



Bandwidth control effects in electron doped manganite $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$ thin films

Kavita Bajaj^{a,b,1}, Vivas Bagwe^a, John Jesudasan^a, Pratap Raychaudhuri^{a,*}

^a Department of Condensed Matter Physics and Materials Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India

^b Department of Physics, Mumbai University, Mumbai 400098, India

Received 25 October 2005; received in revised form 13 January 2006; accepted 5 April 2006 by J. Fontcuberta

Abstract

We report the effect of average A-site cation radius on the structural, magnetic and electrical properties of electron doped manganite $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ thin films. A site cation radius $\langle r_A \rangle$ is varied systematically by partially replacing La^{+3} ions by smaller Y^{+3} ions in the parent compound. The carrier doping, i.e. the fraction of tetravalent Ce atoms at the A-site was kept at 30%. A series of $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$ ($x=0, 0.05, 0.1, 0.15$ and 0.25) thin films were prepared under identical conditions by using pulsed laser deposition technique. Metal–insulator transition temperature (T_p) and the ferromagnetic Curie temperature (T_c) are found to be decreasing significantly with increasing yttrium concentration, i.e. decreasing $\langle r_A \rangle$. The resistivity (ρ) at T_p increases by one order of magnitude when the yttrium concentration is increased from $x=0$ to 0.25 , while magnetization decreases with decreasing $\langle r_A \rangle$. Magnetoresistance as measured under field of 1 T is significant near T_c . Structural analysis reveals the films are having single phase and c -axis lattice parameter decreasing linearly as $\langle r_A \rangle$ decreases. There is no marked difference in surface morphology of samples with different yttrium concentration. From EDX the Y:Ce:Mn ratio were consistent within 5% of the nominal composition.

© 2006 Published by Elsevier Ltd.

PACS: 75.47.Gk; 75.47.Lx; 72.80.+r; 71.28.+d

Keywords: A. Magnetically ordered materials; A. Magnetic films and multilayers; A. Thin films; D. Electronic Transport

1. Introduction

Since, the existence of metal–insulator transition in Lanthanum manganites was established in early 1950s [1], extensive studies have been carried out on this class of materials due to rich variety of electric transport and magnetic properties exhibited by them. But in these mixed valence manganese oxide perovskite ($\text{La}_{1-x}\text{A}_x\text{MnO}_3$) the major focus has been on hole doped compounds in which divalent cation (A) such as Ba, Ca, Sr, Pb, etc. have been substituted at the rare-earth site. Proportionate to the doping level valence state of some of the Mn^{3+} ions with electronic configuration $t_{2g}^3 e_g^1$ in parent compound changes to Mn^{4+} having electronic configuration t_{2g}^3 . However, it was shown that electron doping could be achieved in LaMnO_3 by

replacing some of the La^{3+} ions by Ce^{4+} ions [2,3]. Zener double exchange between Mn^{3+} and Mn^{2+} was suggested to be mechanism responsible for observed ferromagnetism and metal–insulator transition. One interesting observation that emerged from subsequent studies is that Ce doped LaMnO_3 bulk samples of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ cannot form in single phase, but thin films of this compound deposited by pulsed laser deposition technique exist in single phase [4,5]. Furthermore, it was confirmed from X-ray absorption spectroscopy that in epitaxial thin films cerium exist in tetravalent state and manganese in divalent and trivalent state in this system [6,7].

In hole doped manganites structural effects on magnetoresistance and T_c are well studied [8–13]. It was reported that replacing La by small amount of Y in polycrystalline $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ results in decrease in T_c and increase in magnetoresistance [8]. The decrease in T_c is mainly attributed to decrease in Mn–O–Mn bond angle due to decrease in mean ionic radius $\langle r_A \rangle$ of A site cation. In this paper, we report the evolution of magnetic and electric properties of $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$ thin films by changing $\langle r_A \rangle$. We have varied $\langle r_A \rangle$ systematically by partially replacing La^{3+} ions by smaller ions Y^{3+} , While keeping the carrier concentration, i.e. $\text{Mn}^{2+}/$

* Corresponding author. Tel.: +91 22 22782475.

E-mail addresses: bajajkp@rediffmail.com (K. Bajaj), pratap@tifr.res.in (P. Raychaudhuri).

¹ On leave from C.H.M. College, Ulhasnagar, Mumbai, India.

Mn^{3+} fixed at $3/7$. Our main observation is decrease in T_p , T_c and spontaneous magnetization associated with increase in resistivity with decreasing $\langle r_A \rangle$, similar to hole doped compounds [9].

2. Experimental

Bulk samples of $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$ ($x=0, 0.05, 0.1, 0.15$ and 0.25) were prepared by conventional solid-state reaction route. La_2O_3 , Y_2O_3 and CeO_2 powders were heated at 800°C for 12 h. Stoichiometric proportions of La_2O_3 , Y_2O_3 , CeO_2 and MnO_2 were mixed, ground and calcined at 1000°C for 12 h. Mixed powders were reground and sintered at 1350°C for 15 h. Films were deposited by using these sintered targets by pulsed laser deposition technique on single crystal LaAlO_3 substrate using a KrF excimer laser. All the films were deposited under identical condition. Substrate temperature was maintained at 830°C during the growth. Laser energy density was 2.5 J/cm^2 with repetition rate of 10 Hz. Films were grown at the oxygen pressure of 100 mTorr. X-ray diffraction pattern was recorded by using a Siemens X-ray diffractometer. The resistance and magnetoresistance was determined as a function of temperature by using conventional four-probe a.c. method. Frequency kept was 372 Hz. Magnetoresistance was recorded under magnetic field of 1 T and field parallel to current. For magnetization measurement SQUID magnetometer was used. The magnetization data was recorded in magnetic field of 1 kOe. Surface morphology was studied using digital instruments atomic force microscope (AFM) operated in contact mode. Chemical composition was determined using energy dispersive X-ray analysis (EDX).

3. Results and discussion

Fig. 1(a) shows the powder X-ray diffraction pattern of all the films. The pattern reveal single phase of the films oriented along the (001) planes. No impurity phase was observed even by plotting the data on the log scale. Representative AFM images of undoped sample and sample with highest yttrium doping are shown in Fig. 1(b). There is no marked difference in surface morphology of samples with different yttrium concentration. The grain size is about 30 nm. From EDX the Y:Ce:Mn ratio were consistent within 5% of the nominal composition. As the films are grown on LaAlO_3 substrates we cannot estimate the La content since it contains contribution from both the substrate and the film in the EDX spectrum. We have, however, checked the Y:Ce:Mn ratio, which is consistent within 5% of the nominal composition. As expected, the c -axis lattice parameter calculated is found to decrease linearly from 7.7895 \AA to 7.7406 \AA as $\langle r_A \rangle$ decreases from 1.294 \AA for parent compound to 1.25 \AA for the highest doped sample as depicted in Fig. 2. The thickness of all the films was fixed at $1300 \pm 100\text{ \AA}$. Resistivity (ρ) as function of temperature show a metal–insulator transition for all the samples (Fig. 3(a)). This metal–insulator transition coincides within 5 K of the ferromagnetic T_c determined from the temperature dependence of magnetization (Fig.3(b)). Both T_p

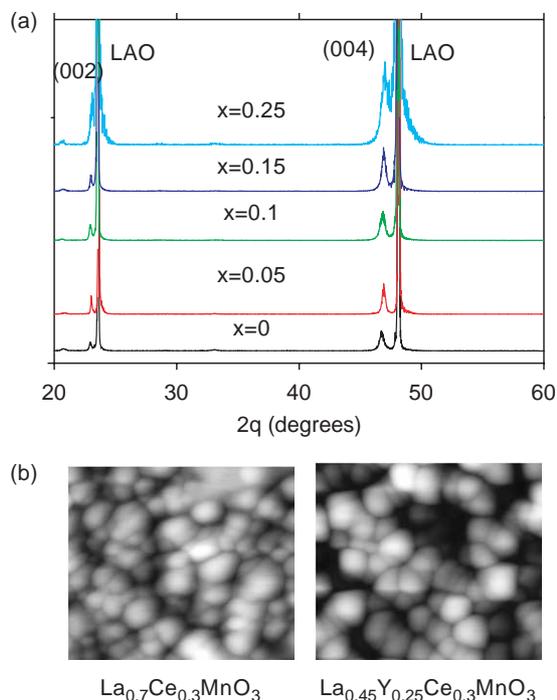


Fig. 1. (a) X-ray diffraction pattern of $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$ films. The intensity is in arbitrary units, (b) AFM image of $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ and $\text{La}_{0.45}\text{Y}_{0.25}\text{Ce}_{0.3}\text{MnO}_3$ films.

and T_c decrease monotonically while resistivity of samples increases with $\langle r_A \rangle$. Resistivity at T_p increases by one order of magnitude when the yttrium concentration is increased from $x=0$ to 0.25 . To show the correlation between structure and the magnetic and transport properties we plot in Fig. 2 the variation in lattice parameter c , T_c and T_p as a function of $\langle r_A \rangle$. There is a perfect consistency between the lattice parameter c , T_c and T_p as all three are decreasing with decreasing $\langle r_A \rangle$. The magnetoresistance of all the samples measured under field of 1 T is significant near T_c . The temperature dependence of resistivity under magnetic field of 1 T and zero field of $\text{La}_{0.6}\text{Y}_{0.1}\text{Ce}_{0.3}\text{MnO}_3$ sample is shown as inset in Fig. 3(a). Fig. 3(b) shows the temperature dependence of magnetization for all the samples. Magnetization decreases by about one

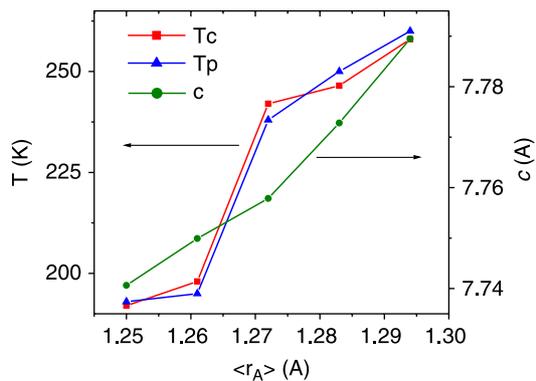


Fig. 2. Curie temperature T_c , metal–insulator transition temperature T_p and c -axis lattice parameter as function of average A site cation radius $\langle r_A \rangle$.

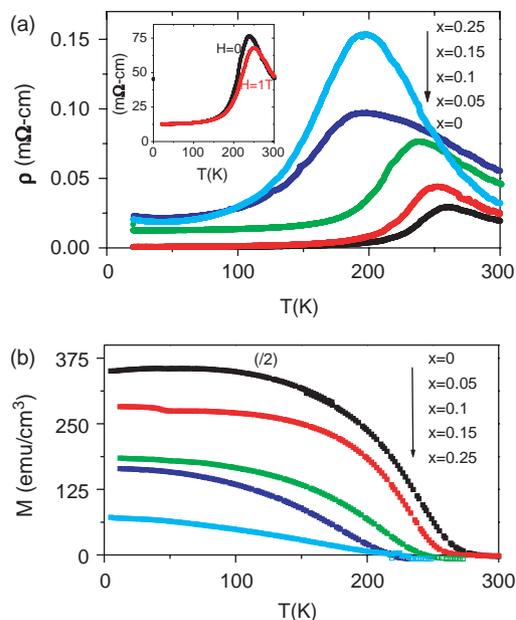


Fig. 3. (a) Resistivity as function of temperature of $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$ films, inset shows resistivity vs. temperature of $\text{La}_{0.6}\text{Y}_{0.1}\text{Ce}_{0.3}\text{MnO}_3$ sample in zero field and in magnetic field of 1 T, (b) magnetization as function of temperature of $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$ films.

order of magnitude when the yttrium concentration is increased from $x=0$ to 0.25. The magnetization decrease with decrease in one electron bandwidth results from the emergence of non-collinear spin structures as the strength of double exchange is weakened. This has been earlier observed in hole doped manganites [12,13].

For the sample with highest yttrium concentration ($x=0.25$) large thermo magnetic irreversibility is observed in the field cooled (FC) and zero field cooled (ZFC) magnetization measured in a field of 50 Oe (Fig. 4), signifying the sample to be behaving like a spin glass. This observation is similar to one reported earlier for narrow bandwidth hole doped manganites [12–14].

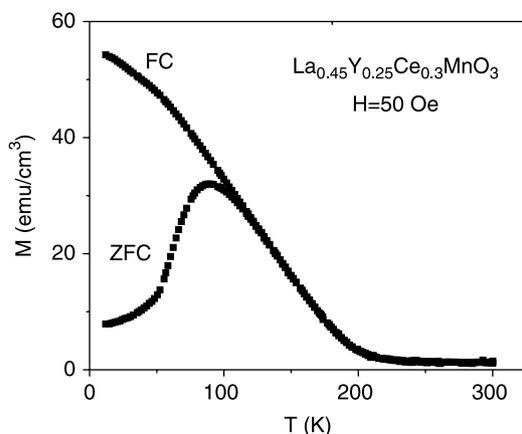


Fig. 4. Magnetization vs. temperature of ZFC and FC (50 Oe) of $\text{La}_{0.45}\text{Y}_{0.25}\text{Ce}_{0.3}\text{MnO}_3$ sample.

Earlier studies have shown that the magnetic and transport properties of hole doped manganites can be varied at constant doping by varying A site cation composition [9–11]. A geometrical factor involving $\langle r_A \rangle$ is ‘tolerance factor’ defined as $t = d_{\text{A-O}}/\sqrt{2}(d_{\text{Mn-O}})$. For perfect cubic structure $t=1$, Mn–O–Mn bond angle is equal to 180° and the undistorted MnO_6 octahedral forms a 3D network. When rare-earth ion (La) is partially replaced by ion of smaller radius, the MnO_6 octahedral gets tilted. This results in lowering of the Mn–O–Mn bond angle and thus reduces the matrix element t_{ij} of electron hopping between Mn^{2+} and Mn^{3+} . There is a direct relation between T_c and carrier bandwidth (W) of e_g band, which in turn depends on Mn–O–Mn bond angle [15]. $W \propto \cos\omega/(d_{\text{Mn-O}})^{3.5}$, where ω is ‘tilt’ angle in the plane of Mn–O–Mn bond ($\omega = [\pi - \langle \text{Mn-O-Mn} \rangle]$) and $d_{\text{Mn-O}}$ is the bond length. The striking similarity in the effect reducing the A-site cation in the electron doped manganite $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ strongly suggests that the mechanism of bandwidth control in this material is very similar to its hole doped counterpart. Thus we have demonstrated that in electron-doped manganites also $\langle r_A \rangle$ plays crucial role in evolution of transport and magnetic properties.

4. Conclusion

We have successfully synthesized a series of electron-doped films, i.e. $\text{La}_{0.7-x}\text{Y}_x\text{Ce}_{0.3}\text{MnO}_3$, where the electron doping is kept constant at 30% and cation size at the A site is gradually reduced. Our results on the transport, magnetization and structural studies on these films suggest that the effect of bandwidth control in this material is very similar to its hole doped counterpart, signifying that the transport mechanism in this material is possibly very similar to its hole doped counterpart.

Acknowledgements

One of the authors K.B. would like to thank Prof. D.C. Kothari for his valuable guidance, Mr S.P. Pai, Mr N. Kulkarni and Ms B. Chalke for technical support. K.B. would like to thank the University Grants Commission for partial support through the Faculty Improvement Program.

References

- [1] G.H. Jonker, J.H. Santen, *Physica* 16 (1950) 337.
- [2] S. Mandal, B. Das, *Phys. Rev. B* 56 (1997) 5073.
- [3] P. Raychaudhuri, S. Mukherjee, A.K. Nigam, J. John, U.D. Vaisnav, R. Pinto, P. Mandal, *J. Appl. Phys.* 86 (1999) 5718.
- [4] C. Mitra, P. Raychaudhuri, J. John, S.K. Dhar, A.K. Nigam, R. Pinto, *J. Appl. Phys.* 89 (2001) 524.
- [5] T. Yanagida, T. Kanki, B. Vilquin, H. Tanaka, T. Kawai, *Solid State Commun.* 129 (2004) 785.
- [6] C. Mitra, Z. Hu, P. Raychaudhuri, S. Wirth, S.I. Csiszar, H.H. Hsieh, H.-J. Lin, C.T. Chen, L.H. Tjeng, *Phys. Rev. B* 67 (2003) 092404.
- [7] J.Y. Lin, W.J. Chang, J.Y. Juang, T.M. Wen, J.M. Chen, *J. Magn. Mater.* 282 (2004) 237.
- [8] S. Jin, H.M. OBryan, T.H. Tiefel, *Appl. Phys. Lett.* 66 (1995) 382.
- [9] H.Y. Hwang, S.W. Cheong, P. Radaelli, M. Marezio, B. Batlogg, *Phys. Rev. Lett.* 75 (1995) 914.

- [10] P.G. Radaelli, G. Iannone, M. Marezio, D. Argyriou, *Phys. Rev. B* 56 (1997) 8265.
- [11] R. Mahesh, R. Mahendiran, A.K. Raychaudhuri, C.N.R. Rao, *J. Solid State Chem.* 120 (1995) 204J.
- [12] M. De Teresa, M.R. Ibarra, J. García, J. Blasco, C. Ritter, P.A. Algarabel, C. Marquina, A. del Moral, *Phys. Rev. Lett.* 76 (1996) 3392.
- [13] P. Raychaudhuri, T.K. Nath, P. Sinha, C. Mitra, A.K. Nigam, S.K. Dhar, R. Pinto, *J. Phys.: Condens. Matter* 9 (1997) 10919.
- [14] C. Mitra, P. Raychaudhuri, S.K. Dhar, A.K. Nigam, R. Pinto, S.M. Patalwar, *J. Magn. Magn. Mater.* 192 (1999) 130.
- [15] W.A. Harrison, *The Electronic Structure and Properties of Solids*, Freeman, San Francisco, 1980.