

**FINAL REPORT**  
**OF**  
**MINOR RESEARCH PROJECT**

(File No.F47-765/13(WRO) 26 MAR 2014)

**Title “Structure–property correlations in hole doped  
manganite”**

**Submitted to**  
**University Grants Commission**  
**Western Region Office, Pune.**

**By**  
**Principal Investigator**  
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**UNIVERSITY GRANTS COMMISSIONS  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI – 110 002  
FINAL REPORT OF THE WORK DONE ON THE PROJECT**

1.	Title of the Project:	Structure–property correlations in hole doped manganite
2.	NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR:	Dr. R. K. Trivedi Shree H. & H. B. Science College, Department of Physics, Yagnik Road, Rajkot – 360 001
3.	NAME AND ADDRESS OF THE INSTITUTION:	Shree H. & H. B. Science College, Department of Physics, Yagnik Road, Rajkot – 360 001
4.	UGC APPROVAL LETTER NO. AND DATE:	F47-765/13(WRO) 26 MAR 2014
5.	DATE OF IMPLEMENTATION:	26 JUN 2014
6.	TENURE OF THE PROJECT:	TWO YEARS
7.	TOTAL GRANT ALLOCATED:	Rs. 1,20,000=00
8.	TOTAL GRANT RECEIVED:	Rs. 75,000=00
9.	FINAL EXPENDITURE:	Rs. 59,228=00
10.	TITLE OF THE PROJECT:	Structure–property correlations in hole doped manganite

11.	OBJECTIVES OF THE PROJECT:
	<p>(a) To synthesize good quality single phasic samples of <math>\text{La}_{1-x-y}\text{Pr}_x\text{A}_y\text{MnO}_3</math> (LPAMO; A = Ca, Sr &amp; Ba) manganites using solid state reaction route</p> <p>(b) To study their structural properties using XRD measurements and Rietveld analysis</p> <p>(c) To carry out the transport studies using R – T and R – H measurements at various temperatures and fields</p> <p>(d) To understand the magnetism of LPAMO manganites</p> <p>(e) To correlate / develop the possible structure – property correlations in the proposed LPAMO manganite systems</p>
12.	WHETHER OBJECTIVES WERE ACHIEVED:
	<p>We have successfully synthesized the proposed doped manganites [i.e. <math>\text{La}_{0.6}\text{Pr}_{0.1}\text{Ca}_{0.3}\text{MnO}_3</math> (L6C), <math>\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3</math> (L5C), <math>\text{La}_{0.6}\text{Pr}_{0.1}\text{Sr}_{0.3}\text{MnO}_3</math> (L6S), <math>\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3</math> (L5S), <math>\text{La}_{0.6}\text{Pr}_{0.1}\text{Ba}_{0.3}\text{MnO}_3</math> (L6B) and <math>\text{La}_{0.5}\text{Pr}_{0.2}\text{Ba}_{0.3}\text{MnO}_3</math> (L5B)] by using conventional solid state reaction.</p> <p>The structure of these oxides has been investigated by XRD technique at room temperature and results of Rietveld refinements reveal the single phasic growth proposed oxides without any detectable impurity within the measurement range. Unit cell volume increases as doping of larger cation element at La-site and unit cell volume decreases as increasing <math>\text{Pr}^{+3}</math> content at La-site due to a small ionic radius of <math>\text{Pr}^{+3}</math>.</p> <p>Room temperature frequency dependent impedance of all the proposed / studied mixed valent manganites has been recorded using LCR meter. Impedance of L6C and L5C manganites decreases with frequency at room temperature due to charge carriers transportation in semiconducting region / state of L6C and L5C manganite samples (since L6C and L5C are semiconductors in nature at room</p>

	<p>temperature), whereas in L6S, L5S, L6B and L5B samples, impedance gets increased with increasing frequency at room temperature due to their metallic nature.</p> <p>The impedance of all the samples decreases with increasing external magnetic field, i.e. negative magnetoimpedance. The negative magnetoimpedance of semiconducting L6C and L5C can be explained by charge carrier transport mechanism and the negative magnetoimpedance of metallic L6S, L5S, L6B and L5B samples can be correlated with the skin effect and magnetic permeability of the samples.</p> <p>All the above mentioned aspects of magnetoimpedance behavior of proposed manganites clearly show an effect of size of the dopant elements and their content at La-site. This shows strong structure-property correlations in the proposed mixed valent manganites.</p>
13.	<p><b>ACHIEVEMENTS FROM THE PROJECT:</b></p> <p>02 (One) international proceedings.</p> <p>Various poster and oral presentations at different national and international events during the tenure of the project.</p>
14.	<p><b>SUMMARY OF THE FINDINGS:</b></p> <p>To summarize, proposed mixed valent manganites can be successfully grown using conventional solid state reaction route. Effect of ionic size of divalent cation (substituted at La-site) and percentage of fluctuating valance ion <math>\text{Pr}^{3+}</math> (at La-site) (i.e. 10% or 20%) on the impedance and magnetoimpedance behavior of the samples understudy has been understood. A strong effect of Pr content as well as size of divalent ion on the structure has been identified in the context of structure – property correlations.</p>

	<p>Further studied on the proposed samples have been carried out by performing R-T under different applied magnetic fields and R-H at different temperatures and data have been received from UGC-DAE CSR, Mumbai center, Mumbai. Analysis on the obtained results is in progress. Shortly the analysis and obtained results will be communicated to reputed international journal for publication.</p>	
15.	<p><b>CONTRIBUTION TO THE SOCIETY:</b></p> <p>The rapid improvement of mobile devices requires smaller components, which can be obtained by designing multifunctional materials. One of the well-known multifunctional material is rare-earth manganites having nominal formula <math>R_{1-x}A_xMnO_3</math> (where R is a rare-earth and A = Ca, Sr, Ba, etc. are divalent alkaline-earth elements) are perovskite oxides which have attracted considerable interest due to their very large magnetoresistance (MR) and dependence on structural and compositional variations. Other than their potential applications in spintronics and data storage industries, their fundamental research aimed at determining the mechanism of the colossal magnetoresistance (CMR) phenomenon has attracted interest in these doped manganites.</p> <p>This project explores the intrinsic physics of doped manganite materials, and lead to new multifunction manganite materials which help to develop better magnetoimpedance sensing devices. Based on the obtained results and studies on presently proposed mixed valent manganites, students of the physics, chemistry and materials science can be inspired and can develop their career in the field of R&amp;D on ceramic technology, manganite applications and spintronic devices.</p>	
6.	<p>WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT:</p>	<p>NO</p>

17.	NO. OF PUBLICATIONS OUT OF THE PROJECT:	01 Attached separately.
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**Annexure -A**

**C. Report of the work done: -**

**I. Brief objective of the project: -**

- (a) To synthesize good quality single phasic samples of  $\text{La}_{1-x-y}\text{Pr}_x\text{A}_y\text{MnO}_3$  (LPAMO; A = Ca, Sr & Ba) manganites using solid state reaction route
- (b) To study their structural properties using XRD measurements and Rietveld analysis
- (c) To carry out the transport studies using R – T and R – H measurements at various temperatures and fields
- (d) To understand the magnetism of LPAMO manganites
- (e) To correlate / develop the possible structure – property correlations in the proposed LPAMO manganite systems

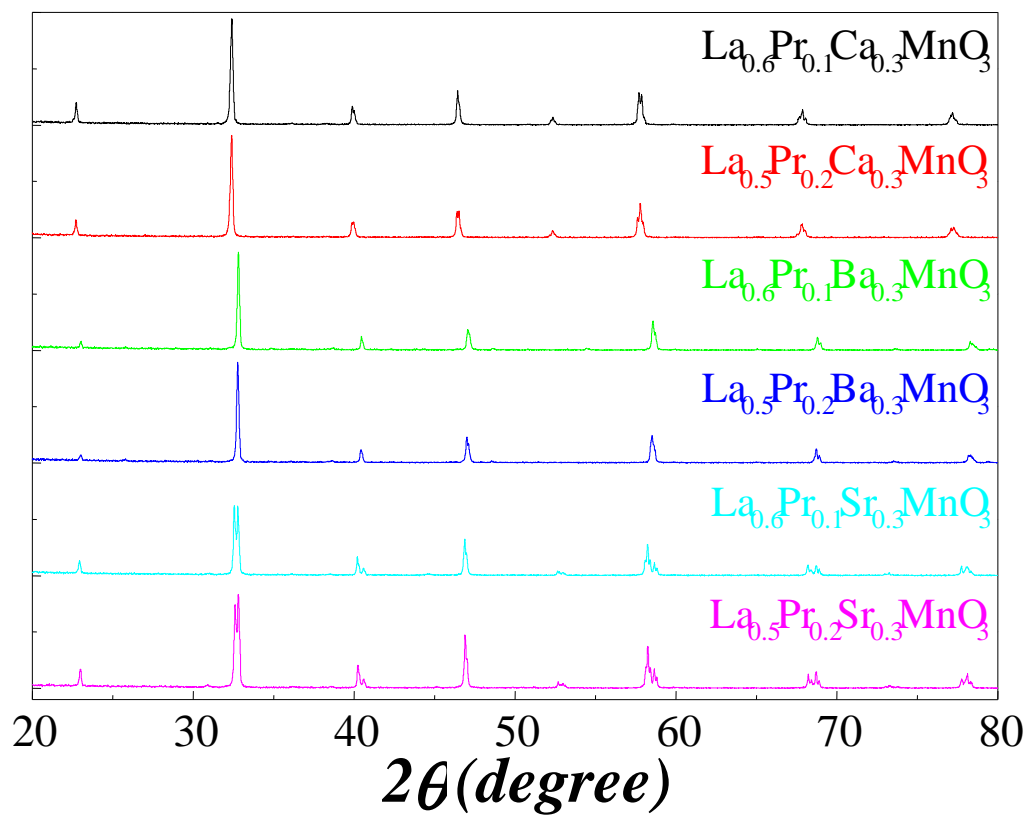
**II. Work done so far and results achieved and publication, if any, resulting from**

All the samples with stoichiometric compositions  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Ca}_{0.3}\text{MnO}_3$  (L6C),  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$  (L5C),  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$  (L6S),  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$  (L5S),  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$  (L6B) and  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ba}_{0.3}\text{MnO}_3$  (L5B) were synthesized using standard solid state reaction route. Different steps used during the synthesis are as

follows: high purity Lanthanum oxide ( $\text{La}_2\text{O}_3$ ), praseodymium oxide ( $\text{Pr}_6\text{O}_{11}$ ), Calcium carbonate ( $\text{CaCO}_3$ ), Barium Carbonate ( $\text{BaCO}_3$ ), strontium carbonate ( $\text{SrCO}_3$ ) and manganese oxide ( $\text{MnO}_2$ ), were taken as starting materials in appropriate stoichiometric ratio. The starting materials were heated in the furnace for making them dry. The materials were ground for three hours for having homogeneous mixtures. Then mixtures were heated for first calcination at  $900^\circ\text{C}$  for 24 hours and were again ground for 3 hours. The second calcination was followed by  $1100^\circ\text{C}$  for 24 hours for all samples. After all the calcinations materials were re-grounded and pelletized. Final heating for sintering was given at  $1250^\circ\text{C}$  for 72 hours. Structural studies were carried out using X-ray diffraction (XRD) patterns recorded on Philips diffractometer (PW 3040/60, X'pert PRO) using  $\text{Cu K}\alpha$  radiation at room temperature (RT). Electrical properties of samples can be understood by impedance spectroscopy in applied frequency range from 1000Hz to 2MHz examined by agilent E4890A precision LCR meter. Magnetic field was applied in parallel direction to the samples to understand change in electrical properties by applied magnetic field upto 1T.

Structural properties of polycrystalline bulk samples  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Ca}_{0.3}\text{MnO}_3$  (L6C),  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$  (L5C),  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$  (L6S),  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$  (L5S),  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$  (L6B) and  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ba}_{0.3}\text{MnO}_3$  (L5B), prepared by conventional solid state reaction method, were analyzed using powder X – ray diffraction method. Recorded intensity of reflecting X – rays is in between  $20^\circ$  to  $80^\circ$  applied  $2\theta$  angle shown in figure 1 for all the samples. XRD pattern illustrates single phasic growth of all the samples without any detectable impurity or presence of any secondary phase in measured range. The change in structural parameters and unit cell volume of all the samples are shown table 1.

**Figure 1:** X – Ray diffraction pattern of all the polycrystalline bulk samples under study.





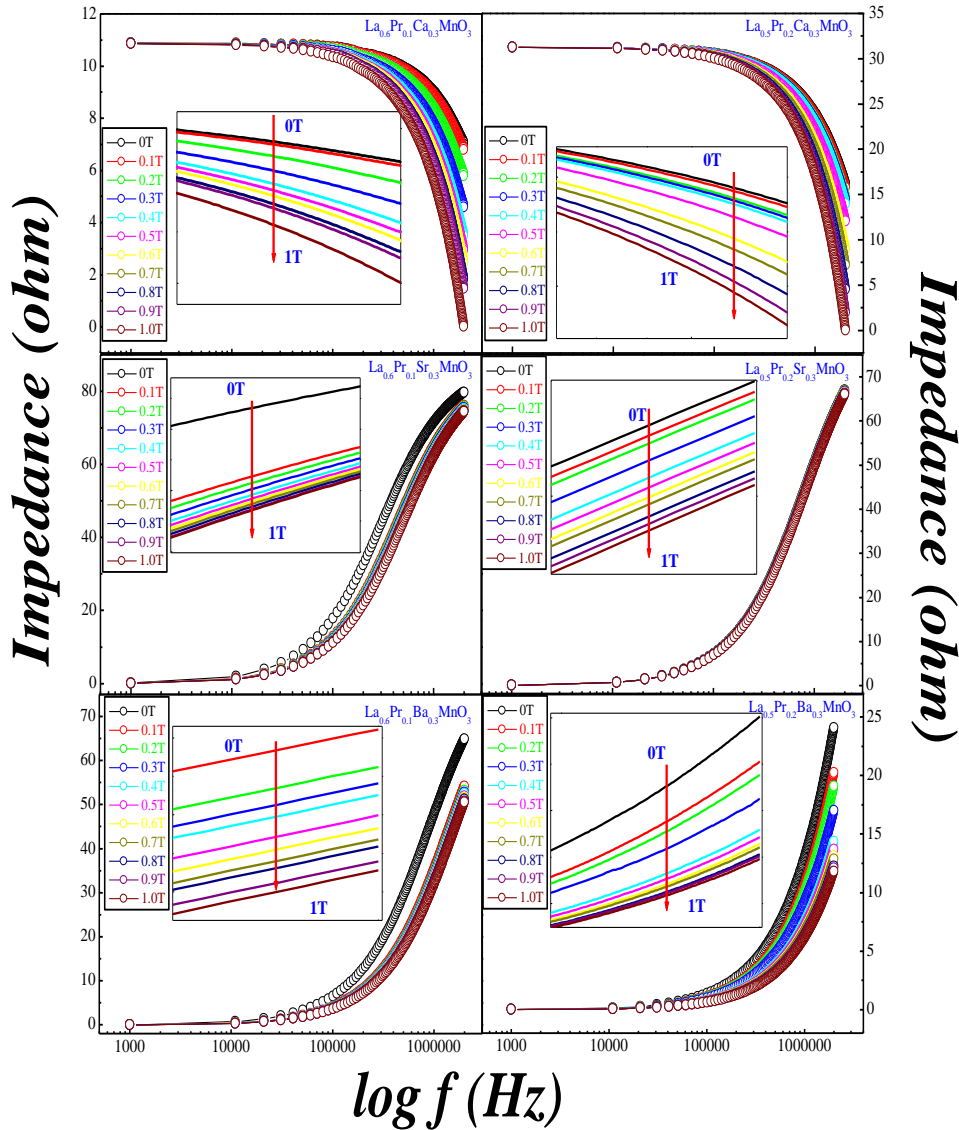
**Table 1:** Lattice Parameters (a,b& c) and cell volume for all the six manganites under study.

Sample Name	a	b	c	Unit cell Volume
La <sub>0.6</sub> Pr <sub>0.1</sub> Ca <sub>0.3</sub> MnO <sub>3</sub>	5.4451	7.7856	5.4328	230.31
La <sub>0.5</sub> Pr <sub>0.2</sub> Ca <sub>0.3</sub> MnO <sub>3</sub>	5.4425	7.7428	5.4321	228.90
La <sub>0.6</sub> Pr <sub>0.1</sub> Sr <sub>0.3</sub> MnO <sub>3</sub>	5.490	7.725	5.530	238.76
La <sub>0.5</sub> Pr <sub>0.2</sub> Sr <sub>0.3</sub> MnO <sub>3</sub>	5.482	7.743	5.528	234.64
La <sub>0.6</sub> Pr <sub>0.1</sub> Ba <sub>0.3</sub> MnO <sub>3</sub>	5.5428	7.7952	5.5469	239.66
La <sub>0.5</sub> Pr <sub>0.2</sub> Ba <sub>0.3</sub> MnO <sub>3</sub>	5.5452	7.7552	5.5464	238.51

The functional oxides are much focused by various scientific groups because of their multi-functional properties, and they show much sensitivity to applied external stimuli such as applied magnetic field, electric field, temperature and pressure. Among functional oxides, one of the most interesting materials are manganese based doped perovskite La<sub>0.7</sub>A<sub>0.3</sub>MnO<sub>3</sub> materials, which possess colossal magnetoresistance (CMR) effect. This compound show metallic conduction below Curie temperature  $T_c$ . At Curie temperature the applied magnetic field tends to align local spin and suppress the resistance largely. Furthermore, most of the research works on La<sub>0.7</sub>A<sub>0.3</sub>MnO<sub>3</sub> have been concentrated on the DC resistance dependence on magnetic field in range of few tesla. The basis for the theoretical understanding of the perovskite oxides is generally the notion of the double exchange interaction, which consider exchange of charge carriers between neighboring Mn<sup>+3</sup> and Mn<sup>+4</sup> with strong Hund's coupling. The Curie temperature is related to the strength of transfer integral  $t_{ij}$  between Mn<sup>+3</sup> and Mn<sup>+4</sup> ions, which dominant conduction. However, recent calculation show that the double exchange alone cannot explain some aspects of the CMR materials and suggested that the electron – phonon

coupling with Jahn –Teller distortion also plays an important role in transport behavior [1,2]. The magnetoimpedance effect in La-Ba-MnO<sub>3</sub> [3], La-Ca-MnO<sub>3</sub> [4] and La-Sr-MnO<sub>3</sub> [5] compound and also at lower frequency (10 kHz–100 MHz) [6] and higher microwave frequency (~GHz) [7] has been studied. In this section, I illustrate the magnetoimpedance effect of prepared La<sub>0.6</sub>Pr<sub>0.1</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> (L6C), La<sub>0.5</sub>Pr<sub>0.2</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> (L5C), La<sub>0.6</sub>Pr<sub>0.1</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (L6S), La<sub>0.5</sub>Pr<sub>0.2</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (L5S), La<sub>0.6</sub>Pr<sub>0.1</sub>Ba<sub>0.3</sub>MnO<sub>3</sub> (L6B) and La<sub>0.5</sub>Pr<sub>0.2</sub>Ba<sub>0.3</sub>MnO<sub>3</sub> (L5B) samples.

**Figure 2:** Impedance study of all the samples in 1000Hz to 2MHz frequency range at different applied magnetic fields.



The ac frequency dependencies of the impedance  $Z$  in the absence of applied magnetic field and in the presence of applied magnetic fields up to 1T for (L6C), (L5C), (L6S), (L5S), (L6B) and (L5B), samples at room temperature are plotted in figure 2. Impedance of L6C and L5C decreases with increasing frequency of applied electric field, whereas impedance of L6S, L5S, L6B and L5B samples are increasing with increasing frequency of applied electric field, but magnetic field dependent impedance responses are same for all the samples. Impedance decreases with increasing magnetic field from 0.0, to 1.0T as shown in figure 2. Inset of figure 2

shows enlarge view of change (decrement) in impedance with applied magnetic field. A similar behavior of impedance with applied magnetic field has been found in a Co-metal based amorphous wire and in Fe metal based nanocrystalline ribbons [8-11].

The Impedance response of L6C and L5C are differing from the impedance responses of L6B, L5B, L6S and L5S samples. The curie temperature  $T_C$  of L6B, L5B, L6S and L5S sample are above the room temperature so they possess metallic behavior at room temperature and the curie temperature  $T_C$  of L6C and L5C are less than room temperature and they possess semiconducting behavior at room temperature. As frequency increases above critical value  $f^*$ , the impedance of metallic L6B, L5B, L6S and L5S samples increase with frequency. This is mainly due to the skin effect of metal state of the sample [3,6], Whereas impedance of semiconducting L6C and L5C decreases with frequency due to the transport process of bound carriers occurring in the samples.

The magnetoimpedance of all the samples was calculated using below given equation:

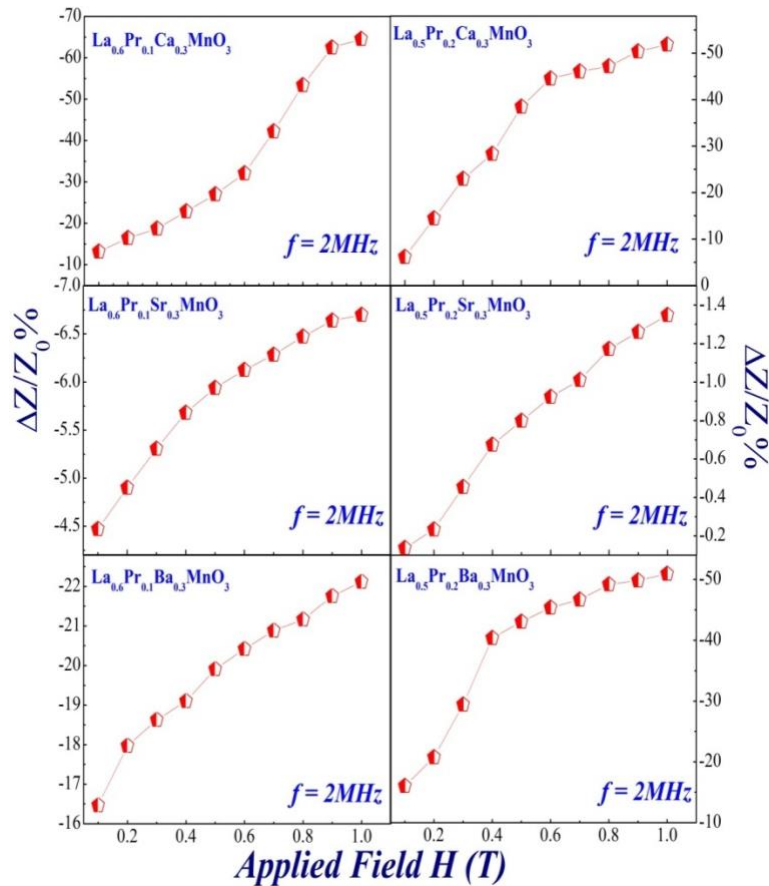
$$\frac{Z_H - Z_0}{Z_0} \times 100 \%$$

Calculated magnetoimpedance at 2MHz frequency for all the samples is plotted in figure 3. Figure shows that all the samples have negative magnetoimpedance at higher frequency (2MHz) and magnetoimpedance decreases with increasing applied magnetic field. The maximum magnetoimpedance is observed in L6C and L5C samples are ~65% and ~55%, respectively, while in L6B and L5B samples it is about ~22% and ~52% respectively and minimum magnetoimpedance is observed in L6S and L5S and it is about ~6.5% and ~1.4% respectively at 1T magnetic field and 2MHz frequency of applied electric field. The magnetoimpedance of semiconducting L6C and L5C samples can be illustrated by charge carrier

localization effect, the charge carriers,  $e_g$  electrons, easily move and hence impedance decreases. Whereas in the metallic L6B, L5B, L6S and L5S samples may be explained with the skin effect and classical electrodynamics, may in this case magnetic permeability decreases with increasing applied magnetic field. The penetration depth can be expressed as  $\delta = \sqrt{2/\omega\sigma\mu_\phi}$ , where  $\sigma$  is the conductivity,  $\mu_\phi$  is the transverse permeability for the circumferential field generated by frequency of applied electric field,  $\omega$  is angular frequency. Generally,  $\mu_\phi$  is the function of frequency of applied electric field and external magnetic field. A decrease in the permeability of the magnetic field results in an increase of the penetration depth  $\delta$ , thus, decreasing impedance of the samples. Similar case has been observed in giant magnetoimpedance of Fe based amorphous materials [9,10].

The magnetoimpedance effect found in the present work reveals a novel aspect of the interplay between magnetism and electronic transport in perovskite manganite oxides and provides a new route for the possible application of such materials in magnetic recording and sensing.

**Figure 3:** Change in magnetoimpedance with applied magnetic field of all the samples.



## References:

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### **III. Has the progress been according to original plan of work and towards?**

#### **Achieving the objective? If not, state reasons**

Yes, we have successfully prepared high quality single phasic LPAMO manganite samples using conventional solid state reaction route. Rietveld analysis reveals the single phasic nature without any detectable impurity within the measurement range studied. Charge transport studies were carried out by performing frequency dependent magnetoimpedance measurements (instead of conventional R-T and MR measurements due to unavailability of PPMS instrument at our collaborative institute, UGC-DAE, CSR, Mumbai). Work has been completed and manuscript will be communicated shortly to reputed international journal shortly. By considering the objectives of the proposed work, recently the data have been received for R-T and MR measurements on all the proposed six samples and as early as possible we communicate the results and analysis to some highly repute journals.

Importantly, the proposed objectives (a), (b) and (e) are completed while for objectives (c) and (d) will be completed shortly, since experimental results are achieved recently.

#### **IV. Please enclose a summary of the finding of the study.**

In the conclusion,  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Ca}_{0.3}\text{MnO}_3$  (L6C),  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ (L5C),  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$  (L6S),  $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ (L5S),  $\text{La}_{0.6}\text{Pr}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$  (L6B) and

$\text{La}_{0.5}\text{Pr}_{0.2}\text{Ba}_{0.3}\text{MnO}_3$  (L5B) perovskite oxide samples have been successfully synthesized by using conventional solid state reaction method. The structure of these oxides is investigated by XRD technique, which reveals single phasic growth oxide without any impurity, and unit cell volume increases as doping of larger ionic radius element at La-site and unit cell volume decreases as increasing doping of  $\text{Pr}^{+3}$  at La-site due to small ionic radius of  $\text{Pr}^{+3}$ . Impedance of L6C and L5C decreases with frequency at room temperature due to charge carriers transportation in semiconducting L6C and L5C, whereas in L6S, L5S, L6B and L5B samples, impedance increases with increasing frequency at room temperature due to metallic behavior of L6S, L5S, L6B and L5B samples at lower temperature than the  $T_C$ . The impedance of all the samples decreases with increasing external magnetic field. The negative magnetoimpedance of semiconducting L6C and L5C can be explained by charge carrier transport mechanism and the negative magnetoimpedance of metallic L6S, L5S, L6B and L5B can be correlated with the skin effect and magnetic permeability of the samples.

The Principal Investigator

**(Dr. Rupal K. Trivedi)**