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# Comparative Study of Magnetic Ordering and Electrical Transport in Bulk and Nano-Grained $Nd_{0.67}Sr_{0.33}MnO_3$ Manganites

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ABSTRACT

We have prepared bulk and nano-sized $Nd_{0.67}Sr_{0.33}MnO_3$ manganites by solid state and low-temperature mild solgel methods respectively. Both the compounds crystallized into an orthorhombic structure with Pbnm space group confirmed from Rietveld refinement of X-ray powder diffraction patterns. Nano-grained compound shows an average particle size of 22 nm with broad grain size distribution revealed from the Transmission electron micrographs. It appeared that the long range ferromagnetic order becomes unstable upon the reduction of the samples dimension down to nano meter scale. DC magnetization and AC susceptibility results showed frustration of spins in nano-grained compound and thereby it could lead to a cluster glass-like behaviour. Temperature dependence of electrical resistivity under different magnetic fields shows the broad maxima at higher temperatures and a low temperature upturn in both the compounds, however, the latter is more prominent in the nano grained compound. Combination of Kondo effect with electron and phonon interactions govern the low temperature resistivity and a small polaron hopping mechanism dominates at high temperatures for both the compounds. The magnetoresistance is understood by the effect of spin polarized tunneling through the grain boundary. The experimental results revealed that the reduction in particle size influences severely on the magnetic, electrical and magneto transport properties.



## 1. Introduction

Doped manganites $A_{1-x}A'_xMnO_3$ (A=trivalent rare earth elements, A'= divalent alkaline earth elements) have attracted enormous scientific interest due to various structural, magnetic and electrical properties associated with it [1]. Due to the strong interplay among charge, spin and orbital degrees of freedom, these compounds exhibit various exotic magnetic phenomena such as colossal magnetoresistance (CMR) and magnetocaloric effect (MCE) [2–4]. The Double Exchange (DE) mechanism is proposed to understand the correlation between ferromagnetism and metallicity and the strong electron-phonon coupling due to the Jahn-Teller (JT) effect explain the resistivity and magnetoresistance in these compounds [5]. Any changes in the valency of the perovskite at the A-site creates ferromagnetism and conduction in these materials. The substitution of the trivalent ($Nd^{3+}$) element by divalent ($Sr^{2+}$) produces an inhomogeneous distribution of mixed valence $Mn^{3+}/Mn^{4+}$ ions to maintain charge neutrality. The coupling between $Mn^{3+}$ and $Mn^{4+}$ ions results from the motion of $e_g$ electron between the two partially filled D- orbitals [6]. $Nd_{1-x}Sr_xMnO_3$ is a ferromagnetic (FM) metal for $x < 0.5$ and an antiferromagnetic (AFM) insulator for $x > 0.6$ whereas the intermediate doping range shows AFM metallic behavior [7]. Among the $Nd_{1-x}Sr_xMnO_3$ series, x=0.33 is known as tricritical point, which separates a first order transition (x=0.3) from a second order transition (x=0.4) [8]. Several authors reported the synthesis and properties of $Nd_{0.67}Sr_{0.33}MnO_3$ (NSMO) by various methods such as pulsed laser deposition, solid state reaction, solgel, PVA gel route and pyrophoric reaction process [8–13]. A commendable work in this direction was done by Venkataiah et al. [10] who reported the electrical resistivity and magnetoresistance (MR) of NSMO by varying the sintering temperature from 800 °C to 1100 °C. Venkatesh et al. reported the critical exponent study combined with MCE and have explained how the PM-FM transition is influenced by the competing order parameters [8]. The low temperature resistivity anomalies of NSMO was reported for microcrystalline sample with grain size greater than 1 μm [11]. However, from the literature it is understood that the magnetic and electrical properties of the materials strongly depend on the crystalline size which vary with the synthetic routes and annealing conditions.

Nano crystalline manganites show unusual physical properties

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when compared to its bulk counterparts [14]. Reduction of the particle size enhances the amount of grain boundaries which results in structural and magnetic disorders in the grain surfaces and thereby influences various magnetic and electrical phenomena significantly. Magnetic nano particle exhibits less value of magnetization and high value of low field magneto resistance [15]. It has been reported that spin glasses or cluster glass are the magnetic systems which exhibit a freezing transition temperature ($T_f$) to a state of order in which spins are aligned in random directions [16]. Moreover, $T_C$ and $T_f$ decrease with the reduction in particle size [16]. However, to the best of our knowledge a limited studies are available in the literature about the effects of particle size reduction on magnetic ordering and electrical transport nature of NSMO. Recently, D.C. Krishna et al. reported the non- linear variation of electrical resistivity and magnetic transition temperature of nano crystalline $Nd_{0.67}A_{0.33}MnO_3$ (A=Ca, Sr, Pb, Ba) on the basis of size variance effect [12]. Among the studied compound, 32 nm crystalline size NSMO sample found to exhibit an interesting phenomena such as double transition and metamagnetic phase, but, the low temperature resistivity on the same was not reported.

In nano materials, synthesis is a key factor in controlling morphology, chemical composition, and grain size distribution [17]. These factors deeply influence the physical and chemical properties of the system. Magnetic materials with nano-sized particles are frequently studied by the scientific community because they exhibit interesting phenomena due to small coercivity as well as increased anisotropy [18]. Therefore in the present article, we take an effort to synthesize nano sized NSMO by mild solgel technique. We have prepared an average particle size of 22 nm NSMO and done a systematic study on effect of particle size reduction on the structural, magnetic and electrical properties in connection with their phase transition behavior.

## 2. Experiment

Microcrystalline and nanoparticles of $Nd_{0.67}Sr_{0.33}MnO_3$ compounds were prepared by the conventional solid state and mild sol-gel techniques [19] respectively. For the bulk composition, stoichiometric amount of $Nd_2O_3$ (Alfa-aesar, 99.9%), $SrCO_3$ (Sigma-Aldrich, 98%), $MnCO_3$ (Sigma-Aldrich, 99.9+ %) were mixed in an agate mortar using distilled water for several hours until the mixture becomes homogenous. The resultant slurry was then dried and calcined at 1100 °C for 12 h. For the nanosized NSMO, stoichiometric amount of $Nd(NO_3)_3.6H_2O$ (Alfa-aesar, 99.9%), $Sr(NO_3)_2$ (Sigma-Aldrich, 99%), $Mn(NO_3)_2.xH_2O$ (Sigma-Aldrich, 98%), were dissolved in deionized water and it is mixed with the solution of citric acid $C_6H_8O_7.H_2O$ (S D Fine-chem limited) and ethylene glycol (Sigma-Aldrich), in the ratio of (0.67 $[Nd^{3+}]$+0.33 $[Sr^{2+}]$+1 $[Mn^{3+}]$) /1.5 [citric acid]/ 2.25 [ethylene glycol]. Ammonia solution was added to the solution till the pH reaches 9. Then heated with constant stirring at 80 °C and converted into a viscous gel. The gel was dried, ground and calcined at 600 °C for 4 hours. The granulated powders were pressed uniaxial into cylindrical pellets of appropriate dimension under a pressure of 100 MPa. The pellets were then sintered at 1350 °C for 12 h (Bulk) and 750 °C for 4 h (Nano) in air and finally cooled to room temperature. The crystal structure and phase purity of the powdered samples were analyzed using X-ray diffraction (PAN analytical X'Pert Pro Diffractometer having Ni filtered Cu Kα radiation, Netherlands). Rietveld refinement of the diffraction pattern was carried out using the GSAS software [20] and Crystal structure was carried out using Crystal Maker software (Crystal maker Software limited, Oxfordshire OX5 1PF, UK). Micro structural analysis was conducted using scanning electron microscope (JEOL-SEM 5601 v, Tokyo, Japan). The morphology and size of the grains were directly investigated by high resolution transmission electron microscopy (HR-TEM). Magnetic and electrical transport measurements of the samples were made as a function of temperature and applied field using a physical property measurement system (Quantum Design Inc., USA).

## 3. Results and discussion

### 3.1. Structural Analysis

The XRD patterns of $Nd_{0.67}Sr_{0.33}MnO_3$ compounds were analyzed, and the structural parameters were determined from Rietveld refinement using GSAS software [20]. The XRD patterns of both the compounds were identified to form a single phase perovskite structure of orthorhombic crystal symmetry and has been indexed with ICDD (International Centre for Diffraction Data) pattern no.89-8474 (Pbnm space group). The refined XRD patterns with the crystallographic structure in the inset are shown in Fig. 1. The refined structural parameters of the same are listed in Table 1. From the refinement analysis, it is evident that there is an excellent agreement between the calculated and experimental fits for both the compounds, considered from the small values of residuals for the weighted pattern $R_{WP}$, pattern $R_P$ and the goodness of fit $\chi^2$. We have obtained a tolerance factor less than 0.9 for NSMO which corroborates the orthorhombic crystal structure obtained from the structural refinement results. It can be seen from Table 1 that the Mn–O–Mn bond angle observed is less than 180° for both compounds and hence deviates from the ideal cubic structure for which the Mn–O–Mn bond angle is 180° [21]. Deviation from the same is an indication of the distortion of the $MnO_6$ octahedra, which further corroborates the orthorhombic crystal structure.

Structural, magnetotransport and magnetic properties of manganites are strongly governed by the grain morphology and grain boundary nature [22]. Fig. 2(a) shows the surface microstructure (inset shows EDAX spectrum) of well densified NSMO bulk compound obtained from SEM analysis. The polygonal grains are almost uniform in size and the grain boundaries are clearly visible. The variation in the grain size as well as grain boundaries will result in variation of bond angle, which affects the DE interaction hence reduce the orbital overlap and hopping of electrons. The micrograph indicates that the surface of the compound is homogeneous. Fig. 2(b), (c) and (d) represent the TEM image (inset shows grain size distribution), EDAX spectrum and SAED pattern of nano NSMO compound respectively. The TEM analysis reveals different sized spherical shaped nano particles with an average particle size of 22 nm with certain grain size distribution. Further, the analysis of chemical composition has been carried out using EDAX at different region of the sample during the SEM and TEM studies to confirm the homogeneity. The EDAX analysis shows that the obtained compositions are nearly identical with the nominal one.

### 3.2. D C magnetic characterization

Temperature variation of magnetization, M(T) of both the compounds has been carried out in zero-field cooled (ZFC) and field cooled (FC) mode from 2–300 K, under an external field of 50 Oe and are depicted in Fig. 3a. In ZFC process, the sample was cooled from 300 K to 2 K in the absence of magnetic field and then the magnetization measurement was performed under 50 Oe during the warming process from 2 K to 300 K. In FC process, the magnetization measurement was carried out under the same magnetic field during the cooling from 300 K to 2 K. The bulk