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Grain Size Induced Metal-insulator Transition in $La_{0.7}Sr_{0.3}MnO_3$ Compounds

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The effect of different synthesis techniques on structural, microstructural and electrical properties of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) was investigated. Two different techniques viz solid state reaction (SSR) and sol-gel (SG) method were used to prepare the samples. X-ray studies have confirmed the single phase formation of LSMO by both the techniques. The average grain size was 2 μm for solid state reaction sample and 22 nm for sol-gel sample. A substantial enhancement in electrical resistivity was observed in the sample with nanosized grains. The micro grain size sample exhibited metallic behaviour whereas nanoparticle sample showed metal-insulator transition around 250 K.

Keywords: Nanomaterials, Manganites, Metal-insulator transition,

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1. INTRODUCTION

Doped perovskite manganites, exhibiting colossal magnetoresistance (CMR) effect have attracted considerable attention not only for fundamental research, but also for potential applications [1, 2]. The magnetic property of ultrafine granular systems is an interesting subject of research for both theoreticians and experimentalists. Considerable difference in magnetization has been observed by varying particle size and have attributed to the presence of nonmagnetic or magnetically dead surface layer [3] or disordered spin orientation in the surface. The nature of interplay between the crystal structure, magnetic and transport properties of manganites is still a matter of discussion in spite of numerous investigations. The size and shape of particle, particle size distribution, and finite size effect and dipolar or exchange interaction between the particles strongly influence the properties of manganites [3, 4]. The underlying physical mechanism is that interactions, one ferromagnetic (FM) and the other antiferromagnetic (AFM), shows variety of physical properties in magnetic (FM or AFM), charge (metal, insulator, or charge ordering), and orbital / lattice degrees of freedom [6]. The phenomenon of metal-insulator transition and electronic phase diagram in doped manganese oxides with perovskite structure has not been satisfactorily explained despite extensive efforts [2]. Most of the investigations show that the ferromagnetic Curie temperature and the metal-insulator transition temperatures in such materials are strongly dependent on composition and synthesis condition. A measurable effect, i.e. field induced modulation of resistance, has also been reported in the CMR manganites [7]. This makes the CMR oxides a likely candidate for use as semiconductors in novel field effect transistors with ferroelectric gate. These devices can be interrogated by reading the resistance (or conductance) of the CMR-based channel. Among all the compositions of $La_{1-x}Sr_xMnO_3$, the $La_{0.7}Sr_{0.3}MnO_3$ shows a variety of structural, electrical and magnetic transitions over a range of temperatures [8].

The physical properties of these materials are usually dependent on their preparation routes [9]. One of the most important aspects is the formation of high quality ceramics and monophasic homogeneous thin films onto the suitable substrates for real applications. For applications a ceramic material consisting of small manganite particles, show a large grain boundary effect at low temperatures could also be interesting. It is therefore important to study the structure and physical properties of the CMR material at nanoscale. The samples with smaller grain sizes possibly show richer electronic and magnetic properties, due to the influence of the structural and magnetic disorders at the grain interfaces. There have been several methods to prepare these manganites by varying micro to nanoparticle size. We choose to prefer solid state reaction (SSR) and sol-gel (SG) technique due to the reason that in SSR, less expensive oxide precursors are used and the procedure is economical where as in SG method, low temperature, quality of precursors, homogeneity of precursors, and particle size can be controlled properly. In addition, a maximum possibility for quality formation of samples can be achieved in these techniques.

In this report, an attempt has been made to systematically investigate the effect of different synthesis techniques on the structural and transport properties of LSMO bulk samples. We propose that metal-insulator transition arises from particle size variation, is a universal feature of electron-correlated manganite nanoparticles.

2. EXPERIMENTAL TECHNIQUE

Powder samples of LSMO were prepared by traditional Solid state reaction (SSR) and sol-gel (SG) techniques. In Solid state reaction method, the stoichiometric amounts of high purity chemicals $La2O_3$, $SrCO_3$ and MnO_2 were mixed in an agate mortar-pestle for several hours. In order to improve the reaction rate and ensure complete phase formation, intermediate grindings were performed. The mix was calcined at 950 °C for 24. The well-calcined mass was pressed into pellets of 12 mm diameter and then sintered at 1100 °C for 24 hours in an ambient air.

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During sol-gel process, $(CH_3COO)_3La.XH_2O$, $(CH_3COO)_2Sr.aq$ and $(CH_3COO)_2Mn.4H_2O$ were used as starting reagents. The precursors were dissolved in triple distilled water containing 30 ml acetic acid. The resulting transparent solution was thoroughly mixed with 100 ml ethylene glycol and then 20 % of ammonium acetate solution was added. This complete solution was heated on a thermal plate under constant stirring at ~ 80 °C to eliminate excess water. A homogeneous brown gel was achieved with heating at 110 °C and finally brown-black powder was formed. The powder was ground for two hours and then calcined at 500 °C for 12 hours. The powder was pressed in the form of pellets and was sintered at 600 °C for 12 hours.

The phase formation and crystal structure parameters of the powder samples were identified by X-ray diffraction (D8 Advance Bruker) using CuKα radiation in the range $10° \leq 2\theta \leq 60°$ with step size of 0.02°. Scanning electron microscope (SEM) was used to obtain the grain structure and size. The electrical resistivity measurement was performed by standard four probe method using a commercial cryostat (Oxford Instruments Inc., UK) in the temperature range $10\ K \leq T \leq 300\ K$.

3. RESULT AND DISCUSSION

3.1 Structural Analysis

Figure 1 reveals the X-ray diffraction patterns for the samples with nominal composition LSMO sintered at 600 °C (SG) and 1100 °C (SSR) respectively. All the prominent peaks indicate the presence of parent compound with orthorhombic (Pnma) and rhombohedral (R3C) lattice structure incase of SG and SSR sample. The grain size obtained through Scherer's formula for nanocrystalline sample was 14 nm which is below the size obtained by SEM with a reasonable agreement.The

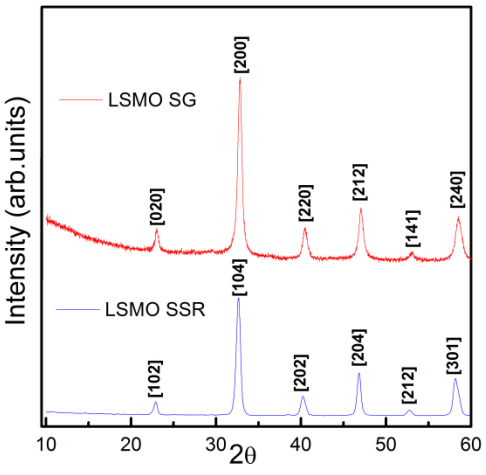

Fig. 1 – X-Ray diffraction patterns for SG and SSR samples

calculated values of lattice parameters along with synthesis conditions are shown in table 1. The XRD pattern of SG prepared sample indicates that the sample is fully crystallized without any kind of impurity. The synthesis of samples through SSR method needs higher temperature (1000-1600 °C) and long sintering time to obtain homogeneous composition and desired structures. High intensity of diffraction peaks for LSMO perovskite phase at high sintering temperature is the clear indication of better sample crystallinity. The SSR sample showed rhombohedral system which agree with early report [10, 11], however, we have observed orthorhombic structure incase of SG sample. The rhombohedral-to-orthorhombic phase transition can be understood as a cooperative Jahn-Teller distortion of MnO_6 octahedra, one long and two short Mn-O bonds with reduced bond angle execute the orthorhombic structure [12, 13] which is possible in nanosized LSMO compound.

3.2 Microstructural Behaviour

Figure 2 shows the polycrystalline samples synthesized by SSR and SG techniques, depict the variable grain sizes observed through Scanning Electron Microscopy (SEM). There is a maximum variation in grain size as it is well known that grain size and grain connectivity varies with varying sintering and synthesis techniques. The samples show spherical shape grains with average size of 2 μm and 22 nm, a marginal variation observed in samples prepared through SSR and SG route. SG prepared samples consisted of agglomerated nanoparticles organized by aggregation of smaller particles. Generally, the grain size increases as the sintering temperature is increased and at temperature above 1000 °C, rapid grain growth results in micron size particles. In general, the samples with large grain size showed linear electric behaviour while the small grain sized sample showed broader and wide metal-insulator transition.

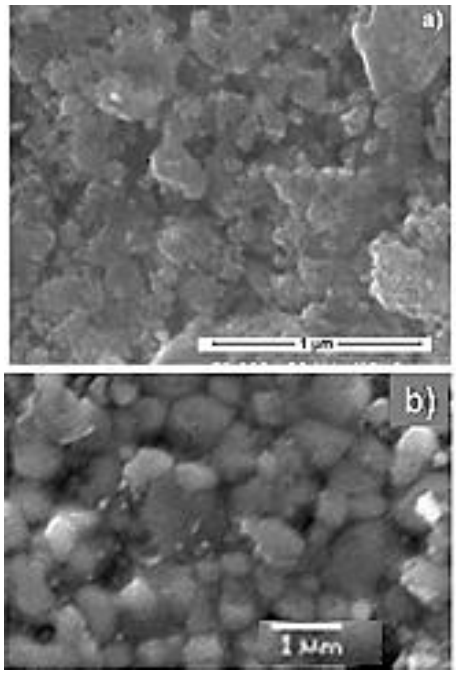

Fig. 2 – Scanning electron micrographs for a) SG and b) SSR samples

3.3 Electrical Resistivity Measurement

To assess the nature of resistivity, we measure the temperature dependent resistivity of LSMO samples

prepared by different synthesis techniques. Figure 3 shows the temperature dependence of normalized zero field resistivity for LSMO SSR and SG samples. It is well known that electrical transport properties depend on grain size and the porosity of the pellets. The resistivity value also appeared to be dependent to a large extent on the synthesis conditions. In order to perceive

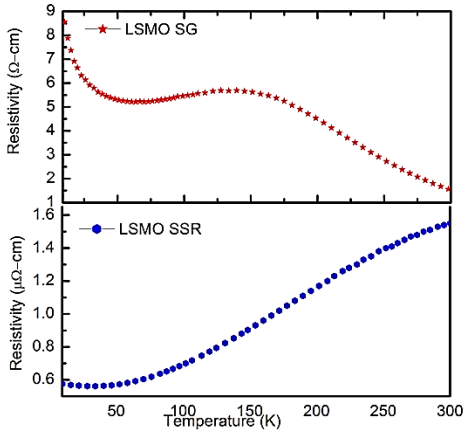

Fig. 3 – Temperature dependence of resistivity under zero fields for SG and SSR samples.

the effect of grain size on the transport properties, our approach was to keep the sintering temperature in both the methods as low as possible. The sample prepared under SSR shows linear metallic behaviour throughout the measured range, however, the sample prepared by SG method shows a metal-insulator transition around 250 K, indicates that the transition has a strong relation with reduced grain size, influenced by sintering and synthesis conditions. The resistivity of the sample increases with decrease in particle size changed by systematic sintering and synthesis method. A low temperature resistivity upturn appears in the SG sample, as a contribution of coulomb Blockade or Kondo effect [14, 15]. We argue that these features are predominantly observed in nanomaterials with a possible existence of new interaction by strong correlation characteristics between the electrons in manganites. From the figure, it is observed that resistivity increases more than one order of magnitude as we move from SSR to SG. This increase in resistivity occurs due to enhanced scattering of the charge carriers by increasing the grain boundaries due to the smaller grain size as observed in SEM images. In SSR method, grain size increases leads to a decrease in grain boundaries and magnetic disorder. The resistivity for the samples with smaller crystallite sizes shows the predominance of the grain boundary in the transport process.

Table 1 – Synthesis conditions and the lattice parameters of $La_{0.7}Sr_{0.3}MnO_3$ samples

Sample Name	Synthesis Technique	Sintering Temperature	a (Å)	b (Å)	c (Å)	V (Å^3)
SSR	Solid State Reaction	1100 °C	5.503	–	13.425	352.071
SG	Sol-Gel	600 °C	5.446	7.712	5.487	230.518

4. CONCLUSION

We synthesized the LSMO sample by solid state reaction and sol-gel method and investigated their structural and transport properties. Both the samples have pure LSMO phase with orthorhombic and rhombohedral unit cells. The sample prepared by SG method had nano range grain size and more disorder surface in comparison with SSR. The samples prepared with SG method restrict the grain growth due to low sintering and precursor temperature effects. The metal-insulator transition appears in finite sized sample is a characteristic feature of strongly electron-correlated manganite system.

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REFERENCES

1. E. Dagotto, *Science* **309**, 257 (2005).
2. Q.A. Pankhurst, J. Connolly, S.K. Jones, J. Dobson, *J. Phys. D: Appl. Phys.* **36**, R167 (2003).
3. M.B. Salamon, M. Jaime, *Rev. Mod. Phys.* **73**, 583 (2001).
4. S. Roy, I. Dubenko, D.D. Edorh, N. Ali, *J. Appl. Phys.* **96**, 1202 (2004).
5. P.E. Jonsson, *Adv. Chem. Phys.* **128**, 191 (2004).
6. M. Suzuki, S.I. Fullem, I.S. Suzuki, L. Wang, C. Zhong, *Phys. Rev. B* **79**, 024418 (2009).
7. Y. Motome, N. Furukawa, *Phys. Rev. B* **71**, 014446 (2005).
8. P. Dey, T.K. Nath, U. Kumar, P.K. Mukhopadhyay, *J. Appl. Phys.* **98**, 014306 (2005).
9. M. Paraskevopoulos, F. Mayr, C. Hartinger, A. Pimenov, J. Hemberger, P. Lunkenheimer, A. Loidl, A.A. Mukhin, V.Y. Ivanov, A.M. Balbashov, *J. Magn. Magn. Mater.* **211**, 118 (2000).
10. P. Dey, T.K. Nath, *Phys. Rev. B* **73**, 214425 (2006).
11. V. Shelke, A. Das, I. Dhiman, R. Yadav, S. Khatarkar, A. Anshul, R.K. Singh, *J. Phys. Condens. Mater.* **20**, 395218 (2008).
12. K.P. Lim, S.W. Ng, S.A. Halim, S.K. Chen, J.K. Wong, *Am. J. Appl. Sci.* **6**, 1153 (2009).
13. J.F. Mitchell, D.N. Argyriou, C.D. Potter, D.G. Hinks, J.D. Jorgensen, S.D. Bader, *Phys. Rev. B* **54**, 6172 (1996).
14. O.L. Lebedev, J. Verbeeck, V. Tendeloo, C. Dubourdieu, M. Rosina, P. Chaudouet, *J. Appl. Phys.* **94**, 7646 (2003).
15. J. Zhang, Y. Xu, S. Cao, G. Cao, Y. Zhang, C. Jing, *Phys. Rev. B* **72**, 054410 (2005).
16. T. Sarkar, M.V. Kamalakar, A.K. Raychaudhuri, *New J. Phys.* **14**, 033026 (2012).