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Structure and magnetic behavior of Zn doped $NdMnO_3$ manganite: Neutron diffraction study

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ABSTRACT

Effect of Zn doping on the structural and magnetic properties of $NdMnO_3$ has been investigated by neutron diffraction and dc magnetic susceptibility measurements. The partial replacement of Mn^{3+} by Zn^{2+} results in the decrease in T_N. In the temperature dependent magnetization measurements, a broad hump and a sharp peak has been observed around ~ 50 K and 10 K respectively for both the samples. Thermal hysteresis in magnetization between cooling and heating runs indicate first-order phase transition. Magnetization measurements on $NdMn_{0.95}Zn_{0.05}O_3$ sample clearly show that, 5% Zn-doping in $NdMnO_3$ results in the suppression in magnetism which is evident from the weakening of Nd–Mn interaction below T_N, and resulting in antiferromagnetic coupling of Mn^{3+} ions along x-axis with Mn^{3+} moments oriented parallel or antiparallel to the x-component of Nd^{3+} moments.

1. Introduction

Studies on manganese based $RMnO_3$ perovskites (R = Rare Earth) are of current interest due to their interesting structural, magnetic and colossal magneto-resistive properties [1]. $RMnO_3$ compounds with R = La, Pr and Nd crystallize in orthorhombic structure [1,2] with *Pnma* space group while compounds with R = Tb, Ho and Yb crystallize in hexagonal structure with space group $P6_3cm$ [3]. $RMnO_3$ compounds exhibit interesting properties, such as, magnetic ordering, unusual transport properties, metal-insulator transition, colossal magneto resistance (CMR), multiferroic properties etc. [4] which are largely influenced by the structure and the nature of the interaction of transition metal ions (within the confined geometry) with the surrounding R ions [5]. Doping of divalent cation at A-site in rare earth manganites with the general formula $R_{1-x}A_xMnO_3$ (R = rare-earth cation, A = alkali or alkaline earth cation) leads to fascinating physical properties due to the creation of Mn^{4+} and double exchange interaction between Mn^{3+} and Mn^{4+} ions [6,7]. It is reported that, $R_{1-x}A_xMnO_3$ manganites undergo antiferromagnetic (AFM) to ferromagnetic (FM) and insulator to metal transition for $x > 0.2$ [8,9]. Moreover, it is also reported that, Mn site (B-site) doping with transition metal ion results in the modification in the magnetism in rare earth based perovskites [10,11]. Substitution of Cu at Mn site in $LaMnO_3$ causes structural distortions and disorder leading to double exchange interactions [10].

In order to understand the magnetic properties of rare-earth based manganites, it is important to study their crystallographic as well as magnetic structure. Amongst all $RMnO_3$ perovskites, $NdMnO_3$ possesses orthorhombic structure and is a weak ferromagnet (WFM) [12]. The strongest magnetic interaction in $NdMnO_3$ is Mn^{3+}–O–Mn^{3+} super-exchange interaction, which is responsible for AFM ordering of Mn ions below T_N while Nd ions remain in the paramagnetic state. Due to the Nd–Mn interactions, Nd ions become polarized below 20 K [13–15].

Considering this, it would be interesting to understand the effect of doping of non-magnetic divalent Zn^{2+} for Mn^{3+} in $NdMnO_3$, wherein, the influence of such valence imbalance will be studied, on both, structural property and magnetic interactions. Neutron Diffraction (ND) technique is one of the powerful tools to investigate the magnetic spin structure. Munoz et al. have observed the ordering of Mn sub-lattice below T_N ~ 78 K with the spin arrangement (C_x, F_y, 0) and Nd sub-lattice with the spin arrangement (0, F_y, 0) below T ~ 13 K in

Abbreviations: ND, Neutron diffraction; NMO, $NdMnO_3$; NMZ5, $NdMn_{0.9}5Zn_{0.05}O_3$; RT, Room temperature; JT, Jahn-Teller; ZFC, Zero Field Cooled; FCC, Field Cooled Cooling; FCW, Field Cooled Warming; BVS, Bond Valence Sum

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$NdMnO_3$ using powder neutron diffraction study [13]. Replacement of Mn ions in small amount leads to the magnetic phase transition in $NdMnO_3$ as a result of a change in ground state of Nd ions [12]. Troyanchuk et al. have reported that, when Mn sub-lattice is heavily substituted with Cr, the magnetic structure having ferromagnetic component and G-type antiferromagnetic components is obtained as a result of ordering of 3d ions, whereas, higher amount of Fe substitution at Mn site results in the antiferromagnetic G-type structure [11]. Mihalik et al. have observed that, the substitution of Fe^{3+} ions for Mn^{3+} ions tunes the superexchange interaction, changing its strength and also changing the ability to polarize the Nd^{3+} ions through the Nd–Mn and Nd–Fe interaction [16]. In A-site substituted $Nd_{0.92}Ca_{0.08}MnO_{2.98}$ system, the transition of Nd ions to FM state has been observed via formation of an intermediate inhomogeneous state subject to the spin reorientation of Nd ions [17,18]. ND studies on $Nd_{0.92}Ca_{0.08}MnO_3$ system shows the development of FM order in a-b plane with canted AFM coupling of the planes perpendicular the c-axis due to ordering of Mn spins and the Nd sublattice orders ferromagnetically at low temperature along the c-axis [19]. In the present work, we communicate the results of studies on the structural and magnetic properties of parent $NdMnO_3$ (NMO) and $NdMn_{0.95}Zn_{0.05}O_3$ (NMZ5) manganites performed using temperature dependent neutron diffraction (ND) and magnetization measurements across its magnetic ordering temperatures.

2. Material and methods

Polycrystalline NMO and NMZ5 samples were synthesized from starting high purity Nd_2O_3, MnO_2 and ZnO powders using solid state reaction method. After initial mixing of oxides using agate mortar and pestle, the powders were calcined at 950° and 1100 °C with intermediate grindings for homogenization followed by final sintering at 1500 °C for 6 h. ND patterns were recorded using focusing crystal based diffractometer, PD-3 with neutrons of wavelength λ = 1.48 Å, at Dhruva reactor, BARC, Trombay, INDIA in the 2θ range of 6–120° at selected temperatures between 2.8 and 300 K [20]. For ND experiment, NMZ5 powder sample was filled in vanadium can of 6 mm diameter and attached to closed cycle refrigerator (A S Scientific, UK) to study the temperature dependent modification in the structural and magnetic behavior. Magnetization measurements of NMO and NMZ5 samples were carried out on a commercial Quantum Design, USA vibrating sample magnetometer (VSM) attached to a commercial 9Tesla physical properties measurement system (QD-PPMS) at UGC-DAE CSR, Mumbai centre.

3. Results and discussion

3.1. Room temperature neutron diffraction studies

Room temperature (RT) neutron diffraction measurements on NMO and NMZ5 samples were carried out to confirm the single phasic nature of the samples. Both the samples possess single phase orthorhombic structure with space group *Pnma* (no. 62). The values of lattice parameters, unit cell volume and Rietveld refined parameters obtained using the analysis of ND data are listed in Table 1. It can be seen that, 5% substitution of Zn^{2+} at Mn^{3+} site results in an increase in the value of lattice parameter 'a' indicating overall expansion of the unit cell.

The change in cell parameters and cell volume can be due to the difference in ionic radii of Mn^{3+} (0.645 Å) and Zn^{2+} (0.74 Å) ions in six coordination number [21]. Table 1 also lists values of selected bond angles and bond lengths for Mn–O ions. In both the samples, we observe the bending of Mn–O angles in MnO_6 octahedra which is similar to that reported by Munoz et al. revealing the presence of distortion in the perovskite structure [13].

Table 1
Room temperature structural parameters obtained from Rietveld refinement of the neutron data taken with λ = 1.48 Å. and space group: *Pnma*.

Parameter	NMO	NMZ5
a (Å)	5.751(9)	5.746(6)
b (Å)	7.578(1)	7.584(4)
c (Å)	5.416(6)	5.417(4)
Volume (Å^3)	236.06(5)	236.10(3)
Mn–O1 (Å)	1.947(4)	1.966(1)
Mn–O21 (Å)	2.146(2)	2.123(3)
Mn–O22 (Å)	1.934(4)	1.945(5)
Mn–O1–Mn (°)	153.13(3)	149.45(5)
Mn–O2–Mn (°)	151.58(2)	152.14(16)
Octahedral distortion (Δ) (Å)	0.0023	0.0016
JT distortion (Å)	0.0970	0.0792

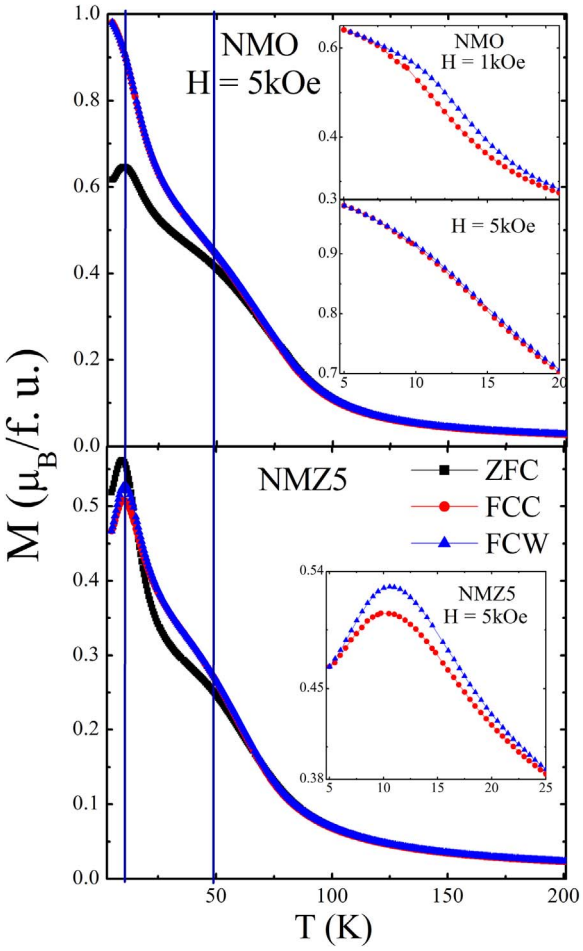

Fig. 1. M–T plots of NMO and NMZ5 samples measured in a field of 5 kOe. The vertical lines in the top and bottom main panels indicate the ordering temperatures. The insets in both the panels show the magnetization in FC condition in the region of phase transition.

3.2. Magnetization studies

In order to understand the low temperature magnetic behavior, dc magnetic magnetization measurements were carried out on both NMO and NMZ5 samples as shown in Fig. 1. It can be clearly seen from Fig. 1 that, with decreasing temperature, magnetization (M) increases monotonically down to 100 K, above which the samples are in the paramagnetic state. Below ~ 80 K, there is a sudden increase in M–T curve and both the samples exhibit slight broad shoulder around 50 K, indicating magnetic correlation around this temperature. On decreasing temperature, M–T curve exhibits a sharp peak in the vicinity of 10 K indicating another magnetic ordering. It is reported that, the Mn