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Variation in Charge Order Magnetic Properties upon Ga Doping in $Pr_{0.63}Ca_{0.37}Mn_{0.98}Ga_{0.02}O_3$ Bulk and Nano Manganites

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***Abstract*—We reported the effect of 2% 'Ga' doping in Mn site and the effect of size reduction on magnetic properties of $Pr_{0.63}Ca_{0.37}Mn_{0.98}Ga_{0.02}O_3$ nano manganites prepared by sol-gel route. The interesting features we have observed are: The emergence of ferromagnetic phase upon 2% 'Ga' doping in antiferromagnetic $Pr_{0.63}Ca_{0.37}MnO_3$ bulk sample and the disappearance of charge order peak upon size reduction in $Pr_{0.63}Ca_{0.37}Mn_{0.98}Ga_{0.02}O_3$ nano manganites. The role of local counter distortion introduced by Ga doping in the appearance of ferromagnetic phase and the enhanced surface pressure preventing the formation of charge order phase in nanosamples is discussed. The occurrence of ferromagnetic transition is further confirmed by hysteresis measurement.**

***Index Terms*— Nanomanganites,Ferromagnetism, Charge order.**

I. INTRODUCTION

Manganites with general formula $R_xA_{1-x}MnO_3$ where R-trivalent rare earth ion like Pr^{3+} Nd^{3+} $Sr^{3+}$and A-divalent rare earth ion like Ca^{2+}, Sr^{2+}, Ba^{2+} etc. are found to exhibit very exiting properties like colossal magneto resistance(CMR), charge ordering/orbital ordering(CO/OO), phase separation(PS) etc. [1-3]. CO is one of the interesting property found in many of the doped manganites and is found to destabilized by two different ways: one is by external perturbation like applying magnetic field [4], irradiating with high energy radiations [5], electric field [6], adding impurities at Mn site are A site [7-8] of manganites etc. second one is by intrinsic way ie reducing the size of the system to a nano scale [9-11]

It is intensively studied that size reduction to a nano scale has direct effect on electric and magnetic properties of manganites. it is shown that structural transition driven by size like transition in shape of coherent precipitates [12] and change in magnetic phase in ferromagnetic (FM) nano system [13] have further high lightened the new physics that arises in size reduced system. Some researchers observed that FM transition temperature (T_C) increases with decrease in size [14,15]. But no change in T_C with decrease in particle size is another observation reported by Lopez-Quintele et.al.[16], in addition they also observed that saturation magnetization (M_S) is decreasing with decrease in particle size which they explained using core-shell model. As the size of the system reduces to few nanometers, manganites are found to exhibit many appreciable phenomena like surface spin glass behavior, Superparamagnetism, low T_C etc, as compared to their bulk counterpart [17-19].

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Many studies have been conducted by doping at the Mn site in $R_{1-x}A_xMn_{1-y}M_yO_3$ manganites as it directly affecting the conducting mechanism of manganites which results in direct modification of manganites properties. D Zhu et al. [20] shown that the introduction of small amounts of Ba or Ga on the A or Mn sites (2%) will induce high FM fractions in $Pr_{1-x}Ca_xMnO_3$ manganites even at low magnetic fields (0.25 T), but unfortunately CO is found to be extremely stable. In contrast to above observation, substitution of magnetic cations in Mn site of $Pr_{1-x}Ca_xMnO_3$ weakens or even destroys the OO-CO state and induces the FM phase at the expense of antiferromagnetic (AFM) phase [21-24] is another observation. Many results on chemical substitution at the Mn site shows the decrease of critical field required to melt the CO-OO in manganites. Zhu et al. [20] proposed that the FM metallic domains produced around the Mn site impurities will grow gradually with the applied field.

The technique of measuring magnetization at different temperature ranging from 0 K-300 K is widely used to study the different magnetic phases exhibited by the manganites. Vibration sample magnetometer (VSM) being the local probe effective in studying the various phase separation exhibited by the mixed valent manganites. Some of the relevant noteworthy features related to the present work are: DC magnetization measurement exhibits a peak at the CO transition and decreases in magnetization with a small peak thereafter towards lower temperature region indicating the presence of AFM phase [25]. For smaller particle size, the destabilization of CO is indicated by broadening of peak and the disappearance of CO is indicated by absence of peak and is observed in $Pr_{0.5}Ca_{0.5}MnO_3$ nano wires [9]. Emergence of FM phase in indicated by sudden rise in magnetization at lower temperature region observed in $Nd_{0.5}Ca_{0.5}Mn0_3$ manganites [26].thus Magnetization measurement gives information about the multitude phases in manganites include FM transition phase.

In this paper, we try to shed light on the controversial findings by comparing the influence of size reduction on magnetic properties of gallium doped $Pr_{0.63}Ca_{0.47}Mn_{0.98}Ga_{0.02}O_3$ (PCMGO) manganites. So far very few magnetization studies are reported to give information about the combined effect of size reduction and doping at Mn site. Here we focus mainly on two factors: The effect of 2% gallium doping in $Pr_{0.63}Ca_{0.37}MnO_3$ manganites and the effect of size reduction on CO property in PCMGO manganites. The emergence of FM phase at T_C=101 K upon 'Ga' doping and weakening of CO peak in bulk PCMGO is observed. Further due to size reduction, the CO peak is found to disappear completely in 15 nm and 35 nm samples. We than confirm the emergence of FM phase by magnetization hysteresis measurement thus corroborating the conclusion of magnetization studies.

II. Experiment

We synthesize the PCMGO sample using sol-gel method. Stoichiometric ratio of highly purity Pr_60_{11} $CaCO_3$, Ga_2O_3 and MnO_3 were dissolved in dilute nitric acid, than equal amount of ethylene glycol is added with continuous starring. The solution is slowly heated on hot plate for about 5 to 6 h to get thick sol. This sol is then heated in furnace at 250^0 C for 6h to get polymeric precursor. The precursor is than sintered at 600^0 C and 800^0 C for about 6 hours to obtain particles of 20 nm and 30 nm. Bulk sample is obtained by sintering the precursor at 1300^0 C for 24 hours. For convenience the samples are named as PCMGO-15 PCMGO-35 and PCMGO-bulk.

The structure and phase purity were confirmed by X-ray diffraction analysis on a rotating powder diffractometer using Cu Kὰ rotation at room temperature and the data were analyzed by Rietveld refinement program called GSAS. The surface morphological studies were carried out using Scanning electron microscope (SEM).compositional analysis is done to check the proper cationic ratio by energy dispersive X-ray analysis (EDAX).

Magnetization measurement on all the powder samples is carried out using vibration sample magnetometer. The change in magnetic behavior with temperature ranging from 0 K-300 K is studied. To corroborate the disappearance of CO and emergence of FM phase in magnetization data, hysteresis behavior at two selected temperatures one above T_C and one below T_C was studied for both the nanosamples.

III. Results & Discussion

X-ray powder diffraction (XRD) is a widely used technique to study the phase formation of a crystalline material and it provides the information of unit cell parameters. The phase formation and absence of impurity signals is confirmed from XRD data. From XRD plot, particle size is calculated using Scherrer formula. The

average size is estimated to be 15 nm and 35 nm for 600^0 C and 800^0 C sintered samples. The diffraction data is than subjected to Rietveld powder diffraction profile fitting technique to find the structural parameters. Figure 1 (a-c) shows the Rietveld powder diffraction fitted XRD fits. The cell parameters, volume of unit cell and the goodness of the fit factors (χ^2 and R_P) for all the samples are listed in Table 1. The volume of the unit cell is found to decrease with increase in particle size. The morphological study for all the samples is done using SEM and is as shown in figure 2 (a-c). From SEM images we can make out an increase in size with increase in sintering temperature.

TABLE I. CELL PARAMETERS AND THE GOODNESS PARAMETERS FOR THE SAMPLES SINTERED AT DIFFERENT TEMPERATURE

Sample	*Particle size*	*a(Å)*	*b(Å)*	*c(Å)*	*V(Å)^3*	*χ2*	*Dwd*	*Rp*
PCMGO	15 nm	5.4610	7.5566	5.3589	221.1459	1.359	0.713	0.0309
	35nm	5.3718	7.5896	5.3701	218.93	1.38	0.72	0.036
	Bulk	5.3633	7.5633	5.3728	217.94	1.905	0.54	0.039

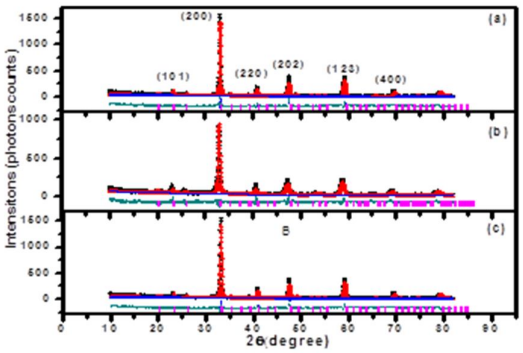

Fig.1 Rietveld fitted powder XRD patterns of (a) PCMGO-15 (b) PCMGO-35 and (c) PCMGO-bulk samples. The experimental points are shown as solid dots. The calculated fit and the difference curves are as shown in the as solid lines. Short vertical lines indicate the calculated reflection positions

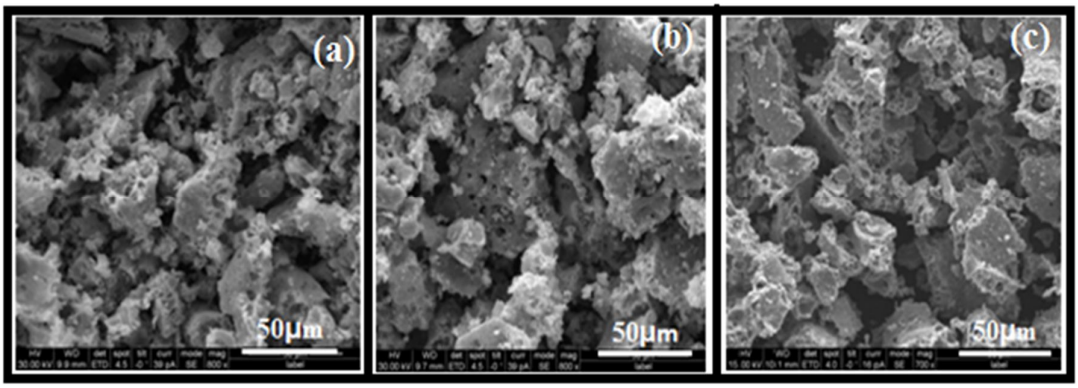

Fig.2 SEM images of (a) PCMGO-15 (b)PCMGO-35 and (c)PCMGO-bulk

Bulk $Pr_{0.63}Ca_{0.37}MnO_3$ system shows CO transiting at T_{CO}=260 K and AFM ordering below T_N=170 K. To study the effect of 'Ga' doping and size reduction, field cooled dc magnetization measurement is carried out for all the three samples at 0.1T as shown in figure 3 (i). The inset shows the CO peak at T_{CO}=235 K for PCMGO-bulk whereas it completely disappeared in 15 nm and 35 nm particle which confirms the suppression of charge order upon size reduction to nano range in PCMGO system. All the three samples show a sudden rise in magnetization at around 100 K indicating the FM transition by suppressing the AFM phase upon gallium doping.

The observations made upon Ga doping in PCMO-bulk sample can be explained in two contests: The first one concerned the CO stability which decreases with increase in Mn^{3+}/Mn^{4+} ion [27].The second is the increase in symmetry of the structure induced by chemical doping either with Ba are Ga called 'counter-distortion' which increases with decrease in the x value in $Pr_{1-x}Ca_xMnO_3$ [20]. Thus introduction of Ga in the distorted octahedral Mn site in $Pr_{0.63}Ca_{0.37}MnO_3$, the

counter-distortion effect is stronger and locally favors the FM state. But unfortunately CO is extremely stable which overcomes the counter-distortion effect and remains unaltered even upon low Ga substitution.

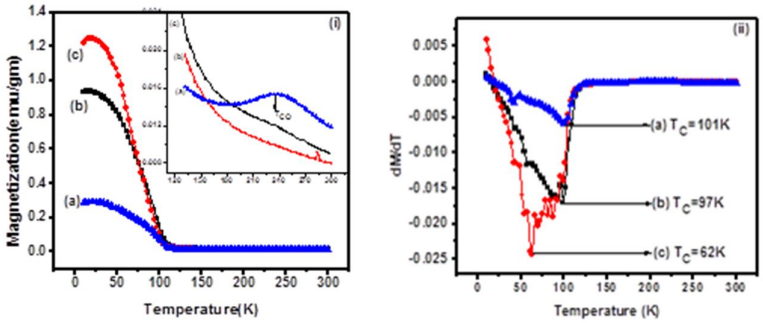

Fig.3 (i) Temperature dependence of field cooled magnetization of (a) PCMGO-15, (b) PCMGO-35 and (c) PCMGO-bulk samples inset shows the expanded view showing the presence of CO peak in PCMGO-bulk. (ii) Derivative of magnetization with respect to temperature Vs. Temperature curve showing ferromagnetic transition temperature for (a) PCMGO-15, (b) PCMGO-35 and (c)PCMGO-bulk samples

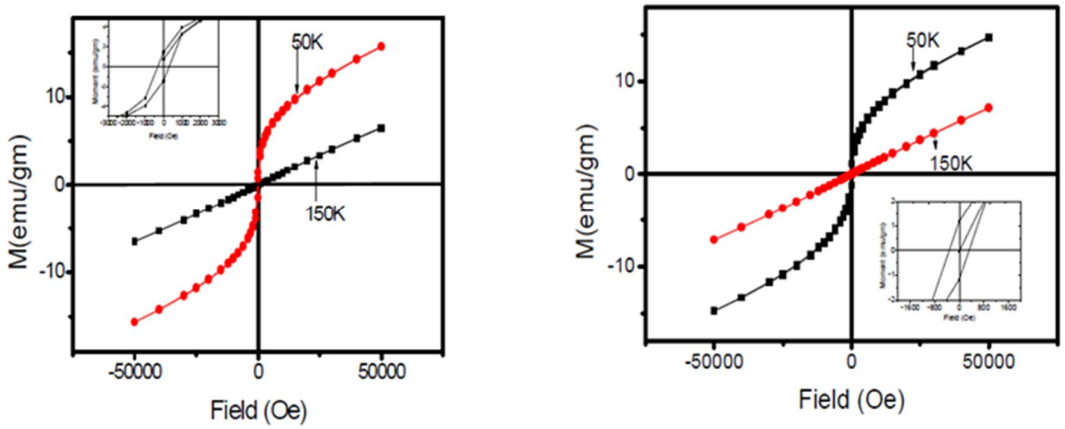

Fig. 4 Isothermal M-H loops measured at temperatures 50K and 150K for (a) PCMGO-15 and (b) PCMGO-35

The disappearance of CO in both nano samples may be due to the enhanced surface pressure which prevents the formation of CO phase and stabilizes the FM state [28].the structural changes driven by the size reduction is also responsible for the disappearance of CO phase [29]. According to core-shell model in a nano sized system [30], due to uncompensated spins present on the surface which destroys the CO/AFM phase which results emergence of FM conducting phase upon size reduction in both the nano samples. The exact ferromagnetic transition temperature is found from infection point of dM/dT vs. T (K) curve to be 65 K, 96 K and 101 K for PCMGO-15 PCMGO-35 and PCMGO-bulk respectively as shown in figure 3 (ii). FM transition is confirmed by magnetic hysteresis for both the nanosamples and is as shown in figure 4. Both the samples exhibit FM hysteresis at 50 K (<TC) and paramagnetic transition ie, linear magnetization cure at 150 K (>TC).

IV. Conclusion

The effect of Ga doping and size reduction on charge order magnetic properties in PCMGO is explained by temperature dependent magnetization measurements. Ga doping in PCMGO bulk do not produce much effect on CO peak but emergence of ferromagnetic phase by overcoming the antiferromagnetic behavior is observed. This ferromagnetic behavior is attributed to the local geometric counter-distortion which is induced around each species by chemical doping (Ga) and CO destabilization in the nano samples is attributed to the enhanced surface pressure and structural change when size is reduced to nano scale. The magnetization hysteresis confirms the conclusions arrived from magnetization data.

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