Experimental observation of charge ordering in nanocrystalline Pr$_{0.65}$Ca$_{0.35}$MnO$_3$

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Observation of charge ordering in single crystalline and bulk polycrystalline systems of various rare-earth based manganites is well documented. However, there is hardly any manifestation of the same when the grain size is reduced to nanoscale. We have observed charge ordering in case of nanocrystalline Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ of average particle size 40 nm. This phenomenon is attributed to the primary role played by the martensitic character of the charge order transition in the material.

PACS numbers: 75.47.Lx, 73.63.Bd

I. INTRODUCTION

The phenomenon charge ordering (CO) in perovskite manganites with general formula $R_{1-x}B_x$MnO$_3$ (where, $R$ is rare-earth, $B$ is bivalent ion) has become a subject of intense research. This intriguing phenomenon is associated with strong interplay between charge, lattice and orbital degrees of freedom and mainly observed for some commensurate fraction of carrier concentration like $x = 1/2, 2/3, 4/5$ etc. However, the formation of CO state is also possible for other incommensurate values of carrier concentration. CO state can be destabilized by magnetic field and gives rise to a large negative magnetoresistance (MR). In literature, there are many studies regarding CO in polycrystalline and singlecrystalline bulk form of the sample. The primary ingredients behind the formation of CO state are emphasized as the competition between the core spins of manganese and the coulomb interaction between electrons of different orbitals of the same manganese-site. The Charge Order transition is accompanied by structural transition. This structural effect has been considered as the secondary effect of CO. More recently, the polarized optical studies have revealed that CO is a martensitic-like transformation. The martensitic strain is another important factor in case of CO. The phenomenon CO is not much explored in case of nanocrystalline form of the samples. The issue is still not clear that which factor plays the dominant role in CO especially, when the particle size of the system is reduced. In this report our primary objective is to address this issue by studying the phenomenon in nanocrystalline material.

The Cd doped Pr- manganites (Pr$_{1-x}$Ca$_x$MnO$_3$) with the doping concentration $0.3 \leq x \leq 0.5$ in bulk form show same generic behavior in their phase diagram. They remain at insulating state in all temperatures in absence of any external perturbation. Charge Order transition occurs below a certain temperature ($T_{CO}$). The antiferromagnetic transition does not coincide with CO. The antiferromagnetic transition temperature, $T_N$, is always less than $T_{CO}$. For the samples having Ca-concentration away from commensurate value ‘0.5’, the antiferromagnetic state is transformed to a canted antiferromagnetic state at low temperature well below $T_N$.

We have performed a detailed experimental study on the nanocrystalline Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ of average particle size ~ 40 nm and CO state has been observed. In case of the bulk Pr$_{0.65}$Ca$_{0.35}$MnO$_3$, $T_{CO}$ and $T_N$ are 225 K and 175 K respectively. The canted antiferromagnetic structure has been stabilized below ~ 100 K.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The nanoparticles of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ have been prepared by sol-gel technique. At the end of the process, the gel is decomposed at about 100º C and a porous black powder has been obtained. The powder is given heat treatment at 1000º C for 6 hour to get nanocrystalline sample. The x-ray diffraction study has confirmed the single phase nature of the sample with orthorhombic crystal structure (pbcm symmetry) similar to the bulk sample. The values of the lattice constants ($a = 5.420 \AA$, $b = 5.449 \AA$ and $c = 7.660 \AA$) of the sample agree quite well with literature values for the bulk sample. Transmission Electron Microscopy (TEM) study has revealed that the average particle size is ~ 40 nm. One typical electron micrograph of the sample has been shown in Fig. 1. The histogram showing particle size distribution as well as the High-resolution Transmission Electron Microscopy (HRTEM) image of the inside portion of a particle has been depicted in the insets of Fig.1. The HRTEM picture (inset [B], Fig. 1) exhibits clear lattice-planes implying good crystallinity inside the particle. The crystallite size of the sample is calculated from the full width of the half maximum (FWHM) of x-ray diffraction peaks using Scherre formula. The correction due to instrumental broadening has been taken into account. The calculated average crystallite size is ~ 36 nm.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Resistivity measurement has been performed in usual four probe method in presence as well as in absence of magnetic field. In absence of the external magnetic field, resistivity increases with the decrease of temperature in
FIG. 1: Transmission Electron Micrograph of nanocrystalline sample of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$. Inset:[A] Histogram showing particle size distribution [B] High-Resolution Transmission Electron Microscopy (HRTEM) image of inside portion of a particle showing lattice resolved planes.

FIG. 2: Resistivity as a function of temperature for nanocrystalline sample of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ of average particle size 50 nm in presence as well as in absence of magnetic field. Inset: Electron Diffraction Pattern of Selected Area (SAED) of the sample at 120 K. The super lattice spots indicated by arrows are signatures of Charge Order transition.

The transport measurements along with electron diffraction study clearly indicate the existence of the CO state in case of the present nanocrystalline sample. The grain boundaries of the nanoparticles are in disordered state and have strong extrinsic effect on transport. The intrinsic character of transition can be affected by this extrinsic effect. To get better understanding of transition, heat capacity measurement has been performed. The temperature dependence of specific heat (Fig. 3) indicates a clear peak at $\sim$ 225 K. The temperature at which the peak is observed is almost same as the reported Charge Order transition temperature ($T_{\text{CO}}$) of the bulk form of the sample.$^{3}$ The peak in specific heat data in case of the nanocrystalline sample indicates CO transi-
FIG. 4: The temperature dependence of zero field cooled dc susceptibility for nanocrystalline sample of Pr0.65Ca0.35MnO3. The measurements have been performed in the presence of 1 kOe magnetic field. Inset:[A] The temperature dependence of susceptibility in high temperature region, CO transition temperature is indicated by arrow. [B] Inverse zero field cooled dc susceptibility at 1 kOe magnetic field has been plotted as a function of temperature. [C] The temperature dependence of zero field cooled and field cooled dc susceptibility in the presence of 100 Oe magnetic field.

The melting of CO state by magnetic field in the bulk sample almost coincides with that obtained for the bulk sample. At low temperature (below ~ 30 K), the susceptibility starts to drop down with the decreasing temperature as seen in case of similar kind of the bulk sample which is believed to be as a result of a spin reorientation transition.

We have also performed the zero field cooled (ZFC) and field cooled (FC) DC susceptibility measurement in presence of the 100 Oe magnetic field (inset [C], Fig. 4). A large bifurcation between FC and ZFC curve has been observed below ~ TC_A. The surface layers of the nanoparticles are in disordered magnetic state comprising of non-collinear spin arrangement as well as defects, vacancies. Due to the existence of this disordered surface layer, the magnetic frustration can occur and as a result, cluster glass state may form. The bifurcation between ZFC and FC susceptibility curve is indication of this glassy behavior.

All the measurements consistently indicate that CO transition occurs in the nanoparticles of Pr0.65Ca0.35MnO3. The CO transition temperature in nanoparticles remains almost same as that of the bulk form of the sample. This result directly contradicts with the previous experimental results for nanocrystalline Pr1.5Sr0.5MnO3 and Nd0.5Sr0.5MnO3. For nanoparticles of Pr0.5Sr0.5MnO3, ferromagnetic transition temperature (TC) remains same as the bulk sample and CO transition is not observed down to 4 K.

In case of Nd0.5Sr0.5MnO3, TC decreases in comparison with the bulk. However CO transition is still invisible down to 2 K. The ferromagnetic transition is governed by DE interaction. There is no evidence of strengthening of ferromagnetic DE interaction (as reflected in the value of TC) due to the reduction of particle size for both the two samples. In spite of this fact, CO transition is hindered. The reduction of particle size has hardly any effect on the on site coulomb interaction. Thus, there may be other factor which plays dominant role in CO in case of nanoparticles. Charge Order transition has all the essential signatures of martensitic transformation. During martensitic transformation, due to the nucleation of new crystal structure with in the parent crystal, lattice misfit arises and it gives rise to a strain known as martensitic strain. This strain has to be accommodated by the system in order to occur the transformation. The development of the martensitic strain depends on the crystal structure of the parent phase and the martensitic phase. It is not easy for nanoparticles to accommodate the martensitic strain.

During the CO transition of Pr0.5Sr0.5MnO3, the high temperature tetragonal crystal structure is changed to CO phase of monoclinic crystal structure. For Nd0.5Sr0.5MnO3, CO transition is accompanied by high temperature orthorhombic crystal structure to the monoclinic crystal structure. In both the cases, CO is associated with the transformation from the higher symmetric crystal structure to relatively lower symmetric crystal structure. On the other hand Pr0.65Ca0.35MnO3 transform...
forms from orthorhombic structure to relatively higher symmetric tetragonal (pseudo) crystal structure during CO transition.\textsuperscript{18,26} It seems that, due to the transition from lower to relatively higher crystal symmetry, the martensitic strain developed during CO transition in Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ is smaller in comparison with Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. As a result, the nanoparticles of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ can accommodate the strain which is rather difficult for other two cases. The charge order transition is possible for the nanocrystals. However, the formation of CO state is largely affected in case of nanocrystalline Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. The observed behaviors of the nanoparticles of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ in the present case and Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ in previous cases\textsuperscript{20,21} show that the martensitic like character of transition itself plays the dominant role in CO transition.

IV. SUMMARY

We have prepared and characterized nanoparticles of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ with average particle size ~ 40 nm. The transport, electron diffraction, heat capacity and magnetization studies have been carried out on the sample. All the measurements indicate that the charge order transition occurs for the sample at almost same temperature as that of the bulk form of the sample. The present experimental results lead to the conclusion that the martensitic nature of the transition is the key factor for the occurrence of CO in nanocrystalline sample of rare-earth manganites.

V. ACKNOWLEDGMENTS

Authors would like to thank Pulak Ray of Saha Institute of Nuclear Physics, Kolkata for providing TEM facility and P. V. Satyam and Jay Ghatak of Institute of Physics, Bhubaneswar, for low temperature electron diffraction measurements.