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STRUCTURAL AND ELECTRICAL PROPERTIES OF HIGH CENCENTRATION IN DOPED $La_{2/3}$ $Ca_{1/3}$ MnO_3

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ABSTRACT. *Structural and electrical properties of high concentration of indium doped ABO_3 typed colossal magnetoresistance $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) perovskite were studied using DC four point probe system, X ray diffractometry, and scanning electron microscopy. $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ (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 $<r_A>$ ionic radius with the decreasing of the cell volume of the samples with increasing Indium concentration. XRD study also show the 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 dropped significantly to lower temperature from 194 K of x=0.0 to 70.9 K at x=0.4 and slightly decreased with further In doping.*

KEYWORDS: Perovskite, Susceptibility

INTRODUCTION

The perovskite manganites $La_{1-x}A_xMnO_3$ (A = Ca, Ba, and Sr) is a magnetic system with diverse magnetic ordering structures that varies with concentration of dopant A (Wollan *et al.*, 1955). The discovery of colossal magnetoresistance (CMR) in the metallic phase as large as 100 fold in polycrystalline (La-Y-Ca) MnO_3 and 10000 fold in $La_{0.67}Ca_{0.33}MnO_3$ epitaxial thin films has revived a great interest in this system (Abdullah Chik *et al.*, 2002). The study of CMR effect is important technologically especially in magnetic sensor industry in order to introduce new novel magnetic sensors and recording devices. The CMR research is also an important fundamental research in understanding 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, dð, in the $RE_{1-x}Ea_xMnO_3$ samples. By changing x with fixed dð or vice versa will essentially bring changes to the Mn^{3+}/Mn^{4+} ratio in these compounds. It is also reported that T_c is also related to the average A-site ionic radius <ðr_A>ð and the tolerance factor t, defined as $(r_A + r_B)$ Öð2$(r_B + r_O)$, where r_A, r_B and r_O are ionic radii at A site, B site, and oxygen respectively (Jonker *et al.*, 1950). A study on doping effects on A site, such as on lanthanum site for $La_{2/3}Ca_{1/3}MnO_3$ may help in our understanding of the lattice effects. In this work a series of polycrystalline samples with nominal composition $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ (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 which is a magnetic trivalent metal. The relationship between A site ionic radius and the structure and electrical properties were studied by substituting lanthanum with indium.

EXPERIMENTAL PROCEDURE

Bulk polycrystalline samples of $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ (x=0.0, 0.4 to 0.6) were prepared via conventional solid-state reaction in air. Stoichiometric mixtures of high purity (99.9%) La_2O_3, $CaCO_3$, $MnCO_3$ and In_2O_3 were ball-milled for 6 hours and later calcined at 900 ^{0}C for 12 hours. The resulting powders were reground, pressed into pellets and sintered at 1300 ^{0}C in air at 2 ^{0}C/min for 24 hrs and then cooled at the same rate to room temperature. X ray diffraction (XRD) patterns were collected by using a Philip x-ray diffractometer with a rotating anode at room temperature with Cu *K*- a 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 (Abdullah Chik *et al.*, 2002).

RESULTS AND DISCUSSION

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.* (1999). 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 qð 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 Å^3, and is decreasing with increasing In doping. It is reported from literature (Coey *et al.,* 1999) 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 (Å)	b (Å)	c (Å)	$c/2^{1/2}$ (Å)	cell volume ($Å^3$)
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

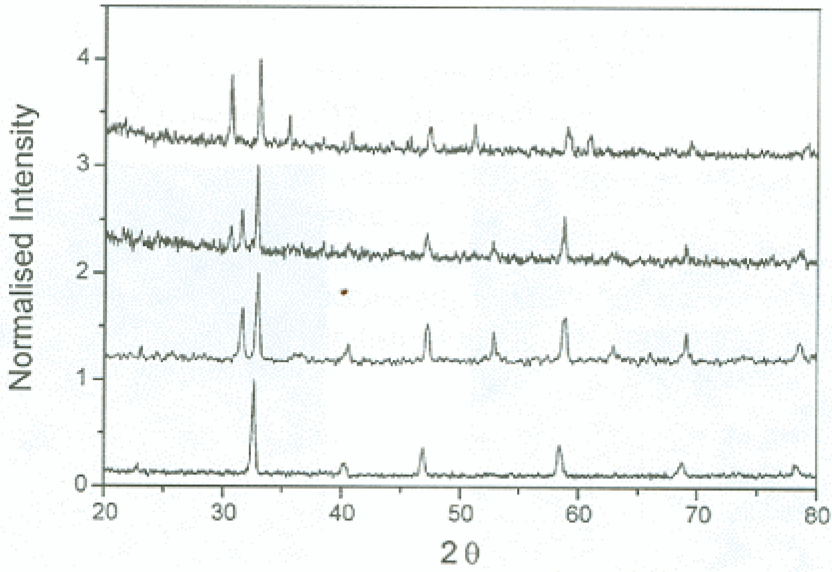


Figure 1. X-ray diffractogram of $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.4,0.5,and 0.6

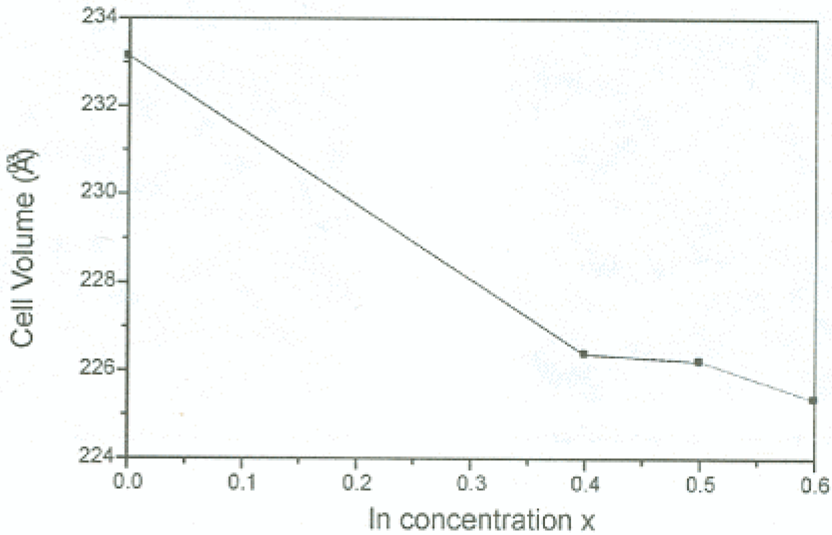
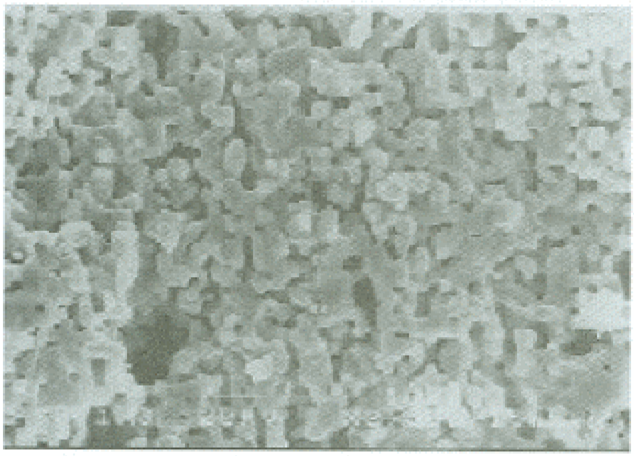


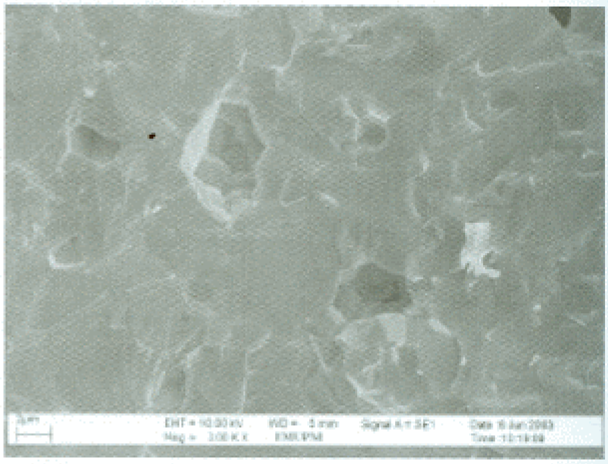
Figure 2. The cell volume variation of In concentration x of $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.4, 0.5, 0.6.

Figure 3 shows the SEM micrographs of LICMO samples. The undoped sample, x=0.0, has uniform grain size with an average of 3mm. It also has high level of porosity and the 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 mm at x=0.4 to 2.5 mm at x=0.6. The level of porosity is reduces at sample x=0.4 and further reduced with increasing In concentration.

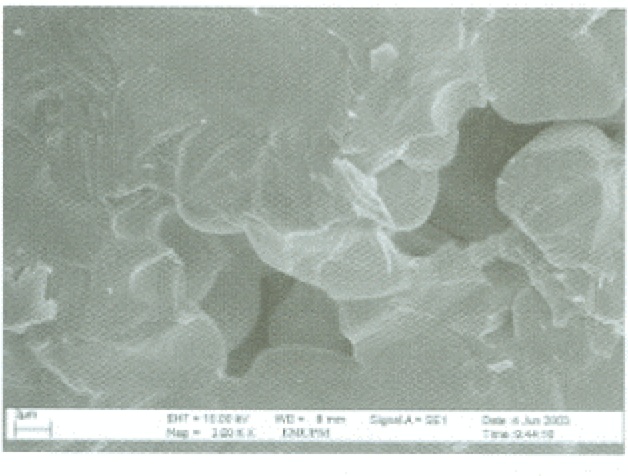
Figure 4 shows the temperature variation of normalized resistance of LICMO samples. The resistance for each sample is normalized with the resistance at temperature 300 K. All LICMO samples show metal to insulator transition at phase transition temperature T_P. The T_p of LICMO sample x=0.0 is 194 K and is still within reported value in literature (Coey et. al., 1999). The T_p for LICMO samples x=0.4, 0.5 and 0.6 is reduced significantly from x=0.0 at 194 K to 70.9 K, 70.4 and 67.8 K respectively as shown in Figure 5. The T_p for LICMO samples is decreased slightly with increasing In doping at higher concentration x=0.4 and above due to weaker DE interactions weakening electronic conductions and thus increases the resistance in the samples.



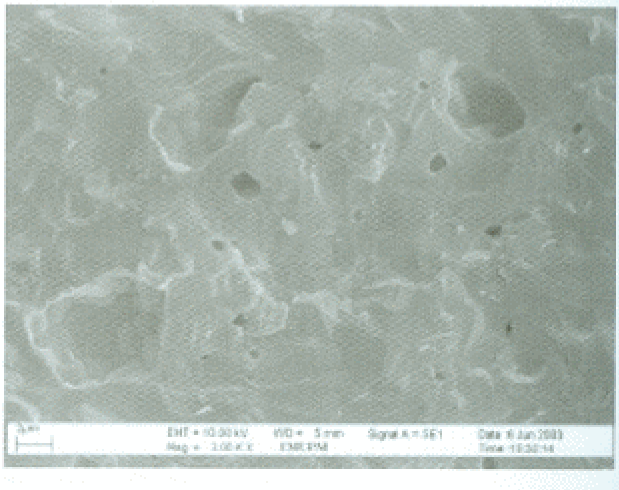
x=0.0



x=0.5



x=0.4



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 at 3.00K X magnification.

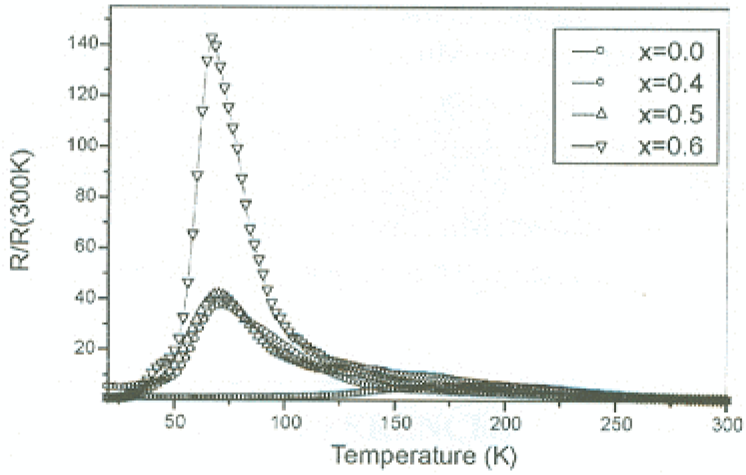


Figure 4. The temperature dependence of normalized resistance of $(L_{1x}In_x)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.4,0.5,and 0.6.

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 the 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.

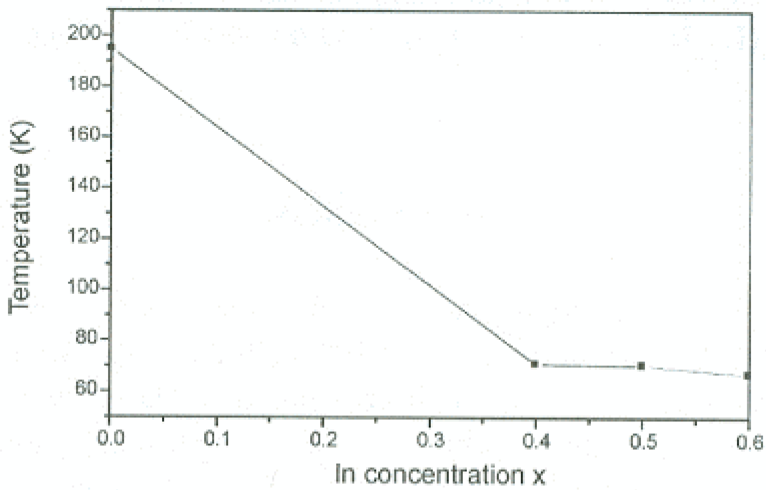


Figure 5. The In concentration variation of phase transition temperature of $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.4,0.5,and 0.6.

As In ions substituted for La in LCMO system, it has been shown to shrink the unit cell volume as well as lanthanide ionic radius $<r_{RE}>$. The experiments reported by Hwang *et al.* (1995) 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 $<r_A>$. The principal effect of decreasing $<r_A>$ 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 $<r_A>$ 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° from undoped LCMO sample, the electrons hopping between Mn sites are getting more and more difficult. Hence the resistance is increases with increasing $<r_A>$ resulting lower T_p with increasing In concentration.

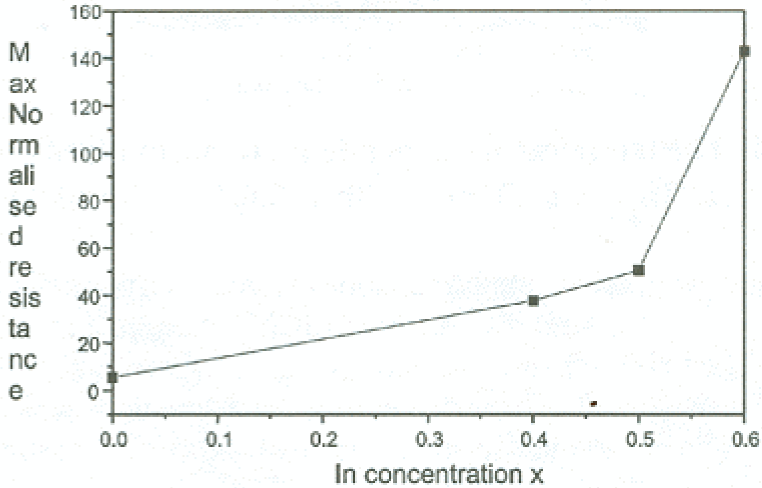


Figure 6. In concentration dependence of maximum normalized resistance of $(L_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.4,0.5,and 0.6

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 μm to 2.5 μm. 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.

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