Indian Journal of Pure & Applied Physics
Vol. 46, May 2008, pp. 325-329

Synthesis and characterization of sodium substituted lanthanum manganite

M P Sharma, S K Jain*, Anjali Krishnamurthy & Bipin K Srivastava

Department of Physics, University of Rajasthan, Jaipur 302 004

*Department of Physics, Apex Engineering College, Jaipur 302 022

E-mail: mps_45@yahoo.com

Received 22 August 2007, revised 3 January 2008; accepted 22 February 2008

Three compositions of sodium substituted lanthanum manganites $La_{1-x}Na_xMnO_3$ (for x = 0.1, 0.2 and 0.5) have been prepared using sol-gel technique followed by two different thermal treatments. Attempts to prepare 50 atomic per cent Na (for La) substituted sample, which would be the maximum permissible amount of Na as per valence consideration, did not yield a compound of correct stoichiometry. Of the two stoichiometric samples, the one with 20 atomic% sodium shows an ordered ferromagnetic state and that with 10 atomic% sodium is disordered ferromagnet.

Keyword: Sol-gel technique, Lanthanum manganites, Ferromagnet, Mott insulator

1 Introduction

Lanthanum manganites with substitutions at both La and Mn sites have drawn considerable attention as they exhibit interesting phenomena such as colossal negative magneto-resistance, magnetic, structural and metal-insulator phase transition and a charge or polaron ordering[1-14]. $LaMnO_3$ is a Mott insulator and has a canted anti-ferromagnetic layered structure. As regards substitutions at La site, compositions with mostly those of divalent cations (like Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}) have been investigated. Substitution of more than $1/3^{rd}$ of La^{3+} atomic fraction by divalent cations leads to ordered ferromagnetic state. As such little work has been done on samples with substitutions by monovalent cations[2]. Another aspect of interest is that of the method of preparation of perovskite samples. Usually these are prepared following the technique of solid state diffusion. Rather recently sol-gel method has been in use. Owing to huge scope for technological applications of these materials, it is of interest to examine the quality of samples prepared using the sol-gel route vis-ã-vis those prepared following the conventional technique of solid state diffusion.

In this paper, work on preparation (following sol gel method) and characterization of three samples with Na substitution in the series $La_{1-x}Na_xMnO_3$ (for x = 0.1, 0.2 and 0.5) has been reported. X-ray diffraction and iodimetric measurements have been made for structural characterization and estimation of oxygen content. Magnetization measurements (field and temperature dependent) have been made for examining the magnetic behaviour. Results have been compared with those on sodium and calcium substituted samples as reported in literature.

2 Experimental Details

$Na(NO_3)$, $La(NO_3)_3.6H_2O$ and $Mn(NO_3)_2.4H_2O$ were used as the starting materials for following sol gel technique. We first worked at preparing samples with compositions corresponding to x = 0.2 and 0.5 in $La_{1-x}Na_xMnO_3$. The sol-gel produce for both the compositions were subjected to two different heat treatments: at 400°C for 18 h and at 900°C for 4 d. The obtained samples are hereafter referred to as 2N400 and 2N900 respectively for x = 0.2. For x = 0.5, these are referred to as 5N400 and 5N900 respectively. Subsequent measurements showed that the sample 2N900 obtained by heat treatment at 900°C is the better one. We then prepared one sample corresponding to x = 0.1 with heat treatment of the sol-gel produce at 900°C for 4 d. This sample is referred to as 1N900.

X-ray diffraction patterns have been recorded on Philips powder diffractometer PW1840 using FeK_α radiation. Oxygen content has been estimated with the help of iodimetric measurements. Magnetization measurements have been made using a vibrating sample magnetometer (PARC make, model 155) in external fields up to 8.5 kOe and in the temperature range 20-300K. For low temperature measurements a closed helium cycle refrigerator cryostat has been

used. Measurements have been made in zero field cooling (zfc) and field cooling (fc) modes. In zfc mode, sample is first cooled in zero magnetic field, from 300K down to 20K, a measuring field is applied and then moment is recorded as a function of temperature as the sample is warmed upto 300K. In fc mode, the sample is cooled from 300K downwards in the presence of a measuring field and the moment is recorded either in this cooling cycle or in the warming cycle; in this study it is recorded in the warming cycle.

3 Results and Discussion

Figures 1(a-e) show X-ray diffraction (XRD) patterns of the samples 2N400, 2N900, 1N900, 5N400 and 5N900 respectively. The pattern of 2N400 gets indexed in cubic symmetry and those of 2N900 and 1N900 get indexed in psuedo-cubic symmetry. Obtained cell constant *a* for all these three samples is ~3.8Å. Iodimetric measurements show the oxygen stoichiometry to be 2.965, 2.995 and 3.035 for 2N400, 2N900 and 1N900 respectively. XRD patterns of the samples 5N400 and 5N900 show that both of these crystallize in dual phase cubic symmetry with cell constants ~3.8Å and ~5.6Å. Oxygen stoichiometry values for 5N400 and 5N900 are 2.803 and 3.272 respectively which are quite off the correct stoichiometric value 3. Thus these higher Na containing samples are dual phase and with quite much of non-stoichiometry. It may be mentioned that as per the valence requirement this is the maximum possible amount of Na that can be substituted in $LaMnO_3$.

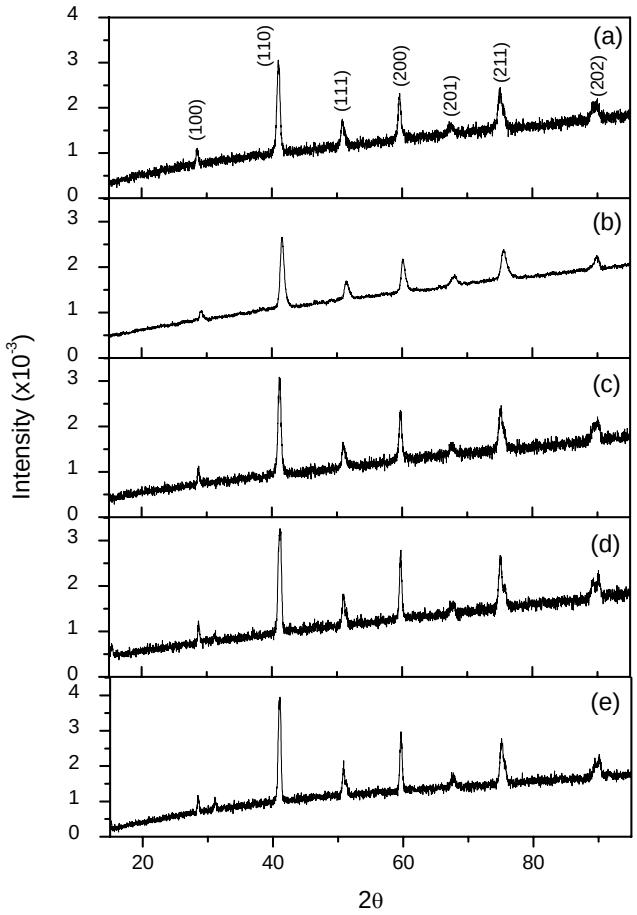

Fig. 1 — X-ray diffraction (XRD) patterns of the samples (a) 2N400, (b) 2N900, (c) 1N900, (d) 5N400 and (e) 5N900

For further characterization, the samples 1N900, 2N400 and 2N900, which have come out as single phase materials, have been put to magnetic measurements. Figure 2 shows magnetization-temperature (*M-T*) measurements on 2N400 recorded in zfc and fc modes under external magnetic field of 11 Oe; measurement in zfc mode is also plotted under a field of 504 Oe. The measurements show (i) a transition from paramagnetic (PM) to ferromagnetic (FM) state spread over a wide temperature range beginning at ~300K, (ii) the nature of broad transition retains at the high field of 504 Oe and (iii) departure between zfc and fc curves starting just immediately below the highest temperature of ~295K. These observations signify relaxation and are representative of disordered magnetic behaviour of the sample 2N400.

M-T measurements on the sample 2N900 (obtained by heating the sol-gel produce at 900°C) under external magnetic fields 12 Oe and 100 Oe are shown

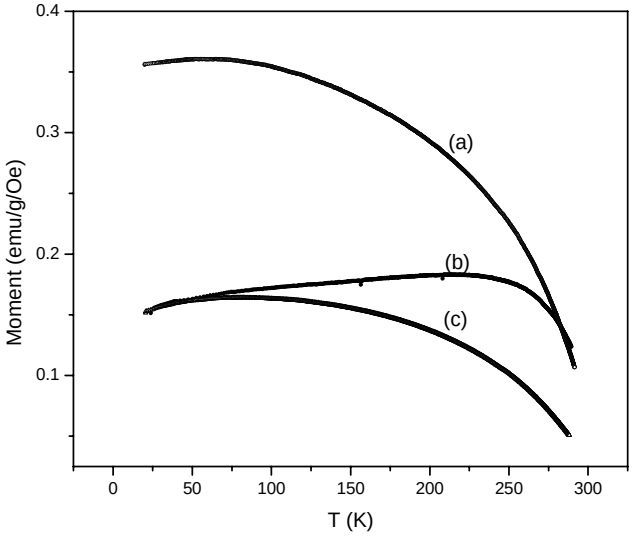

Fig. 2 — Plot of magnetization of 2N400 as a function of temperature (a) in field cooled (fc) mode under a field of 11 Oe, (b) zero field cooled (zfc) mode under 11 Oe and (c) zfc mode under 504 Oe

in Fig. 3. This sample exhibits a sharper PM-FM transition (than does 2N400) at ~290K.

Magnetization-field (*M-H*) measurements on 2N400 and 2N900, at 300K and 20 K, are shown in [Figs 4 and 5]. At 300K, both the samples hardly exhibit any coercivity (H_c) and remanence (M_r). At 20K, 2N400 shows non-zero finite values for the two hysterisis parameters as against near zero values for 2N900. At 20K, the 'near saturation' values of magnetization for 2N400 and 2N900 are 62 emu/g and 85 emu/g respectively. The much sharper magnetic transition and enhanced saturation magnetization for the sample 2N900 are suggestive of its being more ordered and better prepared.

For 10 atomic% Na substituted sample 1N900, *M-T* measurements are shown in Figs 6(a-c). Measurements are shown under external fields of 20 Oe, 200 Oe and 500 Oe. Even at 500 Oe, the PM-FM transition remains spread over a wide temperature range. This observation is suggestive of the 10 atomic% Na containing sample being magnetically disordered. *M-T* measurements for this sample are

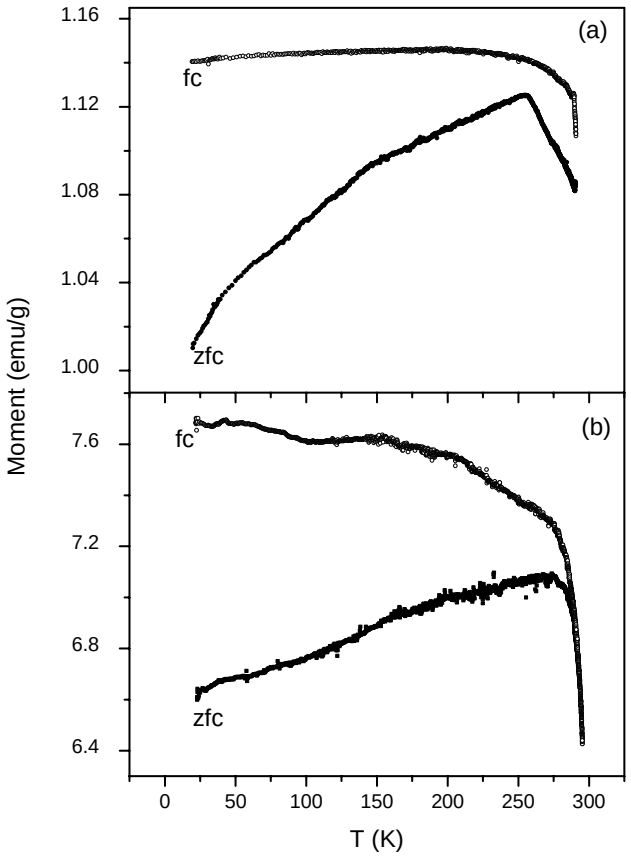

Fig. 3 — Plot of magnetization of 2N900 as a function of temperature in zero field cooled (zfc) and field cooled (fc) modes under a field of (a) 12 Oe and (b) 100 Oe

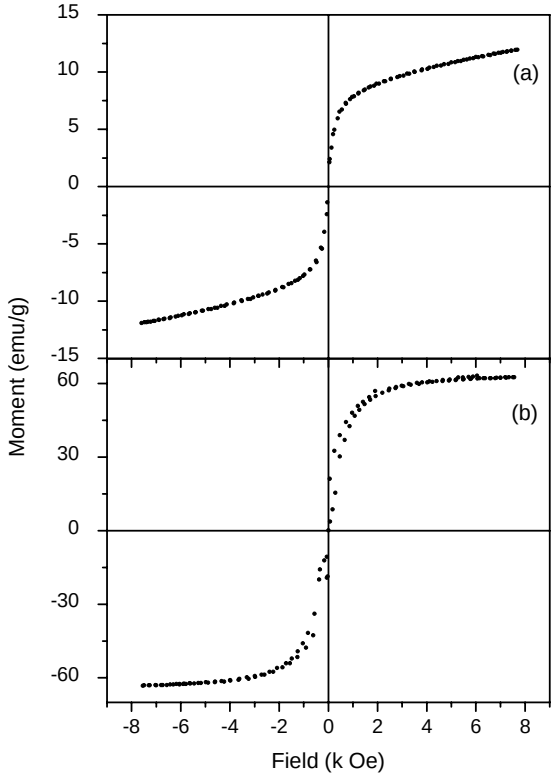

Fig. 4 — Plot of magnetization of 2N400 as a function of magnetic field at (a) 300K and (b) 20K

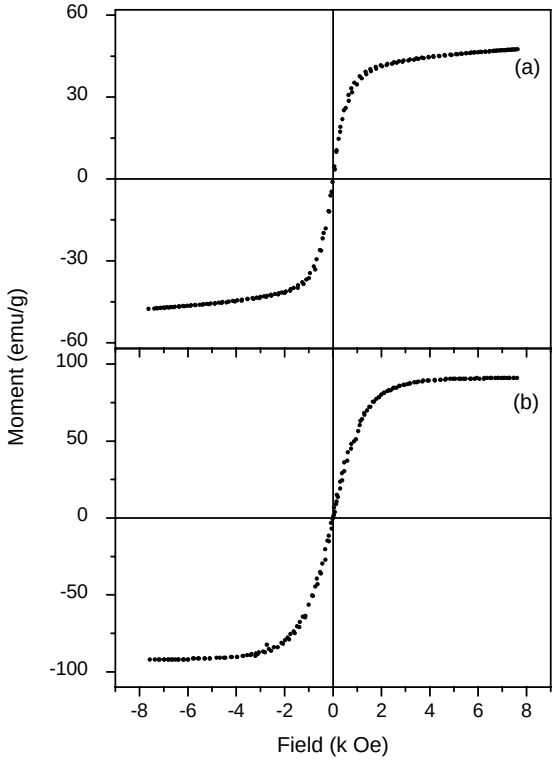

Fig. 5 — Plot of magnetization of 2N900 as a function of magnetic field at (a) 300K and (b) 20K

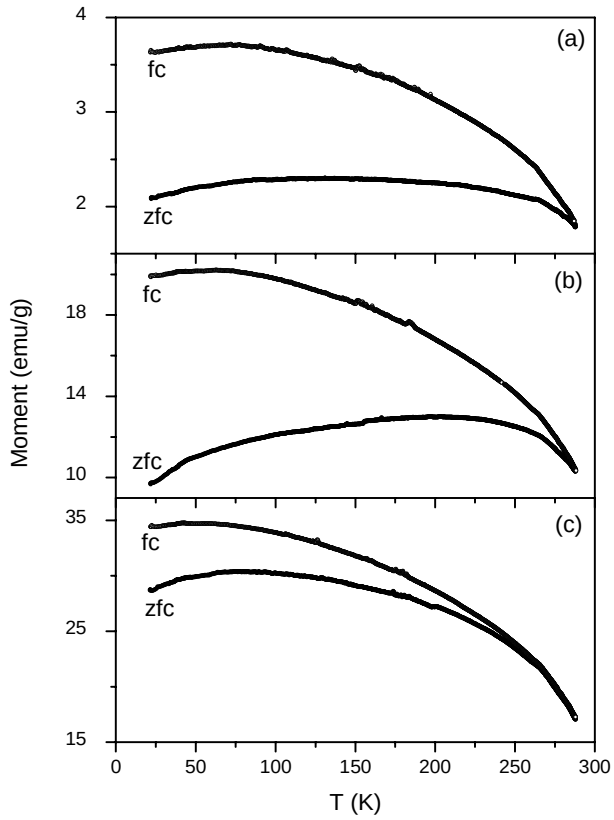

Fig. 6 — Plot of magnetization of 1N900 as a function of temperature in zero field cooled (zfc) and field cooled (fc) modes under fields of (a) 20 Oe, (b) 200 Oe and (c) 500 Oe

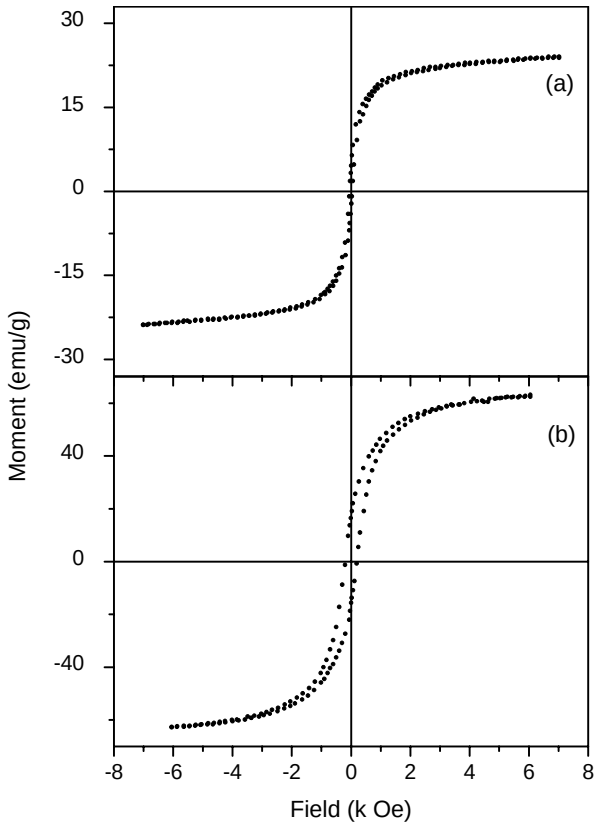

Fig. 7 — Plot of magnetization of 1N900 as a function of magnetic field at (a) 300K and (b) 20K

shown in Figs 7(a and b). At 300 K and also at 20 K, M_r and H_c exhibit finite values which inc
ease at the lower temperature of 20K.

The result that the sample with 20 atomic% ($1/5^{th}$ of) La atoms substituted by monovalent Na^+ shows an ordered FM state merits a special mention. This result supports the inference of the requirement of conversion of a minimum of $1/3^{rd}$ of Mn^{3+} atoms into Mn^{4+} for manifestation of ordered FM state (as inferred in reported studies of divalent cation substituted systems[3]). It is to be noted that substitution of 0.2 Na^+ (as also of 0.4 Ca^{2+}) would result in conversion of 0.4 of Mn^{3+} to Mn^{4+}. It is worth pointing out that $La_{0.6}Ca_{0.4}MnO_3$, prepared with 0.4 of La^{3+} substituted by Ca^{2+}, has a T_c of 260K[7]. This value is quite close to the value 290K of T_c observed in 0.2 Na substituted sample 2N900. Nearly equal ionic radii of Na^+ and Ca^{2+} at 0.97 and 0.99Å respectively[15] would imply that inter-ionic distances and hence strengths of double exchange interactions in the two systems would be nearly the same.

It would be interesting to compare the results of sol-gel route prepared samples of this study with literature report on the conventional ceramic route prepared sample. Itoh *et al.*[2] have reported a Curie temperature of 308K for solid state ceramic method prepared $La_{0.82}Na_{0.16}MnO_3$. This is in reasonable agreement with $T_c \sim 290$K observed for sol-gel route prepared $La_{0.80}Na_{0.20}MnO_3$ sample of this study. As regards the sample 1N900 ($La_{0.90}Na_{0.10}MnO_3$), as it exhibits a magnetic transition spread over a wide temperature range, a comparison is actually not possible, with solid state method prepared samples of close by compositions.

In summary, it has been possible to prepare, following sol-gel method, single phase crystalline samples with substitutions of 10 atomic% and 20 atomic% sodium for La in $LaMnO_3$. Attempt to prepare 50 atomic% sodium substituted sample did not succeed. Sample with 20 atomic% sodium exhibits an ordered FM state and compares well the solid state ceramic technique prepared sample as reported in literature. 10 atomic% sodium substituted sample is magnetically disordered.

Acknowledgement

Authors are grateful to Mr Manoj Kumar for iodimetric measurements. One of the authors (MPS)

is grateful to CSIR for the award of senior research fellowship. The work has been done under a University Grants Commission, Delhi, funded research project and their support is gratefully acknowledged.

References

1 Schiffer P, Ramire A P, Bao W & Cheong S W, *Phys Rev Lett*, 75 (1995) 3336.
2 Itoh Mitsuru, Shimura Tetsuo, Yu Jiang- Ding, Hayashi Toshimasa & Inaguma Yoshiyuki, *Phys Rev B,* 52 (1995) 12522.
3 Gayathri N, Raychaudhuri A K, Tiwari S K, Gundakaram R, Arulraj A & Rao C N R, *Phys Rev B*, 56 (1997) 1345.
4 Mahendiran R, Tiwary S K, Raychadhuri A K, Mahesh R & Rao C N, *Phys Rev B*, 54 (1996) R9604.
5 Ramiraz A P, Schiffer P, Cheong S-W, Chen C H, Bao W, Palstra T T M, Gammel P L, Bishop D J & Zegarski B, *Phys Rev Lett* , 76 (1996) 3188.
6 Mukhin A A, Ivanov Yu V, Travkin V D, Lebedev S P, Pimenov A, Loidl A & Balbashov A M, *J Magn Magn Mater*, 196-197 (1999) 501.
7 Bohigas X, Tejada J, Marinez-Sarrion J, Tripp S & Black R, *J Magn Magn Mater*, 208 (2000) 85.
8 Young S L, Chen Y C, Horrng Lance, Wu T C, Chen H Z & Shi J B, *J Magn Magn Mater*, 209 (2000) 145.
9 Fu C M, Hsu K S, Lin M L & Wen Z H, *J Magn Magn Mater,* 209 (2000) 151.
10 Tai M F, Lee F Y & Shi J B, *J Magn Magn Mater,* 209 (2000) 148.
11 Trukhanov S V, Troyanchuk I O, Szymchzak H & Barner K, *Phys Status Solidi (b),* 229 (2002) 1417.
12 Yates K A, Kapusta C, Riedi P C, Ghivelder L & Cohen L F, *J Magn Magn Mater,* 260 (2003) 105.
13 Vashook V, Vasylechko L, Zosel J & Guth U, *Solid State Ionics,* 8907 (2003) 1
14 Zener C, *Phys Rev,* 83 (1951) 440.
15 Weast R C, *CRC Hand Book of Chemistry and Physics,* 52nd edition, 1971-1972.