

**A COMPARATIVE STUDY ON THE STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES OF THE  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  SYNTHESIZED VIA CO-PRECIPIATION METHOD AND SOLID-STATE REACTION**

Hazar A.Salama, S. A. Halim, W.M.D.W. Yusof, Imad Hamadneh, Noorhana Yahya, Zaidan Abdul Wahab, E. B. Saion and Z. Gebrel

*Faculty of Science and Environmental Studies, Universiti Putra Malaysia  
43400 Serdang, Selangor.*

**ABSTRACT**

The structural, magnetic and electrical properties of lanthanum manganites have been reported.  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  sample synthesized via co-precipitation (COP) method with starting materials derived from metal acetates were compared to the specimens prepared by solid state route (SSR). The Curie temperature,  $T_C$  and the metal-insulator transition temperature,  $T_P$  were obtained by ac susceptibility and four-point probe techniques. The results showed that  $T_C$  and  $T_P$  were 260 K and 276 K respectively for the COP specimen, which is higher than the results obtained for specimen prepared by SSR with  $T_C$  and  $T_P$  were 245 K and 246 K respectively. These results are due to the high chemical homogeneity and high density for the COP specimen as compared to the SSR specimen. The CMR for the COP specimen is observed near the insulator-metal transition with the maximum value of (~ -56%) at 260 K for  $H = 1.06$  T.

**INTRODUCTION**

During the last decade, interest in manganese oxides with perovskite structure (also called manganites) has grown considerably, mainly because of the colossal negative magnetoresistance (CMR) displayed by the mixed-valence members of these materials. Although a change in resistivity induced by a magnetic field is a phenomenon observed in many metals and semiconductors, the magnetoresistance in manganites is remarkable for its size (a decrease in resistivity of more than six orders of magnitude is not uncommon). This makes manganese perovskites are potential candidates for use in magnetic-field sensors and magnetoresistive read heads. Besides the CMR effect, mixed-valence manganites  $\text{T}_{1-x}\text{D}_x\text{MnO}_3$ , where T and D are trivalent and divalent ions respectively can exhibit various magnetic, structural, and electronic phase transitions, leading to a complex physical behavior [1]. The basis of the theoretical understanding of the CMR is usually referred to the double exchange (DE) mechanism proposed by Zener in 1950. However, the DE mechanism alone could not account for the observed transport properties. Other effect such as charge-ordering transition due to the long range coulomb interaction among the carriers, electron phonon coupling, arising from the Jahn-teller distortion of  $\text{Mn}^{3+}$  could also be responsible [2]. It is well known that the magnetic and electrical properties of these oxides are very sensitive to material processing parameters. Accordingly, it is very important to establish a reliable and cost effective scheme for these oxides [3].

Recent studies tend to shift towards more complex oxides systems, such as La-Y-Ca-Mn-O and La-Ca-Mn-Co-O. As more component are involved in the system; it becomes difficult to achieve homogeneity through a conventional materials fabrication scheme based on SSR [3]. The ceramic method has several disadvantages: the starting mixtures are inhomogeneous at the atomic level; the reaction rate is rather slow. Solid-state methods are therefore labour and time intensive and have a tendency towards producing a contaminated product [4]. COP method offers unique advantages including low temperature synthesis, high purity and chemical homogeneity, precise composition control and the production of ceramics with high density and lower particle size. High homogeneity in COP derived materials could easily be achieved due to the fact that the mixing of components occurs at the molecular level in a co-precipitation process.

In this paper we have focused our work to investigate the structural, magnetic and electrical properties of the  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  prepared by two method, co-precipitation method and solid state reaction.

## **PREPARATION AND CHARACTERIZATION**

### **Co-precipitation (COP) method of preparation**

A stoichiometric amount of each metal compound was weighed and dissolved in an optimum amount of acetic acid at 80°C. The solutions were added together to form solution (A) and the temperature dropped to ~ 0-2°C. The oxalic acid was dissolved in water: isopropanol (1:1.5) to have a concentration of 0.5 M at 0-2°C (solution B). Solution (A) was added to the stirred solution (B) in an ice bath and a uniform, stable, white suspension was obtained. Then the slurry was filtered after 5 minutes of reaction. The drying stage was carried out in the temperature range of 80~85°C for 8~12 hours. The powder was calcined at 900°C in air for 12 hours to remove the remaining volatile materials, and calcined powder was reground in a marble mortar for 10 minutes. Then the powder was pressed into pellets. The pellets were sintered at 1300°C for 24 hours and slowly cooled to room temperature at 2°C/minute

### **Solid State Reaction (SSR) preparation**

Starting chemical powders of  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MnCO}_3$  were dry mixing in mortar-pestle for 2 hours, and calcined at 900°C for 12 hours. The calcined powders were reground for 1 hour. The resulting powders were pressed into pellets and sintered at 1300°C for 24 hours in air with increment rate and cooling rate 2°C/minute.

Resistance measurements of the samples were carried out using a four-point probe technique with silver paint contacts. The samples were also examined by X-ray powder diffraction with  $\text{Cu } k_\alpha$  radiation (Phillips PW1830). The microstructure and the grain size were investigate using a scanning electron microscope (SEM) (JEOL6400). The magnetic properties were studied using Ac Susptometer at 125 Hz with different magnetic field ranged from 0.1 Oe to 10 Oe.

## RESULTS AND DISCUSSIONS

X-ray diffraction spectrum of the samples prepared by co-precipitation method and solid state reaction are as shown Figure1. All peaks were attributed to those of orthorhombic perovskite structure. The homogeneity of the phase was preserved in all specimens. The lattice parameters and the unit cell volume were calculated and found in the range as reported in the literature [5]. The COP derived samples possessed larger lattice parameters and the unit cell volume was  $228.71 \text{ \AA}^3$ , compared with  $226.18 \text{ \AA}^3$  for the SSR samples.

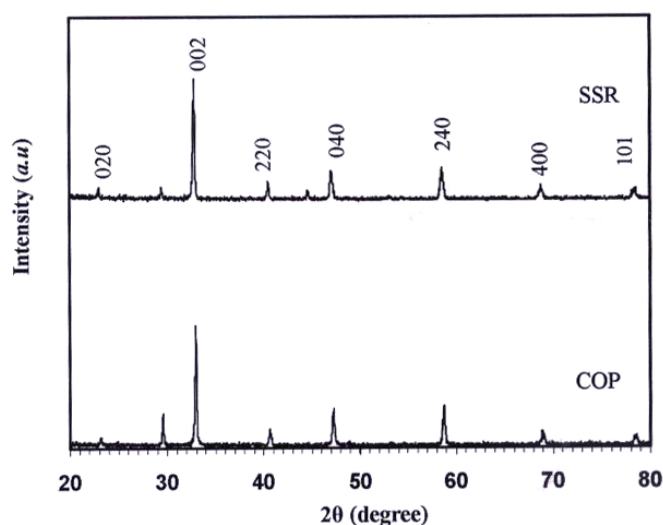


Figure 1: XRD spectrum for COP and SSR specimens

The temperature dependant of the samples resistance at zero magnetic field is presented in Figure 2(a) & 2(b). The samples display a normal phases transition temperature  $T_P$ . At  $T_P$  the curve display metal-insulator transition (MIT), exhibiting the maximum resistivity. For the COP samples the curve display a sharp transition at 276K. This transition is reported in the literature as 245K to 270K. (Balsco et al 1997, Ravindranath, et al 2001). A broad MIT is observed for SSR samples. It shows a lower phase transition temperature at 246K.

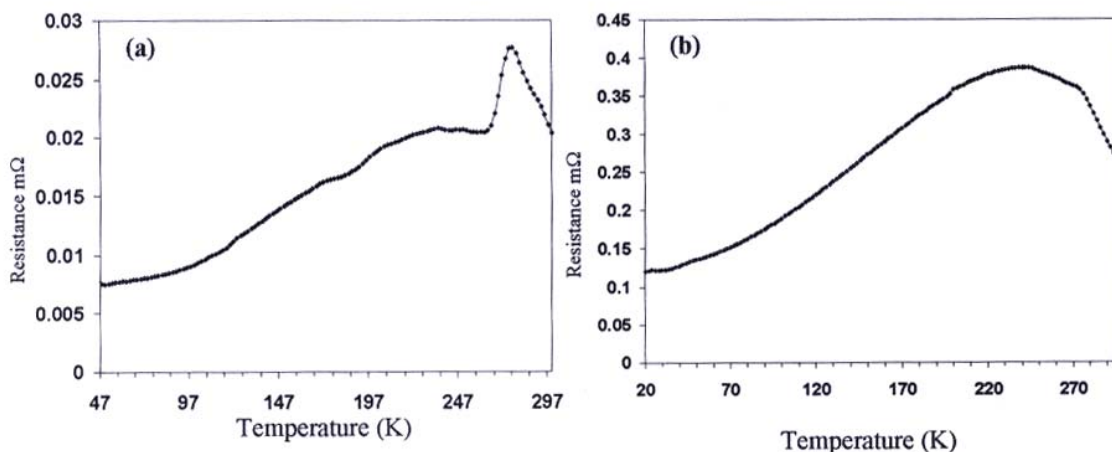


Figure 2: The resistance as a function of temperature for (a) COP samples, (b) SSR samples

The magnetic properties for LCMO system prepared by COP and SSR are shown in Figure 3(a) and 3(b) respectively. Both samples display classical phase transition from paramagnetic state to ferromagnetic state at Curie temperature,  $T_C$ . The sample prepared via COP exhibits the high  $T_C$  at 260 K. Whereas the SSR sample displays lower  $T_C$  at around 245 K. As the magnetic field increases from 0.1 Oe to 10 Oe the SSR sample shows slight increase of Ac susceptibility value. However, as the temperature increases the Ac susceptibility increases.

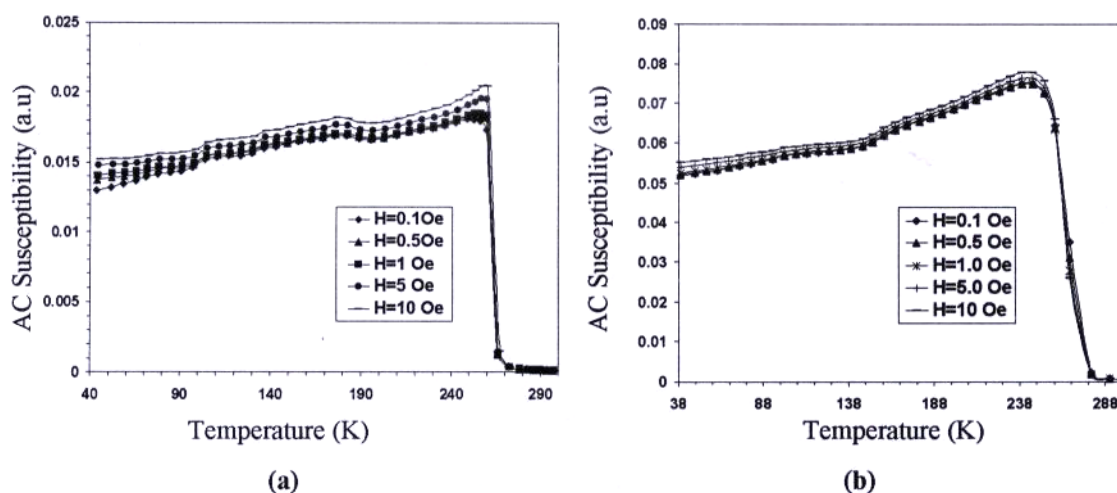


Figure3: Temperature dependant of AC susceptibility of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$   
 (a) COP samples, (b) SSR samples

The CMR as a function of temperature for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  samples at 1.06 Tesla is shown in Figure 4.

The CMR ratio is defined as

$$MR\% = \frac{R(H) - R(0)}{R(0)} \times 100$$

where  $R_H$  is the resistance in the present of magnetic field and  $R_0$  is the zero field resistance. The COP specimen exhibit the maximum CMR value(-56%) at 260K while for the SSR specimen display the maximum CMR value(-34%) at 240K. Each of the specimens displays the maximum CMR value around its  $T_P$ .

The microstructure of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  prepared by COP and SSR are shown in Figure 5(a) and 5(b) respectively. The electron micrograph was taken on fracture surface with magnification of 2000X. The SSR specimen has a uniform grain size of 1- 1.5  $\mu\text{m}$  and has a high level of porosity. The grain size increase drastically to  $\sim 8.7 \mu\text{m}$  with regular shape and are well compact when the specimen is prepared by the COP.

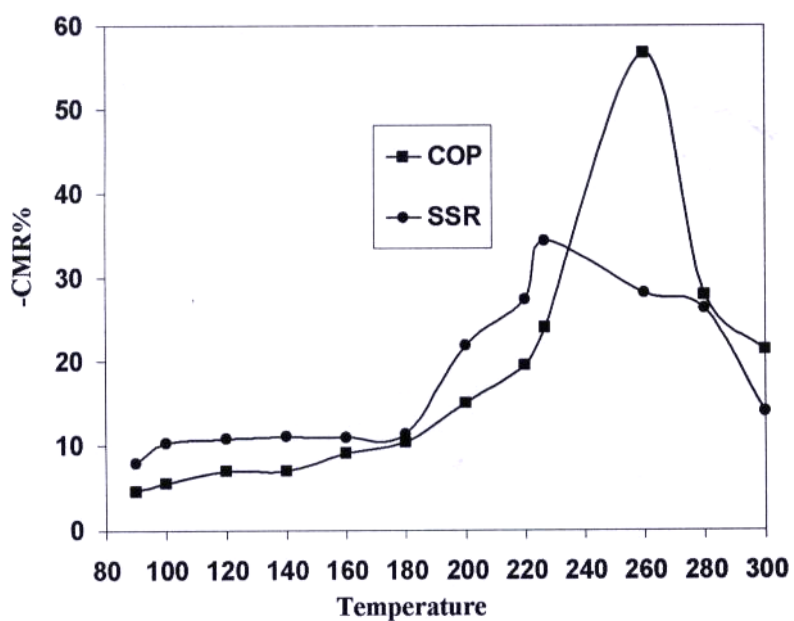


Figure 4: CMR curve of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  as a function of temperature at 1.06 Tesla.

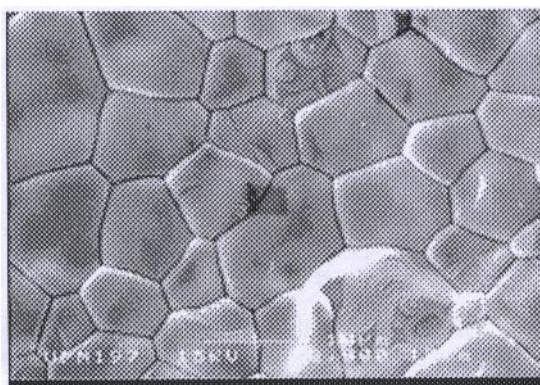


Figure 5 (a): Electron micrograph for COP specimen

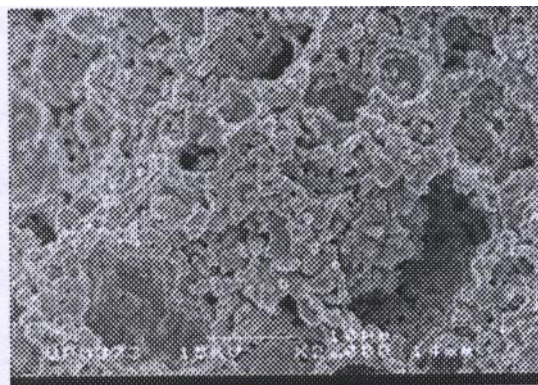


Figure 5 (b): Electron micrograph for SSR specimen

## CONCLUSION

In summary, properties of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  bulk specimen prepared by Co-Precipitation method and Solid State Reaction are investigated. Data on the structural, magnetic and electrical properties show that the COP specimen is more pure and homogeneous than that of the SSR specimen.

## ACKNOWLEDGEMENT

The financial support from the MOSTE, under the IRPA vote: 03-02-04-0374 (Development and Applications of Giant Magnetoresistive and Giant Magnetoresistive Materials) is gratefully acknowledged.

## REFERENCES

- [1] H.Huhtinen, J Raittila, P Paturi, J Salminen and V S Zakhvalinskii *J. Phys.: Condens. Matter* 14 (2002) 7165–7176
- [2] Alvydas Lisauskas Low Frequency Noise in Thin Film Colossal Magnetoresistors September 2000
- [3] S-Y .Bae and S-X.Wang *Appl.Phys Lett* 69 (1) July 1996
- [4] I.Schildermans, M. Van Bale, E. Knaepen, J. Yperman, J. Mullens and L.C. Van Poucke, *Physica C* 278(1997) 55-61
- [5] K. H. ahn, X. W. Wu, K .liu, and C.L. Chien(1997), *J.Appl.Phys*,81(8),5505-507
- [6] Blasco, J. Gracia, J. de Teresa, J. M. Ibarra, M. R. Perez, J. Algarabel, P. A. and Marquina, C. J. physics. *Rev.B*, 55 (14), 1997. 8905-8910.
- [7] Ravindranath. V, Ramachandar Rao, M.S. Rangarajan, M., Yafen Lu., Klein, J., Klingele, R, Uhlenbruck, S. B. Buchner and R. Gross *J.Phys.Rev. B* 63 184434-1-7(2001)