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STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES OF $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$

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ABSTRACT

Structural, magnetic and electrical properties of ABO_3 typed $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ were studied using X-ray diffractometer, AC susceptometer and DC four probe systems. Substitution of x = 0.0, 0.1, 0.2, 0.3, and 0.4 were prepared using the solid-state reaction method. The metal to insulator temperature T_P and the Curie temperature, T_C, decreases as the Indium content increases showing the decreasing of ferromagnetic properties of the compound. For each substitution, there is an enhancement in susceptibility as the field intensity increases from 0.1 Oe to 10 Oe. For x = 0.4, the ac susceptibility shows a cusp around 53 K, suggesting the presence of spin glass state.

Keyword: Manganites, Susceptibility, Spin Glass.

INTRODUCTION

A lot of effort has been put to investigate the magnetic and transport properties in the perovskite manganites (ABO_3) $Ln_{1-x}A_xMnO_3$ (Ln = La, Nd, Pr, etc, A = Ca, Sr, Ba, etc) recently. In these materials the colossal magnetoresistance (CMR) has been observed near the ferromagnetic transition temperature, i.e. the Curie temperature, T_C [1-4]. Magnetoresistance, which has been defined as the variation of the electrical resistance with magnetic field, is very important to the technology of magnetic data storage. A lot of research has been focused on the relationship between the structure and the magnetic properties of the manganites as to ascertain the origin of CMR. Hwang et al. [5] and other authors have shown a closed dependence of magnetic and transport properties on the average ionic radius of the A site $\langle r_A \rangle$ [6-8]. At about 30 % of doping level of divalent alkaline ion, the T_C is shown by the established phase diagrams to be 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 [1-4]. A study on the doping effects on A site may benefit our understanding of the lattice effects.

EXPERIMENTAL PROCEDURE

Polycrystalline samples $(La_{1-x}In_x)_{0.67}Ca_{0.33}MnO_3$, x = 0.0, 0.1, 0.2, 0.3 and 0.4, were prepared by the conventional solid-state reaction method. A well-mixed stoichiometric mixture of La_2O_3, $CaCO_3$, $MnCO_3$, In_2O_3 with purities higher than 99.9% was ball milled with acetone for 6 h and dried in the oven at 110 °C overnight. The dried mixture was calcined at 900 °C in air for 12 h. The product obtained was reground, palletized with the pressing at 6.5 kN, and sintered in air at 1300 °C for 24 h. Characterizations of the samples were performed on a Philip x-ray diffractometer with a rotating anode. Resistance was measured by the conventional four-probe method in the temperature range of 20 to 300 K. Ac susceptibility was measured at 0.1, 0.5, 1.0, 5.0 and 10.0 Oe by a Lake Shore Cryotronics AC susceptometer (Model 7000) in the temperature range of 30-300 K using a close-cycle helium cryostat.

RESULTS AND DISCUSSION

The lanthanum calcium manganites $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) samples were doped with indium on the A site, stoichiometrically to reduce the content of the lanthanum on each sample. As the indium content increases, figure 1 shows a detectable secondary phase. The intensity of the secondary phase also increases as the indium content increases, notable for higher indium content (x = 0.2, 0.3 and 0.4). A slight shift for a standard LCMO peaks to a higher 2θ degrees is also observed. Table 1 shows the lattice constants and the unit volume from the XRD pattern, as well as the calculated values for LCMO by Blasco, J et al. [9]. Blasco, J et al, shows it from the calculated values that LCMO is orthorhombic, indexed to a space group of Pbnm (62). Our LCMO sample has a unit cell volume of 233.06 Å compared with the calculated values of 230.25 Å. As the content of Indium increases, all the lattice constants, and the unit cell volumes have decreases slightly for each samples. The sample with x = 0.4 has the smallest unit volume of 226.4Å.

Table1: Lattice constant and unit volume of the $(La_{1-x}In_x)_{2/3}Ca_{1/3}MnO_3$ calculated from the XRD pattern for x = 0.0, 0.1, 0.2, 0.3 and 0.4. A first row values are from Blasco, J. et al. for LCMO.

X	A (Å)	B (Å)	C (Å)	Volume (Å)^3
0.0	5.472	5.457	7.711	230.2500
0.0	5.462	5.481	7.785	233.0613
0.1	5.457	5.498	7.757	232.7301
0.2	5.445	5.446	7.672	227.5014
0.3	5.420	5.443	7.684	226.6861
0.4	5.425	5.427	7.690	226.4049

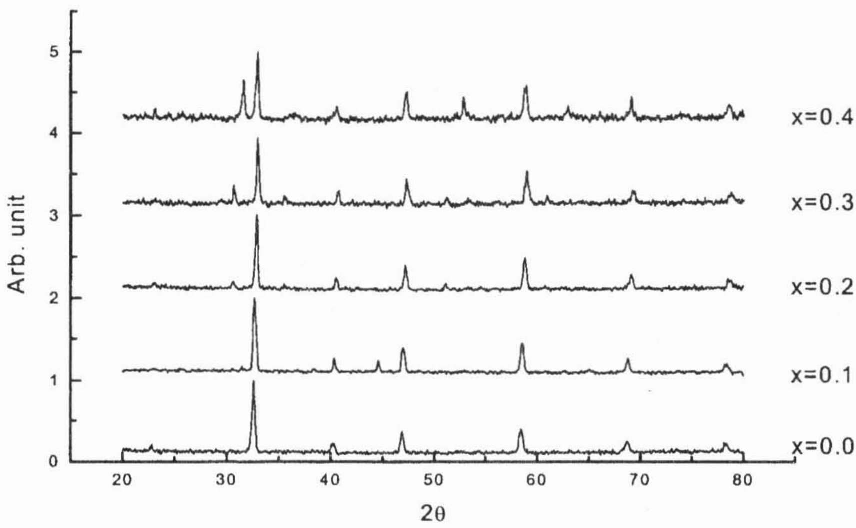


Figure 1: Powder x-ray diffraction pattern for $(La_{1-x}In_x)_{0.67}$ $Ca_{0.33}$ MnO_3 with x=0.0, 0.1, 0.2, 0.3 and 0.4 respectively.

Figure 2 shows the temperature variation of resistance for increasing indium content (x = 0.0 – 0.4). The maximum resistance of 1% indium doped sample is significantly reduced from that of LCMO, but for the higher percentage of Indium doping, there is a tendency of increasing maximum resistance as x increases. The sharpest peak occurs at x = 0.4 and the maximum resistance is lowest at x = 0.1.

The maximum resistance shows the tendency of gradually increasing for higher x, but the susceptibility intensity shows the opposite tendency, gradually decreasing as the x increases, as shown in Figure 3. By gradually replacing the trivalent lanthanum by a nonmagnetic trivalent indium, the samples indicate the decrease of ferromagnetism ordering, thus the increasing tendency of the maximum resistance for higher x. This characteristic of resistance is possibly attributed to the decreasing of spin alignment within the samples, i.e. spin dependent conduction. According to Anderson and Hasegawa, the combined itinerant/local-moment system lowers its total energy by aligning the spins ferromagnetically and thus allowing the itinerant electrons to gain kinetic energy, enhancing the conduction [10].

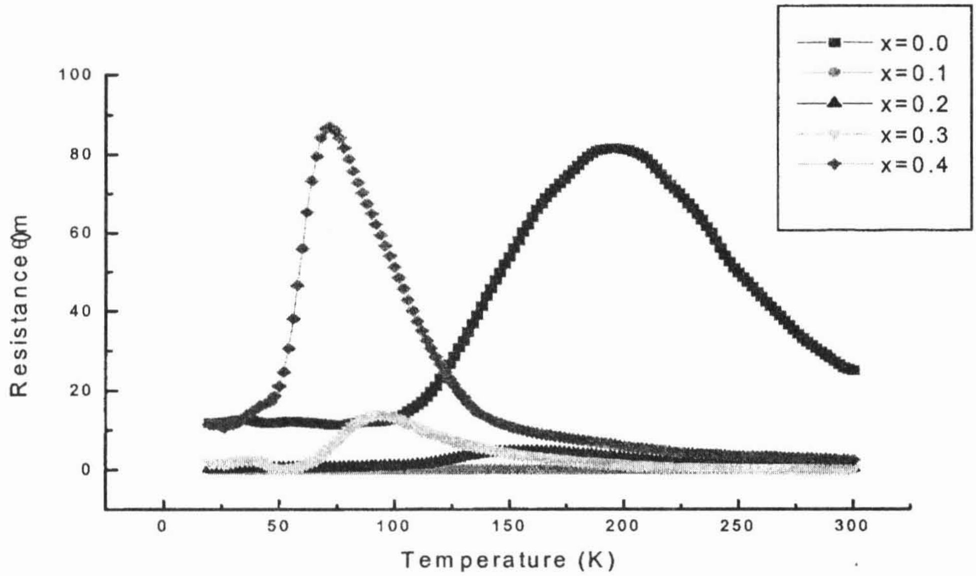


Figure 2: Temperature variation of resistance of $(La_{1-x}In_x)_{0.67}$ $Ca_{0.33}$ MnO_3 with x = 0.0, 0.1,0.2, 0.3 and 0.4 respectively.

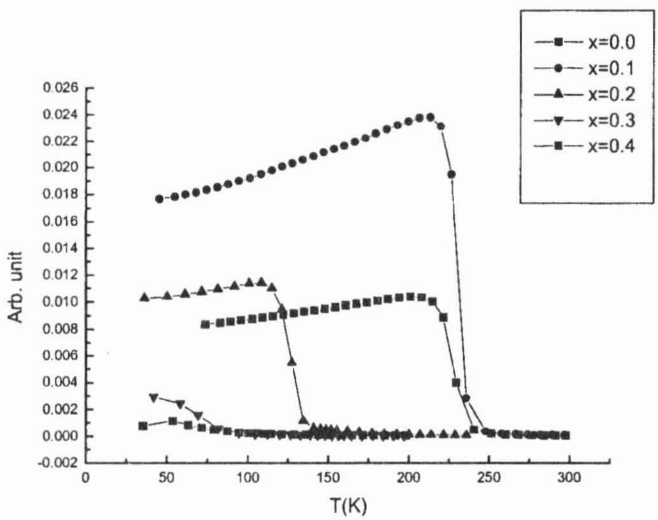


Figure 3: Temperature dependence of AC susceptibility for $(La_{1-x}In_x)_{0.67}$ $Ca_{0.33}$ MnO_3 with x = 0.0, 0.1,0.2, 0.3 and 0.4 for field intensity of 1.0 Oe.

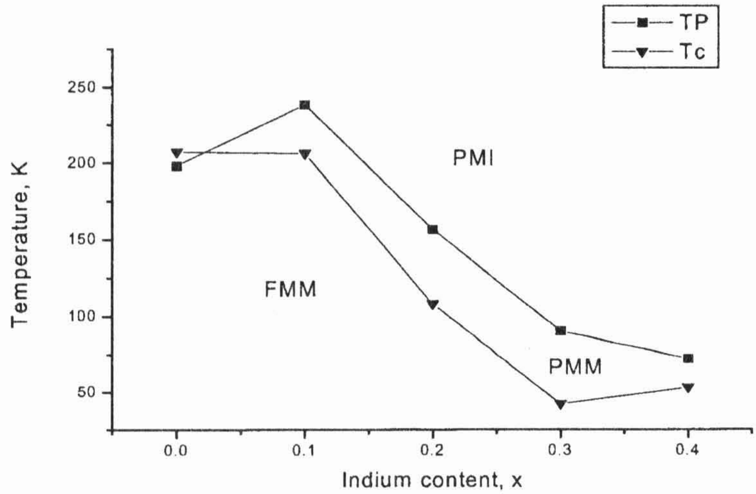
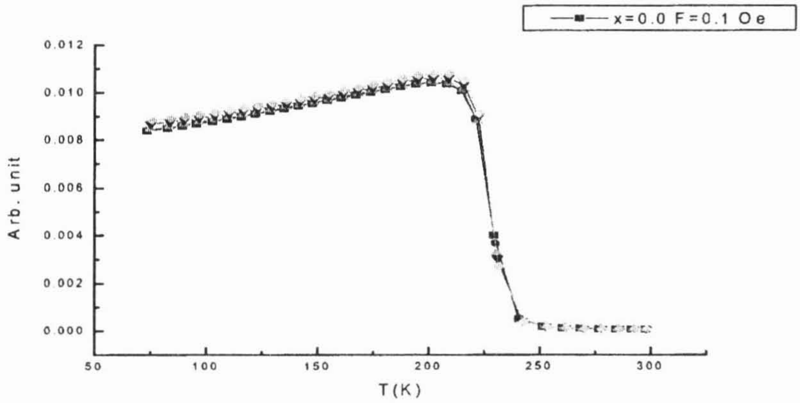


Figure 4: The variation of T_C and T_P with temperature for $(La_{1-x}In_x)_{0.67}Ca_{0.33}MnO_3$ with x = 0.0, 0.1,0.2, 0.3 and 0.4.

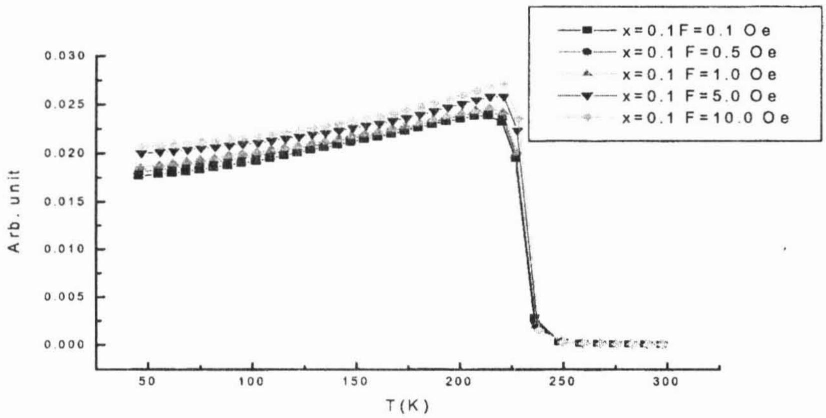
It is shown that AC susceptibility measurements are strongly influenced by the average radius of A site cation, $\langle r_A \rangle$. Figure 3 shows that for larger size of A site cation, $\langle r_A \rangle$ (x=0.0), a classical ferromagnetic behaviour with T_C around 210 K is observed. For an intermediate $\langle r_A \rangle$, corresponds to increasing indium content, (x = 0.1, 0.2), a decrease of T_C is observed. For a higher content of indium, (x = 0.3, 0.4), there is a sharp decrease of susceptibility. The magnetic behaviour of the compounds with $x \geq 0.3$ does not exhibit a classical ferromagnetic behaviour. It is possibly that the ferromagnetic tendency is replaced by the spin glass behaviour, a distinct characteristic relates to a magnetic ordering below spin freezing temperature, shown by the cusps formed at low temperature around 41 K and 53 K. However, the cusp in AC susceptibility is not a characteristic property of spin glasses alone. For example, $U_3Cu_4Si_4$, which is a collinear antiferromagnet down to 1.5K as shown from the neutron diffraction studies, also exhibits a cusp at 50K in the AC susceptibility [11]. In most of the cases, the low temperature anomaly in AC susceptibility can be caused by the changes in the domain wall displacement, which is either frozen because of narrow walls or stopped by domain wall pinning effects [12].

Figure 4 shows the temperature variation of the phase transition temperature, T_P, and the Curie temperature, T_C. It is observed that T_P shifts to lower temperature as the indium content increases. The reducing of T_P is possibly related to the decreasing value of the average ionic radius of A site <A>, since the ionic radius of indium is smaller than that of lanthanum. The T_P is only slightly higher for x = 0.1 but dropping steadily for higher x. The T_C, however, only drops slightly for x = 0.1, dropping faster for x = 0.2 and 0.3, and increases slightly for x = 0.4. The material exhibits phase changes from ferromagnetic metallic to paramagnetic metallic and finally into paramagnetic insulating behaviour.

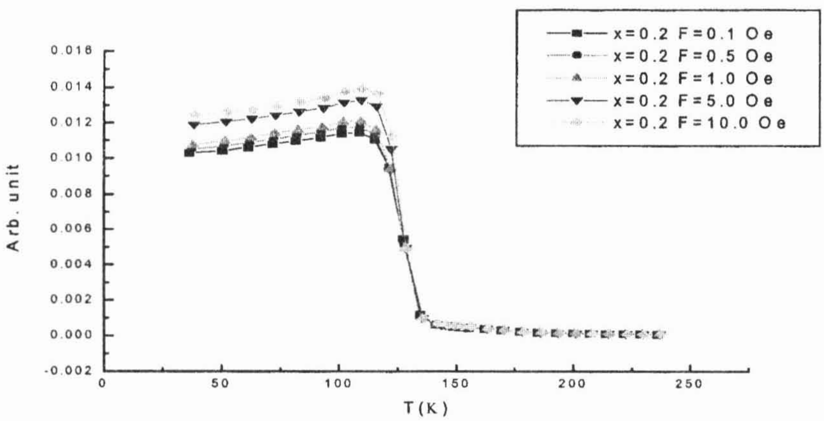
Figure 5 shows the temperature and field dependence of AC susceptibility for increasing indium content, (x=0.0 – 0.4). For each samples, the measurement was done with increasing field intensity of 0.1, 0.5, 1.0, 5.0 and 10.0 Oe. For a larger $\langle r_A \rangle$, (x=0.0), there is a slight increase in susceptibility with increasing field intensity. A significant increase of susceptibility is observed for an intermediate $\langle r_A \rangle$ (x=0.1 – 0.3). A sharp increase of susceptibility can be seen for an indium content of x = 0.4. It is seen from these measurements that, the enhancement of AC susceptibility corresponds to the reducing of $\langle r_A \rangle$, or to the increasing of indium content, x.


x=0.0 F=0.1 Oe
Arb. unit
0.012
0.010
0.008
0.006
0.004
0.002
0.000
50
100
150
200
250
300
T(K)

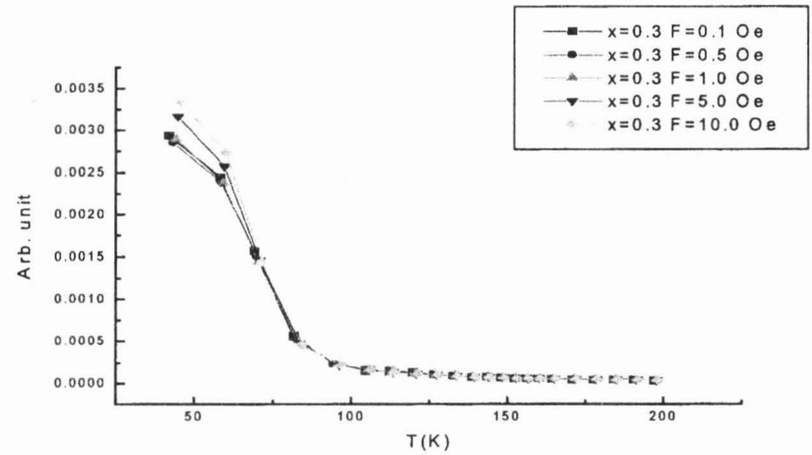
(a)


x=0.1F=0.1 Oe
x=0.1 F=0.5 Oe
x=0.1 F=1.0 Oe
x=0.1 F=5.0 Oe
x=0.1 F=10.0 Oe
Arb. unit
0.030
0.025
0.020
0.015
0.010
0.005
0.000
50
100
150
200
250
300
T(K)

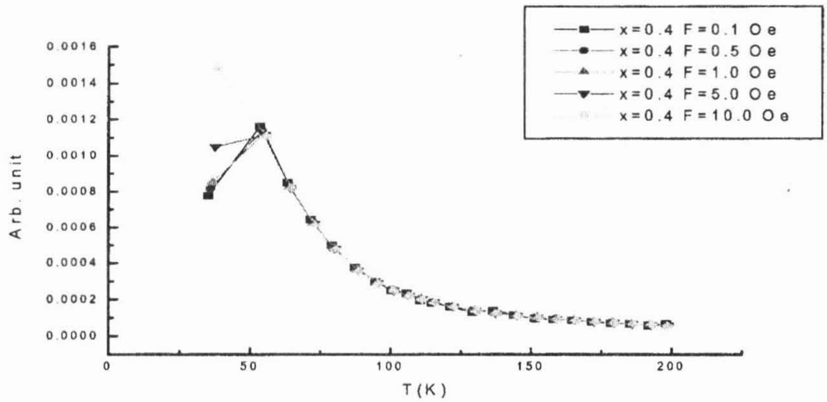
(b)


x=0.2 F=0.1 Oe
x=0.2 F=0.5 Oe
x=0.2 F=1.0 Oe
x=0.2 F=5.0 Oe
x=0.2 F=10.0 Oe
Arb. unit
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
-0.002
0
50
100
150
200
250
T(K)

(c)



(d)



(e)

Figure 5: Temperature variations of AC susceptibility of $(La_{1-x}In_x)_{0.67}Ca_{0.33}MnO_3$ with (a) x=0.0, (b) x=0.1,(c) x=0.2, (d) x=0.3 and (e) x=0.4.

CONCLUSION

In summary, the structural, magnetic and electrical properties of ABO_3 typed $(La_{1-x}In_x)_{2/3}$ $Ca_{1/3}$ MnO_3 are investigated. As the indium content increases, there is a phase shift in the XRD pattern, reduced intensity of the standard peaks as well as reduced unit cell volume. The Curie temperature and the metal-insulator transition temperature are also reduced, albeit a higher T_P for x=0.1, possibly due to reduced average ionic radii, from the smaller indium ionic radius. The ferromagnetism tendency is maximum for x=0.1, but gradually decreasing for higher x. The opposite happens for maximum resistance, which is minimum for x = 0.1, but gradually increasing for higher x, which is possibly due to spin dependent conduction. For even higher x, i.e. x = 0.3 and 0.4, the samples shown a possible spin glass characteristic. All samples show enhancement of susceptibility with the increasing field intensity.

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