Research Article

Magnetotransport Behaviour of Nanocrystalline Pr$_{1-x}$Sr$_x$MnO$_3$ (0.40 ≤ x ≤ 0.60)

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The nanocrystalline samples of Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) (x = 0.40, 0.50, 0.55, and 0.60) were synthesized by wet-chemical sol-gel route. Structural, magnetic, and magnetotransport properties have been studied systematically. It is found that Pr$_{1-x}$Sr$_x$MnO$_3$ samples with Sr content x = 0.40 and 0.50 show paramagnetic to ferromagnetic (PM-FM) transition at $T_C \sim 308$ K with no trace of FM-AFM transition within the temperature range of 77–350 K. However, interestingly a second transition is observed at $T \sim 273$ and 255 K, respectively, for samples $x = 0.55$ and 0.60 corresponding to an A-AFM magnetic structure. This indicates that samples $x = 0.40$ and 0.50 are ferromagnetic below $T_C$, while other samples ($x = 0.55$ and 0.60) have a mixed phase consisting of FM and A-type AFM phases. Resistivity versus temperature ($\rho$-T) curves show that the resistivity of all the samples is much larger than the single crystals of corresponding compositions due to large contribution of grain boundaries in the present nanocrystalline samples. Moreover, the decrease in metallic component at higher Sr concentration is also evidenced by the successive reduction in magnetoresistance (MR) with increasing Sr content from $x = 0.40$ to 0.60.

1. Introduction

Several experimental and theoretical studies have focused on the exploration of grain size effect on the structural, magnetic, and electrical transport properties of alkaline-earth doped rare earth perovskite manganites chemically represented by RE$_{1-x}$AE$_x$MnO$_3$ (RE = rare earth cation and AE = alkaline earth cation) because of their unusual magnetic and electronic properties like colossal magnetoresistance (CMR), charge ordering, orbital ordering, and phase separation [1–10]. These studies focus on and clearly highlight the significance of broken Mn–O–Mn exchange bonds at the grain surface and their likely impact on the magnetic and electrical transport properties. Since size reduction leads to increased contribution from the surface regions, the broken Mn–O–Mn bonds are indeed expected to have a definite impact on magnetoelectrical properties in manganites. However, in view of the fact that manganites exhibit a strong competition and correlation between various structural and electronic degrees of freedom even more intriguing and complex phenomena are expected. It has been shown that in nanomanganites, size reduction below ~100 nm renders the charge and orbitally ordered (CO–OO) ground state with unstable antiferromagnetic (AFM) spin order, giving rise to a ferromagnetic (FM) ground state [3, 11]. Size induced transition from the AFM/CO to the weak ferromagnetic (WFM) state was observed in both nanowires [3] and nanoparticles [4]. It has been shown by Lu et al. [11] that destabilization of the AFM/CO state and formation of an FM order can result in an enhancement of magnetization by two orders of magnitude. The WFM ground state in nanomanganites resulting from the destabilization of AFM ground state has been regarded as a direct consequence of size reduction because when the size is small enough (e.g., 20 nm), the effect of surface spin disordering would become more evident. However, WFM induced by the destabilization of the AFM order has been also
reported in single crystals [12, 13] as well as epitaxial thin films [14]. This suggests that the evolution of WFM out of the AFM-CO state cannot be a consequence of material down sizing to nanometric scale alone and that some additional effects such as orbital disordering may also be equally important [13–17].

The effect of material down sizing can have more dramatic effect in the vicinity of compositions that possess strong magnetic phase coexistence and hence show bicritical/multicritical points. Among the manganites, Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) has larger bandwidth than Nd$_{1-x}$Sr$_x$MnO$_3$ (NSMO) and exhibits PM-FM transition at $T_C \sim 320$ K for $x \sim 0.30–0.40$ [15, 17, 18]. In single crystals, epitaxial thin films, and large grain polycrystalline bulk, insulator to metal (I-M) transition is also observed to be simultaneous with the PM-FM transition. At higher Sr concentrations ($x > 0.50$), it transforms into an A-type AFM metal and when $x$ exceeds 0.75 the magnetic structure becomes C-type AFM insulator. Therefore, it is interesting to study the behavior of this compound in this critical range, $x = 0.40$ to 0.60, for its nanocrystalline particles.

In view of the above, we have tried to understand the magnetic and magnetotransport behaviour of nanocrystalline Pr$_{1-x}$Sr$_x$MnO$_3$ in this critical range, $x = 0.40$ to 0.60. The Pr$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.40, 0.50, 0.55,$ and 0.60) nanoparticles are prepared by wet-chemical sol-gel route and their magnetic and magnetotransport properties for their nanometric size (∼40 nm) grains are studied.

2. Experimental Procedure

The wet-chemical sol-gel route has been adopted to synthesize Pr$_{1-x}$Sr$_x$MnO$_3$ (with $x = 0.40, 0.50, 0.55,$ and 0.60) nanosized particles at a significantly lower sintering temperature as compared to conventional solid-state reaction method. In this technique, the aqueous solution of high purity Pr(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$·4H$_2$O, and Mn(NO$_3$)$_2$·4H$_2$O has been taken in the desired stoichiometric proportions. An equal amount of ethylene glycol has been added to this solution with continuous stirring. This solution is then heated on a hot plate at a temperature of ∼100–140°C till a dry thick brown colour sol is formed. At this temperature ethylene glycol polymerizes into polyethylene glycol, which disperses the cations homogeneously forming a cation polymer network. The polymerized ethylene glycol assists in forming a close network of cations from the precursor solution and helps the reaction in enabling the phase formation at low temperatures as compared to that in bulk synthesis via solid state route. The gel forms a resin and the high viscosity of the resin prevents different cations from segregating and ensures a high level of homogeneity. This has been further decomposed in an oven at a temperature of ∼250°C to get a polymeric precursor in the form of a black resin-like material. This material was then finely ground into powder. The same procedure was used to synthesize all the samples and then pellets were made for each sample. A pellet from each sample was finally sintered at ∼900°C for about 12 hrs. All the synthesized samples have been subjected to phase identification and structural characterizations using a powder X-ray diffractometer [XRD, Philips PW1710] using CuKα radiation at room temperature and microstructural characterization by the scanning electron microscopic technique [SEM, Philips XL20]. The magnetotransport measurements have been performed by standard dc four-probe technique in the temperature range of 300–77 K at an applied magnetic field of 3 kG. The magnetic characterizations have been carried out by temperature dependent ac susceptibility measurements in the temperature range of 77–350 K.

3. Results and Discussion

3.1. Structural and Microstructural Characterization. The powder X-ray diffraction (XRD) patterns of Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) ($x = 0.40, 0.50, 0.55,$ and 0.60) samples are shown in Figure 1. All the samples are single phase polycrystalline and possess orthorhombic structure (space group Pbnm). The degree of crystallinity remains almost unaffected by the value of $x$ (Sr content). In all the samples, the most intense diffraction maxima corresponds to the (112) plane followed by (312)/(132), (220), and so forth. The lattice parameters of all the PSMO samples were evaluated from the XRD data and are listed in Table 1. For clarity, the variation of the lattice parameters and unit cell volume with Sr content ($x$) is plotted in Figures 2 and 3, respectively. From the XRD data of Table 1 and Figure 2, it is clear that as the Sr content increases, the in-plane lattice parameters, namely, $a$ and $b$, come closer, and the structure becomes nearly tetragonal. The out-of-plane lattice parameter $c$ first decreases and then again

![Figure 1: XRD patterns of Pr$_{1-x}$Sr$_x$MnO$_3$ samples with $x = 0.40$, 0.50, 0.55, and 0.60.](image-url)
Table 1: Variation of CSs, lattice parameters, and unit cell volumes of Pr$_{1-x}$Sr$_x$MnO$_3$ samples with different Sr concentrations.

<table>
<thead>
<tr>
<th>Sr concentration ($x$)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume of unit cell (Å$^3$)</th>
<th>Crystallite size (CS) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>5.489</td>
<td>5.467</td>
<td>7.703</td>
<td>229.293</td>
<td>19</td>
</tr>
<tr>
<td>0.50</td>
<td>5.494</td>
<td>5.452</td>
<td>7.662</td>
<td>229.502</td>
<td>18</td>
</tr>
<tr>
<td>0.55</td>
<td>5.494</td>
<td>5.467</td>
<td>7.667</td>
<td>230.283</td>
<td>17</td>
</tr>
<tr>
<td>0.60</td>
<td>5.487</td>
<td>5.485</td>
<td>7.672</td>
<td>230.898</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 2: Variation of lattice parameters of Pr$_{1-x}$Sr$_x$MnO$_3$ with different Sr concentration ($x$).

Figure 3: Variation of unit cell volume of PSMO samples with different Sr concentration ($x$).

Figure 4: Variation of crystallite size of PSMO samples with different Sr concentration ($x$).

increases slightly. This variation in the lattice parameters is in agreement with the previously reported results [15, 17]. However, in the present case, the in-plane lattice parameters are slightly larger than the previously reported values. This could be due to the nanocrystalline nature of the present samples where strain is expected to be more dominant than in microcrystalline samples.

The average crystallite size (CS) of the samples is obtained by the X-ray line width using Scherer formula, $CS = \frac{k\lambda}{\beta \cos \theta}$, where $k = 0.89$ is the shape factor, $\lambda$ is the wavelength of X-rays, $\beta$ is the actual FWHM due to CS only, and $\theta$ is the angle of diffraction. The average CS of samples having Sr content $x = 0.40$, 0.50, 0.55, and 0.60 is found to be approximately equal to ~19 nm, 18 nm, 17 nm, and 15 nm, respectively. This suggests that Sr concentration ($x$) also affects the crystallite size. The variation of CS is plotted in Figure 4. The CSs, lattice parameters, and unit cell volumes obtained for the different samples are listed in Table 1.

The surface microstructure of the samples, as revealed by scanning electron microscopy (SEM), was found to consist of nanometric grains. The average grain size is found to be ~40 nm in all the samples. This grain size is larger than
the crystallite size calculated from the XRD data. This difference is due to the fact that grains are composed of several crystallites, probably due to the internal stress or defects in the structure. A representative typical micrograph showing the surface morphology of the fractured portion of $x = 0.40$ sample is shown in Figure 5. The crystallite size was also determined by TEM. All the samples were observed to consist of nanocrystalline crystallites of average size $\sim$40 nm and in majority of cases these nanocrystals were found to be present in the form of clusters. The TEM investigations also revealed that the crystallite size was not uniform and in some areas crystals as large as 60–70 nm were also observed. However, the density of such crystals was relatively small. A representative TEM micrograph unraveling local area microstructure and the corresponding selected area electron diffraction pattern showing the presence of nanocrystals and nanocrystalline cluster are shown in Figure 6.

3.2. Magnetic Characterization. The magnetic phase characterization was carried out by the temperature dependent AC susceptibility ($\chi-T$) which was measured using the lock-in technique. The variation of AC susceptibility with temperature is shown in Figure 7 (left panels). The paramagnetic to ferromagnetic (PM-FM) phase transition temperature ($T_C$) was determined from the first-order temperature derivative ($d\chi/dT$) of the $\chi-T$ data, which is plotted in the right panel of Figure 7. The $T_C$ has been defined as the temperature corresponding to the peak in the $d\chi/dT$ curve. The sample with Sr content $x = 0.40$ shows onset of transition around 315 K and a sharp PM-FM transition at $T_C = 308$ K (value corresponding to the peak in the first-order derivative of $\chi$). This value is nearly equal to the values reported for single crystals of similar composition [15] and similar to the bulk samples. There is no trace of FM-AFM transition within the temperature range of 77–350 K. The half doped sample with Sr content $x = 0.50$ also shows transition from PM-FM state at around 308 K, but, in this case, the transition width has slightly larger value, as shown by relatively broader peak in the $d\chi/dT$. On the lower temperature side, the susceptibility decreases around $T \sim 225$ K. This could be due to appearance of A-type AFM ordering. In samples with Sr content $x = 0.55$ and 0.60, the FM transition temperature is found to decrease slightly to $T_C \sim 300$ K and the transition width also increases. But the most interesting observation is the occurrence of a second transition for the samples with Sr content $x = 0.55$ and 0.60 that generally corresponds to an A-AFM magnetic structure. The PM-FM transition is followed by a kink and change in the slope of the $\chi-T$ curve (marked by double arrow in Figure 7). The smaller peak, which occurs at $T \sim 273$ and 255 K, respectively, for sample $x = 0.55$ and 0.60, in the $d\chi/dT$ curve corresponds to this transition. This is due to the presence of a second magnetic phase that has a lower magnetic moment, such as the A-AFM phase that consists of two-dimensional ferromagnetic sheets coupled in an antiferromagnetic manner. In samples having Sr concentration $x = 0.55$ and 0.60, the presence of the AFM phase is also evidenced by sharp decrease in the susceptibility in the lower temperature regime. Thus, the present results show that at $x = 0.40$ and 0.50 samples are ferromagnetic below $T_C$, while other samples ($x = 0.55$ and 0.60) have a mixed phase consisting of FM and A-type AFM phases. In nanomanganites with an AFM ground state, the superexchange interaction drives AFM, which is diluted by the surface disorder [6, 16, 19, 20]. This induces a reorganization of the disordered surface spins and has been explained in terms of the core-shell model [19, 20].

3.3. Electrical Transport Characterization. Electrical transport characterization of all samples was performed by resistance measurements in zero magnetic field as well as a DC magnetic field $H = 3$ kOe by four-probe technique. The resistivity was calculated from the formula $\rho = \rho_L/A$, where $R$ is the resistance, $\rho$ is the resistivity, $L$ is the distance between the voltage probes, and $A$ is the cross-sectional area of the sample. Percentage magnetoresistance/magnetoresistivity (MR) was calculated by $MR = (\rho_0 - \rho H) \times 100/\rho_0$, where $\rho_0$ is the resistivity at zero magnetic field and $\rho_{H}$ is the resistivity at $H = 3$ kOe. The temperature dependence of resistivity (in the temperature range of 4.2–350 K) and MR (in the temperature range of 77–300 K) is plotted in Figure 8. The resistivity of all the samples is much larger ($\sim$ few $\Omega$-cm) than the single crystals of corresponding composition [15, 18] which is of the order m$\Omega$-cm or even smaller. This is due
Figure 7: Temperature dependent AC susceptibility (left panel) and corresponding temperature derivatives (right panel) of Pr$_{1-x}$Sr$_x$MnO$_3$ samples with $x = 0.40$, 0.50, 0.55, and 0.60.
Figure 8: The temperature dependent resistivity (left) and MR (right) plots of Pr$_{1-x}$Sr$_x$MnO$_3$ samples with $x = 0.40, 0.50, 0.55,$ and $0.60$. 
to large contribution of the grain boundaries in the present nanocrystalline samples. Because of the increased surface area which leads to increased grain boundary disorder as discussed in a previous section, the carrier scattering is strongly enhanced in the GB region. As seen in the $\rho$-$T$ curves plotted in Figure 8, for the sample $x = 0.40$ the resistivity first increases on lowering the temperature up to 165 K and then shows an insulator to metal (I-M) transition, which is much lower than the PM-FM transition temperature $T_C$. In case of $x = 0.50$ sample, the resistivity first increases on lowering the temperature and then shows a hump- or plateau-like region. However, no I-M transition is seen in this case and, in fact below the humped region, the resistivity shows a very strong enhancement. Nearly similar trend is showing samples having higher Sr concentration ($x = 0.55$ and 0.60). Disappearance of the I-M transition at $x = 0.50$ or higher is indicative of the fact that in these samples metallic component is reduced. In the composition range $x = 0.50$–0.60, the electrical characteristic is determined by competing metallic and insulating phases. The metallic phases are generally contributed by FM and A-AFM phases, while the insulating characteristics are mainly due to the presence of grain boundaries. The absence of I-M transition shows that the contribution of grain boundaries is rather dominant in these samples ($x = 0.50$–0.60) and one possible scenario is that the induced FM phase is not metallic but insulating or has relatively lower conductivity. This can be attributed to the nanocrystalline nature of the sample. Because of the small grain/crystallite size the electrical transport is dominated by the contribution from the grain boundaries. The grain boundary contribution envelopes the I-M transition, which occurs in the vicinity of $T_C$ in single crystalline materials.

The decrease in the metallic component at higher Sr concentration is also evidenced by the successive reduction in the magnetoresistance (MR) as Sr content increases from $x = 0.40$ to 0.60. As seen in the right panel of Figure 8, sample $x = 0.40$ shows the highest MR ~12% at 77 K and $H = 3$ kOe. The MR values are measured to be ~8, 4.5, and 3.5% for $x = 0.50$, 0.55, and 0.60, respectively. This gradual and systematic decrease in MR magnitude confirms the conjecture that induced FM phase in the present nanocrystalline samples may not be metallic.

4. Conclusions

We have synthesized Pr$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.40$, 0.50, 0.55, and 0.60) nanocrystalline samples by wet-chemical sol-gel route and studied their structural, magnetic, and electrical transport properties. All the samples are single phase and possess orthorhombic structure with space group Pbnm. The samples with $x = 0.40$ and 0.50 show a paramagnetic to ferromagnetic (PM-FM) transition at $T_C \sim 308$ K. However, interestingly, a second transition is observed at $T \sim 273$ and 255 K, respectively, for samples $x = 0.55$ and 0.60 correspond to an A-AFM phase which indicates that, below $T_C$, samples with $x = 0.55$–0.60 have a mixed phase consisting of FM and A-type AFM phases. In these nanocrystalline samples, the resistivity is much larger than the single crystals of corresponding compositions due to large contribution of grain boundaries. Moreover, the gradual decrease in the MR from ~12 to 3.5% is observed with the Sr content from $x = 0.40$ to 0.60 which also indicates the decrease in the metallic component at higher Sr concentrations.

References


[20] T. Zhang, T. F. Zhou, T. Qian, and X. G. Li, “Particle size effects on interplay between charge ordering and magnetic properties in nanosized La$_{0.25}$Ca$_{0.75}$MnO$_3$,” *Physical Review B*, vol. 76, no. 17, Article ID 174415, 7 pages, 2007.