

# STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF HIGH CONCENTRATION IN DOPED $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$

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*Abstract:* Structural and electrical properties of high concentration of indium doped  $\text{ABO}_3$  typed colossal magnetoresistance  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LCMO) perovskite were studied using DC four point probe system, X ray diffractometry, and scanning electron microscopy.  $(\text{La}_{1-x}\text{In}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LICMO) samples of concentration  $x = 0.0, 0.4, 0.5$  and  $0.6$  with sample  $x=0.0$  as a reference were prepared using the solid state reaction method. XRD study shows Indium doped samples exhibit the effect of reduced  $\langle r_A \rangle$  ionic radius with the decreasing of the cell volume of the samples with increasing In concentration. XRD study also shows appearance of secondary phase with increasing intensity with incorporation of indium. SEM micrographs shows porosity decreased with high In doping with fused grains and unclear grain boundaries. Electrical transport studies show the metal to insulator transition temperature  $T_p$  is hugely dropped to lower temperature from 194 K of  $x=0.0$  to 70.9 K at  $x=0.4$  and is slightly decreased with further In doping. Ac susceptibility shows that ferromagnetic interactions are decreasing with increasing In content suggesting weakening DE interactions.

Keywords: Perovskite, Susceptibility

## INTRODUCTION

The perovskite manganites  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Ca}, \text{Ba}, \text{and Sr}$ ) is a magnetic system with diverse magnetic ordering structures that varies with concentration of dopant A [2]. The discovery of colossal magnetoresistance (CMR) in the metallic phase as large as 100 fold in polycrystalline  $(\text{La}-\text{Y}-\text{Ca})\text{MnO}_3$  and 10000 fold in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  epitaxial thin films has revived a great interest in this system [6]. The study of CMR effect may be important technologically for a new generation of magnetic sensors and recording devices as well as fundamentally in helping our understanding of the strongly correlated electron systems. Research in these compounds indicates that CMR occurs near its  $T_c$ , the ferromagnetic to paramagnetic transition temperature, which is also usually near the phase transition temperature,  $T_p$ . It is known by now that  $T_c$  and  $T_p$  are very sensitive to the doping concentration,  $x$ , and the oxygen deficiency,  $\delta$ , in the  $\text{RE}_{1-x}\text{Ea}_x\text{MnO}_3$  samples. By changing  $x$  with fixed  $\delta$  or vice versa will essentially bring changes to the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio in these compounds. It is also reported that  $T_c$  is also related to the average A-site ionic radius  $\langle r_A \rangle$  and the tolerance factor  $t$ , defined as  $(r_A + r_B) / \sqrt{2}(r_B + r_O)$ , where  $r_A$ ,  $r_B$  and  $r_O$  are ionic radii at A site, B site, and oxygen respectively [4]. A study on doping effects on A site, such as on lanthanum site for  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  may help in our understanding of the lattice effects. In this work a series of polycrystalline samples with nominal composition  $(\text{La}_{1-x}\text{In}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LICMO) with high In concentration,  $x = 0.4$  to  $0.6$  and  $x=0.0$  as a reference were investigated. Indium is a nonmagnetic trivalent metal and has ionic radius smaller than that of lanthanum, a magnetic trivalent metal. By replacing lanthanum with indium the relationship between A site ionic radius and the structure and the electrical properties were studied.

## MATERIALS AND METHODS

Bulk polycrystalline samples of  $(\text{La}_{1-x}\text{In}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  ( $x=0.0, 0.4$  to  $0.6$ ) were prepared via conventional solid-state reaction in air. Stoichiometric mixtures of high purity (99.9%)  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MnCO}_3$  and  $\text{In}_2\text{O}_3$  were ball-milled for 6 hours and later calcined at  $900^\circ\text{C}$  for 12 hours. The resulting powders were reground, pressed into pellets and sintered at  $1300^\circ\text{C}$  in air at  $2^\circ\text{C}/\text{min}$  for 24 hrs and then cooled at the same rate to room temperature. The samples structures were checked by x ray diffraction (XRD) by using a Philip x-ray diffractometer with a rotating anode at room temperature

with Cu  $K\text{-}\alpha$  radiation. The electrical properties of the samples were evaluated using conventional DC four probe method with closed cycle helium refrigerator in the temperature range of 20 to 300 K [1].

## RESULTS AND DISCUSSIONS

Figure 1 shows the x ray diffractogram for LICMO samples. It is shown that samples  $x=0.0$  has pure LCMO phase as reported by Coey et. al. [5]. Samples with In concentration  $x=0.4$  to  $0.6$  show an appearance of a secondary phase due to incorporation of higher In concentration at La site. A slight shift of  $2\theta$  from the pure phase is also detected for  $x=0.4$  to  $0.6$  with increasing intensity of secondary phase. Table 1 shows the lattice constants and the cell volumes of LICMO samples from the XRD diffractogram. It is shown that the LICMO samples  $x=0.0$ ,  $x=0.4$  and  $x=0.5$  are orthorhombic but sample LICMO  $x=0.6$  is tetragonal. The cell volume of the pure sample  $x=0.0$  is  $233.12 \text{ \AA}^3$ , and is decreasing with increasing In doping. It is reported from literature [5] the structure of LCMO is slightly distorted from cubic structure due to Jahn Teller distortion in order to accommodate smaller A site ionic radius due to incorporation of Ca cation. With incorporation of In at La site, the smaller In ionic radius causes the Jahn Teller distortion to reduce the cell volumes further as shown in figure 2.

Table 1: Lattice parameters of  $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5,$  and  $0.6$ .

X	a	b	C	$c/2^{1/2}$	Cell volume
0.0	5.40	5.54	7.78	5.51	233.12
0.4	5.41	5.45	7.69	5.44	226.38
0.5	5.40	5.45	7.69	5.42	226.21
0.6	5.42	5.42	7.67	5.40	225.35

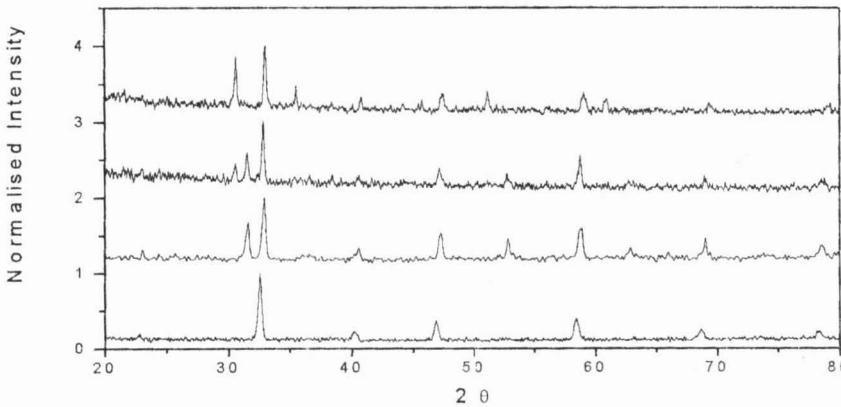


Figure 1: X-ray diffractogram of  $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5,$  and  $0.6$

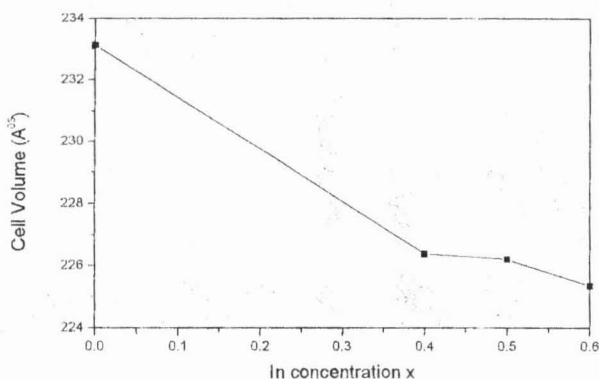
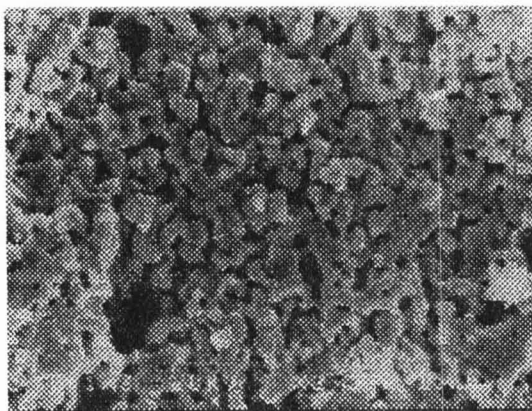


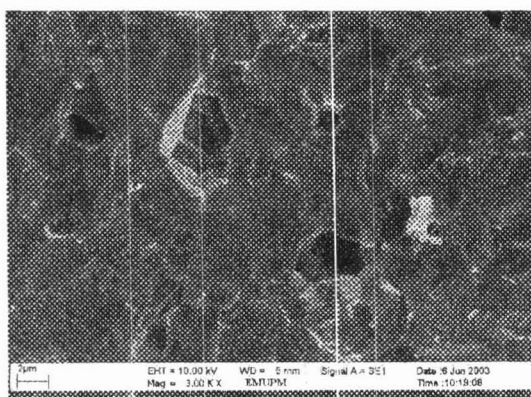
Figure 2: The cell volume variation of In concentration  $x$  of  $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5, 0.6$

Figure 3 shows the SEM micrographs of LICMO samples. The undoped sample,  $x=0.0$ , has uniform grain size with an average of  $3\mu m$ . It also has high level of porosity and lowest density among the samples. At samples  $x=0.4$  to  $0.6$ , the grains tend to fuse with no clear grain boundary is observed. The average grain size decreases to within range of about  $2.1\mu m$  at  $x=0.4$  to  $2.5\mu m$  at  $x=0.6$ . The level of porosity is reduces at sample  $x=0.4$  and further reduced with increasing In concentration.

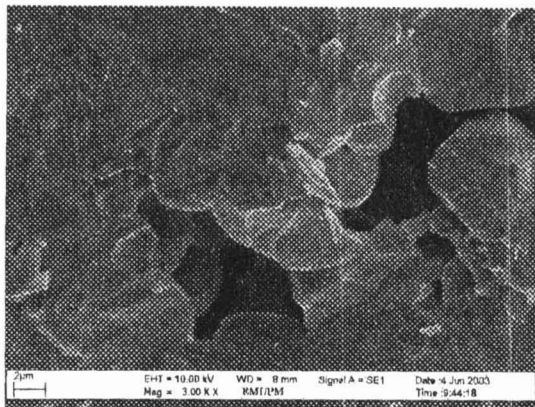
Figure 4 shows the temperature variation of normalized resistance of LICMO samples. The resistance for each sample is normalized with the resistance at temperature  $300\text{ K}$ . All LICMO samples show metal to insulator transition at phase transition temperature  $T_p$ . The  $T_p$  of LICMO sample  $x=0.0$  is  $194\text{ K}$  and is still within reported value in literature [5]. The  $T_p$  for LICMO samples  $x=0.4, 0.5$  and  $0.6$  is sharply dropped from  $x=0.0$  at  $194\text{ K}$  to  $70.9\text{ K}, 70.4$  and  $67.8\text{ K}$  respectively as shown in figure 5. The  $T_p$  for LICMO samples is DE interactions weakening electrical conductions and thus increases the resistance in the samples.



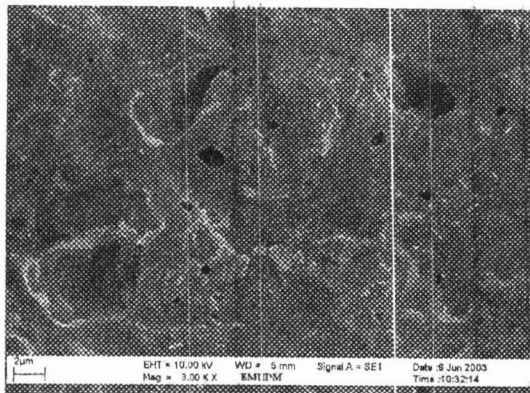
$x=0.0$



$x=0.4$



x=0.5



x=0.6

Figure 3: SEM micrograph of  $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5,$  and  $0.6$

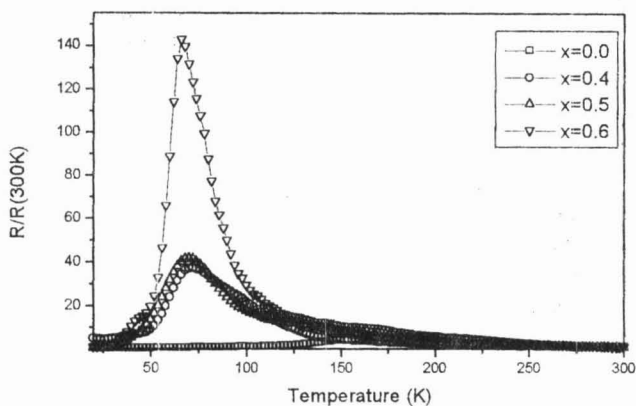


Figure 4: The temperature dependence of normalized resistance of  $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5,$  and  $0.6$

Figure 6 shows the In concentration variation of maximum normalized resistance of LICMO samples. The maximum normalized resistance for LICMO samples increases slightly from  $x=0.0$  to  $x=0.4$  and  $x=0.5$ . The maximum normalized resistance increases sharply from  $x=0.5$  to  $x=0.6$  indicating increased resistance due to decreasing DE interactions which is caused by decreasing Mn-O-Mn bond angle due to Jahn Teller distortion to accommodate smaller A site ionic radius.

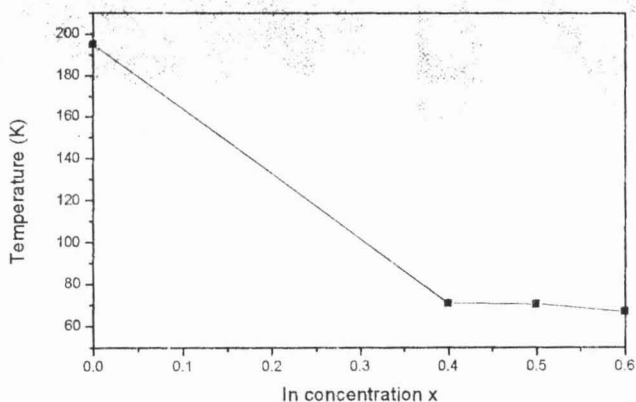


Figure 5: The In concentration variation of phase transition temperature of  $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5,$  and  $0.6$

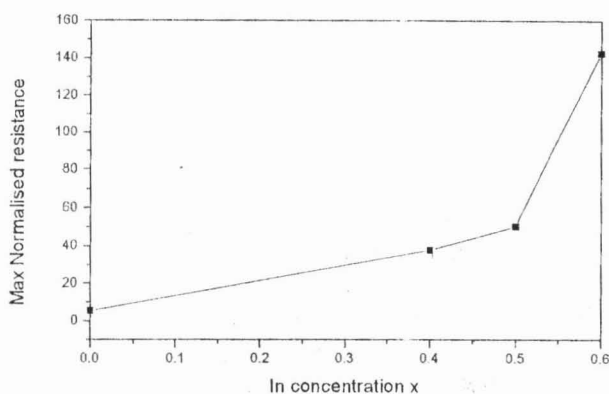


Figure 6: In concentration dependence of maximum normalized resistance of  $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5,$  and  $0.6$

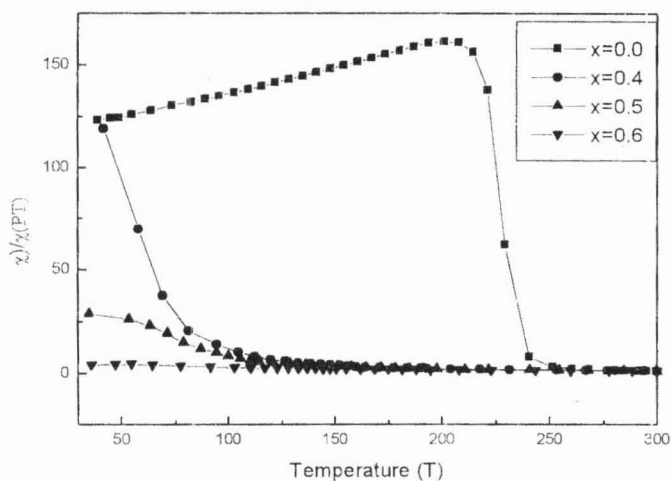


Figure 7: Temperature dependence of normalized susceptibility for  $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$  with  $x=0.0, 0.4, 0.5,$  and  $0.6$

Figure 7 shows the temperature variation of normalized susceptibility of LICMO samples. Sample LICMO with In concentration  $x=0.0$  shows typical ferromagnetic to paramagnetic transition with  $T_C$  around 210 K. Sample with In concentration  $x=0.4$  shows a beginning of a transition from paramagnetic phase to ferromagnetic phase at lower transition temperature around 52K while sample with In concentration  $x=0.5$  and  $0.6$  shows a much lower susceptibility intensity suggesting decreasing ferromagnetic interactions with higher In doping at lower temperature.

As In ions are substituted for La in LCMO system, it has been shown to shrink the unit cell volume as well as lanthanide ionic radius  $\langle r_{RB} \rangle$ . The experiments reported by Hwang et al. (1995) [3] showed that when La is partially substituted by Y or Pr in the  $La_{0.7}Ca_{0.3}MnO_3$  compound, significant changes in resistance, magnetoresistance and Curie temperature occur. It is indicated that substituting smaller rare-earth ions for La with fixed carrier concentration in La-Ca-Mn-O reduces the average ionic radius of the A site  $\langle r_A \rangle$ . The principal effect of decreasing  $\langle r_A \rangle$  is to decrease the Mn-O-Mn bond angle, and cause the Mn ions to get closer to each other and hence change the electron hopping between the Mn sites. In LICMO samples, it is observed that there is a relationship between the  $T_p$  and  $\langle r_A \rangle$  for  $x=0.4$  to  $x=0.6$ . The substituting effect of In for this range of concentration is to reduce the  $T_p$  of LICMO samples slightly from 70.9 K to 67.8 K as well as the cell volume. As the Mn-O-Mn bond angle reduces from  $161^\circ$  from undoped LCMO sample, the electrons hopping between Mn sites are getting more and more difficult. Subsequently, double exchange interactions among Mn-O-Mn bond are

reduced and ferromagnetic interactions resulting from the electrons exchange are less favoured. Hence the resistance is increased with increasing  $\langle r_A \rangle$  resulting lower  $T_P$  with increasing In concentration.

## CONCLUSION

LICMO samples with In doping at La site show the effect of reduced Mn-O-Mn bond angle by incorporation of smaller In ionic radius. XRD study shows increasing intensity of secondary phase with decreasing LCMO phase with In concentration. The cell volume is also decreased due to distortion in the orthorhombic structure with increasing In concentration which transform LICMO samples  $x=0.6$  to tetragonal structure. SEM micrographs shows decreasing level of porosity with In content. The grain boundaries also fused with average grains size within  $2.0 \mu\text{m}$  to  $2.5 \mu\text{m}$ . Resistance measurement indicates all samples show metal to insulator transition at temperature  $T_P$  with overall decreasing trend with increasing In dopant while the maximum normalized resistance is increased with In dopant indicating weakening of DE interactions which inhibit conduction within samples. This weakening DE interactions can be confirmed by ac susceptibility studies that shows weakening ferromagnetic interactions with increasing In doping.

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