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Magnetic dynamics of charge ordered $Nd_{0.80}Na_{0.20}MnO_3$ compound

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ABSTRACT

The magnetic dynamics of charge ordered $Nd_{0.8}Na_{0.2}MnO_3$ compound was studied by measuring the temperature variation of magnetization for different magnetic fields up to 7 T and, the field variation of magnetization at different temperatures down to 5 K. This sample exhibits a charge-ordering transition at 180 K, followed by a weak ferromagnetic (FM) transition at around 100 K and a spin glass like transition below 40 K. Suppression of charge-ordering and spin glass like transition and increase in FM T_C were observed with an increase in magnetic field. A reversible metamagnetic transition above a threshold field (H_f) of 4.5 T was observed at 130 K, followed by a saturation magnetization of 3.2 μ_B/f.u. However at 5 K, an irreversible field induced first order phase transition from charge ordered state to FM state was observed at H_f=5 T. For comparison, the temperature and field variations of magnetization were studied on a FM compound from the same series with the composition $Nd_{0.90}Na_{0.10}MnO_3$. A clear FM transition with a T_C of 113 K and a saturation magnetization of 4.3 μ_B/f.u was observed.

1. Introduction

The hole doped manganites $R_{1-x}A_xMnO_3$ (R=rare earth element and A=alkaline earth element) have been the subject of intense studies due to the interplay of magnetism, electric transport and crystallographic distortion. These materials exhibit transition from paramagnetic insulator to ferromagnetic metallic state upon cooling with colossal magnetoresistive behavior [1,2]. They are explained on the basis of Zener double exchange (DE) ferromagnetic (FM) interaction in Mn^{3+}–O^{2-}–Mn^{4+} networks [3]. The other factors such as mixed valency, ionic size mismatch, Mn–O bond length, ∠Mn–O–Mn bond angle, strong electron–phonon interaction [4], etc. also play a considerable role on CMR behavior [5]. The coexistence of ferromagnetic metallic (FMM) and antiferromagnetic (AFM) charge or orbital ordered insulating phases due to magnetic phase separation plays a considerable role in colossal magnetoresistance phenomena [2]. These properties depend upon the hole doping level and average A-site ionic radius ($\langle r_A \rangle$), which in turn control the effective e_g electron band width. The Nd–Mn–O series falls in the category of medium size e_g bandwidth, where one can tune the bandwidth by appropriate Nd site substitution such that the system varies from DE dominated large bandwidth to charge ordered (CO) dominated low band width of e_g electrons. In Nd–Mn–O series, several authors have studied the magnetic properties by doping divalent alkaline earth elements such as Ca, Ba and Sr in place of Nd ions [6–12]. Charge-ordering in Ca doped materials [13,14] and the suppression of charge-ordering by the application of magnetic field have been reported [14–17].

Unlike the case of divalent alkaline earth element doped Nd–Mn–O series, the work on monovalent alkali ion doping in the same series is limited. Charge-ordering followed by a weak FM transition was reported in two samples of $Nd_{1-x}Na_xMnO_3$ for x=0.20 and 0.25 [18,19]. Tang et al. [20] reported a FM insulating behavior in $Nd_{1-x}Na_xMnO_3$ system for x=0.10 to 0.25. PM to FM transition along with spin glass like transition and spin canting is reported in (Nd, Ag)–Mn–O series [21]. Ferromagnetic and metal–insulator transition along with colossal magnetoresistance of the order of 60% for 1 T magnetic field have been reported in $Nd_{1-x}K_xMnO_3$ (x=0.10–0.20) series [22] with T_C in the range of 116–128 K. In order to systematically study the magnetic dynamics in a CO/AFM system, where different magnetic ground states are dominant at different temperatures, we have prepared $Nd_{1-x}Na_xMnO_3$ compounds for x=0.10 and 0.20. It is shown that as the doping concentration approaches x=0.20, the system undergoes transition from DE-FM dominated phase to CO phase.

2. Experimental details

Polycrystalline samples of $Nd_{1-x}Na_xMnO_3$ (x=0.10 and 0.20) were prepared by the conventional solid state reaction method. The final sintering in pellet form was carried at 1200 °C for 24 hr. X-Ray diffraction patterns (XRD) were recorded using Bruker D8

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Advance XRD machine with CuK_α radiation and they were refined using Rietveld refinement technique and fullprof program [23]. Recording of microstructure images and compositional analysis were carried out using LEO scanning electron microscope (SEM) equipped with Oxford energy dispersive spectrometer (EDS).

The temperature variations of zero field cooled (ZFC) and field cooled (FC) magnetization (M) were measured using a Lakeshore model no. 7410 vibrating sample magnetometer. The magnetization loop measurements were carried out by varying the field up to ± 10 T by Quantum Design superconducting quantum interference device (SQUID) magnetic property measurement system. The temperature variation of electrical resistivity was measured by a standard linear four probe method in the absence of magnetic field. The oxidation state of Mn was determined by a chemical titration method, in which the samples were dissolved in dilute sulfuric and phosphoric acids with an addition of excess amount of $Fe(NH_4)_2(SO_4)_2$ and were titrated against self indicating $KMnO_4$ solution.

3. Results and discussions

The prepared samples of $Nd_{1-x}Na_xMnO_3$ series for $x=0.10$ and 0.20 are found to be in single phase form as per the XRD results. Their patterns could be refined using Pbnm space group in orthorhombic cell. The typical XRD patterns along with Rietveld refinement are shown in Fig. 1 for $x=0.10$ and for $x=0.20$ samples. The typical lattice parameters for $x=0.10$ are $a=5.4221(06)$ Å, $b=5.4950(07)$ Å and $c=7.6769(09)$ Å. The lattice parameters are comparable to those of the previous reports on Na doped and Ag doped samples of Nd–Mn–O series [20–22]. The chemical compositions determined from EDS analysis are found to be comparable to the nominal starting composition. The average Mn valence values for $x=0.10$ and 0.20 samples are found to be 3.34 and 3.47, respectively.

Fig. 2 shows the temperature variation of magnetization of $x=0.10$ and 0.20 samples in zero field cooled (ZFC) and field cooled (FC) conditions for an applied magnetic field of 200 Oe. The $x=0.10$ sample exhibits PM to FM transition at 113 K followed by a low temperature spin glass like transition at 40 K. The FM T_C value is comparable to the other monovalent alkali ion doped $NdMnO_3$ compounds [20–22]. The Curie–Weiss law fit of the inverse susceptibility of the same sample in the paramagnetic region is shown in the inset of Fig. 2(a) and Curie temperature is found to be 136 K. Unlike $x=0.10$ sample, the magnitude of magnetization of $x=0.20$ sample is found to be quite small and it also exhibits a broad hump at around 180 K as shown in Fig. 2(b) with a signature of charge-ordering phenomenon. A similar behavior has been reported in $Pr_{0.75}Na_{0.25}MnO_3$ system at $T\approx 220$ K [24]. The Mn^{4+}/Mn^{3+} ratio of the present $x=0.20$ compound is 47:52, and it is quite close to the half doped CO system in manganites, where the Mn^{3+} and Mn^{4+} ions undergo charge ordering. So, it is not surprising that $x=0.20$ sample exhibits charge-ordering at 180 K. The present CO temperature is comparable to that observed by Liu et al. [19] in $Nd_{0.75}Na_{0.25}MnO_3$ sample. A secondary rise in magnetization below 100 K followed by a sharp peak at around 40 K is observed. It can be ascribed to the presence of weak FM followed by competing magnetic interaction such as reentrant spin glass (RSG) and AFM behavior. This can be substantiated from the observed large irreversibility between ZFC and FC magnetization especially below 40 K. The inset of Fig. 2(b) shows the inverse susceptibility along with Curie–Weiss law fit. The presence of CO transition can be clearly seen and the impending weak FM is manifested from the positive value of the Curie temperature. In order to understand the complex magnetic properties of $x=0.20$ sample, we have carried out M–T measurement under different magnetic fields ranging from 1 to 7 T as shown in Fig. 3. The applied magnetic field is found to enhance the low temperature FM phase with a large increase in the magnitude of magnetization along with a shift in FM T_C towards high temperature, i.e 85 K for $H=1$ T to 166 K for $H=7$ T. Moreover, the sharp fall in magnetization observed at low temperature due to possible spin glass like behavior is shifted further downwards and ultimately it disappears for $H=7$ T. Thus the applied magnetic field tends to stabilize the FM phase at the expense of other competing magnetic phase. On the other hand, the CO transition temperature observed at 180 K is found to be field independent and it could be seen prominently up to a magnetic field of 5 T. The disappearance of CO transition for $H=7$ T could be either due to the quenching of charge-ordering or the merging of the CO transition with the enhanced FM signal.

To further study the magnetic properties, we have carried out measurement of field variation of magnetization up to ± 10 T magnetic field at different temperatures. All the measurements

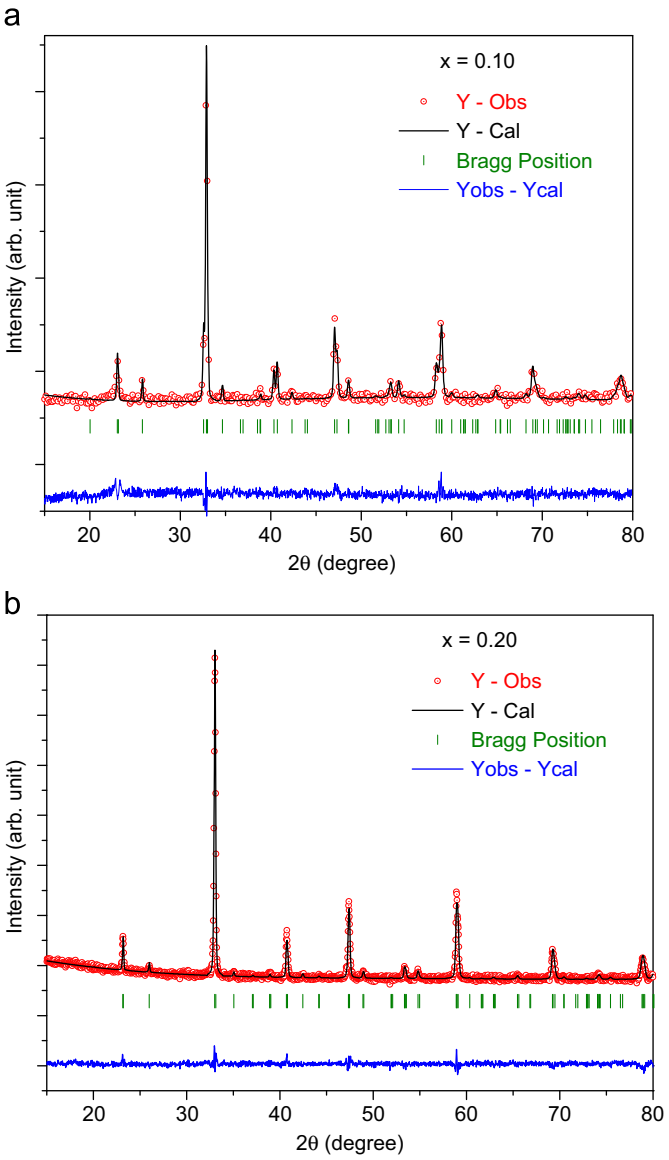

Fig. 1. XRD pattern for the samples (a) $x=0.10$ and (b) $x=0.20$. The circles represent experimental points and the solid line represents Rietveld refined data. The bottom line shows the difference between experimental and refined data. The vertical bars correspond to allowed Bragg peaks.