SUPPRESSION OF CHARGE AND ANTIFERROMAGNETIC ORDERING IN Ga-DOPED \( \text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3 \)

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Abstract. We investigate the structural, magnetic and magnetotransport properties of the Ga doped compounds \( \text{La}_{0.4}\text{Ca}_{0.6-x}\text{Mn}_x\text{Ga}_x\text{O}_3 \). The undoped compound \( \text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3 \) (LCMO) shows an antiferromagnetic (AFM) ground state and charge ordering (CO) at low temperatures. The partial replacement of manganese ions by non magnetic d\(^{10}\) Ga\(^{3+}\) ions can disrupt the charge, orbital, spin ordering. The magnetic and magnetotransport measurements showed that CO and AFM phases are weakened with increasing Ga content; \( T_{\text{CO}} \) and \( T_N \) shift to lower temperatures. Below 100 K, the AFM/CO phase was partially transformed in ferromagnetic (FM) clusters which grow with increasing Ga content. Non-magnetic Ga, doped in LCMO increases the magnetism in the samples. The compounds have semiconducting behavior in the whole investigated temperature range. The samples showed negative magnetoresistance (MR) that is not much affected by the Ga content. The maximum value of MR \( \sim 30 \% \) (for 7 T) was always reached at the base temperature (75 K), suggesting that this behavior is mainly decided by extrinsic factors, such as grain boundaries, disorder and charge carriers localization. The magnetic and electrical properties of these compounds at low temperatures, suggest that they are composed of a mixture of charge ordered and charge disordered phases of various proportions.

Key words: Manganites, Charge ordering, Magnetic transition.

1. INTRODUCTION

Complex rare earth manganese oxides have attracted an increasing interest in the last three decades due to the discovery of colossal magnetoresistance (CMR) effect, that is very promising in technical application such as in magnetic sensors and in computer memory systems [1]. This effect was extensively studied mainly in \( \text{Ln}_{1-x}\text{A}_x\text{MnO}_3 \) compounds where \( \text{Ln} = \) lanthanide, \( \text{A} = \) divalent alkaline elements and Mn has a mixed valence of Mn\(^{3+}/\)Mn\(^{4+}\) ions. The cation substitution either at the Ln and Mn site leads to changes within the 3 D manganese-oxygen network and in the number of charge carriers which will result in a large variety of magnetotransport phenomena [1–3].

The properties of these materials are driven by a strong coupling between magnetic, charge and lattice degrees of freedom, which have been shown to result in electronic phase separation between two or more magneto-electronic phases at low temperatures [4]. One of the most interesting phenomena observed in some mixed valence manganites, which is associated with phase separation, is charge ordering (CO) which occurs on cooling below a certain temperature for a certain range of Mn$^{3+}$/Mn$^{4+}$ ions ratio. This phase implies the real space alternate ordering of the Mn$^{3+}$ and Mn$^{4+}$ ions in the nodes of the lattice. In the case of the La$_{1-x}$Ca$_x$MnO$_3$ compounds, the CO phase occurs for $x \geq 0.5$ [3, 5, 6], it has insulating behavior and it becomes antiferromagnetic (AFM) at low temperatures. Close to $x = 1$, the state becomes “canted” having coexisting AFM and FM characteristics [7, 8]. The CO phase can be “melted” by applying a high magnetic external field [7, 9], by reducing the size of the particles [10], by A-site disorder [11, 12], or by Mn-site substitution [13] with various d ions in Ln$_{1-x}$A$_x$MnO$_3$ manganites. The scenario of phase separation in systems with charge ordering was also theoretically described in Ref. [14].

The perovskite manganites La$_{1-x}$Ca$_x$MnO$_3$ attracted significant research interest for their abundant physics. La$_{0.4}$Ca$_{0.6}$MnO$_3$ is characterized by a stable antiferromagnetic (AFM) ground state ($T_N \sim 160$ K) and charge ordering (CO) below $T_{CO} \sim 267$ K [8, 9]. In this paper we studied the influence of Ga-doping on the magnetic properties and on the electrical conduction mechanism of AFM/CO La$_{0.4}$Ca$_{0.6}$MnO$_3$ manganites. Since Ga has the same valence 3+ as Mn$^{3+}$ it preferentially will replace those ions. The ionic radius of d$^{10}$Ga$^{3+}$ is 0.620 Å, rather close to the Mn$^{3+}$ ionic radius of 0.645 Å, and this is why we do not expect significant distortion of the lattice. In spite of these, Ga$^{3+}$ is a d$^{10}$ ion and this fact will have a strong influence on the physical properties of the doped compounds. These ions will locally destroy the alternating order of the Mn$^{3+}$ and Mn$^{4+}$ ions, and consequently the charge/orbital/spin ordering in the system. Our detailed study demonstrated the depreciation of CO phase and the enhancement of magnetism, by the substitution of non magnetic d$^{10}$ Ga$^{3+}$ ions for the manganese ions in La$_{0.4}$Ca$_{0.6}$MnO$_3$.

2. EXPERIMENTAL

Ceramic samples with nominal composition La$_{0.4}$Ca$_{0.6}$Mn$_{1-x}$Ga$_x$O$_3$ ($x = 0.0, 0.1, 0.15, \text{ and } 0.2$) were synthesized using the conventional solid state reaction method, using high purity precursors (better than 99.9%): La$_2$O$_3$, CaCO$_3$, Ga$_2$O$_3$, and MnO$_2$. The powders were calcined at 1100° C and then pressed in pellets and sintered in air at 1300 °C for 24 h with intermediate grindings. The X-ray powder diffraction patterns were recorded using a Brucker Advance D8 AXS diffractometer with CuK$_\alpha$ radiation. Data were refined by the Rietveld method.
using the program FULLPROF. To check the magnetotransport properties, the resistivities were measured in a cryogen-free magnet cryostat (Cryogenic Ltd.) by the four probe method in the temperature range from 5 to 300 K and magnetic fields up to 7 T. Another cryogen-free, VSM magnetometer (Cryogenic Ltd.) was used for magnetization measurements in the temperature range 5–300 K and in magnetic fields up to 12 T. The thermal variation of magnetization, $M(T)$, was recorded on warming, in zero field-cooled (ZFC) and field-cooled (FC) modes under 1 T magnetic field. To analyse the magnetic behaviour of the samples in high magnetic fields the isothermal magnetization measurements were performed at selected temperatures, ramping up the magnet from 0 to 12 T.

3. RESULTS AND DISCUSSIONS

The room temperature X-ray diffraction pattern for the analysed samples is shown in Fig. 1. The diffraction patterns indicated that all studied compounds were single perovskite phase. The Rietveld refinement plot of the X-ray diffraction data for the sample with $x = 0$ is depicted in Fig. 2. The La$_{0.4}$Ca$_{0.6}$Mn$_{1-x}$Ga$_x$O$_3$ samples have orthorhombic ($Pnma$) symmetry and their lattice constants are indicated in Table 1. As can be seen, there are small changes in lattice constants of doped samples in comparison with those of the undoped one, because the dimensions of Ga$^{3+}$ and Mn$^{3+}$ ions are very close.

![X-ray diffraction pattern](image_url)

**Fig. 1 –** Powder X-ray diffraction patterns for La$_{0.4}$Ca$_{0.6}$Mn$_{1-x}$Ga$_x$O$_3$ samples with $x = 0.00–0.20$. 

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$</th>
<th>Lattice Constants</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.4}$Ca$</em>{0.6}$Mn$_{1-x}$Ga$_x$O$_3$</td>
<td>0.00</td>
<td>$a$, $b$, $c$</td>
<td>$Pnma$</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>$a'$, $b'$, $c'$</td>
<td>$Pnma$</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>$a''$, $b''$, $c''$</td>
<td>$Pnma$</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>$a'''$, $b'''$, $c'''$</td>
<td>$Pnma$</td>
</tr>
</tbody>
</table>
Figure 2 – Rietveld refinement plot of the X-ray diffraction data for the sample with \( x = 0 \). Observed and calculated, profiles are plotted on the same scale. The Bragg peaks are indicated tick marks.

Figure 3 presents the magnetization as a function of temperature \( M(T) \) for the analyzed samples, taken in ZFC and FC regime in a magnetic field of 1 T. The undoped sample (Fig. 3a), exhibit the typical CO peak at \( T_{CO} \sim 266 \, \text{K} \), in full agreement with earlier reports [8, 10, 15]. At lower temperature the AFM transition occurs at \( T_N \sim 162 \, \text{K} \), suggested by a small feature in \( M(T) \) curve. The upturn in this curve at low temperature suggest a possible canted AFM state.

Table 1
Quantitative data for the \( \text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3 \) compounds

<table>
<thead>
<tr>
<th>sample ( x )</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>( T_{CO}(\text{K}) )</th>
<th>( T_N(\text{K}) )</th>
<th>( T_S(\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.408</td>
<td>7.588</td>
<td>5.386</td>
<td>–</td>
<td>162</td>
<td>266</td>
</tr>
<tr>
<td>0.10</td>
<td>5.402</td>
<td>7.569</td>
<td>5.389</td>
<td>48</td>
<td>160</td>
<td>236.4</td>
</tr>
<tr>
<td>0.15</td>
<td>5.424</td>
<td>7.607</td>
<td>5.394</td>
<td>96.4</td>
<td>156</td>
<td>201</td>
</tr>
<tr>
<td>0.20</td>
<td>5.411</td>
<td>7.583</td>
<td>5.384</td>
<td>101</td>
<td>157</td>
<td>201</td>
</tr>
</tbody>
</table>

In doped samples (Figs. 3b and 3c), a progressively decrease of \( T_{CO} \) and a broadening of CO transition originated peak with increasing Ga content, (as compared to the undoped), was observed. The magnitude of the magnetization is much larger than that of the undoped sample (more than three times, for \( x = 0.2 \)).

The difference between ZFC \( M(T) \) and FC \( M(T) \) curves increases with dopant concentration, at low temperatures. These behaviors are illustrated in the
Figs. 3b and 4c for the samples with \( x = 0.1 \) and \( x = 0.20 \) respectively. \( T_{CO}, T_G \) (temperatures associated with the formation of the FM clusters (when \( M(T) \) has an inflection point)) and \( T_N \) are indicated in Table 1 and in Figs. 3a,b,c. As can be seen, the relative height of the peak in \( M(T) \) curves (that marks the occurrence of the CO phase) decreases, while the magnetization at the base temperature increases with increasing Ga content.

Isothermal \( M(H) \) curves, taken at selected temperatures, and up to 4 T were mostly straight lines, as expected, for the undoped sample (Fig. 4a). In the case of the doped samples these \( M(B) \) curves are no longer straight lines at low temperature, showing a more rapid increase and having a convex shape, as shown in Fig. 4b for the sample with \( x = 0.15 \). The magnetic behaviors of these samples strongly suggest the occurrence of a cluster-glass state below \( T_G \), when the magnetizations begin to increase. Such a state, containing coexisting phases, was also found in other doped manganites [11, 16].
Low temperature magnetic measurements indicated a linearly increase of magnetization with increasing doping content. In Fig. 5 is presented the magnetization taken at 5 K and 4 T, $M(5\text{ K}, 4\text{ T})$ as a function of Ga content. High field (up to 12 T) magnetization measurements (Fig. 6) allowed us to estimate a saturation magnetization of these FM clusters, of about $M_S = 0.11\ \mu_B/\text{f.u.}$ at 5 K for the sample with $x = 0.2$. We have found narrow magnetic hysteresis loops $M(B)$ for the doped samples, and a small hysteresis loop shift ($\mu_0H_b = 0.14\ \text{T}$), as shown in the inset of Fig. 6.

This resembles with an exchange bias effect and it indicates the presence of some FM clusters grown in an AFM matrix [3, 9]. All these findings suggest a phase separation scenario at low temperatures, the coexistence of a minority phase consisting of charge disordered FM clusters embedded in a CO-AFM matrix. Ga doping in La$_{0.4}$Ca$_{0.6}$MnO$_3$ locally destroys the CO phase and it leads to the
formation of a minority of charge disordered FM clusters. The Jahn-Teller effect which is very important for orbital/spin ordering is weakened when a Mn ion is replaced by a spherical d$^{10}$ Ga$^{3+}$ ion [17]. The CO-AFM phase is progressively depreciated with increasing content of Ga, while the FM clusters grow, at low temperatures. The doped samples have magnetic behaviors which look rather similar with charge-order breaking and ferromagnetism enhancement upon reduction of the grain size down to nanometer scale found in La$_{0.4}$Ca$_{0.6}$MnO$_3$ [10, 12]. Figure 7 shows the temperature dependence of the resistivities of the studied samples La$_{0.4}$Ca$_{0.6}$Mn$_{1-x}$Ga$_x$O$_3$ with $x = 0.0, 0.1, 0.15$, and $0.2$ in zero applied magnetic field and in the temperature range from 50 to 300 K.

![Graph showing temperature dependence of resistivity](image)

**Fig. 7** – Temperature dependence of resistivity $\rho(T)$ in zero applied magnetic field for the samples with $x = 0.0 – 0.20$. The inset shows the fitting of $\ln(\rho)$ as a function of $T^{-1/4}$.

All the samples have typical semiconducting behaviour, with increasing resistivity when the temperature decreases. The resistivity $\rho(T)$ of the doped samples is shifted upward in comparison with that of the undoped one, probably due to the disorder introduced in system by doping. This behavior also suggest that the FM clusters either they are not metallic or they are very small and cannot compensate the increase of resistivity generated by disorder. The conduction behaviour of the samples can be well depicted by using the VRH (variable range hopping) model [18]: $\rho = \rho_0 \exp[(T_0/T)^{1/4}]$ (where $\rho_0$ is the prefactor and $T_0$ is the characteristic temperature) as shown in the inset of Fig. 7. In Fig. 8a, b the field dependence (from 0 to 7 T) of the magnetoresistance $MR$, is shown at various
temperatures for the sample with $x = 0.0$ and $x = 0.20$, respectively. The studied samples show negative magnetoresistance $MR = [\rho(H) - \rho(0)]/\rho(0)$, which increases with decreasing temperatures indicating the dominant role of the grain boundaries in this process [3]. This effect, also masks the possible decrease of resistivity inside of FM clusters (induced by the double exchange interaction).

Fig. 8 – Field dependence of the magnetoresistance $MR$, for the sample with $x = 0$ (a) and $x = 0.20$ (b), at selected temperatures.

For all the studied samples $MR$ approach to about 30% in 7 T at the base temperature of 75 K. The magnetoresistance does not change substantially with increasing doping, indicating again that $MR$ effect in these compounds is a result of disorder and of some other defects.

4. CONCLUSIONS

$\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ has a stable AFM ground state ($T_N \sim 160$ K)/charge ordering (CO) below $T_{\text{CO}} \sim 267$ K. The partial replacement of manganese ions by non magnetic $d^{10} \text{Ga}^{3+}$ ions can disrupt the charge/orbital/spin ordering. CO and AFM phases are weakened with increasing Ga content, leading to the formation of a minority of charge disordered FM clusters. The magnetization at low temperatures and high magnetic fields $M(5K;4T)$ was found to linearly increase with the Ga content. Non-magnetic Ga doped in LCMO enhanced the magnetism of the system. The magnetotransport properties, indicate semiconducting behaviour for all the analysed samples, and negative magnetoresistance, dominated mostly by grain boundaries and other defects effects, rather than by the possible decrease of resistivity in FM clusters. The magnetic and electrical behaviors of these samples can be understand presuming the coexistence of minor charge disordered FM and major CO AFM phase, in a phase separation scenario.
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