LETTER TO THE EDITOR

Effect of Internal Pressure on Charge-Ordered Rare Earth Manganates

C. N. R. Rao,*,†,[1] P. N. Santhosh,* R. S. Singh,† and A. Arulraj*

* *Solid State and Structural Chemistry Unit and CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560 012, India; and*
† *Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India*

The effect of internal pressure on charge-ordered rare earth manganates of the composition $Ln_{1-x}A_xMnO_3$ ($Ln =$ La, Pr, Nd and $A =$ Ca, Sr) has been studied by varying the average radius of the A site cations ($\langle r_A \rangle$). Increasing $\langle r_A \rangle$ is generally accompanied by an increase in the ferromagnetic transition temperature and a decrease in the charge-ordering transition temperature. On increasing the size of the A site cations by appropriate substitution, charge-ordered insulators such as $Pr_{0.7}Ca_{0.3}MnO_3$ and $Nd_{0.5}Ca_{0.5}MnO_3$ become ferromagnetic, accompanied by an insulator-metal transition. In $Pr_{0.5}Sr_{0.5}MnO_3$, substitution of La in place of Pr destroys the antiferromagnetic transition and favors the ferromagnetic metallic state. © 1998 Academic Press

Rare earth manganates of the composition $Ln_{1-x}A_x$ MnO_3 (Ln = La, Pr, Nd and $A =$ Ca, Sr) not only exhibit colossal magnetoresistance, but also fascinating effects due to charge-ordering of the Mn^{3+} and Mn^{4+} ions (1–3). Charge-ordering is favored when the proportions of Mn^{3+} and Mn^{4+} are comparable (say, $x = 0.5$) and is very sensitive to the weighted average ionic radius of the A site cation, $\langle r_A \rangle$. This is because $\langle r_A \rangle$ determines the $\langle$Mn–O–Mn$\rangle$ angle or the one-electron bandwidth. Two types of charge-ordering in the manganates have been delineated (3, 4). When $\langle r_A \rangle$ is fairly large, as in $Nd_{0.5}Sr_{0.5}MnO_3$ ($\langle r_A \rangle = 1.24$ Å), the manganate transforms from a ferromagnetic metallic (FMM) state to a charge-ordered (CO) antiferromagnetic (AFM) state (CE type), and the latter can be melted by the application of a magnetic field (5). However, when $\langle r_A \rangle$ is very small, as in $Y_{0.5}Ca_{0.5}MnO_3$, the cooperative Jahn–Teller effect becomes more important than the magnetic interactions, and the material remains a charge-ordered insulator down to the lowest temperature without exhibiting ferromagnetism; magnetic fields have no effect on the insulating state of this manganate (4, 6). $\langle r_A \rangle$ in the rare earth manganates also determines the ferromagnetic Curie temperature, with T_c increasing with $\langle r_A \rangle$, analogous to the effect of external pressure (7, 8). We have investigated the effect of internal pressure on charge-ordered manganates by varying $\langle r_A \rangle$ through appropriate cation substitutions in the A site. Such a study was expected to show how the Curie point, T_c, the charge-ordering temperature, T_{CO}, and the electronic properties vary with internal pressure and demonstrate how the properties of these manganates can be finely tuned by this means. Since we initiated the study, we have noticed a paper by Moritomo *et al.* (9) on the effect of pressure on the charge-ordering transition of manganates. The present study involving a variety of manganate systems, however, helps to establish unambiguously the effect of varying the internal pressure by chemical substitution.
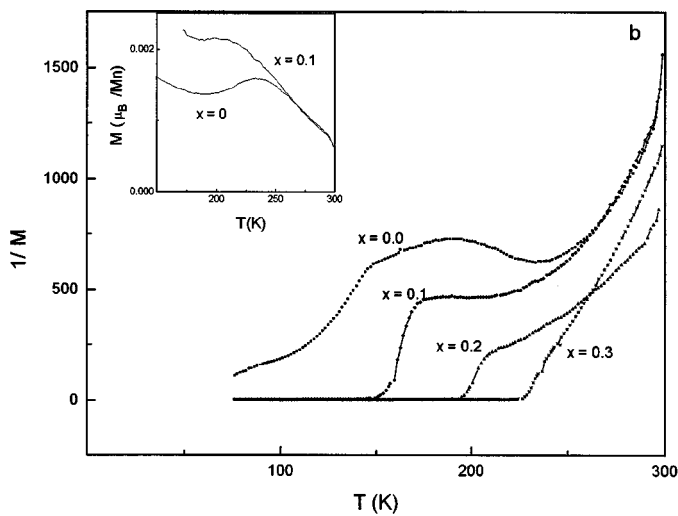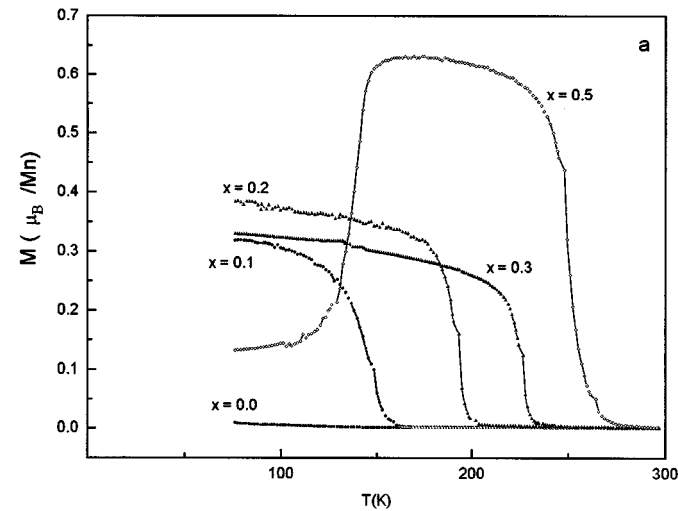
To study the effect of internal pressure on charge-ordering in $Ln_{1-x}A_xMnO_3$, we have investigated the following systems: (1) $Nd_{0.5}Ca_{0.5-x}Sr_xMnO_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.5$); (2) $Nd_{0.5-x}La_xCa_{0.5}MnO_3$ ($x = 0.0, 0.25$); (3) $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x = 0.0, 0.1, 0.2, 0.3$); (4) $Pr_{0.7-x}La_xCa_{0.3}MnO_3$ ($x = 0.0, 0.4$); and (5) $Pr_{0.5-x}La_xSr_{0.5}MnO_3$ ($x = 0.0, 0.1, 0.2, 0.5$). In systems 1 and 2, we are able to study the effect of substitution of Sr in place of Ca, or La in place of Nd in $Nd_{0.5}Ca_{0.5}MnO_3$, which is a charge-ordered insulator with a small $\langle r_A \rangle$ (1.17 Å) and a fairly high T_{CO} of 240 K (10). The $X = 0.5$ composition in 1 transforms from a FMM state to an AFM CO state around 150 K in a first-order fashion (5). Systems 3 and 4 afford a study of the effect of substitution of Sr in place of Ca, or La in place of Pr, in the charge-ordered insulator $Pr_{0.7}Ca_{0.3}MnO_3$ ($\langle r_A \rangle = 1.17$ Å) with a charge-ordering transition at ~ 220 K (11). System 5 represents the effect of substitution of La in place of Pr in $Pr_{0.5}Sr_{0.5}MnO_3$ which transforms from a ferromagnetic state to an AFM state (A type) without a clear sign of charge-ordered state at the Néel temperature (12).

The manganates samples were prepared by the conventional ceramic method using appropriate mixtures of oxides and/or carbonates of the constituent elements. The mixtures were first heated at 1200°C in air and finally at

---

[1] To whom correspondence should be addressed.

1400°C/1500°C. The phase purity was established by recording the X-ray diffraction patterns with a JEOL JDX-8P diffractometer. The lattice parameters of the various compositions along with the respective $\langle r_A \rangle$ values are listed in Table 1. Electrical resistivity measurements were carried out from 300 to 20 K by the four-probe method. DC magnetization measurements were made with a vibrating sample magnetometer (Lakeshore 7300) in an applied magnetic field of 100 Oe.

In Fig. 1a, the magnetization data of the $Nd_{0.5}Ca_{0.5-x}Sr_xMnO_3$ system are shown. We see that the Curie temperature, as indicated by the sharp increase in the magnetization (M), increase with increases in x. The $x = 0$ composition does not show ferromagnetism and remains in the CO state down to low temperatures. The charge-ordering transition temperature in this composition at 240 K is
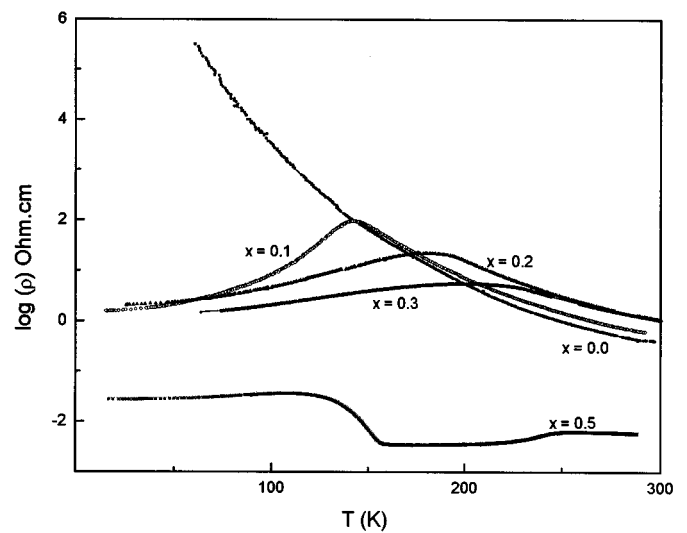
TABLE 1
Structure Parameters of the Manganates

System/Composition	Lattice parameters (Å)				
	$\langle r_A \rangle$ (Å)	a	b	c	V (Å^3)
$Nd_{0.5}Ca_{0.5-x}Sr_xMnO_3$					
$x = 0.0$	1.17	5.389	5.415	7.611	222.10
$x = 0.1$	1.18	5.406	5.430	7.619	223.67
$x = 0.2$	1.20	5.415	5.452	7.638	225.49
$x = 0.3$	1.21	5.417	5.460	7.639	225.93
$x = 0.5$	1.24	5.424	5.478	7.619	226.38
$Nd_{0.5-x}La_xCa_{0.5}MnO_3$					
$x = 0.0$	1.17	5.389	5.415	7.611	222.10
$x = 0.25$	1.19	5.420	5.422	7.645	224.81
$Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$					
$x = 0.0$	1.18	5.436	5.481	7.661	228.23
$x = 0.1$	1.19	5.449	5.486	7.698	230.12
$x = 0.2$	1.21	5.452	5.493	7.699	230.55
$x = 0.3$	1.22	5.462	5.495	7.701	231.16
$Pr_{0.7-x}La_xCa_3MnO_3$					
$x = 0.0$	1.18	5.436	5.481	7.661	228.23
$x = 0.4$	1.19	5.458	5.469	7.715	230.29
$Pr_{0.5-x}La_xSr_{0.5}MnO_3$					
$x = 0.0$	1.24	5.402	5.402	7.780	227.03
$x = 0.2$	1.25	5.425	5.425	7.789	229.23
$x = 0.4$	1.26	5.466	5.485	7.687	230.46
$x = 0.5$	1.26	5.482	5.488	7.716	232.14

evidenced from the broad minimum in the inverse magnetization curve (Fig. 1b) or the maximum in the magnetization curve (see inset of Fig. 1b). In the $x = 0.1$ composition, the charge-ordering transition is shifted to ~ 210 K. Thus, there is an increase in T_c and a decrease in T_{CO}, with increasing internal pressure, induced by increasing $\langle r_A \rangle$.

FIG. 1. Temperature variation (a) of the magnetization and (b) of the inverse magnetization of $Nd_{0.5}Ca_{0.5-x}Sr_xMnO_3$. Inset in (b) shows the variation of magnetization of two compositions over a narrow range.

FIG. 2. Temperature variation of the logarithm of resistivity of $Nd_{0.5}Ca_{0.5-x}Sr_xMnO_3$.

The magnetization behavior in Fig. 1 is reflected in the resistivity data (Fig. 2). The $x = 0$ composition is an insulator down to very low temperatures. With the substitution of Ca by Sr, an insulator–metal (I–M) transition manifests itself, with the transition temperature increasing with x. The temperatures corresponding to the I–M transition, T_{im}, are comparable to the T_c values from Fig. 1a. In $Nd_{0.5-x}La_x Ca_{0.5}MnO_3$, the material becomes ferromagnetic when $x = 0.25$, with a T_c of ~ 160 K, accompanied by an I–M transition around that temperature (Fig. 3). This result again shows how an increase in $\langle r_A \rangle$ by substitution of La in place of Nd transforms a CO state to a FMM state.

Substitution of Sr in place of Ca in $Pr_{0.7}Ca_{0.3}MnO_3$ brings about drastic changes in the magnetization and electrical resistivity. In Fig. 4a, we show how with increase in x in $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$, T_c increases. The $x = 0.1$ compositon has a T_c of 150 K while the $x = 0.3$ composition
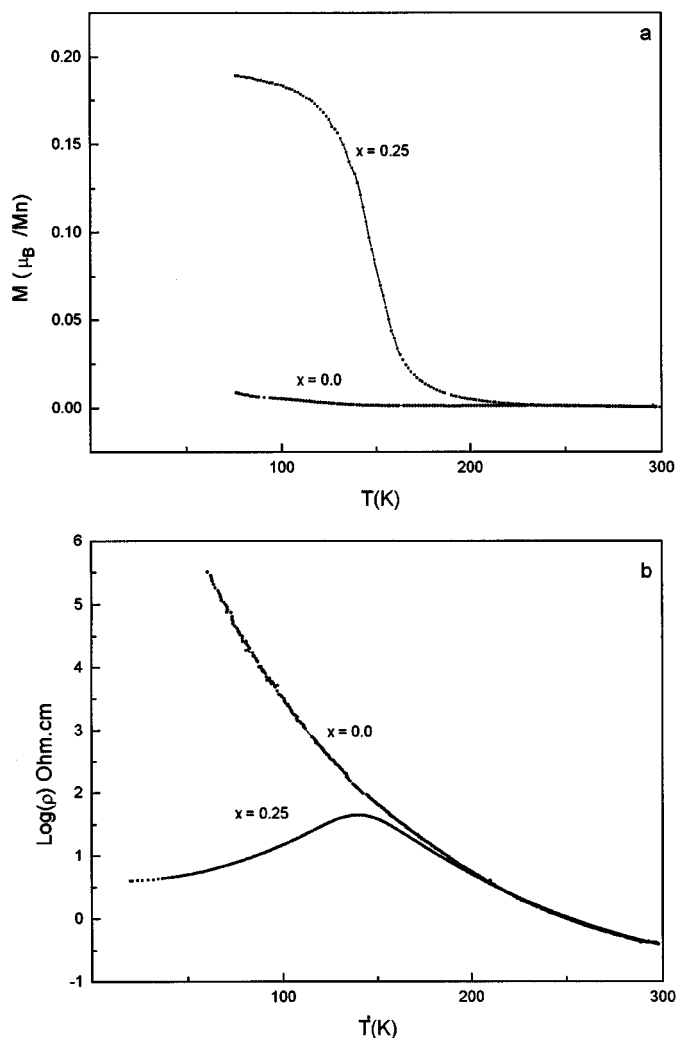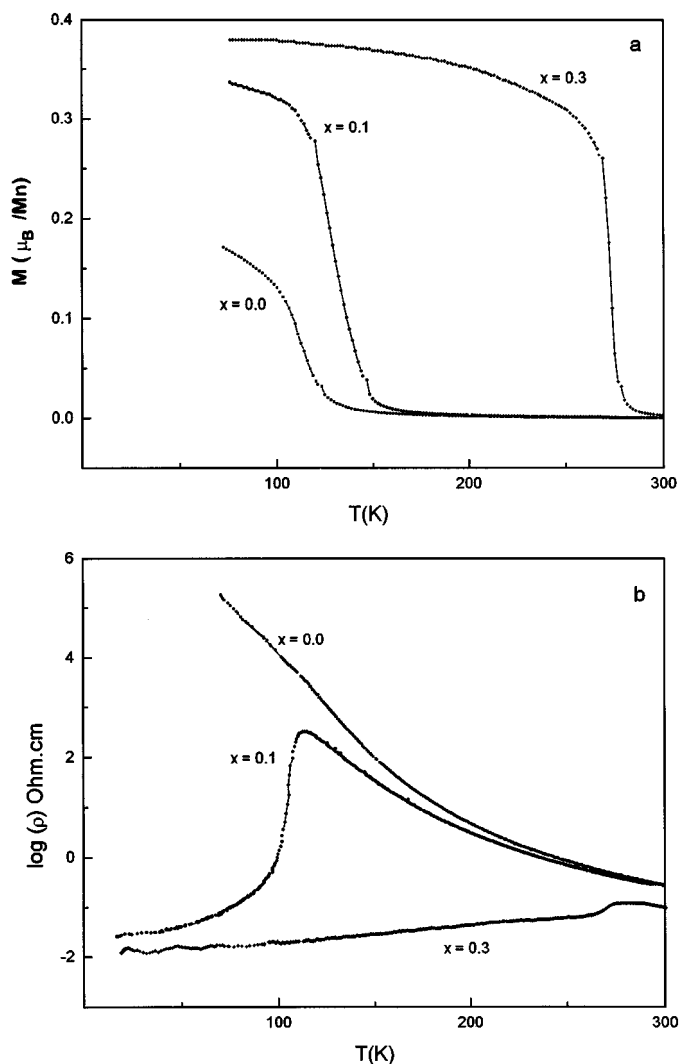

FIG. 4. Temperature variation (a) of the magnetization and (b) of the logarithm of resistivity of $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$.

FIG. 3. Temperature variation (a) of the magnetization and (b) of the logarithm of resistivity of $Nd_{0.5-x}La_xCa_{0.5}MnO_3$.

has a T_c of ~ 275 K. We see weak spontaneous magnetization in $Pr_{0.7}Ca_{0.3}MnO_3$ below 120 K due to spin–glass behavior (13). With increasing x, the temperature of the I–M transition also increases (Fig. 4b). The T_{im} and T_{CO} values are comparable. The effect of substitution of La in place of Pr in $Pr_{0.7}Ca_{0.3}MnO_3$ is comparable to that of Sr in place of Ca. Thus, the $x = 0.4$ composition shows a T_c of ~ 140 K, and the I–M transition occurs around 100 K (Fig. 5).

In Fig. 6, we show the effect of substitution of La in place of Pr in $Pr_{0.5}Sr_{0.5}MnO_3$. The $x = 0$ composition shows the ferromagnetic T_c around 260 K, and a transition to the AFM state (A type) at ~ 140 K (12). The $x = 0.2$ composition shows a well-defined Néel temperature but the $x = 0.4$ and $x = 0.5$ compositions do not. With progressive substitution of Pr by La, there is a marked increase in T_c
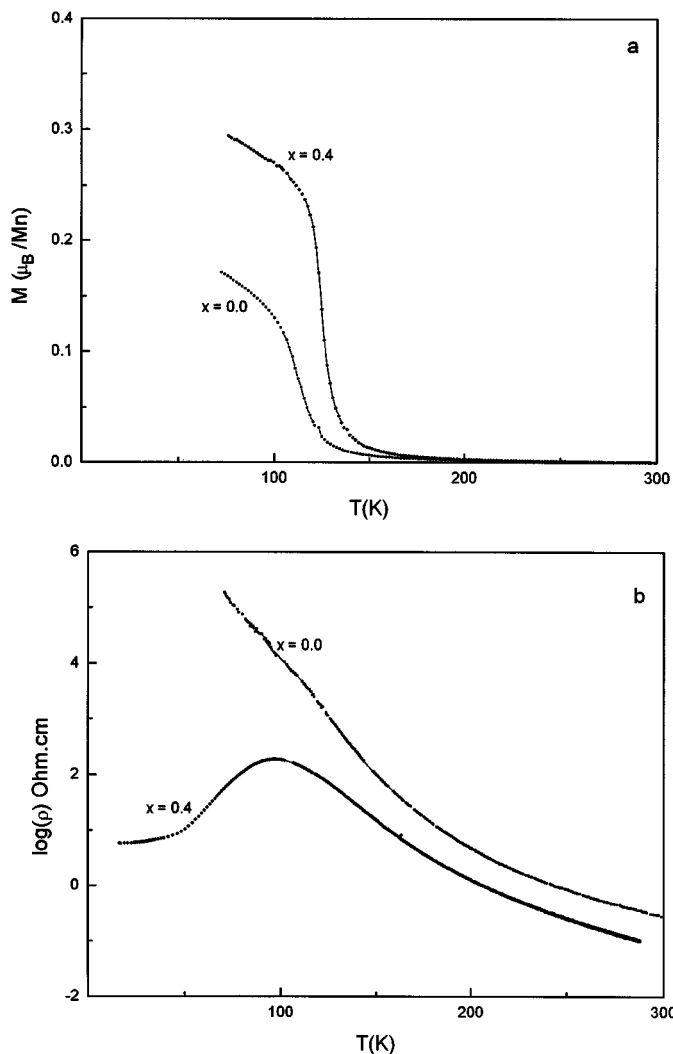
FIG. 5. Temperature variation (a) of the magnetization and (b) of the logarithm of resistivity of $Pr_{0.7-x}La_xCa_{0.3}MnO_3$.

FIG. 6. Temperature variation (a) of the magnetization and (b) of the logarithm of resistivity of $Pr_{0.5-x}La_xSr_{0.5}MnO_3$.

(Fig. 6a). The resistivity of the $x = 0$ sample shows metallic behavior below T_c and an increase in resistivity around T_N (Fig. 6b). The $x = 0.2$ sample shows a comparable behavior, but the increase in resistivity below T_N is smaller in magnitude. The $x = 0.4$ and 0.5 compositions exhibit metallic behavior from 300 to 100 K, but there is an upward trend in resistivity below 100 K (see inset of Fig. 6b). When Nd in $Nd_{0.5}Sr_{0.5}MnO_3$ is partly substituted by Pr, we have found that both T_c and T_N increase, suggesting the nature of the AMF interaction to be different after the substitution (possibly of CE type).

In conclusion, the present study of charge-ordered manganates demonstrates how $\langle r_A \rangle$ crucially determines the magnetic and electrical properties of these materials. A small increase in $\langle r_A \rangle$ or the internal pressure destroys the charge-ordered state, rendering the material ferromagnetic. Insulator–metal transitions occur in such ferromag-
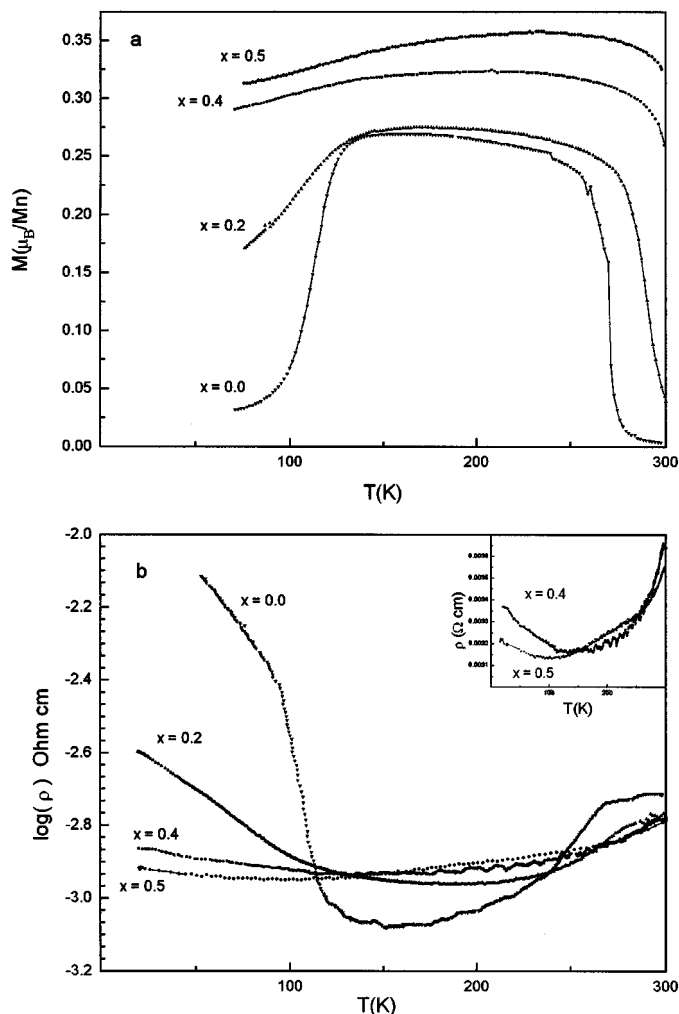
netic compositions, with T_{im} values comparable to T_c values. The ferromagnetic T_c increases with an increase in internal pressure, while T_{CO} decreases. The present results are consistent with the observations of Moritomo et al. (9) based on the effect of external pressure on charge-ordered manganates.

REFERENCES

1. Y. Tokura, Y. Tomioka, H. Kuwahara, A. Asamitsu, Y. Moritomo, and M. Kasai, *J. Appl. Phys.* **79,** 5288 (1996).
2. C. N. R. Rao, A. K. Cheetham, and R. Mahesh, *Chem. Mater.* **8,** 2421 (1996).
3. C. N. R. Rao and A. K. Cheetham, *Science* **276,** 911 (1997).
4. N. Kumar and C. N. R. Rao, *J. Solid. State. Chem.* **129,** 363 (1997).

5. H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, *Science* **270,** 961 (1995).

6. A. Arulraj, R. Gundakaram, N. Gayathri, A.K. Raychaudhuri, and C. N. R. Rao, *Phys. Rev. B.*, in press.

7. H. Y. Hwang, S.-W. Cheong, P. G. Radelli, M. Marezio, and B. Batlogg, *Phys. Rev. Lett.* **75,** 914 (1995).

8. R. Mahesh, R. Mahendiran, A. K. Raychaudhuri, and C. N. R. Rao, *J. Solid State Chem.* **120,** 204 (1995).

9. Y. Moritomo, H. Kuwahara, Y. Tomioka, and Y. Tokura, *Phys. Rev. B* **55,** 7549 (1997).

10. T. Vogt, A. K. Cheetham, R. Mahendiran, A. K. Raychaudhuri, R. Mahesh, and C. N. R. Rao, *Phys. Rev. B* **54,** 15303 (1996).

11. Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, *Phys. Rev. B* **53,** 1689 (1996); M. R. Lees, J. Baratt, G. Balakrishnan, D. McK. Paul, and M. Yethiraj, *Phys. Rev. B* **52,** 14303 (1995).

12. H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara, and Y. Tokura, *Phys. Rev. Lett.* **78,** 4253 (1997).

13. H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, *Phys. Rev. B* **52,** 13145 (1995).