

Effect of Zn substitution on para- to ferromagnetic transition temperature in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ colossal magnetoresistance materials

V. P. S. Awana,^{a)} E. Schmitt, and E. Gmelin

Max-Planck-Institut für Festkörperforschung Heisenbergstr-1, D-70569 Stuttgart, Germany

Anurag Gupta, A. Sedky, and A. V. Narlikar

National Physical Laboratory, K. S. Krishnan Marg, New Delhi 110012, India

O. F. de Lima and Claudio A. Cardoso

Instituto de Física, "Gleb Wataghin," UNICAMP 13083-970, Campinas, SP, Brazil

S. K. Malik

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400005, India

W. B. Yelon

Research Reactor Facility, University of Missouri, Columbia, Missouri 65211

Structural, magnetic, and thermal measurements are carried out on the $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ system with $x=0.0-0.50$. The structural characterization of the samples is done by Rietveld analysis of their neutron diffraction patterns. Zn substitutes at Mn site isostructurally until $x=0.30$. Oxygen content remains nearly invariant with x . Magnetic and thermal measurements as well as the electrical resistance show a para- to-ferromagnetic transition at T_p , which decreases with an increase of x . For low Zn concentration (until $x=0.075$) the decrease dT_p/dx is smaller than for the larger concentrations of Zn. Relative decrease dT_p/dx at higher concentrations ($x>0.10$) is similar to that observed earlier for the $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ system. For the transition at T_p , the related change of magnetic entropy (ΔS_{trs}) are calculated from the heat capacity data and indicate that for $x=0$ the expected value $\Delta S_{\text{trs}}=12.8\text{ J/mol K}$ is recovered. © 2000 American Institute of Physics. [S0021-8979(00)26508-0]

I. INTRODUCTION

The invention of high temperature superconductivity (HTSc) in perovskite oxide cuprates^{1,2} initiated a hectic research of material scientists towards similar perovskite oxides, which might not be cuprates or even not superconductors. A novel material, with the nominal formula $\text{RE}_{1-x}\text{Ea}_x\text{MnO}_{3\pm\delta}$ (where $\text{RE}=\text{La, Pr, Nd, Sm, etc}$, $\text{Ea}=\text{Ca, Sr, Ba, Pb, etc}$), belonging to perovskite oxide magnetites, was reinvented in 1993.^{3,4} These compounds show a very large colossal magnetoresistance (CMR) that makes them interesting for practical applications. Besides their potential practical applicability, the fundamental research on knowing the actual mechanism of the CMR phenomenon has also attracted great interest.⁵⁻¹² What is known by now is that T_p , the paramagnetic-to-ferromagnetic (pf) transition temperature, where the CMR occurs, is highly sensitive to x , the doping concentration and δ , the oxygen deficiency in $\text{RE}_{1-x}\text{Ea}_x\text{MnO}_{3\pm\delta}$ samples.⁸⁻¹² By changing x with fixed δ or vice versa, one essentially changes the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio in these compounds.^{7,13} There exists a clear relation between T_p and the amount of Mn^{4+} ions. In addition, most of these compounds go through a structural phase transition (trigonal to orthorhombic) often coupled with the pf transition and accompanied with a change in sign of charge carriers at T_p .^{14,15}

The doping mechanism for changing $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio in the CMR materials is quite similar to that as followed for

the HTSc compounds to control effective Cu valency. In both cases variation of the Mn/Cu valency is achieved by either aliovalent substitution and/or by changing overall oxygen content which determines the value of T_p or T_c ^{1,2,7} (T_c , superconducting transition temperature). Similar to HTSc compounds, both Cu and Mn can be substituted partially by other 3d metals like Co, Ni, Fe, and Zn. In case of CMR compounds, Mn-site (3d) metal substitutions were also carried out¹⁶⁻²² and the results were explained in terms of changed $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. T_p decreased monotonically with increasing Fe concentration and disappeared for 18 at. % Mn/Fe substitution.¹⁶⁻¹⁸ Keeping in mind that Cu/Zn substitution in HTSc cuprates resulted in interesting physics, it seemed useful to study the same in CMR materials also. This is the aim of present study. T_p decreases with an increase of x as it is seen from resistivity, magnetization, and heat capacity versus temperature measurements. The relative decrease of T_p with Mn/Zn substitution is similar to that observed for other 3d metal substitutions on Mn-site,¹⁹⁻²¹ but different to Fe.¹⁶⁻¹⁸ We could find only few reports^{21,22} on Mn-site Zn substitution in CMR materials and that also for fixed Zn concentration of 5 at. %²¹ and 15 at. %.²²

II. EXPERIMENT

Samples of the series $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ with $x=0.0-0.50$ were synthesized through a solid-state reaction route. Magnetization measurements were performed on a physical property measurement system from Quantum Design, in an applied dc field of 0.5 T. Heat capacity measurements were carried out in temperature range from 100 to 300

^{a)}Electronic mail: awana@tilux.mpi-stuttgart.mpg.de

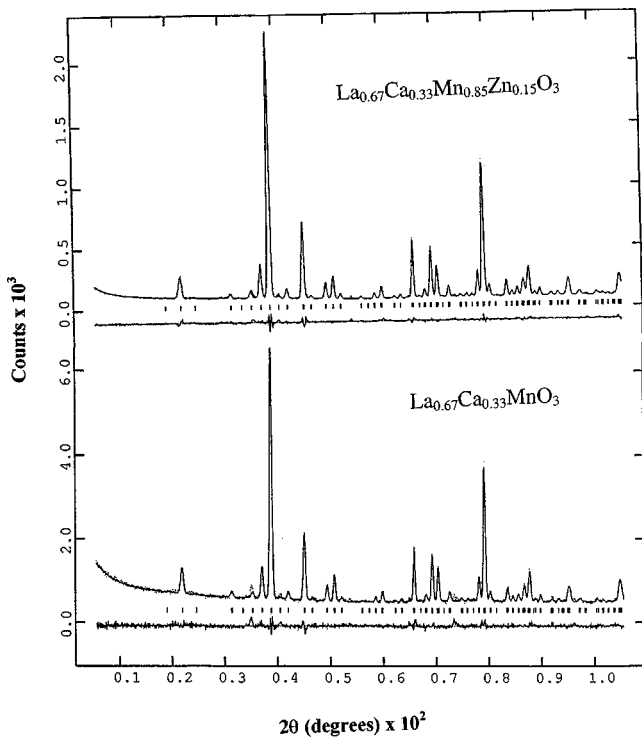


FIG. 1. Fitted and observed Neutron diffraction patterns for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ system with $x=0.0$ and 0.15 , taken at room temperature. The vertical bars marked at the bottomset of fitted and observed spectrum are for the LaCaMnO_3 (CMR compounds) with space group $Pnma$.

K using a commercial scanning calorimeter (DSC-2, from Perkin Elmer). Neutron diffraction patterns at room temperature were obtained using the research reactor facility at the University of Missouri.

III. RESULTS AND DISCUSSION

Figure 1 shows the neutron diffraction patterns for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ with $x=0.0$ and 0.15 . Both the patterns are similar from which we conclude that Zn substitutes isostructurally at the Mn site in these compounds. Also,

TABLE I. Lattice parameters, oxygen content, fractional occupancies, and selected bond lengths for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ ($x=0.0, 0.05, 0.10$, and 0.15). The numbers in parentheses give the estimated deviation in the last significant digit(s). Typical atomic positions, which vary slightly depending on the composition, are La,Ca (0.0, 1/2, 0), Mn,Zn (0, 0, 1/2), O(1) (1/2, 1/4, 0), and O(2) (1/4, 0, 3/4).

	$x=0.0$	$x=0.05$	$x=0.10$	$x=0.15$
$a(\text{\AA})$	5.4610(7)	5.4503(7)	5.4548(5)	5.4532(4)
$b(\text{\AA})$	7.7155(10)	7.6978(10)	7.7020(7)	7.7008(5)
$c(\text{\AA})$	5.4779(7)	5.4673(6)	5.4690(5)	5.4684(4)
O(1)	0.99(2)	1.02(3)	1.03(2)	1.07(2)
O(2)	1.0×2	1.0×2	1.0×2	1.0×2
Oxygen content	2.99(2)	3.03(2)	3.03(3)	3.07(2)
Mn-O(1) (\AA)	1.9554(10)	1.9450(8)	1.9511(6)	1.9524(6)
Mn-O(2) (\AA)	1.957(5)	1.943(4)	1.9549(31)	1.9579(30)
	1.968(5)	1.974(4)	1.9656(30)	1.9606(30)
wR_p	0.0454	0.0531	0.0549	0.0466
R_p	0.0335	0.0372	0.0395	0.0340

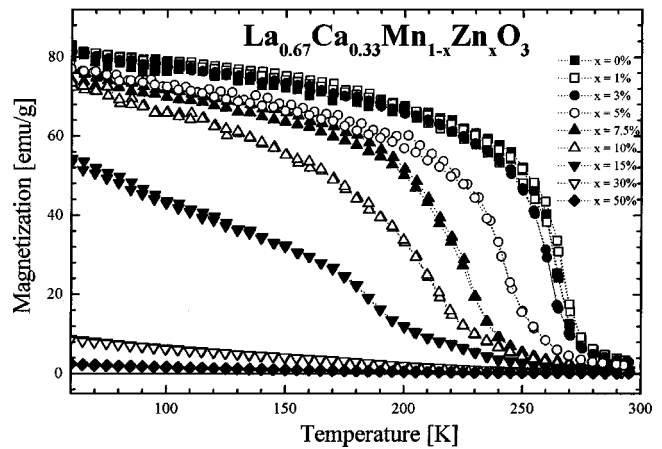


FIG. 2. Magnetization vs temperature plots for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ system.

x-ray diffraction patterns of all the $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ samples show that Zn substitutes isostructurally up to $x=0.30$ beyond which the x-ray patterns contain some extra lines. Lattice parameters, oxygen content, and selected bond lengths for these samples deduced from Rietveld analysis of the neutron diffraction data are listed in Table I. The lattice parameters and oxygen content are nearly the same for all x up to 0.15 due to nearly similar ionic size of $\text{Mn}^{3+,4+}$ and Zn^{2+} . The Mn-O(1) and Mn-O(2) bond distances also are nearly unchanged. Some oxygen occupancies refine to more than one which may be renormalized to conclude some deficiency in metal ions.

Figure 2 depicts the magnetization (M) versus temperature. Obviously the pf-transition temperature (T_p) decreases with increasing x . This is corroborated by the insulator-to-metal transition temperature seen as a large anomaly in the electrical resistivity measurements (plots are not shown). As expected, for most of the polycrystalline bulk materials T_p is not sharp, but the pf transition takes place over a broad temperature range of nearly 5–50 K, depending on x . The transition temperature $T_p(M)$ derived from $M(T)$ curves are tabulated in Table II. They were determined as the crossing point between the $M(T)$ curve, extrapolated from high temperatures, and the tangent on the inflection point on the high-

TABLE II. Para- to ferromagnetic transition temperatures (T_p) for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ system deduced from magnetization $M(T_p)$ and heat capacity $C_p(T_p)$, change of entropy ($\Delta S'_{\text{trs}}$) reflected to pf transition deduced from specific heat curves in the range 100–300 K and taking $x=0.30$ as reference, and ΔS_{trs} , the transition entropy corrected by contributions estimated from below 100 K and from the magnetic part of $x=0.30$ sample.

Sample	$T_p(M)$ (K)	$T_p(C_p)$ (K)	$(\Delta S'_{\text{trs}})$ (J/mol K)	ΔS_{trs} (J/mol K)
$x=0.0$	277	274	6.4	12.8
$x=0.03$	270	271	6.5	12.8
$x=0.05$	255	253	5.1	10.7
$x=0.075$	238	240	3.75	8.9
$x=0.10$	220	225	2.9	7.7
$x=0.15$	185	...	2.3	7.3
$x=0.30$

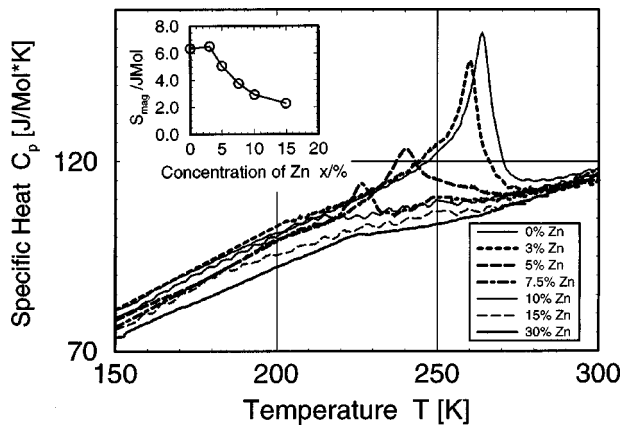


FIG. 3. Heat capacity (C_p) vs temperature plots for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zn}_x\text{O}_3$ system, measurements have been made down to 100 K. Inset shows $\Delta S'_{\text{trs}}$ as a function of x .

temperature side of the $M(T)$ anomaly. For $x > 0.15$, T_p is no more clearly seen neither in both, M vs T and R vs T measurements, nor in the specific heat C_p .

Figure 3 shows the heat capacity (C_p) versus temperature plots. The samples ($x = 0, 0.03, 0.05, 0.075$) show well defined peaks, but only a less pronounced hump for $x = 0.1$ and no anomaly for $x = 0.15$ and 0.30 (similar to the M vs T and R vs T experiments). The transitions $T_p(C_p)$ shift to lower temperatures with increased x values and coincide excellently with $T_p(M)$ (see Table II). Thereby, $T_p(C_p)$ have been calculated by application of the same method as used for the determination of $T_p(M)$ (see earlier). The change of entropy (ΔS_{trs}) related with T_p can be calculated from $C_p(T)$ by subtracting the lattice contribution. Theoretically, the expected entropy change ΔS_{trs} for magnetic ordering of a mixture of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ions is: $\Delta S_{\text{trs}} = 0.67R \ln 5 + 0.33R \ln 4 = 12.8 \text{ J/mol K}$, since for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (similar to other CMR compounds) 1/3 of the Mn ions are Mn^{4+} with spin $S = 3/2$ and 2/3 are Mn^{3+} with $S = 2$. Obviously the peaks displayed in Fig. 3 show $\Delta S_{\text{trs}} \ll 12.8 \text{ J/mol K}$, as observed by other groups.^{23,24} However, it is noticed that for magnetic transitions near 280 K, a considerable part of entropy is contained in $C_p(T)$ below 100 K.²⁵ Therefore, in a first step we took the $C_p(T)$ curve (in the range 100–300 K) for $x = 0.3$ (without anomaly) as approximated lattice heat and subtracted this curve from all others. The resulting $\Delta S'_{\text{trs}}$ is given in Table II. $\Delta S'_{\text{trs}}$ as a function of x decreases as shown in the inset of Fig. 3. The following estimate however shows that for $x = 0$ the expected full entropy is presumably engaged: (i) the entropy below 100 K amounts to $\Delta S_{\text{cor}}(< 100 \text{ K}) \cong 2.5 \text{ J/mol K}$ according to Ref. 22, (ii) assuming a magnetic heat of 2.5 J/mol K for $x = 0.3$ (the present lattice reference) would give an additional ΔS_{cor} , around transition $\cong 3.7 \text{ J/mol K}$. The full entropy estimated includes these corrections yield: $\Delta S_{\text{trs}} = [(6.4 + 2.5 + 3.7) \pm 1.5] \text{ J/mol K}$ (for $x = 0.0$). For the other samples the values, decreasing with x are listed in Table II.

The effect of depression of $T_p[dT_p/dx(\text{Zn})]$ by substitution of Zn is similar to that observed when $3d$ metals sub-

stituted in LaCaMnO_3 for $x > 0.10$.^{16–22} But for low x values ($x < 0.10$) it appears that dT_p/dx is much slower [$dT_p/dx(\text{Zn}) = 4.9 \text{ K/at. \%}$] in the present case, which [$dT_p/dx(\text{Fe})$] is 24 K/at. \% for Fe substitution.¹⁶ A similar situation is reported in Refs. 21 and 22, where two fixed concentrations of Zn, respectively 5 and 15 at. % are studied. Relatively higher valence substitution of $\text{Fe}^{3+,4}$ at Mn site in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ might decrease the Mn^{4+} ratio faster in the system when compared with partial substitution of Mn by fixed valent Zn^{2+} . This might be a possible explanation why dT_p/dx decreases less at low x in the present case.

ACKNOWLEDGMENTS

V.P.S.A. acknowledges the Brazilian Science Agency FAPESP for financial support through Contract No. 97/12325-7 during preliminary stage of this work. Part of the work at MURR was supported by US Department of Energy Grant No. DF-FG02-90ER4527.

- ¹J. G. Bednorz and K. A. Müller, Z. Phys. B: **64**, 189 (1986).
- ²R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zharuk, and D. Werder, Nature (London) **329**, 423 (1987).
- ³R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
- ⁴G. Radaelli, D. E. Cox, M. Marezio, S. W. Cheong, P. E. Schiffer, and A. P. Ramirez, Phys. Rev. Lett. **75**, 4488 (1995).
- ⁵A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).
- ⁶C. N. R. Rao, R. Mahesh, A. K. Raychaudhuri, and R. Mahendiran, J. Phys. Chem. Solids **59**, 487 (1998).
- ⁷J. B. Goodenough, J. Appl. Phys. **81**, 5330 (1997).
- ⁸Y. Moritomo, A. Asamitsu, and Y. Tokura, Phys. Rev. B **51**, 16491 (1995).
- ⁹I. V. Medvedeva, Y. S. Bersenev, K. Bärner, L. Haupt, R. Mandal, and A. Poddar, Physica B **229**, 194 (1997).
- ¹⁰G. C. Xiong, Q. Li, H. L. Ju, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **66**, 1689 (1995).
- ¹¹S. Jin, T. H. Tiefel, M. McCormack, H. M. O. Bryan, L. H. Chen, R. Ramesh, and D. Schurig, Appl. Phys. Lett. **67**, 557 (1995).
- ¹²K. M. Satyalakshmi, B. Fisher, L. Patlagan, G. Koren, E. Sheriff, R. Prozorov, and Y. Yeshurun, Appl. Phys. Lett. **73**, 402 (1998).
- ¹³H. L. Ju, C. Kwon, Qi. Li, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **65**, 2108 (1994).
- ¹⁴J. Barratt, M. R. Lees, G. Balakrishnan, and D. Mck Paul, Appl. Phys. Lett. **68**, 424 (1996).
- ¹⁵A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, Nature (London) **373**, 407 (1995).
- ¹⁶K. H. Ahn, X. W. Wu, K. Liu, and C. L. Chien, J. Appl. Phys. **81**, 5505 (1997).
- ¹⁷G. Kallias, M. Pissas, E. Devlin, A. Simopoulos, and D. Niarchos, Phys. Rev. B **59**, 1272 (1999).
- ¹⁸A. Tkachuk et al., Phys. Rev. B **57**, 8509 (1998).
- ¹⁹N. Gayathri, A. K. Raychaudhuri, S. K. Tiwary, R. Gundakaram, A. Arulraj, and C. N. R. Rao, Phys. Rev. B **56**, 1345 (1997).
- ²⁰M. Rubinstein, D. J. Gillepsie, J. E. Snyder, and T. M. Tritt, Phys. Rev. B **56**, 5412 (1997).
- ²¹K. Ghosh, S. B. Ogle, R. Ramesh, R. L. Greene, T. Venkatesan, K. M. Gapchup, R. Bathe, and S. I. Patil, Phys. Rev. B **59**, 533 (1999).
- ²²R. Yonghong, X. Zhuan, Y. Wihua, J. Zhengkuan, and Z. Qirui, D. W. Xuebao **19**, 293 (1997) (Chinese Journal).
- ²³A. P. Ramirez, S.-W. Cheong, and P. Schiffer, J. Appl. Phys. **81**, 5337 (1997).
- ²⁴L. Ghivelder, I. C. Abrego, N. M. Alford, G. J. Tomka, P. C. Rieldi, J. M. Driscoll, A. K. M. A. Hossain, and L. F. Cohen, J. Magn. Magn. Mater. **189**, 274 (1998).
- ²⁵J. E. Gordon, R. A. Fisher, Y. X. Jia, N. E. Phillips, S. F. Reklis, D. A. Wright, and A. Zettl, Phys. Rev. B **59**, 127 (1999).