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Investigation of structural, magnetic, and electronic properties of Co doped $NdMnO_3$

Farooq H. Bhat [a], G. Anjum [b], Jan Asifa [a], Tanveer A. Dar [a], Ravi Kumar [c], Manzoor A. Malik [d]

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Highlights

- The spontaneous orthorhombic strain (s) decreases with rising Co concentration, which indicates a reduction in lattice distortion.
- The magnetic properties are understood in terms of the different valence and spin states of both Mn and Co ions.
- The hysteresis studies indicate the existence of a ferromagnetic state.
- The increasing value of coercive field show the system under study is highly anisotropic.
- XAS and XPS confirm the existence of Mn and Co in mixed valence states and the microscopic reason for the magnetic properties of the samples.

Abstract

Polycrystalline $NdMn_{1-x}Co_xO_3$ (x=0.0, 0.3, 0.7) samples were synthesized utilizing the conventional ceramic method. TheX- ray diffraction patterns subjected to Rietveld refinement uncover the single-phase orthorhombic crystal structure for all the samples. Temperature-dependent magnetization executed at 0.05T and 1.0T reveal the transition from ferromagnetic to paramagnetic phase at Curie temperature T_c (~ 60–140K). In all the samples, zero field cooled (ZFC) and field cooled (FC) curves separate at thermo-magnetic irreversibility temperature (T_{irr}), except in$x$=0.0 sample, at a higher field of 1T. The ZFC curve displays the cusp showing maximum at temperature T_m. T_m and T_{irr} shift to lower temperatures with a broad maximum in ZFC as the external field is increased in$x$=0.3 & 0.7 samples indicating ferromagnetic ordering. At a temperature of 10K, magnetization versus magnetic field (M–H) curves undoubtedly imply the ferromagnetic interactions at low fields up to 3T, and at fields greater than 3T a distinctive antiferromagnetic character is evident that is pronounced in$x$=0.7 sample. At T = 150K, the M–H curve indicates paramagnetic behavior in$x$=0.0 & 0.7 samples; however, inx=0.3 sample, a slight non-linearity suggests feeble ferromagnetic interactions at tiny fields typically below 1T.

The detailed analysis of X-ray absorption spectroscopy (XAS) spectra at $L_{3,2}$- edges of manganese (Mn) and cobalt (Co) ions along with O K-edge reveal that Mn exhibits mixed valent states i.e. Mn^{3+}/Mn^{4+} and Co shows high spin Co^{2+} and high/low spin Co^{3+} state. These results are confirmed using charge transfer multiplet calculations done at $L_{3,2}$ edges of Mn and Co ions. X-ray photoelectron spectroscopy (XPS) conducted at Mn2p, Co2p, and O1s –edges serves to reinforce and validate the XAS results.

Introduction

The perovskite manganites $RMnO_3$ (R=La, Nd, Pr, Gd, etc.) continue to be the focus of thorough research. This is primarily due to the intricate interplay of electronic, magnetic, and structural phases. The substitution of rare-earth element La or Mn at the B site, for a divalent alkaline earth cation like Ca or a 3d element like Co, respectively, results in a variety of attributes such as ferro-/antiferro-magnetism, metal–insulator transition, and colossal magnetoresistance [1], [2], [3], [4], along with other properties involving spin, charge, and orbital ordering [5]. Additionally, strong entanglement among various lattice, electronic, spin, and orbital degrees of freedom has been observed in doped $RMnO_3$ compounds [6]. Therefore, these compounds have a potential for practical use in spintronics, magnetic storage, etc.

The oxidation state of transition metal ions in these compounds, too demonstrates a vital role in governing their different magnetic and electric properties, e.g. half-metallic ferromagnetism (FM) [7] and charge and orbital ordering [8]. The low temperature ground state of $RMnO_3$ oxides was established long back to be antiferromagnetic (AFM) [9], [10]. However, as mentioned above it was discovered that doping of Sr at the La site induces FM in it, accompanied by a sharp decrease in resistivity [9], or doping of Co at the Mn site in the $LaMnO_3$ perovskite brings FM in it [4], [11], [12], [13]. Recently, Co-doped $LaSrMnO_3$ has shown FM behavior at room temperature, accompanied by increased electrical resistivity [14]. In a separate study on Co-doped $LaSrMnO_3$ the existence of FM, spin-glass behaviour, and Griffith phase [GP] is observed; which along with the electrical properties was explained in terms of different spin states of Co and Mn [15], [16]. Wang et al. [17] explored structural, magnetic, electrical transport, magnetoresistance (MR), and magnetocaloric effect (MCE)of Ba-doped $LaMnO_3$ observing the existence of GP with FM clusters in the paramagnetic (PM) region. Remarkably, the material demonstrated a large MR (~45%) and ideal MCE at room temperature. In a different study of Pt/$LaMnO_3$ heterostructures, the coexistence of FM and weak AFM phases, alongside a spin glass (SG) state, and the exchange bias (EB) effect was observed at low temperatures by Wang et al. The SG state was attributed to the competition between FM double-exchange and AFM super-exchange interactions at the interface. These findings suggest the potential for tuning the magnetic properties of AFM-LMO-based thin films [18].

It is learnt that very few studies have been done on the B-site doping in $NdMnO_3$. Troyanchuk et al. [19] showed that on substitution of Mn for Al, Fe, Cr, and Zn, the FM component increases significantly while Neel temperature T_N decreases slightly. The magnetization measurements reveal a sharp decrease in the net magnetization with a decrease in temperature. In a separate study of fifty percent Fe and Cr doping at the Mn site, Troyanchuk[20] showed that the ordering of magnetic spins of transition metal ions leads to a change in the magnetic structure. Sazonov et al. [21] found partially ordered Co and Mn ions in $Nd_2CoMnO_{6+\delta}$ (δ up to 0.12), significantly influencing the magnetic properties. They showed that Co^{2+} /Mn^{4+} are the predominant valence states of Co and Mn ions respectively. In $Nd_2CoMnO_{6,}$ the observed ionic disordering was found to enhance components like spin glass (SG).

As is well known and mentioned above in $LaMnO_3$, type-A AFM insulator, doping of Co at Mn site induces FM [4], [11], [12], [13], [14], [15], [16], [17]. It has been explained through mechanisms like superexchange (SE) interactions among Mn^{3+} ions [11] and Mn^{3+}-Mn^{4+} double exchange (DE) mechanism [22]. Replacing the non-magnetic La by rare-earth magnetic sublattice like Nd or Pr preserves the electronic configuration of Mn ions and

establishes an orbitally ordered AFM ground state of A-type [23]. Wang et al. have done quite extensive work on different properties of manganite perovskites like $NdMnO_3$ [24], [25], [26] and $SrMnO_3$ [27]. In their findings, the $NdMnO_3$ was found to exhibit semiconducting properties and showed MR effect though weak and a very good temperature coefficient of resistance (TCR) [24]. It was also found to display magnetization reversal, critical behaviour, and MCE providing a renewed understanding of this phenomenon in the light of magnetic ordering of Nd and Mn moments [25]. In Sr doped $NdMnO_3$ the increasing Sr content leads to increased magnetization owing to DE between Mn^{3+} and Mn^{4+}. The doped samples display critical phenomena near the Curie temperature (T_C) and a significant MCE was observed, with the strength of this effect varying across different Sr doping levels. The study highlights that Sr concentration influences the formation of ferromagnetic clusters in the paramagnetic state, a characteristic linked to the Griffiths phase observed in these compounds [26]. The four-layered AFM $SrMnO_3$ manganite is found to have a hexagonal structure that displays the existence of MR. It also has the maximum temperature coefficient of resistance (TCR) of 4.34% K^{-1} near room temperature [27].

These findings indicate that the materials studied exhibit significant potential for magnetic refrigeration applications near room temperature. Additionally, they hold great promise for advancing research and development in spintronics, AFM, and insulating electronic materials, as well as their incorporation into innovative electronic devices.

Hence, in context to the above investigating the structural and magnetic property alterations resulting from the substitution of La with Nd, as well as exploring the impact of Co doping at the Mn site in $NdMnO_3$ within the substitution range (x=0.0, 0.3, & 0.7), will be an intriguing avenue of study.

In this paper, we substituted Co at the Mn site in $NdMnO_3$ to study the crystal structure, magnetic properties, and electronic structure of the $NdMn_{1-x}Co_xO_3$ (x=0.0, 0.3 & 0.7) system. Magnetic studies suggest the presence of a possible ferromagnetic interaction, which is corroborated by the observed unsaturated magnetization and high value of coercivity, indicating the anisotropic nature of the studied samples. To understand the underlying origin of these properties, we investigated the electronic structure using XAS and XPS. XAS measurements have been performed at the $L_{3,2}$- edge of Mn and Co ions in addition to the O K-edge followed by Charge transfer multiplet (CTM) calculations for different ions to authenticate the valence states and symmetry of ions in the system under study. XPS results further substantiate the findings from XAS.

Section snippets

Experimental procedure

The samples of $NdMn_{1-x}Co_xO_3$ (x=0.0, 0.3, 0.7) (NMCO) were prepared in a single phase by solid-state reaction method. The stoichiometric amounts of high purity, Aldrich made, oxides of Nd_2O_3, MnO_2, and Co_3O_4 were mixed and grounded vigorously in an agate mortar to achieve a homogenous form. This homogenous mixture was pre-calcinated at 800 °C (1073 K) for 12 h followed by sintering at 900 ^{0}C (1173 K) for 20 h with a repetition of this step. The sintered powder was grounded thoroughly and then …

X-ray diffraction (XRD) studies

Fig. 1 shows the Rietveld refined XRD diffraction patterns of NMCO samples. The observed patterns agree well with the fitted spectra, and the refinement findings show that the NMCO samples depict an orthorhombic perovskite structure that is a single phase having space group Pbnm. The various parameters obtained after refinement are given in Table 1. It is noticed that $\mathbf{c}/\sqrt{2} < \mathbf{a} < \mathbf{b}$ for $NdMnO_3$ (NMO)**;** hence it takes Ó type orthorhombic structure. For the remaining samples $\mathbf{a} < \mathbf{c}/\sqrt{2} < \mathbf{b}$**;** thus have O …

Conclusions

The polycrystalline samples of NMO, NMCO3, and NMCO7 were prepared using the ceramic method. The analysis of XRD data using Rietveld refinement revealed their single- phase formation with the orthorhombic crystal structure and Pbnm as space group. The XAS and XPS studies show the presence of mixed valence of Mn (Mn^{3+}/Mn^{4+}) and Co(Co^{2+}/Co^{3+}) in both NMCO3 and NMCO7 samples while as NMO has the presence of only Mn^{3+} ions. The magnetic properties of the prepared samples are understood in terms of …

CRediT authorship contribution statement

Farooq H. Bhat: Writing – original draft, Visualization, Validation, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **G. Anjum:** Writing – review & editing, Software, Methodology, Formal analysis. **Jan Asifa:** Writing – review & editing, Software, Data curation. **Tanveer A. Dar:** Software, Data curation. **Ravi Kumar:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. …

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. …

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