Characterization of Doped Rare Earth Manganites, \( \text{La}_{0.68-x} \text{A}_x \text{Ca}_{0.32} \text{MnO}_3 \) where \( \text{A} = \text{Y, Gd} \) (\( x = 0.00, 0.08 \))

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Abstract. \( \text{La}_{0.68-x} \text{A}_x \text{Ca}_{0.32} \text{MnO}_3 \), where \( \text{A} = \text{Y, Gd} \) (\( x = 0.00, 0.08 \)) have been studied by XRD, Magnetoresistance amplitude measurement and SEM (Scanning Electron Microscopy) grain size determination, magnetic measurement of \( x = 0.00 \). The bulk sample was prepared by the solid state reaction method (standard ceramic technique) between the corresponding metallic oxides in stoichiometric ratio. We measured the magnetoresistance amplitude of these compounds in 5 T magnetic field at annealing time 8 h and 15 h in Oxygen. The room temperature resistivity and \( T_c \) were decreased after annealing at 1350°C for 15 h in Oxygen. These annealing shows that the magnetoresistance ratio increases. It depends upon annealing time. These results can be explained on the basis of the weakening of the Double Exchange (DEX) interaction.

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1 Introduction

The magnetoresistance (MR) in perovskite like Lanthanum manganites \( \text{La}_{1-x} \text{Ca}_x \text{MnO}_3 \) has recently been the subject of attention due to enormous changes of resistivity observed in these materials compared with those occurring in metallic based multilayer or granular structure. Very high magnetoresistance values have been reported for bulk polycrystalline compounds [1] and thin film [2,3]. Perovskite structured Lanthanum manganite (LaMnO3) exhibits both strong ferromagnetism and metallic conductivity by partial substitution of La ions (3+ valence) with A (2+) valence ion such as Ca, Ba, Sr, Pb. Mixed Mn\(^{3+}/\text{Mn}^{4+}\) valence states, and canting of Mn spin are created when La\(^{3+}\) is replaced by A (2+ valence) ion [4-8]. The magnetoresistance has also been observed in single crystal. The preparation condition, the level of A-doping the Oxygen content and the perovskite lattice parameter plays an important role in determining the characteristics of La\(_{1-x}\)A\(_x\)MnO\(_3\) compounds.
The transport properties of the hole doped manganites can be modified by the substitution of the La sites. Jin et al. [9] first reported that replacing La by a small amount of Yttrium in polycrystalline La$_{0.67}$Ca$_{0.33}$MnO$_3$ led to increase in MR amplitude of up to about 10,000% – a value comparable to that obtained in thin film. This has been recently confirmed by subsequent studies of Hwang et al. [10] and Fontcuberta et al. [11]. Similar attempt has been made by V.S. Teodorescu et al. [12]. They have studied the structural and magnetotransport properties of La$_{0.60}$Y$_{0.07}$Ca$_{0.33}$MnO$_3$ in bulk and thin film. The MR amplitude was 680% on the perovskite thin film (deposited by pulsed laser deposition on MgO crystal using an exciter laser) at 2 T magnetic field and MR amplitude 280% at 221 K in the bulk sample (prepared by the solid state reaction method). The amplitude variations of the MR from bulk to thin film were explained by the difference between the average grain size (lower grain size in the thin film) with a direct implication in the electronic scattering on the grain boundaries.

Many researchers have carried out the substituted ions viz. Tb, Gd on La site. J.M. De Teressa et al. [13] studied the transport properties of compound (La$_{3/4}$Tb$_{1/4}$)$_{2/3}$Ca$_{1/3}$MnO$_3$. They have found magnetoresistance (MR) amplitude as large as 70000% at 12 T in bulk sample. $T_c$ changes from $\approx 265$ K for the undoped compound to $\sim 103$ K for this compound. The main reason is that Tb weakens the double exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ lowering the value of $T_c$. Z.B. Guo et al. [14] have studied the magnetic, magnetoresistance (MR) behavior of polycrystalline La$_{0.67-x}$Gd$_x$Ca$_{0.33}$MnO$_3$ in which gadolinium content plays an important role for MR amplitude. The sample with $x = 0$ and $x = 0.5$ shows MR $\sim 42\%$ and $68\%$ at $T_c$ respectively at field of 1.5 T. The value $x = 0.10$ exhibits a broad MR. MR is 65% over an extended temperature range $\sim 30$ K and it is 90% over some extended temperature range in $x = 0.15$. J.R. Sun et al. [15] studied the magnetoresistance properties of compound La$_{0.7-x}$Gd$_x$Ca$_{0.33}$MnO$_3+\Delta$ by synthesizing the different starting materials. Starting materials are La(OH)$_3$ and La$_2$O$_3$. La$_{0.67-x}$Gd$_x$Ca$_{0.33}$MnO$_3$ was prepared from either La(OH)$_3$ or La$_2$O$_3$ and La(OH)$_3$. They have found different amplitudes. In this case it is found that La$_2$O$_3$ and La(OH)$_3$ coexist and inhomogeneous distribution occurs in the Oxygen content of compounds and La$_2$O$_3$ causes considerable Oxygen deficiency in resulting sample. With this view, we investigated (La/R)$_{1-x}$Ca$_x$MnO$_3$ where La was systematically substituted by element R = Y, Gd.

2 Experimental

The compounds La$_{0.68-x}$A$_x$Ca$_{0.32}$ MnO$_3$, where A = Y, Gd with $x = 0.00$, 0.08 were prepared by standard ceramic techniques of MnO$_2$ (purity above 99%), Y$_2$O$_3$ (Alderich, 99.9%), Gd$_2$O$_3$ (Alderich, 99.9%) CaCO$_3$ (above 99%), La$_2$O$_3$ (Alderich, 99.9%) mixed according to the desired stoichiometry in a sil-
ica crucible and silica crucible prefired in the air around 1000°C. The mixture is heated by the home made furnace at 1300°C for 24 h with binder and pressed by hydrostatic pressure machine in pelletization process and sintered at 1300°C and 1350°C and annealed in Oxygen for 8 h and 15 h at 1350°C.

### 3 Result and Discussion

The prepared materials were characterized by X-ray diffractometer. The X-ray diffraction pattern for La$_{0.68}$ Ca$_{0.32}$MnO$_3$ is shown in Figure 1. A total of 8 peaks are observed in X-ray diffraction patterns. Table 1 shows XRD which is attached herewith. Sample La$_{0.68}$ Ca$_{0.32}$MnO$_3$ shows the single phase with no detectable secondary phase along with cubic structure. The lattice parameter for La$_{0.68}$Ca$_{0.32}$MnO$_3$ is $a = 3.8571$ Å. XLAT program confirms this value of lattice parameter. This value is changed slightly with the substitution of Y, Gd. Table 2 shows the EDXS analysis of La$_{0.68}$Ca$_{0.32}$MnO$_3$. This shows that samples of La$_{0.68}$Ca$_{0.32}$MnO$_3$ are having correct composition form similarly La$_2$O$_3$, CaCO$_3$, MnO$_2$ are mixed with correct composition. We used the JSM 840 Scanning Electron Microscopy manufactured by JEOL Ltd.

The photographs (Figure 2) show the average size of the grain for different magnifications.

For ×5000 magnification the size is 1 μm to 2.16 μm, for ×3500 magnification, the size is 1.11 μm to 2.22 μm, for ×2500 magnification, the size is 1.37 to 2.75 μm for La$_{0.68}$Ca$_{0.32}$MnO$_3$. We can infer that the average size is around 1 μm to 2.75 μm for La$_{0.68}$Ca$_{0.32}$MnO$_3$ and having 5 to 10% porosity. The

![Figure 1. Diffraction pattern of La$_{0.68}$Ca$_{0.32}$MnO$_3$.](image)

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Table 1. Data of Diffraction pattern of La$_{0.68}$Ca$_{0.32}$MnO$_3$

<table>
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Table 2. EDXS analysis for La$_{0.68}$Ca$_{0.32}$MnO$_3$

<table>
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<tr>
<th>No</th>
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</table>

curve in Figure 3 shows history dependent and irreversible behaviour. When the temperature increases, the magnetisation decreases. History dependent behaviour means that the value of magnetic moment depends on the magnetic field and temperature changes. Field cooled gives some amount of irreversibility and the data has collected on cooling and gives optimal Mn$^{4+}$ content for ferromagnetism.

The curve in Figure 4 is not linear and reversible. This curve is named as virgin curve.

The room temperature resistivity of all samples dropped rapidly after annealing at 1350°C for 15 h in Oxygen. Temperature was decreased from 240 K
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Figure 3. Magnetization vs. temperature, for La$_{0.68}$Ca$_{0.32}$MnO$_3$ at 1 T of applied field.

Figure 4. Magnetization vs. applied magnetic field at 5 K for La$_{0.68}$Ca$_{0.32}$MnO$_3$.

to 210 K and 180 K for substitution of La by small amount of Gd and Y in La$_{0.68}$Ca$_{0.32}$MnO$_3$. The MR ratio is calculated by \( \Delta R/R_0 = (R_H - R_0)/R_H \), where \( R_0 \) is the zero field resistance and \( R_H \) is the resistance in the applied magnetic field of 5 T. The MR is found to be 1700% at 240 K for La$_{0.68}$Ca$_{0.32}$MnO$_3$ (A) and 3300% at 210 K for La$_{0.68}$Gd$_{0.08}$Ca$_{0.32}$MnO$_3$ (B) and 6300% at 180 K for La$_{0.6}$Y$_{0.08}$Ca$_{0.32}$MnO$_3$ (C) (see Figure 5).

Table 3 shows the MR ratio of different compounds for the annealing time 8 h and 15 h. MR is found to be the highest for an optimum annealing time of 15 h. Temperature decreases due to the change in Mn-O-Mn bond angle. In the perovskite structure Mn ions occupy B site which is surrounded by Oxygen octahedra for cubic structure, the Mn-O-Mn bond angle is equal to 180°. Upon substitution of La by cations with a smaller radius viz. cations of Y and Gd the Mn O$_6$ octahedra are forced to rotate in order to compensate for the reduced size.

Table 3:

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<th>Compound</th>
<th>MR Ratio</th>
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<tr>
<td>La$<em>{0.68}$Ca$</em>{0.32}$MnO$_3$ (A)</td>
<td>1700%</td>
</tr>
<tr>
<td>La$<em>{0.6}$Gd$</em>{0.08}$Ca$_{0.32}$MnO$_3$ (B)</td>
<td>3300%</td>
</tr>
<tr>
<td>La$<em>{0.6}$Y$</em>{0.08}$Ca$_{0.32}$MnO$_3$ (C)</td>
<td>6300%</td>
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</table>

Figure 5. Magnetoresistance vs. temperature for annealed samples of La$_{0.68}$Ca$_{0.32}$MnO$_3$ (A), La$_{0.6}$Gd$_{0.08}$Ca$_{0.32}$MnO$_3$ (B), La$_{0.6}$Y$_{0.08}$Ca$_{0.32}$MnO$_3$ (C).
Table 3.

<table>
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<th>Annealing time, h</th>
<th>La$<em>{0.68}$Ca$</em>{0.32}$MnO$_3$</th>
<th>MR ratio in %</th>
<th>La$<em>{0.6}$Gd$</em>{0.08}$Ca$_{0.32}$MnO$_3$</th>
<th>La$<em>{0.6}$Y$</em>{0.08}$Ca$_{0.32}$MnO$_3$</th>
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<tbody>
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<td>15</td>
<td>1700</td>
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<td>6300</td>
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</table>

The substitution of MnO$_6$ octahedra lowered the Mn-O-Mn bond angle. The increase in Mn$^{4+}$ proportion increases the Oxygen content which influences the ordering temperature. Annealing has also got a strong effect on the Curie temperature. Annealing increases the intrinsic character and the magnitude of the resistivity in the semiconducting range but lowers the residual value in the ferromagnetic range, hence causing an overall increase in the MR in the present investigation. Small lattice polarons were exhibited above $T_c$ in these annealed samples. The formation of small lattice polaron are due to the strong electron phonon coupling at this temperature. The activation energy for resistivity and thermopower are observed in this temperature range. Below $T_c$, there remain sign indication of spin scattering and polaronic collapse. The collapse of large polarons in the ferromagnetic stage reduces the effective exchange coupling via the double exchange mechanism and a metal insulator transition. Jahn-Teller lattice effects with the double exchange picture seem to be of this type of sample. The temperature was decreased and MR was seen at below $T_c$.

References

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