Size Dependent Magnetic Properties of \( \text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) Nanomanganite

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Abstract: Nanoscale materials show different properties compared to bulk materials. Due to the size dependent properties the nanoscale materials have potential applications in industry. In this paper the size dependent magnetic properties of \( \text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) nanomanganite have been investigated. \( \text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) nanoparticles were prepared by low temperature sol-gel method. X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and EDAX techniques were used to understand the structure, grain size and composition. Nanoparticles prepared were of the sizes 15 nm, 19 nm and 25 nm respectively. SQUID magnetometer was used to study the magnetic behavior of the nanoparticles. Field cooled (FC) and zero field cooled (ZFC) magnetization of all the nanosamples with respect to temperature was studied and compared. We have observed drastic changes in magnetic properties of 15 nm particles compared to the other nanoparticles. The ‘charge order peak’ was seen to have disappeared in 15 nm particles while it was present in the other nanoparticles. All the nano particles exhibit superparamagnetism whose blocking temperature decreases as a function of decreasing particle size. The possible reasons for the influence of the particle size on the magnetic properties are discussed.

1. Introduction

Studies on perovskite rare earth manganites of general formula \( \text{A}_{1-x}\text{B}_x\text{MnO}_3 \) (where \( \text{A} \) is a trivalent rare earth ion such as \( \text{La}^{3+}, \text{Pr}^{3+} \) etc. and \( \text{B} \) is a divalent alkaline earth ion such as \( \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+} \)) have been a very active research area in the last few years in condensed matter physics due to their technological applications\([1-3]\). These materials show coexisting/ competing electronic and magnetic phases. Charge ordering (CO) is one of the fascinating properties exhibited by manganites. It is an insulating phase that is unstable under various perturbations such as magnetic field, electric field and pressure. We have shown \([4-7]\) that it is also unstable to size reduction to nanoscale. Recent research on manganites focuses on the effect of the particle size reduction on the physical properties of these materials \([8-9]\). The particles with smaller grain sizes show richer magnetic and electronic properties due to the influence of the disorder on the surface. The published reports on nanomanganites show the interesting effects of the reduction in size in these systems.

Quintel’s group \([10]\) has studied the electronic and magneto transport properties of sol-gel derived nanoparticles of \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \). They show that the saturation magnetization and magneto calorific effect (MCE) decrease linearly with surface/volume ratio. Zheng et. al \([11]\) have shown that \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) nanoparticles with diameter below 60 nm exhibited surface phonon modes which disappeared above that particle size. The softening and hardening of the stretching and bending modes of phonons were observed respectively with the decrease of particle size from 140 to 20 nm. It was also shown that the metal-insulator transition temperature \( T_{\text{MI}} \) shifts towards lower temperatures with the decrease in the grain size while the Curie temperature \( T_c \) is insensitive to the grain size. Dutta et.al \([12]\) have studied the effect of particle size on magnetic and electronic properties on sol-gel
derived nanoparticles of $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$. It has been shown that no signatures of structural phase transitions are observed with the decrease of particle size at room temperature. There is an increase of $T_c$ and $T_{MI}$ with the decrease of particle size. Zhangyz et al., [13] studied the sol-gel prepared nanosized $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ particles. With the grain growth, there is a structural phase transition from cubic perovskite phase to orthorhombic phase. Magnetization increases with the decrease of particle size and a small decrease in the Curie temperature $T_c$ with the grain growth is also reported. Our group has not observed any monotonic increase or decrease in magnetization in $\text{Pr}_{0.57}\text{Ca}_{0.41}\text{Ba}_{0.02}\text{MnO}_3$ nanoparticles [4-7]. Some other reports have concluded that the magnetization decreases as particle size increases [14]. The published reports on nano manganites show the interesting effects of the reduction in size in these systems though many results are contradictory to each other. To understand the size dependent magnetic properties of manganites more in detail we have investigated the $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanomanganite.

The bulk $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ manganite shows an insulating behavior in a large temperature range (5-240K) due to CO of Mn$^{3+}$ and Mn$^{4+}$ cations ($T_{CO}=240K$) but exhibits a ferromagnetic ordering below $T_c=120K$. It shows that the ferromagnetic ordering of manganese cations does not induce a transition to a metallic state in contrast to what is observed in many other manganites which exhibit a metallic state due to the double exchange mechanism. Therefore $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is a rare combination of CO and ferromagnetic insulating phase. In this study we present the magnetic properties of $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanomanganite. We have mainly focused on the charge order region and the ferromagnetic region of the system.

2. Experimental

$\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanoparticles were prepared by sol-gel method. The preparation of a homogeneous polymeric precursor is the most crucial step in this synthesis procedure. The advantage of this method is its versatility and the possibility to obtain high purity materials, control over stoichiometry, homogeneity and the precise size control of the particles. Stoichiometric proportions of high purity $\text{Nd}_2\text{O}_3$, $\text{CaCO}_3$, and $\text{MnCO}_3$ were dissolved in concentrated nitric acid and an appropriate amount of triple distilled water was added to this mixture. Then an equal amount of ethylene glycol was added with continuous stirring. Initially the mixture was heated to 100$^\circ$C and at this stage the water evaporates. Further the mixture was heated to 140$^\circ$C. Excess ethylene glycol is then removed by heating to about 180$^\circ$C and at this stage a thick sol was formed. This sol was further heated at 250$^\circ$C in a furnace for about 6 hours to get the polymeric precursor. This precursor was then sintered at 700$^\circ$C, 900$^\circ$C and 1100$^\circ$C for about 6 hours each to obtain particles of different sizes.

3. Characterization

X-ray diffraction experiments were carried out on all the samples using a Philips powder diffractometer (Cu-Kα; $\lambda = 1.54056$ Å) at room temperature to confirm the phase formation and to estimate the crystallite size. Elemental composition analysis was done by Energy dispersive X-ray analysis (EDAX). Further the particle size of 700$^\circ$C sintered samples was also estimated using transmission electron microscopy (TEM). D. C. magnetization measurements were carried out using a commercial SQUID magnetometer at 1000 G on all the three nano samples in the temperature range of 10-300K.

4. Results and Discussions

4.1 Structural details

Figure 1 shows the X-ray diffraction patterns of the three nanosamples. The average grain diameter/size (d) was evaluated indirectly from the XRD data by applying the Scherrer formula $d = k\lambda / \beta$. 
/β cos θ (where k = 0.89 is a shape factor, λ is the wavelength of X-Rays, β is the full width at half maximum of the peaks and θ is the angle of diffraction). The average crystallite sizes estimated from XRD for 700°C, 900°C and 1100°C sintered samples are 15 nm, 19 nm and 25 nm respectively. Figure 2a shows the X-ray diffraction profiles for the most intense peak of the Nd0.7Ca0.3MnO3 nanosamples. It was observed that for the 15 nm particles the broadening is more compared to 19 nm and 25 nm particles. The structure was studied by the Rietveld powder diffraction profile fitting technique (Fig. 2b). All the samples crystallize in the orthorhombic space group Pbn.
The particle size of 700\(^\circ\) C (NCMO7) sintered sample was also determined directly by employing transmission electron microscopy. Figure 3(a,b) show the TEM pictures of 700\(^\circ\) C sintered sample. The average particle size of 700\(^\circ\) C sintered sample estimated using TEM was 15 nm and is in good agreement with the average grain size estimated by XRD. The TEM observations reveal that the particles are nearly spherical in shape. EDAX measurements have shown the good stoichiometry for all the three nanosamples.

**Fig. 2b** Observed (dots) and Rietveld fitted (continuous lines) powder diffraction pattern of 15 nm particle

**Fig. 3 (a b)** High resolution TEM image of 15 nm particles (c) the SAED pattern showing diffraction spots indicating polycrystalline behavior
4.2 Magnetization studies

Figure 4 shows the field cooled (FC) dc magnetization curves for the three nanosamples at 0.1T. The inset shows a clear picture of the melting of charge order in 15 nm particle whereas the CO peak is seen for both 19 nm and 25 nm particles at 235 K. It confirms that size reduction melts the charge ordering in manganites.

![Figure 4 Comparison of field cooled (FC) dc Magnetization vs. Temperature for all the 3 nanosamples (inset shows the melting of CO in 15 nm particle)](image)

Fig. 4 Comparison of field cooled (FC) dc Magnetization vs. Temperature for all the 3 nanosamples (inset shows the melting of CO in 15 nm particle)

$T_C$ is determined from the inflection point of the field cooled magnetization curve as observed in the dM/dT vs T curve (Fig.5). $T_C$ values increase with an increase in particle size ie. 85 K, 105 K and 110 K for 15 nm, 19 nm and 25 nm particles respectively. Among the three samples maximum magnetization was observed for the lowest particle size ie for 15 nm particles.

![Fig. 5 dM/dT curve showing the $T_C$ of different nano-particles](image)

Fig. 5 dM/dT curve showing the $T_C$ of different nano-particles
Figure 6 (a, b, c) shows the temperature dependence of the field cooled (FC) and zero field cooled (ZFC) magnetization. Zero field cooled (ZFC) magnetization was measured as a function of temperature while warming the sample under a field of 0.1 T.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6.png}
\caption{Temperature dependence of the zero field cooled and field cooled magnetization of the nanosamples showing the decrease in blocking temperature for the 15 nm particles.}
\end{figure}

In M(T) curves we obtained two different curves for zero-field-cooling (ZFC) and filed-cooling (FC) for super paramagnetic materials. In ZFC curve, the moment increased with the increase in temperature and then decreased, while the moment decreased in FC curve with increase in temperature. All the samples show irreversibility between FC and ZFC curves with ZFC magnetization exhibiting prominent peak at $T_B$ where $T_B$ is called the blocking temperature. The region below $T_B$ ($T < T_B$) is called blocking region, here the net magnetization of the individual particles is zero since the particles are oriented in different directions. Once the temperature is increased in the presence of the field the particles try to align in the field direction and hence
magnetization increases with increase in temperature and a peak is observed in the magnetization curve of ZFC i.e. the blocking temperature\[15]. Above $T_B$ the magnetization decreases since the moments no longer align in the field direction. The region $T > T_B < T_C$ is called superparamagnetic region. Above $T_C$ the moments of individual particles get disordered and the material becomes paramagnetic\[16]. The variation of $T_C$ and $T_B$ as a function of particle size is as shown in figure 7. The $T_C$ increases with increase in temperature and the blocking temperature decrease with decrease in particle size. Disappearance of charge order in the 15 nm particles is one of the interesting observations of our studies. This is in consistency with our earlier reports.

$$T_B = E_a / k_B \ln(t_f) \quad --- (1)$$

$$T_B = KV/k_B \ln(t_f) \quad --- (2)$$

where $E_a$ is the anisotropy barrier and can be obtained by $E_a = KV$ (K = anisotropy energy density constant and V is the volume of particle), t is the experimental measuring time and $k_B \ln(t_f_0)$ is treated as constant. \[17-20\]. From equation 2 it is clear that $T_B$ is directly proportional to volume of the particle. For small particles, they have small volume and thus lower energy barrier and lower blocking temperature. Hence $T_B$ decreases with decrease in particle size.
5. Conclusions

We have successfully prepared nanoparticles of NCMO by polymer-assisted sol-gel method. The nanoparticles were characterized by various techniques like XRD, TEM, EDAX and SQUID. Magnetization measurements show interesting temperature and also particle size dependence. Except 15 nm particles all other particles show charge ordering. The disappearance of charge order in nanosystem is quite interesting as it provides a new intrinsic way of melting the CO in addition to the external perturbations. Blocking temperature is seen to decrease with decrease in particle size. We have observed the strong dependence of magnetic properties with respect to particle size.

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