STRUCTURAL, ELECTRICAL AND MAGNETORESISTANCE OF La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ AT DIFFERENT SINTERING TEMPERATURES

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ABSTRACT

The structural, electrical and magnetoresistance of La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ perovskites have been investigated. The materials were prepared using co-precipitation method (COP) at sintering temperature of 1120 °C, 1220 °C and 1320 °C, respectively. Characterization by X-Ray diffraction showed that they have orthorhombic structure with $Pbnm$ space group. Insulator metal transition, $T_{im}$ increased from 261 K to 272 K with increasing of sintering temperature. Magnetoresistance (MR) measurements were carried out in the presence of magnetic fields from 0.1 T to 1 T at room temperature. In the present investigation, the percentage of MR of all the materials are found to increase with increasing magnetic field. MR values almost increase with increasing sintering temperature and this trend can be explained by the conduction mechanism due to the grain growth of materials.

Keywords: manganites; magnetoresistance;

INTRODUCTION

Perovskite manganites with the form R$_x$A$_{1-x}$MnO$_3$ (R is the rare-earth ion, A is alkaline-earth divalent ion) have attracted considerable attention in recent years because of the discovery of colossal magnetoresistance effect (CMR) in this materials and their potential applications in magnetoresistive transducer and sensors [1]. Substitution on La$^{3+}$ site by a divalent alkaline earth ions (A$^{2+}$) results in a mixed valence of Mn$^{3+}$/Mn$^{4+}$, where Mn$^{4+}$ lacks $e_g$ electron and hence the itinerant hole associated with the Mn$^{4+}$ ions may hop to Mn$^{3+}$ but, because of a strong on-site exchange interaction (Hund’s rule) with the localized Mn electrons, only hoping between sites with localized parallel spins is favored [2]. Recent studies on these materials revealed that CMR phenomenon is attributed not only to the double exchange (DE) mechanism but also to the interactions such as electron-phonon coupling, electron-magnon interaction, and the complicated band structure [2, 3]. La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) has high magnetic transition temperature $T_c$, while La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) exhibits high magnetoresistance (MR) [3]. In order to have a CMR material system with both high $T_c$ and high MR, a series of La$_{0.67}$Ca$_{0.33-x}$Sr$_x$MnO$_3$...
has been investigated [3]. Change et al. also found the raising of sintering temperature induced the formation of an interfacial phase near the grain boundaries of La$_{0.67}$Sr$_{0.33}$MnO$_3$ and Nd$_{0.67}$Sr$_{0.33}$MnO$_3$ [4]. In view of these fact, it is interesting to study the structural and electrical properties of magnetoresistive La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ (LCSMO) at different sintering temperatures.

**EXPERIMENTAL DETAILS**

The La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ samples were prepared by using co-precipitation method. Lanthanum acetate, calcium acetate, strontium acetate and manganese acetate were weighted and dissolved in glacial acetate acid. 0.5M oxalic acid was added to the solution in an ice bath until white suspension was obtained. The resulting slurry was filtered after 5 min of reaction and dried in an oven at 80°C for 8 hours. The powders were calcined at 900°C in air for 12 hours and then cooled to room temperature at 2°C/min. The samples were examined using X-ray diffraction (XRD) and scanning electron microscope (SEM). The temperature dependence of resistivity was measured using the standard DC four probe method. The MR measurements have been done by measuring the resistance of the samples with magnetic field from 0.1 T to 1 T at room temperature.

**RESULTS AND DISCUSSION**

X-ray diffraction patterns of the samples are single perovskite phases with orthorhombic structure (space group $Pbnm$) as shown in Figure 1. The grain size increased with increasing of sintering temperature (Figure 2). The same results have been reported by Siwach et al. in the series of La$_{0.7}$Ca$_{0.3}$MnO$_3$ that synthesized at 500, 600, 900 and 1300 °C [5]. By looking at the SEM images, sample that sintered at 1120 °C has well separated smaller grains and the grains do not seem to connect tightly. While for samples sintered at 1220 °C and 1320 °C, well-formed granular crystallites with larger grain size than sample sintered at 1120 °C can be seen. The effect of grain size on charge-ordering and phase segregation of Nd$_{0.5}$A$_{0.5}$MnO$_3$ (A= Ca & Sr) has been investigated [6]. The sample with smaller grain size which was sintered at 1173 K showed greater ferromagnetic (FM) interaction at lower temperature due to phase segregation compared to sample with the largest grain size that sintered at 1673 K [6].
Figure 1: X-Ray diffraction patterns of La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ prepared at different sintering temperatures

Figure 2: Scanning electron micrographs of La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ at different sintering temperatures (a) 1120, (b) 1220 and (c) 1320

Figure 3 shows the temperature dependence of the resistivity for La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ sintered at 1120°C, 1220°C and 1320°C, respectively. The $T_{im}$ value is found to increase from 261 K to 271 K with the increased of sintering temperature. In sol-gel prepared La$_{0.67}$Ca$_{0.33}$MnO$_3$ samples, the decreased in grain size creates a non-magnetic surface layer that has nano crystalline size around the grain [2]. Here, the shifting of $T_{im}$ towards higher temperature region can be explained as the enhancement of grain growth that improved the connectivity between the grains and reduced the existing of the pores and voids as shown in Table 1.
Table 1: Grain size, $T_{im}$, density and porosity of La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ at different sintering temperatures

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>Grain size (µm)</th>
<th>$T_{im}$ (K)</th>
<th>Density ($\rho_{\text{exp}}$) (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1120</td>
<td>18</td>
<td>261</td>
<td>4.64</td>
<td>24.8</td>
</tr>
<tr>
<td>1220</td>
<td>33</td>
<td>266</td>
<td>5.25</td>
<td>15.0</td>
</tr>
<tr>
<td>1320</td>
<td>38</td>
<td>271</td>
<td>5.62</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Figure 3: Resistivity versus temperature curves of La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ at different sintering temperatures

Figure 4: Magnetoresistance (%) versus magnetic field (B) of La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$ at different sintering temperatures
MR measurements were carried out in the presence of magnetic field from 0.1 T to 1.0 T at room temperature. A typical plot of percentage of MR over magnetic field is shown in Figure 4. The percentage of MR of all materials are found to increase with increasing magnetic field. Furthermore, the MR values almost increased with increasing in sintering temperature and it can be explained by the conduction mechanism due to better grain growth of the samples.

CONCLUSION

In conclusion, the insulator-metal transition temperature ($T_{im}$) shifted to higher temperature with increasing of sintering temperatures. The MR values are found to increase with increasing magnetic field and can be explained by the suppression of the magnetic spins scattering with the application of magnetic field and causing the local ordering of the magnetic spins. The MR values almost increase with increasing in sintering temperatures and it may due to the grain growth of the materials. Grain growth mechanism plays an important role in determining the structural, electrical and magnetoresistance of magnetoresistive La$_{0.7}$Ca$_{0.28}$Sr$_{0.02}$MnO$_3$.

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