Investigation of the Structural and Magnetic Properties of $La_{0.9}Ca_{0.1}(Mn_{0.1}Co_{0.9})O_3$ Prepared by Sol-Gel Route

S.K. Jain, Sudhish Kumar, Anjali Krishnamurthy, and B.K. Srivastava

Abstract**—**Structural and Magnetic properties of $La_{0.9}Ca_{0.1}(Mn_{0.1}Co_{0.9})O_3$ has been investigated using temperature, time and field dependent dc magnetization measurements in the temperature range of 20K - 300 K and in fields up to 8.5 kOe. Polycrystalline sample of $La_{0.9}Ca_{0.1}(Mn_{0.1}Co_{0.9})O_3$ was prepared using sol-gel route and characterized by powder X-ray diffractometry. Field dependent magnetization curve recorded down to 20K display ferromagnetic hysteresis loops below 180K and the saturation magnetization increases with decrease in temperature. Appearance of two peaks in the ZFC mode of magnetization curve and clear departure between the ZFC and FC modes indicates cluster glass like ferromagnetic behaviour with a paramagnetic – ferromagnetic transition below 300K. ZFC curves recorded in the presence of different magnetic fields, display shifting of the peaks towards lower temperature with increasing fields and time dependence of magnetization gives evidence of the field induced type ferromagnetic transition and presence of ferromagnetic clusters in $La_{0.9}Ca_{0.1}(Mn_{0.1}Co_{0.9})O_3$.

Keywords**—**Sol Gel, Doped Perovskites, Magnetic properties, Hysteresis, Ferromagnetic clusters.

I. INTRODUCTION

THE perovskite lanthanum manganite and its substituted analogues have been the subject of intense investigation in the last few decades due to their unusual electrical properties; colossal magneto-resistance included, and associated magnetic behaviour. Special attentions have been paid to the Ca doped manganites $La_{1-x}Ca_xMnO_3$ because of their rich variety of electrical conduction and unusual magnetic properties [1-12]. $La_{1-x}Ca_xMnO_3$ is a ferromagnetic conductor in the range of $0.2 \leq x \leq 0.4$, while the end members, $LaMnO_3$ and $CaMnO_3$ are antiferromagnetic insulators. $LaCoO_3$ is a nonmagnetic insulator below 50K and acquires Curie-Weiss susceptibility above 100K followed by disappearance of the charge gap between 450 and 600 K. Hole doping of the Co d bands by substitution of La with Ca leads to a strong magnetic response.

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Now it is pretty well established that in $LaMnO_3$, when trivalent lanthanum is substituted by 1/3rd (atomic%) or more of divalent Ca, the system attains a long range ferro-magnetic order; with varying temperature it exhibits insulator- metal transition coinciding with that of paramagnetic- ferromagnetic transition. Beyond this level of substitution of La by divalent cations, variety of systems with substitutions by different atoms at the Mn site has been thoroughly investigated [4]. For lower level substitutions by a divalent cation, the systems exhibit disordered magnetic behaviour. This region has not been so thoroughly studied. One point under discussion has been whether in such samples the magnetic state is one of a canted nature or one where ferromagnetic regions are present in the presence of anti-ferromagnetic regions [2], [5], [9]. Bulk single crystals of $La_{0.9}Ca_{0.1}MnO_3$ display mixed magnetic state, constituted by coexisting canted antiferromagnetic matrix and nanometer sized ferromagnetic clusters, and the nanocrystalline $La_{0.9}Ca_{0.1}MnO_3$ is a well ordered ferromagnet [3]. In addition in recent past an interesting development has been the use of wet sol-gel process for preparation of perovskite oxides. Inspired by the extensive research work on doped manganates, we have carried out detailed magnetization studies on a sol gel route prepared sample of $La_{0.9}Ca_{0.1}(Mn_{0.1}Co_{0.9})O_3$.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of Ca doped manganate- cobaltate system $La_{0.9}Ca_{0.1}(Mn_{0.1}Co_{0.9})O_3$ (hereafter referred to as LMC90) has been prepared by a metal-salt routed sol-gel processing method and subsequent heating in air at 9500C for 5 days. For phase purity and single phase characterization powder X-ray diffraction patterns (XRD) were recorded at room temperature on a Philips make X-ray powder diffractometer (PW1840) with FeKα radiation. DC magnetization measurements, viz., variation of magnetization with temperature (M – T), time (M-t) and field (M – H), have been made in the temperature range 20K – 300K and in fields up to 8.5 kOe using a vibrating sample magnetometer (PARC make, model 155), a closed helium cycle refrigerator (CCR) cryostat and an electromagnet. M – T curves have been recorded in zero field cooled (ZFC) and field cooled (FC) modes. For measurements in ZFC mode, sample is first cooled from 300K down to 20K in the absence of any external

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magnetic field, then a measuring field is applied and moment is recorded in the warming cycle as the sample is heated up to 300K. In FC mode the sample is cooled from 300K down to 20K in the presence of a measuring field and moment is recorded in the warming cycle as the sample is again heated up to 300K. Measurements on temporal relaxation of magnetization have been made at a low temperature and under different magnetic fields after zero field cooling of the sample.

III. Results And Discussion

Fig. 1 displays the room temperature XRD pattern of LMC90, indicates that all the peaks can be indexed on the basis of rhombohedral perovskite cell (space group: R-3c) without any impurity. Due to weak filtering of the FeK_{β} radiation in the diffractometer, Bragg peaks corresponding to this wave length were also observed for the most intense reflections. However these peaks can be easily indexed in the same rhombohedral perovskite cell. The XRD data analysis confirm that the sample crystallize in single phase with a slight rhombohedral distortion (from cubic symmetry) and in agreement with the published reports [2], [4], [10], [11].

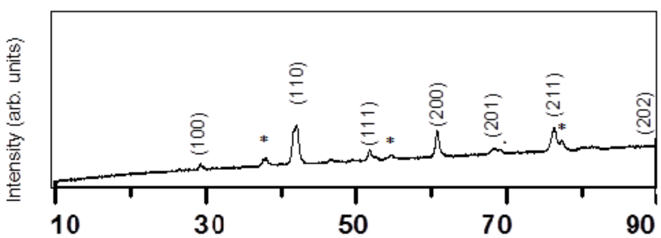

Fig. 1 Indexed X-ray diffraction patterns of LMC90 recorded at room temperature. (* - Peaks corresponds to Fe K_{β} Peak).

The field dependence of magnetization (M – H curves) for LMC90 at different temperature down to 20K is shown in Fig. 2. The 300K M-H curve is a typical reversible magnetization curve and confirm the paramagnetic nature of the sample at room temperature. The 180K and 20K M-H curves display beautiful hysteresis loop and indicative of the ferromagnetic nature of the sample below 180K. It is to be noted that the magnetization does not get saturated up to the highest field of 8.0kOe. Interestingly the maximum value of magnetization at 20K and 8.0kOe is three times higher than that of 180K. In comparison to other compounds in these type of perovskites, the observed values of coercivity and remanent magnetization for LMC90 are found to be large and are in agreement with the inference of large anisotropy for this composition [8].

Fig. 3 exhibits, M – T measurements in ZFC and FC modes for LMC90. Features in the curves are suggestive of one major transition at temperatures above 150K and another anomaly in the temperature range ~30K – 60K. The transition at the higher temperature is paramagnetic–ferromagnetic one. Hysteresis (M–H) measurements made at different temperatures (Fig. 2) support this conjecture.

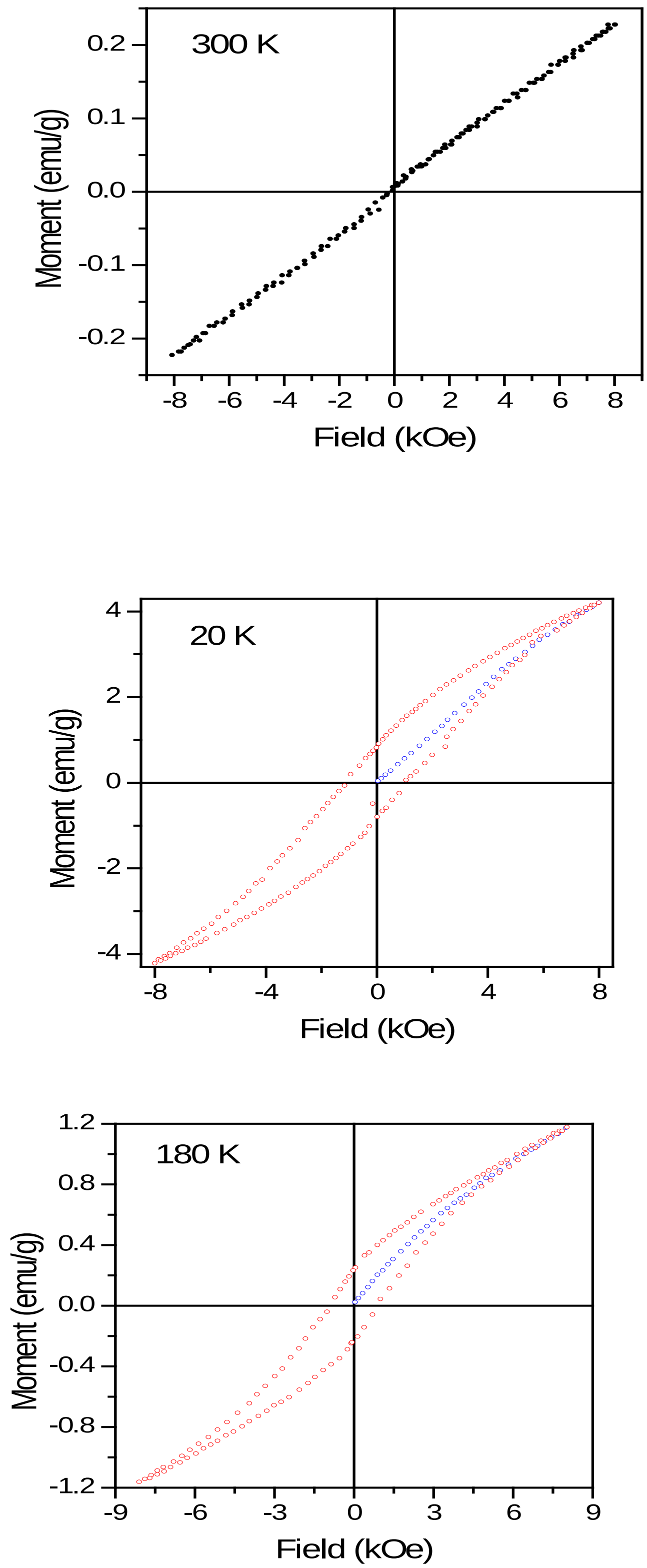

Fig. 2 Field dependence of magnetization for LCMC90 at different temperatures.

Wide departures between FC and ZFC curves are suggestive of magnetic relaxation and also indicative of the existence of magnetic clusters in this material. These types of feature have also been reported in other materials like doped Fe_2P based systems and in ferrites [13-16]. However some of them display well ordered ferromagnetic structure [14] and in other complicated magnetic structures/states were also observed [15]. Therefore in order to clarify the relaxation phenomenon, temporal relaxations of the magnetization were recorded.

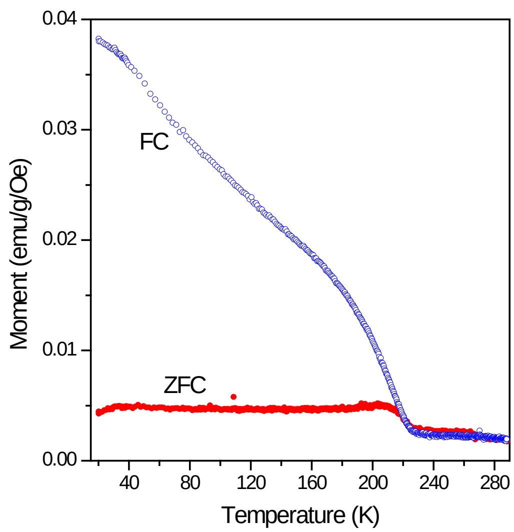

Fig. 3 Temperature dependent ZFC and FC Magnetization for LMC90

Fig. 4 exhibit magnetization versus logarithm of observation time for LMC90 at 20K. It has been observed that for LMC90 the fields needed for observing relaxation behaviour are high. Thus, 90% Co substitution for Mn in $La_{0.9}Ca_{0.1}MnO_3$ results in high magnetic anisotropy energy, which would be suggestive of either large anisotropy constant or large cluster sizes (but in the nano- size range) or a combination of both [2], [5], [8], [13-16].

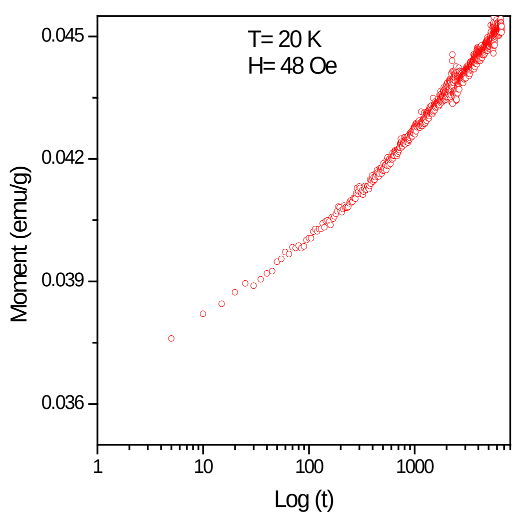

Fig. 4 Magnetization versus logarithm of observation time.

Fig. 5 shows M – T curves for LMC90, recorded in ZFC mode in the presence of different low magnetic fields. The peak at the higher temperature displays clear shift towards low temperature side with increasing field. This observation is a strong supportive of the display of magnetic clustering behaviour by LMC90. The low temperature anomaly also shows a shift towards lower temperature with increasing field but the amount of the shift is much less. We attribute the low temperature anomaly to spin glass like re-entrant behaviour in these magnetic clusters. This is in agreement with literature reports [6], [13], and [16]. It is to be noted that this low temperature anomaly becomes quite prominent in LMC90. This shows that Co atoms do not take part in double exchange and only aid to indirect exchange resulting in frustrated state [6], [7], [13].

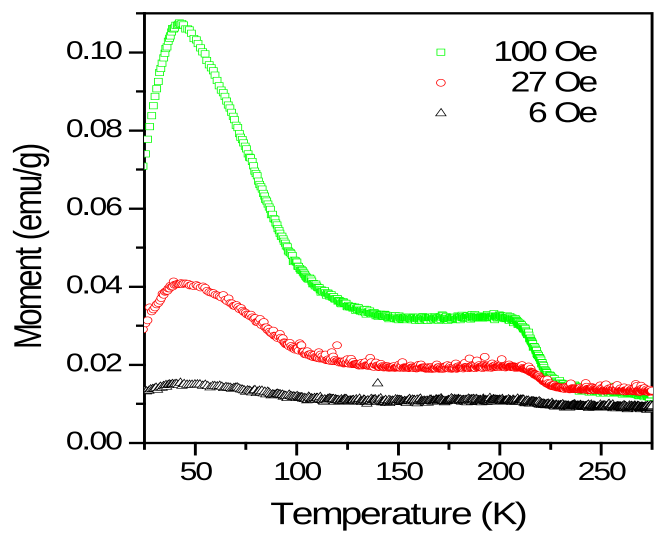

Fig. 5 M – T curves for LCMC90, recorded in ZFC mode at different magnetic fields.

IV. Conclusion

Single phase polycrystalline samples of Ca doped manganate- cobaltate system $La_{0.9}Ca_{0.1}(Mn_{0.1}Co_{0.9})O_3$ can be easily prepared using sol-gel route at low temperatures. The system exhibit long time magnetic relaxation associated with a disordered system of ferromagnetic clusters. Co atoms do not take part in double exchange and aid in indirect exchange which results in spin glass like frustrated state. Low temperature anomaly is prominent in this system and can be attributed to a spin glass like state.

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