



On magnetic ordering in heavily sodium substituted hole doped lanthanum manganites



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ABSTRACT

Mixed valence manganite system with monovalent sodium substituted lanthanum manganites form the basis of the present work. Lanthanum manganites belonging to the series $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ with $x=0.5-0.9$ were synthesized using modified citrate gel method. Variation of lattice parameters and unit cell volume with Na concentration were analyzed and the magnetization measurements indicated ferromagnetic ordering in all samples at room temperature. Low temperature magnetization behavior indicated that all samples exhibit antiferromagnetism along with ferromagnetism and it has also been observed that antiferromagnetic ordering dominates ferromagnetic ordering as concentration is increased. Evidence for such a magnetic inhomogeneity in these samples has been confirmed from the variation in $\text{Mn}^{3+}/\text{Mn}^{4+}$ ion ratio from X-ray Photoelectron Spectroscopy and from the absorption peak studies using Ferromagnetic Resonance Spectroscopy.

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1. Introduction

Manganites (AMnO_3) belonging to the class of perovskites are hotly pursued the world over by scientists and engineers. From a fundamental point of view these class of materials are considered to be a store house of rich and fascinating physics since they represent a strongly correlated system where correlation exists between charge, spin and lattice degrees of freedom. Early investigation pertaining to their structural, electrical and magnetic properties dates back to the 1950s and various properties exhibited by these class of materials are explained based on double exchange mechanism, Jahn Teller distortion, crystal defects and oxygen deficiencies [1–3]. Such theories governing the transport and magnetic properties made these materials highly resourceful and in the late 1990s the application potentials of these materials were realized [4–6].

Catalytic activity of manganites, particularly, lanthanum manganites (LMO) is utilized in the oxidation of CO and hydrocarbons [7,8]. Different valence ion substitution at La or Mn sites (called

doped LMO) lead to cation or anion vacancies providing enhanced mobility and reactivity of oxygen ions essential for the catalytic activity [9]. Another major area dominated by doped LMO are in solid oxide fuel cells (SOFCs) where they serve as cathode materials similar to yttria substituted zirconia (YSZ) electrolytes due to their excellent electronic and ionic conductivity, thermal, mechanical and chemical stability [10,11]. The importance and demand for these materials is growing at a faster rate ever since the discovery of Colossal Magneto-Resistance in Ca doped rare earth manganites ($\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$) in 1994 [12,13]. From an applied perspective they can find applications in a wide area ranging from magneto-resistive random access memory (MRAM), magnetic tunnel junctions (MTJs), data storage, read-write heads to bolometric sensors [1,14]. These materials are a fertile area for material scientists since they exhibit interesting structural, electrical and magnetic properties. These properties are dependent on the nature of substitution, their concentration and are also influenced by temperature dependent structural phase transitions [15–17].

The unique characteristic of manganites is identified to be this tunable nature of charge carriers which results in mixed valence states of Mn ions responsible for the diverse structural, magnetic and electron transport properties. The d orbital alignment and

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orientation of probable valence states of Mn such as Mn^{4+} , Mn^{3+} and Mn^{2+} in the crystal lattice control the charge as well as orbital ordering mechanisms which has direct consequence on Mn–O–Mn bond length and bond angle, Jahn Teller distortion and the structure or phase of material, charge transport mechanism and conduction. An exceedingly investigated property of manganites is magnetism and can be explained based on the double exchange interaction by Zener based on the different valence states of Mn [18]. With the emergence of multiferroic materials, lanthanum manganites and its derivatives ($\text{La}_{1-x}\text{A}_x\text{MnO}_3$; $\text{A}=\text{Ca}^{2+}$, Sr^{2+} , Ba^{2+} , Ce^{4+}) (electron doped or hole doped) are again revisited as they exhibit varied magnetic transitions coupled with metal insulator transition, thus providing a close linkage between magnetic and electronic transport properties. Active research is on in these materials with the anticipation of developing a possible component exhibiting simultaneous ferroelectric (FE) and ferromagnetic (FM) characteristics [19,20]. In addition to divalent and trivalent substitutions, monovalent ion substitutions for La sites called hole doped manganites is another way of inducing mixed valency for manganese ions [21–24]. It is known that with monovalent doping, hole concentration could be doubled with respect to divalent doping. Sodium ion (Na^+) is an ideal candidate among the monovalent ions since ionic radius of Na^+ (116 pm) is close to La^{3+} (117.2 pm) and within the tolerance limits. The amount of Na can be varied in the composition and this alters the amount of Mn^{3+} and Mn^{4+} ions which play a significant role in deciding the magnetic property of manganites. Reports exist in literature pertaining to magnetic behavior in $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ (LNMO) series with lower substitution levels of Na [25–29]. However no reports could be found dealing with higher substitutions of Na beyond 40 percent. It is this particular observation from literature survey that we find compositions with Na substitutions from 50 percent to 90 percent will be of interest to the scientific community.

One of the difficulties in synthesizing these compositions is the upkeep of Na stoichiometry because of its volatility at high temperatures and hence their substitution leads to the formation of vacancies at lanthanum and oxygen sites in the lattice. These vacancies also play a crucial role in determining the material properties including magnetic ordering. A survey of literature reveals that the preparation technique adopted for LNMO series plays a significant role in maintaining the desired composition of series. Hence adoption of an appropriate preparative technique is highly essential for synthesizing a stoichiometric compound where the desired and actual composition are the same. So search for room temperature ferromagnetic ordering in La–Na manganite is important from an applied perspective as well as from a theoretical point of view. In such a study adoption of an appropriate technique which inhibits the loss of sodium during synthesis assumes importance. Evaluation of $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio using techniques like X-ray Photoelectron Spectroscopy also assume significance. Present work focuses on the synthesis of 50 percent to 90 percent Na substituted LMO by an appropriate technique wherein the loss of Na is kept minimal. Influence of higher Na doping on structural and magnetic properties are discussed in the present paper along with surface analysis using X-ray Photoelectron Spectroscopy (XPS) and the possible mechanisms contributing to magnetic ordering is identified. Ferromagnetic Resonance (FMR) studies for analyzing the magnetic behaviour are also carried out. Analysis will be with respect to 50 percent Na substituted sample (coded as LNMO5) which has already been published by these authors [30]. The present work is a sequel to the above investigation.

2. Experimental techniques

Preparative technique adopted in this investigation is a

modified citrate gel method. Required amounts of precursors namely lanthanum oxide, manganese nitrate and sodium carbonate corresponding to the composition $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ ($x=0.5$ – 0.9) were dissolved in de-ionized water and an adequate amount of citric acid was added. An appropriate amount of nitric acid was added to the solution to convert all the constituents to nitrates and was heated to a temperature of 80°C with continuous stirring; the solution boiled, frothed, turned dark and caught fire giving a spongy dark powder. The resultant powder was then fired at a temperature of 1100°C for several hours. Samples are assigned the codes LNMO6, LNMO7, LNMO8, LNMO9 corresponding to 60 percent, 70 percent, 80 percent and 90 percent Na substitutions respectively.

All the synthesized samples were subjected to structural characterization using X-ray powder diffraction (XRD) [Rigaku D max-C, (30 kV and 20 mA)] and fine structure refinement was carried out using Rietveld refinement [FullProf Studio, version2]. Magnetization studies at room temperature and high temperature (303–393 K in steps of 10 K) were carried out using Vibrating Sample Magnetometry (VSM)[DMS 1660 VSM] and Field Cooled (FC) – Zero Field Cooled (ZFC) measurements (10–300 K) using SQUID Magnetometer. An elaborate and accurate understanding of the structure as well as the properties of the Na doped LaMnO_3 was carried out using X-ray Photoelectron Spectroscopy (XPS) [Omicron Nanotechnology XPS system with a monochromatic Al K_α radiation ($h\nu=1486.6$ eV), source voltage: 15 kV and emission current: 20 mA]. XPS spectra was then deconvoluted using Casa XPS program (Casa Software Ltd, UK) in which the background correction was simulated using Shirley function and peak fitting using a Gaussian Lorentzian function. The recorded Binding energy (BE) spectra were calibrated employing BE of aliphatic carbon at 284.6 eV with a sensitivity of ± 0.2 eV. Ferromagnetic Resonance (FMR) studies were utilized for analyzing the ferromagnetic nature in the samples.

3. Results and discussion

3.1. Structural and magnetic studies

Lanthanum manganite samples with five different substitutions of Na, namely LNMO5, LNMO6, LNMO7, LNMO8 and LNMO9 subjected to structural characterization using XRD showed distorted orthorhombic structure and the XRD pattern is depicted in Fig. 1. For XRD pattern of LNMO5, refer [30]. It may be noted here that monovalent ion substitution can result in distorted perovskite as suggested by Shimura et al. [31]. Orthorhombic structure is exhibited by higher Na substituted compositions of lanthanum manganites and is usually in a mixed state with rhombohedral phase for heavily doped samples [21]. Peaks are more clearly

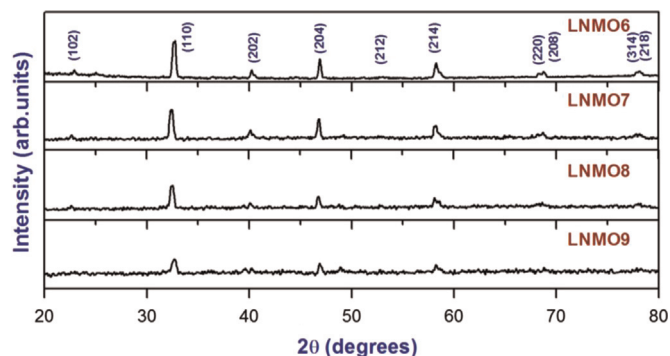


Fig. 1. XRD pattern of Na substituted LaMnO_3 samples, LNMO6 to LNMO9.

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