Grain Size Effect on Electrical and Magnetotransport Properties of La$_{0.67}$Ca$_{0.33}$MnO$_3$ synthesized via Sol-Gel Method

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Abstract. The effect of grain size on electrical resistivity and magnetoresistance (MR) effect on La$_{0.67}$Ca$_{0.33}$MnO$_3$ prepared via sol-gel method was reported with different sintering temperature starting from 600°C to 1200°C. X-ray diffraction (XRD) patterns show that La$_{0.67}$Ca$_{0.33}$MnO$_3$ was in single phase and had orthorhombic structure with space group Pbnm (62). The crystallite size as well as particle size show strong dependence on sintering temperature (Ts). The metal-insulator transition (TMI) and the magnitude of magnetoresistance are significantly influenced by the effective grain boundaries in LCMO polycrystalline. The TMI and its resistivity increases as the grain size and crystallite size increases (Ts increase). The highest low-field magnetoresistance (LFMR), which extrinsic percentage of MR is more dominant, observed in LC-SG8 (-12.89%) with nano-sized distribution that showing double crystallite structure. However, the highest CMR is found in LC-SG10 (-23.48%) at 80 K with 1 Tesla. These percentage variations of MR for all samples were influenced by the grain size and crystallite size variations which consequently affect the spin polarized-tunneling scattering at the grain boundary layer.

1. Introduction
Perovskite manganites with general formula La$_{1-x}$A$_x$MnO$_3$ where A is a divalent alkaline earth cation (e.g. Ca, Ba, Sr) has attracted extensive attention in the last few decades due to its special physical properties and potential applications in magnetoresistive devices [1]. It is proved that Jahn-Teller effect and double exchange (DE) mechanism that attributed to paramagnetic insulator state or antiferromagnetic insulating state and ferromagnetic metallic state is mostly conceived to be the relation of the rich physical properties in CMR materials. The effect of grain size on magnetic behaviors of different types of manganites had been studied by many researchers [2,3]. Goutam et al., (2006) [4] studied the effect of Ts from 600°C to 1000°C in nanophase La$_{0.7}$Ca$_{0.3}$MnO$_3$ manganites synthesized through polymeric precursor route and they observed that as Ts increased, both crystallite size and the particle size were increased due to the congregation effect. The decrease in magnetoresistance in these oxides becomes extremely large near the transition temperature and this phenomenon gives huge interest to information storage applications. The magnitude of MR which depends on the magnitude of external magnetic field applied becomes colossal only in the presence of great fields at the transition temperature, which in depends on the composition. Therefore, in order to
enhance the magnitude of MR in the presence of relatively low fields and at high temperatures, grain size reduction [5], substitution doping [6], distribution of the manganite grains in a non-magnetic insulating matrix and magnetic insulating matrix are used as alternative approaches [7]. Thus, sol-gel technique has more advantages than solid state method to obtained ultrafine nano sized powders with precise stoichiometry and better uniform size. Besides, sol-gel method has the advantage of lower processing temperatures, short annealing times, high purity of materials, good control of size and shape of the particles and particle size well below 100 nm at the lower processing temperature [8]. The effect of sintering temperature on structure, microstructure, electrical and magneto-transport properties of single phase \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) were synthesized using sol-gel reaction method was reported in this work.

2. Materials and Method

\( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) compound were prepared via sol-gel method by dissolving a stoichiometric mixture of nitrates cation (\( \text{La(NO}_3)_3\cdot6\text{H}_2\text{O}, \text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O} \) and \( \text{Mn(NO}_3)_2\cdot4\text{H}_2\text{O} \)) in distilled water. Stoichiometric amount of the nitrate solution was stirred and heated at 70°C for 2 hours. Then, the aqueous solution of citric acid was added to the cationic mixture and after a while the ethylene glycol was added to the mixed solution. Finally, the whole solution was heated at 80°C with 250 rpm using magnetic stirrer until the gel is formed. On further heating, the gel was dried in the oven at 120°C until the gel was decomposed and produced a fluffy dried mass. The fluffy dried mass was ground and calcined at 500°C in ambient atmosphere for 5 hours with the heating and cooling rate of 2°C/min. Then, this powders were sintering with various temperature starting from 600°C until 1200°C [1,2].

The structural and microstructure of the samples were characterized by X-ray diffraction (XRD, Phillips PW 3040/60 Xpert Pro) using a CuKα radiation at room temperature and field emission scanning electron microscopy (FESEM, LEO1455 VSPEM, with an OXFORD INCA ENERGY 300EDXattachment). The magnetic behaviors were measured by vibrating sample magnetometer (VSM, LakeShore 7440) at room temperature. The Lake Shore Hall Effect measurement system 7604 was used to characterized and analyzed the metal insulator transition temperature (\( T_p \)) and magneto transport properties with temperature control (80 – 300 K) and magnetic field (0 and 1 T).

3. Results and Discussions

Figure 1(a) shows the XRD spectrums of LCMO with different sintering temperature from 600°C to 1200°C via sol-gel method labeled as LC-SG6, LC-SG7, LC-SG8, LC-SG9, LC-SG10, LC-SG11 and LC-SG12, respectively. Overall, all samples are completely formed into polycrystalline single phase without any detectable impurities with orthorhombic structure having \( \text{Pnma} \) space group (62) (ICSD collection code: 82820). The crystallite size was determined from the most intense of \( \{121\} \) peak using Scherrer’s formula. The intensity of the X-ray peaks for the LCMO perovskite phase increases as sintering temperature increases from 600°C to 1200°C reflecting the growth of crystalline phase in all samples. Rietveld Refinement analysis conformed all samples were in orthorhombic system, where not changes of lattice constant \( (a, b, c) \) and cell volume, \( V \) were observed. However, crystallite size is increased with sintering temperature.

The micrographs revealed an increment of sintering temperatures (\( T_s \)) starting from 600°C to 1200°C significantly promotes grain growth and the porosity decreases. The variation of the crystallite sizes (CS) obtained from the width of the X-ray diffractions peaks and the grain size (GS) for the all LCMO samples were plotted in Figure 1(b). The growth rate of the crystallite size is slower as compared to grain size and reach saturated after 1000°C. The difference between CS and GS was more pronounced at higher sintering temperature. Both crystallite sizes (CS) and the grain size (GS) increases with sintering temperature (\( T_s \)) due to congregation of the grains because a grain may subsists of several crystallite domains and these domains arises due to twinning and other structure defects, such as vacancies, dislocations, and stacking faults in the grain [9]. Overall, at low sintering temperature (600°C and 700°C), it is expected that only single crystallite on each grain. Meanwhile, at higher temperature (1000°C-1200°C), the grain might consist of multi crystallite.
In this section, metal-insulator transition temperature ($T_{MI}$) was measured in the temperature range of 80 – 300 K by four probe technique with/without an external applied magnetic field. All samples of LCMO at 0 and 1 T were plotted in Figure 2. The $T_{MI}$ of polycrystalline samples is an extrinsic property that strongly depends on the synthesis conditions and microstructure (e.g. grain boundaries or magnetic disorder layers). As lowering sintering temperature, a large dropped of the $T_{MI}$ and a substantial increase in resistivity at $T < T_{MI}$. Siwach et al. (2008) [10] emphasized the importance of a spin-polarized tunnelling below phase temperature and the domain wall contribution. They suggested that in small particles and noticed electrical resistivity increase at low temperatures is due to the enhanced scattering of the charge carriers through the higher density of magnetic disorder in grain boundaries. Thus, the $T_{MI}$ at lowest sintering labelled as LC-SG6 goes down to 155 K (0 T). The strong suppression of the $T_{MI}$ is caused by induced disorders and also by the increase in the non-magnetic phase fractions, due to enhanced grain boundary densities as a consequence of lower sintering temperature. This is also causes the increase in the carrier scattering leading to a corresponding enhancement in the resistivity. Therefore, lowering of sintering temperature reduces the metallic transition temperature and hence, increased in resistivity. However, by apply an external magnetic field 1 T, the transition temperature shifts to higher values with increasing the particle size leading to decrease in the GB’s and the associated disorder. Thus, resulting decrease in scattering of the carriers expressed by decreasing in the resistivity.

The simultaneous electronic transition can be clarify by double exchange (DE) mechanism model, the shifted $T_{MI}$ is most probably due to strong interaction between the Mn$^{3+}$ and Mn$^{4+}$ spin. Goutam et al., (2006) [11] reported that in the presence of applied magnetic field, the localized electron spins ($t_{2g}$) are favorably oriented along the field direction and therefore, the electron can transferred more easily from Mn$^{3+}$ to Mn$^{4+}$, hence resulting in the improved conductivity and consequently decrease in the resistivity and $T_{MI}$ shifted to the higher temperature has been observed.
Figure 2: Temperature dependence of the resistivity for LCMO at sintering temperature from 600°C to 1200°C.
The percentage of MR curve for all LCMO samples were measured from 80 – 300 K with an external magnetic field up to 1 Tesla as shown in figure 3. At 80 K, the MR values were measured to be (-7.62%), (-11.61%), (-12.89%), (-12.08%), (-12.31%), (-11.21%), (-11.27%) for sample LC-SG6, LC-SG7, LC-SG8, LC-SG9, LC-SG10, LC-SG11, LC-SG12, respectively at the field of 0.1 T. The highest LFMR value, which extrinsic MR is more dominant, is observed for LC-SG8 with nano-sized distribution that showing pseudo-domain structure as suggested in. However, the highest CMR is found in LC-SG10 (-23.48%) at 80 K with 1 Tesla applied field.

The MR curves gave two significant different regions or gradient, which is faster drop of MR value from 0 – 0.1 T and follow by a linear or slow decrease of resistance at 0.1 T – 1.0 T. Generally, low field magnetoresistance (LFMR) is a significant MR, which observed at low magnetic field with always related to the extrinsic MR and Radaelli et al. (1997) [12] reported that commonly this kind of behavior is show in polycrystalline form that can be interpreted in terms of spin dependent tunneling and spin dependent scattering through electron barriers across the grain boundaries. The large scattering and tunneling effects occurred when the spin alignment disordered at the grain boundaries. When a low field is applied, the disorder spin among neighboring will align parallel with the magnetic field. Thus, this will enhanced the electron hopping and leads to the steep decrease in resistance at low fields. All LCMO systems with different sintering process have not achieved saturation with a magnetic field up to 1 Tesla, meaning that higher magnetic field is required to fully align all localized spin. This might be due to obtain of some disordered region at the grain boundary.

The appearance of peak in the MR-T curve around TMI depicts in which all samples as shows in figure 4, there is a presence of the intrinsic component of MR, which arises due to the double exchange mechanism around TMI. However, around TMI the peak in the MR-T curve of the sample LC-SG12 (bigger in particle size) is significantly higher at all applied magnetic fields as compared to other samples. The magnitude of MR peak around TMI decreases as we lower the sintering temperatures (smaller in particle size) as well as the magnitude of the applied magnetic field is reduced. The peak MR values are (-23.94%), (-19.47%), (-14.76%), (-12.69%), (-11.53%) at 1 Tesla applied magnetic field for LC-SG12, LC-SG11, LC-SG10, LC-SG9 and LC-SG8, respectively whereas for sample LC-SG6, and LC-SG7 there is a hump in the MR variation around TMI. In the case of nanostructure manganites, magnetotransport studies reveal that the volume fraction of highly disordered grain boundaries play an important role in these materials. As the surface to volume ratio become larger, that is, grain size reduced, the effective of the grain boundaries will increase and as a result the intrinsic properties reduced, thus, humped the MR peaks. These studies clearly depict that sol-gel technique is an effective method to enhance ferromagnetic ordering temperature along with improving of low field magnetoresistance. Thus, the intrinsic of magnetoresistance follows the expected DE behavior with steady increase in temperature, meanwhile, the extrinsic of magnetoresistance improved that the nature of the surface region of nanosize grains plays a very crucial role in enhancement of magnetotransport behavior of nanodimensional system [13].
Figure 3: The percentage of MR curve for LCMO with different sintering temperature from 600°C to 1200°C as a function of magnetic field at various temperatures.
Figure 4: The percentage of MR versus temperature curve for LCMO with different sintering temperature from 600°C to 1200°C.

4. Conclusion
The effects of sintering temperature (grain size) on the electrical and magneto-transport properties of nanoparticles of polycrystalline La$_{0.67}$Ca$_{0.33}$MnO$_3$ ceramics synthesized by sol-gel method was demonstrated. The T$_{MI}$ at lowest sintering labelled as LC-SG6 goes down to 155 K (0 T). The strong suppression of the T$_{MI}$ is caused by induced disorders and also by the increase in the non-magnetic phase fractions, due to enhanced grain boundary densities as a consequence of lower sintering temperature. The highest LFMR value, which extrinsic MR is more dominant, is observed for LC-SG8 with nano-sized distribution that showing double crystallite. However, the highest CMR is found in LC-SG10 (-23.48%) at 80 K with 1 Tesla applied field. All LCMO systems with different sintering process have not achieved saturation with a magnetic field up to 1 Tesla, meaning that higher magnetic field is required to fully align all localized spin. This might be due to obtain of some disordered region at the grain boundary.

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