Magnetic and Dielectric Measurements of Mn Substituted $LaFeO_3$ Compounds

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Abstract

$LaFeO_3$ is a known orthoferrite which shows multiferroic behaviour and magnetoelectric coupling at room temperature. In the present report we present our data of magnetic and dielectric measurements in Mn substituted $LaFeO_3$. Samples are prepared using solid state reaction. Weak ferromagnetic behaviour is observed in samples for $LaFeO_3$ and $LaFe_{0.75}Mn_{0.25}O_3$ with orthorhombic structure. Higher Mn concentration($x>0.5$) indicate rhombohedral structure and subsequently anti ferromagnetic behaviour. Dielectric measurements show that for $LaFe_{0.25}Mn_{0.75}O_3$, dielectric constant has value of order 50×10^4 and loss factor value is of order 50000, whereas for $LaFe_{0.75}Mn_{0.25}O_{3.13}$, the same are 1.15×10^7 and 1400 respectively. The loss factor of these order indicate a leakage phenomenon.

Introduction

The origin and understanding of coupling phenomena between different physical properties within one material is a central subject of solid state science. It has fascinated physicists for decades. In 1865, James Clerk Maxwell proposed four equations governing the dynamics of electric fields, magnetic fields and electric charges, which are now known as Maxwell's equations. They show that magnetic interactions and motion of electric charges, which were initially thought to be two independent phenomena, are intrinsically coupled to each other [1].

In1888 Rontgen discovered that a moving dielectric became magnetized when placed in an electric field, which was followed by observation of the reverse effective ie the polarization of a moving dielectric in a magnetic field, 17 years later [2]. In 1894 Curie pointed out the possibility of intrinsic Magnetoelectric Effect behaviour of (non-moving) crystals on the basis of symmetry considerations [3]. The term 'magnetoelectric' was coined by Debye a few years after the first (unsuccessful) attempts to demonstrate the static ME effect experimentally [4].

A considerable amount of research currently concentrates on multifunctional materials in which several physical properties could potentially be used simultaneously. One of the key questions for the future development and understanding of multifunctional materials concerns the mutual coupling between the properties, its underlying mechanism and whether it can be used in applications. In this context

multiferroics (MF) are multifunctional materials par excellence, because they simultaneously possess several so-called ferroic orders such as ferromagnetism, ferroelectricity and/or ferroelasticity (figure 1). The cross-coupling of these ferroic orders reflects interesting electron-phonon interactions, and they have great potential for new spintronic devices.

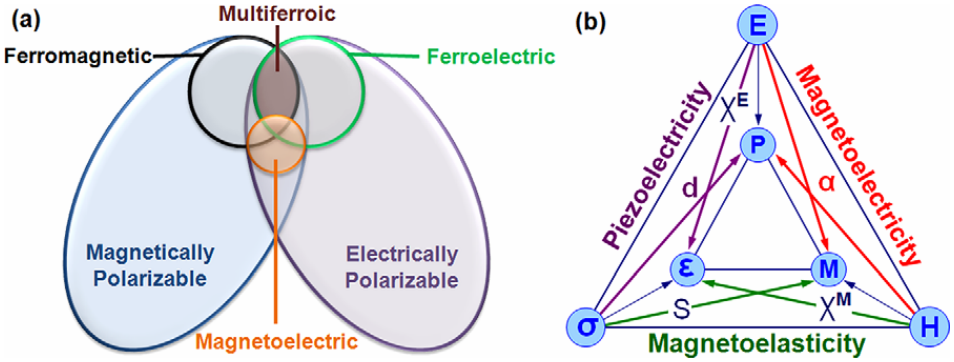


Figure 1: (a) Relation between magnetoelectric and multiferroic materials, (b) Different types of coupling present in materials. [6]

Most of the MF materials are usually transition metal perovskites. Among the rare earth orthoferrites, lanthanum orthoferrite ($LaFeO_3$) is a very well known canted antiferromagnetic material with a high value of Néel temperature (T_N =740 °C) [5]. Actually, it crystallizes in an orthorhombically distorted perovskite oxide with a space group Pbnm. The lattice parameters are a=5.557 Å, b=5.565 Å and c=7.854 Å. In this report, we present our results of magnetic and dielectric measurements made on $LaFe_{(1-x)}Mn_{(x)}O_3$ (x= 0, 0.25 and 0.5, 0.75 and 1).

Experimental

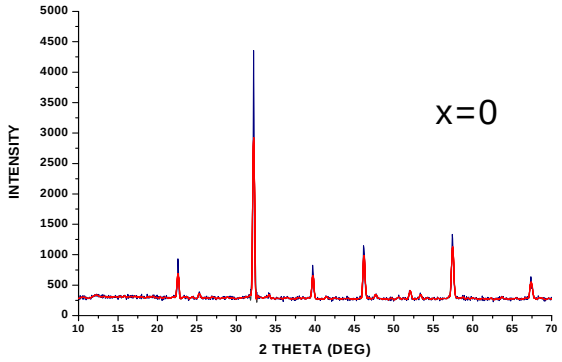
Samples of manganese substituted Lanthanum orthoferrite **$LaFe_{1-x}Mn_xO_3$** were synthesised for x = 0, x=0.25, x=0.5, x=0.75 and x= 1 through solid state reactions. The starting materials used were La_2O_3 (Alpha aesar), Fe_2O_3, and Mn_2O_3(Alpha aesar).The starting materials were preheated at 200^0C for two hours to remove impurities and moisture and were weighed in proper stoichiometry before mixing to make samples of 10 gm each. After mixing together, each sample was ball milled for two hours in a ball milling unit with four Zirconium balls. After each milling session for half an hour, a break of ten minutes was taken to prevent excessive heating of the samples.

The as milled samples of $LaFeO_3$ (for x = 0), $LaFe_{0.75}Mn_{0.25}O_3$ (for x = 0.25), $LaFe_{0.5}Mn_{0.5}O_3$ (for x = 0.5), $LaFe_{0.25}Mn_{0.75}O_3$ (for x=0.75) and $LaMnO_3$ (for x=1) were heated at 800^0C for eight hours. The heating was performed in a muffle furnace in air. The sintered samples were again thoroughly grounded in a mortar pestle (agate). The grounded samples were pelletized in a hydraulic press. Two Pellets of 10

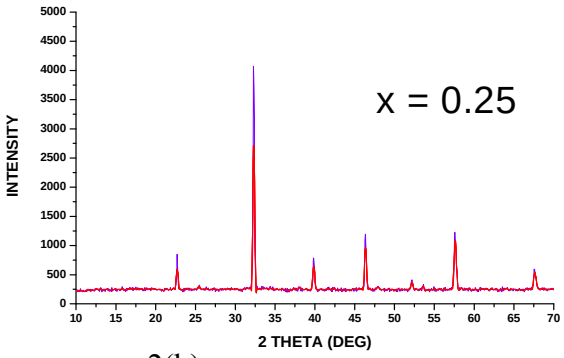
mm diameter and thickness of approximately 2.5 mm to 4 mm were made for each sample. The sample pellets were further sintered at 1200^0C for ten hours. One pellet from each sample was grounded and powdered for X-ray diffraction and magnetic measurements. The other pellet from each sample was used for dielectric measurements. XRD was taken for all the samples using Maxima 7000S (Cu Ka′1 radiation at wavelength λ = 1.5406) at a slow scan rate with step size 0.05 deg. Magnetic hysteresis measurements were done using Princeton Micromag Alternating gradient magnetometer (AGM). For the magnetic measurements, the samples were packed in small packets in Aluminium foil of approximately 0.5 mm by 0.5 mm dimension with each packet having approximately weight ten to fifteen mg of the corresponding sample. The diamagnetic background of aluminium foil was subtracted from the sample data. The dielectric measurements for the samples were performed using Agilent E4980A (20 Hz to 2 MHZ) precision LCR meter. For dielectric measurements, the sample temperature was varied from 40^0C to 300^0C and the dielectric constant and dissipation factor was found as a function of temperature.

Results

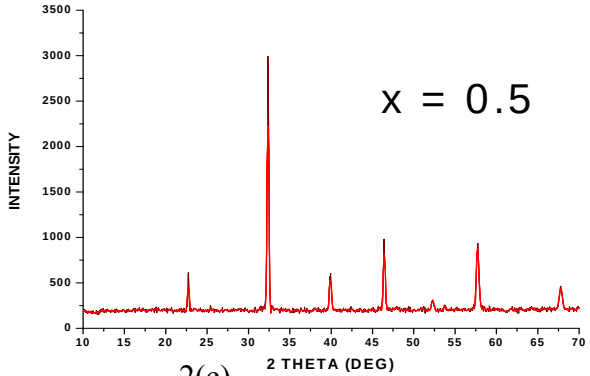
The X-ray diffraction patterns of the samples are shown in figure 2(a) to 2(e).



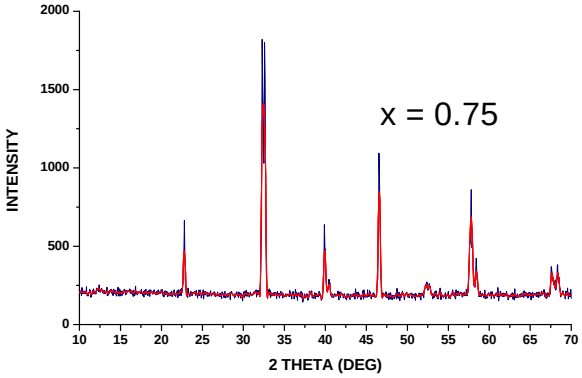
2(a)



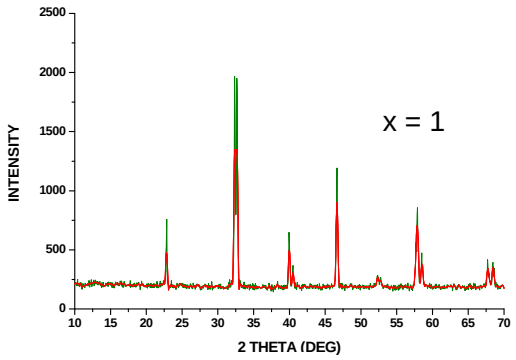
2(b)



2(c)



2(d)



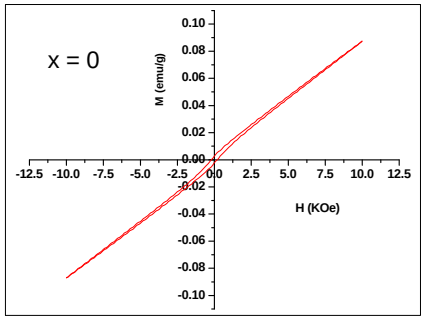
2(e)

From JCPDS data (card no 037-1493), the crystal structure for sample (x =0) is found to be that of $LaFeO_3$ which is orthorhombic with space group Pn*a. The lattice parameters are a = 5.5669, b =5.5530, c = 7.8547. In case of x = 1, the crystal structure is rhombohedral and is matching with that of $LaMnO_{3.13}$ (JCPDS data card no 058-0580) instead of $LaMnO_3$. The change in oxygen stoichiometry may be due to high heating temperature of 1200^0C, since after previous heating at 800^0C, the structure is found to be matching with that of $LaMnO_3$, which is also orthorhombic (JCPDS card no 035-1353). The space group for $LaMnO_{3.13}$ is

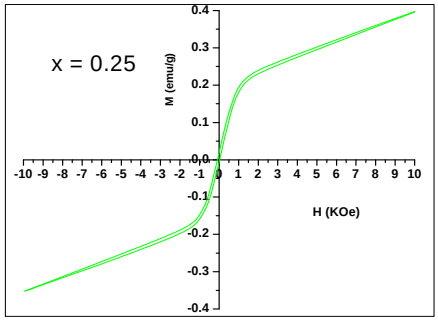
R-3c (167). The lattice parameters are a = 5.5159AU, c = 13.2868 AU. The peaks for x=0, x = 0.25 and x = 0.5 are positioned at similar 2 theta values, which suggests that crystal structures of samples for x = 0.25 and x = 0.5 are orthorhombic too. The peaks for x = 0.75 are matching with that of $LaMnO_{3.13}$, which suggests that the structure here is rhombohedral. Thus the crystal structure is obtained as orthorhombic in samples with concentration of manganese varying between zero to 50%. For higher concentration of manganese, the structure changes to rhombohedral.

Magnetic Measurements

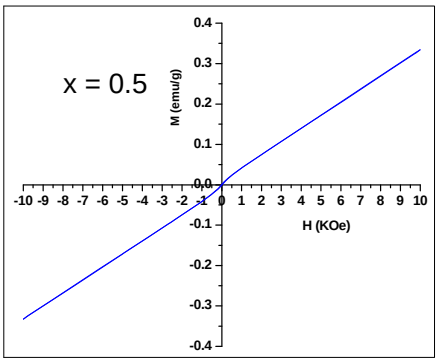
The M vs H hysteresis loops are shown in figure 3(a) to 3(e). The values of saturation magnetic moment, remanent magnetization and coercivity are given in Table 1.



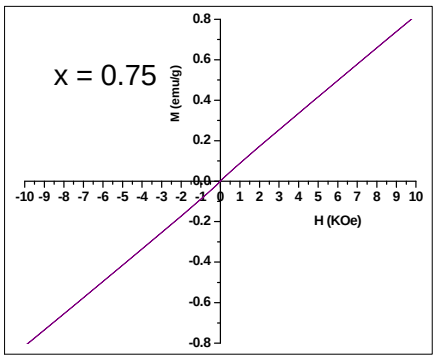
3(a)



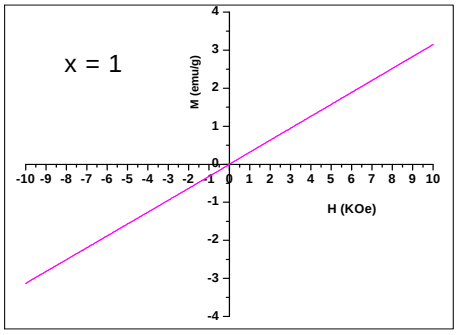
3(b)



3(c)



3(d)



3(e)

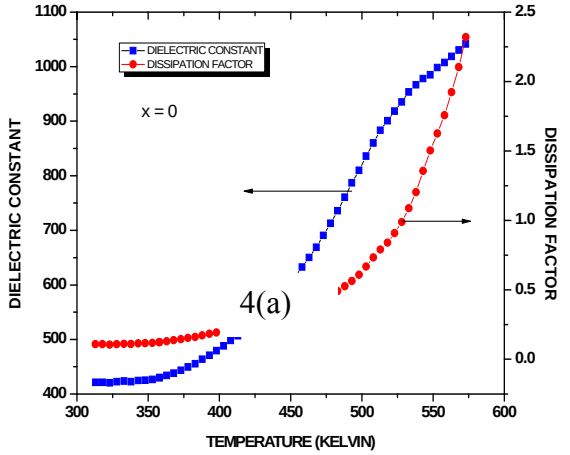
Table 1:Saturation and remanent magnetization as well as coercivity data for x = 0, 0.25, 0.5, 0.75, 1.

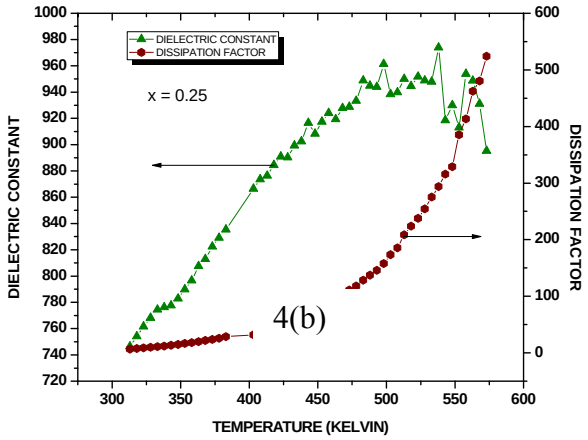
Sample $LaFe_{(1-x)}Mn_{(x)}O_3$	Saturation Magnetic moment (M_S) emu/g	Remanent magnetic moment (M_R) emu	Coercivity H_C (Oersted)
$LaFeO_3$ (x = 0)	0.087	0.0024	207
$LaFe_{0.75}Mn_{0.25}O_3$ (x = 0.25)	0.398	0.0128	55.93
$LaFe_{0.5}Mn_{0.5}O_3$ (x = 0.5)	0.333	0.0013	23.10
$LaFe_{0.25}Mn_{0.75}O_3$ (x = 0.75)	0.817	0.0010	9.728
$LaMnO_{3.13}$ (x = 1)	3.141	0.0055	12.744

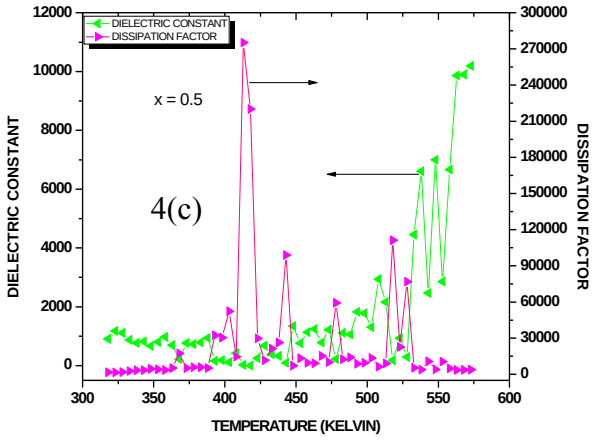
The non linear hysteresis M-H loops for x = 0 to x = 0.5 clearly indicate magnetic ordering. The low magnetic moment (M_S = 0.087 in cgs units) for x = 0 is in agreement with earlier data [5]. The linear nature of the curves for x = 0.75 and x = 1 suggests suppression of magnetic ordering. Sample (x = 1) shows a M_S value of 3.141 in cgs unit. The maximum value of M_R in cgs units is observed for sample (x =0.25) also in. The coercivity of sample (x = 0) is found to be at 207 Oe.

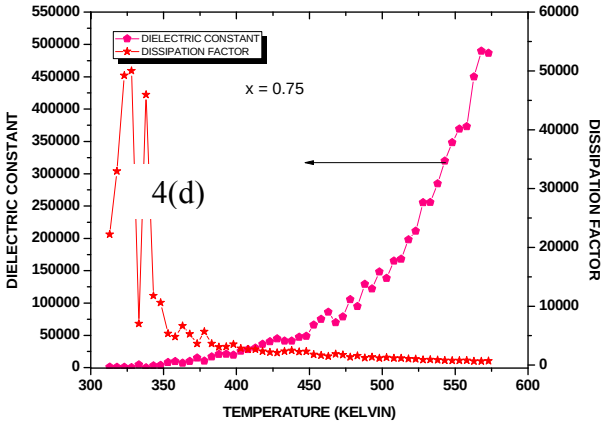
Dielectric Measurements

The variations of Dielectric constant vs Temperature are shown in 4(a) to 4(e). The measurements were taken at frequency 1 KHz. All the samples show rise in dielectric constant with temperature. For x = 0 and 0.25, value of the dielectric constant is approximately 1000 at 580 K, whereas for x = 0.5, it is 11000 at the same temperature. For x = 0.75 and 1, the value of dielectric constant is seen to be of higher magnitude at higher temperatures and is ~55000 for x=0.75 and ~1.1 $\times 10^7$ for x = 1, respectively at 580 K.

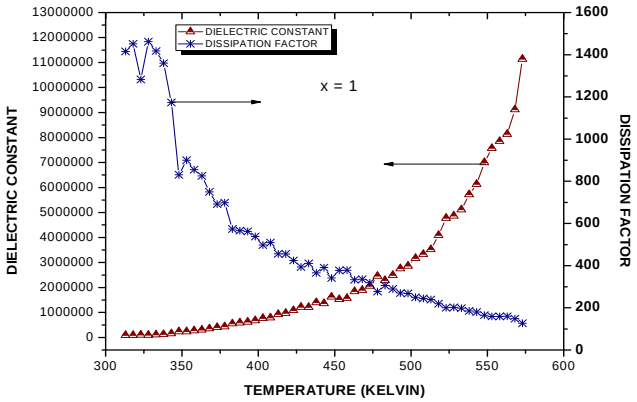








4(e)



Dissipation (loss) Factor

The measurements of Dissipation Factor D vs Temperature at 1 KHz are shown in Figure 4(a) to 4(e). The dissipation factor or loss factor as it is also called, shows a rise with temperature for samples x= 0 and 0.25. On the other hand, D falls with rise of temperature for x = 0.5 and 0.75 and 1. For x = 0, the maximum value of D is at ~2.5 and the same is at ~ 650 (x = 0.25) at temperature ~ 580 K. In case of sample x = 0.5, D shows anomaly of 7.2×10^6 at 418 K (145^0C). D shows maximum value of 1.45×10^5 observed at 338 K (65^0C) for x = 0.75. The maximum dissipation factor in case of sample x = 1 is ~1450 and it falls down to a value of ~125 at temperature 580 K.

Conclusion

Manganese substituted lanthanum orthoferrite samples were successfully synthesized using solid state reaction technique. XRD analysis confirmed the crystal structures of the synthesized samples. Samples of $LaFeO_3$, $LaFe_{0.75}Mn_{0.25}O_3$, and $LaFe_{0.5}Mn_{0.5}O_3$ have orthorhombic structure, whereas $LaFe_{0.25}Mn_{0.75}O_3$ and $LaMnO_{3.13}$ showed rhombohedral structure. Ferromagnetic behaviour with magnetic hysteresis is seen for samples $LaFeO_3$ and $LaFe_{0.75}Mn_{0.25}O_3$. With increasing Mn concentration, the antiferromagnetic component predominates and a linear M-H behaviour is observed.

Dielectric measurements of samples show that samples $LaFe_{0.25}Mn_{0.75}O_3$, $LaMnO_{3.13}$ have relatively large dielectric constants. Dissipation factors of $LaFe_{0.5}Mn_{0.5}O_3$ and $LaFe_{0.25}Mn_{0.75}O_3$ are very large indicating that these samples have high loss factor.

In short, a series of ABO3 oxides, with A=La and B = Fe, Mn in varying ratios have been successfully synthesized, with the observed structure in conformity with those previously reported. Magnetic and dielectric measurements ascertain the multiferroic nature of the samples with higher Fe content. The predominance of antiferrromagnetic behaviour reduces this nature with increasing Mn concentration. Further work on the electric polarization with varying fields would throw light on the magneto-electric coupling in the multiferroic systems.

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