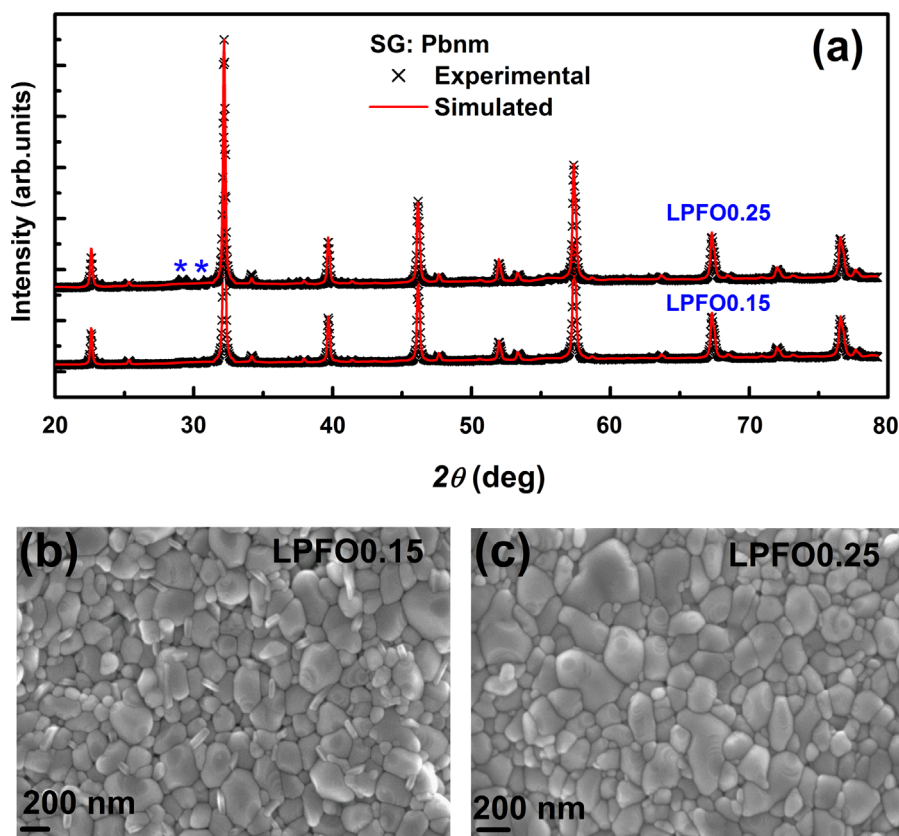


Fig. 1. (a) XRD spectra of La_{1-x}Pb_xFeO₃ ($x=0.15, 0.25$) polycrystalline samples; (b and c) shows the FESEM images of La_{1-x}Pb_xFeO₃ ($x=0.15, 0.25$) polycrystalline samples.

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