

**EFFECT OF SUBSTITUTION OF  $Mn^{3+}$  BY OTHER TRIVALENT CATIONS ON THE COLOSSAL MAGNETORESISTANCE AND RELATED PROPERTIES OF THE MANGANATES:  $La_{0.7}A_{0.3}Mn_{1-x}M_xO_3$  (A = Ca, Sr, Pb; M = Al, Cr, Fe, Co)****M. Sugantha<sup>1</sup>, R.S. Singh<sup>1</sup>, A. Guha<sup>2</sup>, A.K. Raychaudhuri<sup>2</sup>, and C.N.R. Rao<sup>1\*</sup>**<sup>1</sup>Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India<sup>2</sup>Department of Physics, Indian Institute of Science, Bangalore 560 012, India

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**ABSTRACT**

Investigations of the manganates of the general formula  $La_{0.7}A_{0.3}Mn_{1-x}M_xO_3$  with A = Ca, Sr, or Pb and M = Al, Cr, Fe, or Co in the x range 0.00–0.20 have shown that the ferromagnetic  $T_c$  and the insulator–metal transition temperature,  $T_p$ , generally decrease with increase in x, accompanied by an increase in the resistivity at  $T_p$ . The value of the saturation magnetization and, hence, the saturation moment also decrease with increase in x. The magnitude of magnetoresistance is generally smaller in the Fe and Co substituted systems when A = Pb. However, with A = Sr, we find enhanced colossal magnetoresistance in the 50–250 K range when x = 0.1 for M = Fe and Co. Interestingly, these systems exhibit a nearly flat resistivity curve over this temperature range. © 1998 Elsevier Science Ltd

**KEYWORDS:** A. oxides, C. X-ray diffraction, D. electrical properties, D. magnetic properties

**INTRODUCTION**

Rare-earth perovskites of the general formula  $Ln_{1-x}A_xMnO_3$  (Ln = rare earth, A = alkaline earth) exhibiting fascinating properties such as ferromagnetism and the associated insulator–metal (I–M) transition, colossal magnetoresistance (CMR), and other properties have been

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investigated extensively in the last 3 years [1]. Cation-deficient  $\text{LaMnO}_3$  has been shown to exhibit properties similar to  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  [2]. Investigations of cation-deficient  $\text{La}_{1-x}\square\text{MnO}_3$  and  $\text{LaMn}_{1-x}\square\text{O}_3$  have shown that while  $\text{La}^{3+}$  vacancies are tolerated up to 10% without destroying CMR and related properties, vacancies in the  $\text{Mn}^{3+}$  site have a detrimental effect because the  $\text{Mn}^{3+}$  ions are part of the active electrical network in these oxides [3]. There have been a few recent studies on the effect of substitution of  $\text{Mn}^{3+}$  in  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  by other trivalent cations such as Al and Fe. The substitution of  $\text{Fe}^{3+}$  in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  [4] or of  $\text{Al}^{3+}$  in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  and  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  [5,6] generally appear to decrease the I–M transition temperature,  $T_p$ , without significantly affecting CMR, when the dopant concentration is not very high. We considered it important to carry out a systematic study of the variation of  $T_p$ , the ferromagnetic Curie temperature  $T_c$ , and the CMR in  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  with different A-site ions as well as with different dopant ions. The purpose of this study was not only to examine the systematics, but also to determine whether CMR can be optimized with respect to its magnitude as well as the temperature range. In this context, it is noteworthy that CMR is favored by a decrease in temperature and increase in resistivity at  $T_p$  [7]. In the present study, we have investigated  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  with  $\text{M} = \text{Al}, \text{Cr}, \text{Fe},$  or  $\text{Co}$  and  $x = 0.01\text{--}0.05$ ,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  with  $\text{M} = \text{Fe}, \text{Co}$  and  $x = 0.0\text{--}0.2$ , and  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  with  $x = 0.00\text{--}0.15$ .

## EXPERIMENTAL

$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $\text{M} = \text{Al}, \text{Cr}, \text{Fe},$  and  $\text{Co}$ ) samples were prepared as follows: To solutions of the dopant metal (Al, Cr, Fe, or Co) in nitric acid were added the required quantities of the oxides/carbonates of La, Ca, and Mn. The nitrate cake thus obtained was decomposed at 773 K in air and the resulting powder was heated at 1173 K and then sintered at 1273 K for 24 h. Manganates of the type  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $\text{M} = \text{Fe}, \text{Co}$ ) samples were prepared by a similar method, except that the nitrate precursor was heated at 1273 K and then sintered at 1573 K for 24 h. The  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  samples were prepared by the nitrate route, but the sintering temperature was 1273 K.

The manganates were characterized by X-ray diffraction (XRD), using a Rich-Seifert XRD-3000TT diffractometer. The  $\text{Mn}^{4+}$  content was estimated by redox titrations. Magnetization of the samples were measured with a VSM instrument (Lakeshore model 3300) in a field of 0.01 T. Electrical resistivity and magnetoresistance measurements were performed on bar-shaped pellets, with the four-probe technique in the temperature range 15–350 K. Magnetic fields up to 6T were employed for magnetoresistance measurements.

The XRD patterns of the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  samples were indexed on a pseudocubic unit cell. The unit-cell parameters were in the  $7.72 \pm 0.01 \text{ \AA}$  range. The XRD patterns of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $\text{M} = \text{Fe}, \text{Co}$ ) and  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  were indexed on a rhombohedral unit cell. The rhombohedral  $a_R$  parameter is constant ( $\sim 5.456 \text{ \AA}$ ) up to a tolerance factor  $\tau$  of 0.936. When  $\tau > 0.936$ , as in  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ,  $a_R$  increases. The range of variation of  $a_R$  is from 5.456 to 5.500  $\text{ \AA}$ .

## RESULTS AND DISCUSSION

Typical resistivity data of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $\text{M} = \text{Cr}, \text{Fe}$ ) are shown in Figure 1. As  $x$  increases, the temperature at which the resistivity maximum occurs due to the I–M transition,

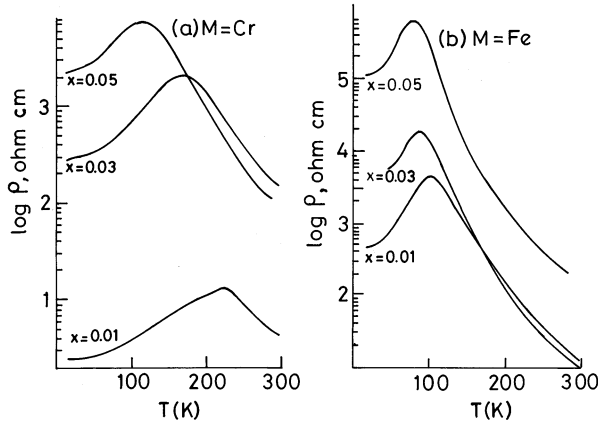


FIG. 1

Resistivity behavior of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  (a) with  $M = \text{Cr}$  and (b) with  $M = \text{Fe}$ .

$T_P$ , shifts to lower values. The resistivity of the material also increases with the increase in the  $x$  value. From Figure 2, we notice a similar behavior in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $M = \text{Fe}, \text{Co}$ ). The  $T_P$  in the parent compound,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.0$ ), is above 300 K. The  $T_P$  remains above 300 K for  $x \leq 0.03$  and gradually decreases to lower temperatures with increasing  $x$  value; the  $x = 0.2$  composition is insulating. The resistivity behavior of  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  is comparable to that of the  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $M = \text{Fe}, \text{Co}$ ) system. However, the I–M transition in the former, which occurs at 330 K in the parent compound with  $x = 0.0$ , sharply decreases to 227 K for  $x = 0.01$ . In all the manganates,  $\text{La}_{0.7}\text{A}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $A = \text{Ca}, \text{Sr}, \text{and Pb}; M = \text{Al}, \text{Cr}, \text{Fe}, \text{and Co}$ ), the percentage of  $\text{Mn}^{4+}$  decreases somewhat with the increase in the  $x$  content ( $x \geq 0.08$ ). This possibly is due to a small decrease in the oxygen content. Thus, when  $A = \text{Sr}$ , the  $\text{Mn}^{4+}$  content is  $\sim 20\%$  when  $x = 0.15$  for both  $M = \text{Fe}$  and  $\text{Co}$ . The same is true for  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ . An interesting feature in the resistivity curves in Figure 2 is that, close to  $x = 0.10$ , the maxima are broad, especially in the Co-substituted manganate. For all practical purposes, the resistivity in this system is nearly constant over a broad temperature range of 25–300 K.

In Figure 2 we show typical magnetization data for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $M = \text{Fe}, \text{Co}$ ). We note that the  $T_c$  is generally greater than  $T_P$  and that, like  $T_P$ ,  $T_c$  decreases with an increase in  $x$ . The value of the saturation magnetization,  $M_S$ , decreases with an increase in  $x$ . Thus, the saturation magnetic moment,  $\square_S$ , decreases progressively from  $3.6\square_B$  for  $x = 0.0$  to  $1.8\square_B$  for  $x = 0.10$ . This is consistent with the fact that the insulating state in the manganates is not ferromagnetic. The  $M_S$  and  $\square_S$  values decrease with  $x$  in a similar manner in  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ .

In Figure 3a, we show the variation of  $T_P$  with  $x$  in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ . The  $T_P$  decreases sharply for  $x = 0.01$  and then decreases marginally with further increase in  $x$  when  $M = \text{Al}, \text{Fe}, \text{or Co}$ . When  $M = \text{Cr}$ , there is a linear decrease of  $T_P$  with  $x$ . The peak resistivity,  $\rho_P$ , at the I–M transition increases markedly up to  $x = 0.01$  and then less significantly for higher values of  $x$ , when  $M = \text{Cr}, \text{Fe}, \text{or Co}$  (Fig. 3b). For  $M = \text{Al}$ ,  $\rho_P$  is nearly constant for  $x > 0.01$ . We have not observed any significant effect due to magnetic interactions between  $\text{Mn}^{3+}$  and  $\text{M}^{3+}$  ions in any of the systems we have studied, including

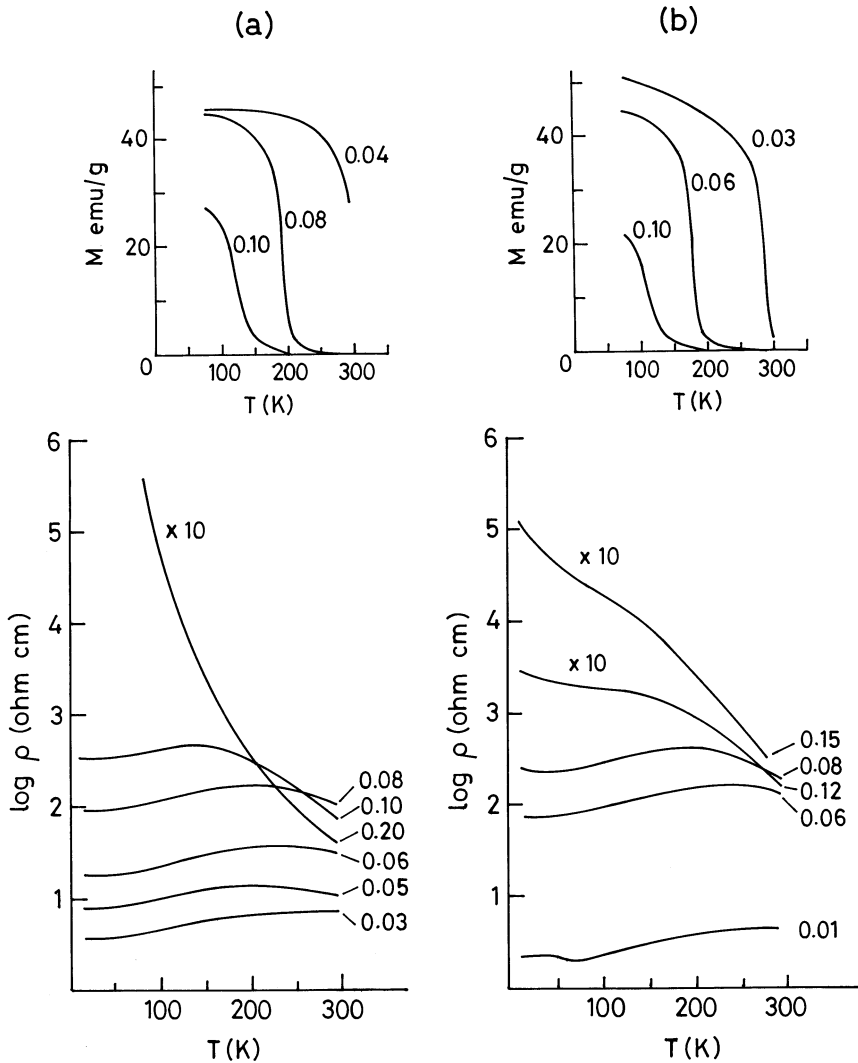


FIG. 2

Resistivity behavior of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  (a) with  $M = \text{Fe}$  and (b) with  $M = \text{Co}$ . Magnetization data are shown for a few compositions of the  $M = \text{Fe}$  and  $\text{Co}$  systems.

the  $\text{Cr}^{3+}$ -substituted compounds, where there can be ferromagnetic superexchange between  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$ .

In Figure 4, we show the variation of  $T_P$  and  $\rho_P$  with  $x$  for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $M = \text{Fe}, \text{Co}$ ) and  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ . The  $T_P$  decreases smoothly with the increase in  $x$  in the Sr system (Fig. 4a), accompanied by an increase in  $\rho_P$ . In the Pb-substituted system, the  $T_P$  decreases with the increase in  $x$ , but there is a plateau-like behavior for  $x = 0.04 \pm 0.02$ . In this region, the  $\rho_P$  also shows a plateau, although there is a general increasing trend with the increasing  $\text{Fe}^{3+}$  content.

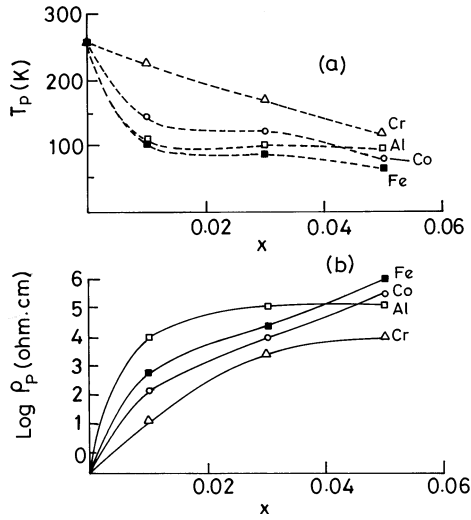


FIG. 3

Variation of (a) the insulator metal transition temperature,  $T_p$ , and (b) the peak resistivity at the transition,  $\rho_p$ , in  $La_{0.7}Ca_{0.3}Mn_{1-x}M_xO_3$  with  $x$ .

In Figure 5, we show the temperature variation of the magnetoresistance (MR) of a few compositions of  $La_{0.7}Sr_{0.3}Mn_{1-x}M_xO_3$  and  $La_{0.7}Pb_{0.3}Mn_{1-x}M_xO_3$  ( $M = Fe$  and  $Co$ ). In  $La_{0.7}Sr_{0.3}Mn_{1-x}M_xO_3$ , the magnitude of MR is smaller in the  $x = 0.03$  compositions

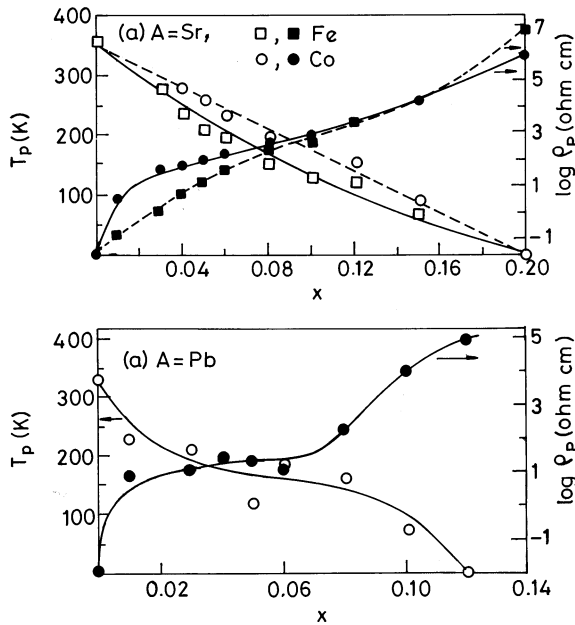


FIG. 4

Variation of  $T_p$  and  $\rho_p$  in (a)  $La_{0.7}Sr_{0.3}Mn_{1-x}M_xO_3$  ( $M = Fe, Co$ ) and (b)  $La_{0.7}Pb_{0.3}Mn_{1-x}Fe_xO_3$ .

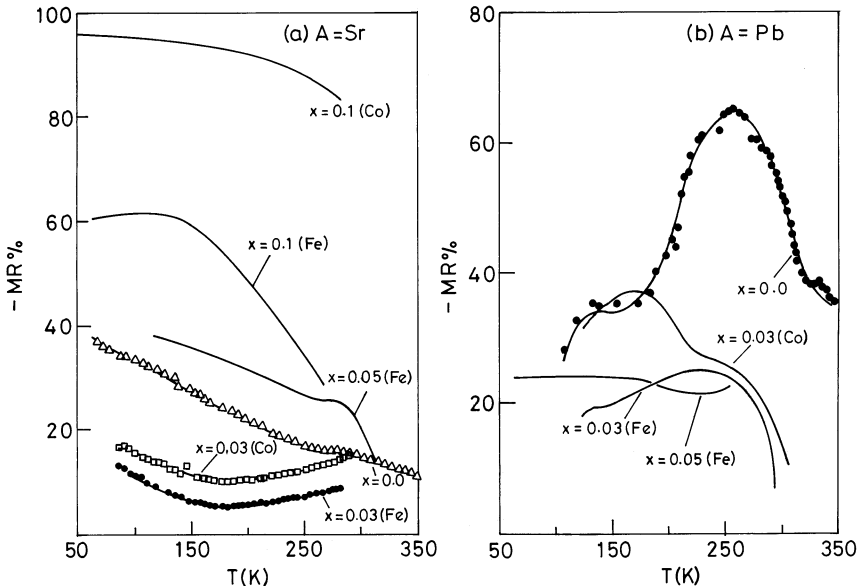


FIG. 5

Temperature variation of the magnetoresistance in (a)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $\text{M} = \text{Fe}, \text{Co}$ ) and (b)  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{M}_x\text{O}_3$  ( $\text{M} = \text{Fe}, \text{Co}$ ).

compared to the parent  $x = 0.00$  composition. The magnitude of MR is higher when  $0.05 \leq x \leq 0.10$ , especially in the  $x \approx 0.10$  compositions, where the resistivity maxima are broad (Fig. 2). This could be due partly to the effect of grain size. The nearly constant and very high CMR (80–90%) in the  $x = 0.10$  ( $\text{M} = \text{Co}$ ) composition is noteworthy (see Fig. 5a). In the Pb system, MR is generally lower in both the Fe- and Co-substituted compositions (Fig. 5b).

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