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Negative magnetoresistance and conduction mechanism in $LaMn_{1-x}Co_xO_3$ thin films

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Abstract

The present work involves the deposition of $LaMn_{1-x}Co_xO_3$ (0.0, 0.2, 0.4, 0.5, 0.7) thin films on $LaAlO_3$ substrate with (100) orientation using the pulsed laser deposition technique. X-ray diffraction, Energy Dispersive Analysis of X-rays, four-probe technique, and a 7-T SQUID Magnetometer were used to investigate structural, elemental overlay, electrical transport, and magnetic properties of the mentioned thin film samples. The temperature dependent resistivity data indicates the semiconducting behaviour of the samples and the negative magnetoresistance effect arises in $LaMn_{0.8}Co_{0.2}O_3$. At higher temperatures, all the samples adhered to Arrhenius law and the small polaron hopping model whereas at the mid-temperature range and lower temperatures, nearest-neighbour hopping and Mott-variable range hopping is followed respectively. The observation of small polaron hopping at high temperatures indicates strong electron-phonon interaction in the above mentioned samples, as confirmed by the large values of electron-phonon coupling parameter (γ_p). Magnetic studies showed a paramagnetic to ferromagnetic phase transition in doped samples with coexisting ferromagnetic and antiferromagnetic interactions.

Introduction

ABO_3-type perovskites, in which A is either a rare earth metal: La, Gd, Nd, Pr; or an alkaline earth metal: Sr, Ca, etc. , and B is a transition metal like Mn, Fe, and Ni; have piqued interest worldwide for the past few years due to their exceptional magnetic and electrical properties including colossal magnetoresistance (CMR) [[1], [2], [3], [4]], ferromagnetism (FM)/anti-ferromagnetism (AFM) [5], catalyses, ferroelectricity besides spin, lattice, and orbital degrees of freedom [[6], [7], [8]]. Manganites ($RMnO_3$, R=La, Gd) are materials in this class that have significant technological utility in terms of computer memory systems, magnetic sensors, and magnetoresistive transducers [4,9], including the applications based on CMR effect. When considering other oxide families, manganites stand out due to their crystal structure's ability to accommodate a wide variety of atomic substitutions. $LaMnO_3$ (LMO) is a type-A antiferromagnetic insulator with $T_N \approx 140K$, where T_N represents the Néel temperature [6,8,10]. Doping of transition metal ions like Co at the Mn site induces mixed valence Mn^{3+}/Mn^{4+} for Mn, leading to the onset of FM in $LaMn_{1-x}Co_xO_3$ [4,11] along with other important magnetic and electrical properties. The onset of FM has been elucidated through processes such as double exchange (DE) interaction between Mn^{3+}-Mn^{4+} [12,13], superexchange (SE) interaction among Mn^{3+} ions [14], and positive superexchange interaction between Mn^{4+} and Co^{2+} ions [15,16].

The electrical and magnetic characteristics of lanthanum manganites are influenced by their structural features, notably the Jahn-Teller (JT) distortion [17]. This distortion, observed in polycrystalline orthorhombic perovskites, serves to eliminate degeneracy within the octahedral molecular complex. The 3d states of Mn^{3+} split into two sets of orbitals, t_{2g} and e_g. In LMO perovskite, singly occupied e_g orbitals further split, resulting in the elongation of the MnO_6 octahedron [17]. Several investigations of these materials have also indicated a robust electron-phonon (e-ph) interaction, attributed to the significant involvement of JT distorted ions in the transport mechanism [18].

Various studies have been carried out on the transport mechanism of lanthanum manganites by different authors to elucidate their detailed transport characteristics. W. Khan et al. [19] examined the transport properties of $LaMn_{1-x}Fe_xO_3$ ($0.1 \leq x \leq 0.6$) bulk samples. They observed that the resistivity data showed Mott-variable range hopping (Mott-VRH) behaviour across the entire temperature range studied (77–300K). Additionally, they found that the samples exhibited non-adiabatic small polaron hopping (SPH) conduction, accompanied by subtle changes in the Fe-O-Fe and Fe-O-Mn bond angles and bond lengths. These findings indicate that the transport properties can be attributed to the enhanced charge carrier localization caused by Fe doping. F. A. Khan et al. [10] investigated the transport and magnetic properties of $La_{1-x}Pb_xMnO_3$ ($0 \le x \le 0.20$) bulk samples and found that except for parent compound i.e., LMO, all other Pb doped samples display metal-semiconductor transition (MST). For the semiconducting region, the transport behaviour was elucidated through VRH and SPH models, noting a systematic decrease in hopping distance and hopping energy suggesting a low energy requirement for the hopping process. The resistivity data for the metallic region was interpreted by using the relation $\rho(T) = \rho_o + \rho_{2.5} T^{2.5}$ [10] which indicates the existence of electron-magnon scattering in the system. The magnetic study of samples revealed paramagnetic (PM) to weak ferromagnetic transition with the increase in Pb concentration beyond x=0.10, which could be explained based on the DE mechanism between Mn ions. A. Zahrin et al. [20] investigated the impacts of substituting K^+ ions in place of Ba on the magnetic and electrical properties of $La_{0.7}Ba_{0.3-x}K_xMnO_3$ (x=0.0, 0.4) bulk samples. The transport measurements revealed a decrease in resistivity and metal-insulator transition temperature (T_{MI}), with T_{MI} shifting to higher temperatures upon the introduction of K^+ ions into the system. This behaviour can be associated with an increase in the rate of e_g electron hopping due to an increase in the Mn-O-Mn bond angle and electronic bandwidth. Further, the transport mechanism in the insulating region was investigated using VRH and SPH models, and the metallic behaviour displayed by the samples at low temperatures was fitted with the relation $\rho(T) = \rho_o + \rho_2 T^2 + \rho_{4.5} T^{4.5}$. Magnetic studies indicated the FM nature of the samples which gets strengthened with the substitution of K^+ ions due to the enlargement of grain size. V. Kumar et al. [21] examined the transport properties of $LaCo_{1-x}Ni_xO_3$ ($0 \le x \le 0.5$) bulk specimens in different temperature ranges employing Arrhenius and Effros-Shklovskii (ES) type VRH model and suggested that the conduction mechanism is governed by disorder-induced localization of charge carriers. They also studied the magnetic properties of the samples and found that the magnetic nature is dependent on the doping concentration. Samples with $x < 3$ show PM to AFM transition at low temperatures, whereas those with $x > 3$ display spin glass behaviour within the same temperature range. A. Kumar et al. [22] examined the transport properties of $LaCo_{1-x}Ni_xO_3$ (x=0.0, 0.3) thin films and the electrical measurement suggests the semiconducting behaviour for the samples in the measured temperature range (100–300K). They carried out an extensive analysis of the conduction mechanism controlling the transport behaviour of these thin films in different temperature ranges using the Arrhenius law and ES-type VRH model, indicating disorder-controlled transport in these films. Z. Shan et al. [23] investigated the electrical transport properties of La_xMnO_3 thin films with varying contents of La^{3+} vacancies using the Mott-VRH model. They observed that reducing the number of La vacancies resulted in weakened electron localization. Further, the magnetic study revealed the FM nature of the films which becomes strong with the decrease in La vacancies.

Although, extensive research has been conducted on bulk LMO and its derivatives; however, the rise of nanotechnology has increased interest in nanoparticles and thin films. Thin films offer a platform to explore and create novel materials with distinct properties, differing from their bulk counterparts. Additionally, the substrate plays a crucial role in determining thin film structure and physical properties (like Curie shift) as a result of lattice misfit. Therefore, examining the electrical transport and magnetic properties of Co-doped LMO thin films presents an intriguing avenue for investigation. Thus, in this study, we examined the structural, electrical transport, and magnetic properties of $LaMn_{1-x}Co_xO_3$ thin films of thickness 238 nm. The composition and uniformity of the samples were confirmed using Energy Dispersive analysis of X-rays. We have identified the possible conduction mechanisms prevailing across different temperature ranges and also studied the existence of magnetoresistance (MR) in the aforementioned thin films.

Section snippets

Experimental details

A set of $LaMn_{1-x}Co_xO_3$ bulk targets with varying Co content (x=0.0, 0.2, 0.4, 0.5, and 0.7; LMO, LMCO2, LMCO4, LMCO5, and LMCO7) were synthesized using conventional solid-state reaction method. LMO/LMCO thin films, with a thickness of ~238 nm (confirmed by 3D optical profilometer), were deposited on $LaAlO_3$ (LAO) substrate with (100) orientation utilizing the Pulsed Laser Deposition (PLD) technique at UGC-DAE CSR, Indore. The deposition process involved ablating the bulk LMO/LMCO targets …

XRD studies

The XRD diffraction patterns of LMO, LMCO2, LMCO4, LMCO5, and LMCO7 thin film samples are depicted in Fig. 1. The bulk end members of this series viz. LMO (JCPDS# 01-087-2012) and $LaCoO_3$ (JCPDS# 48–0123) possess orthorhombic and rhombohedral structures respectively. From Fig. 1, it is clear that with increasing Co doping, there is a peak shift towards higher diffraction angles compared to LMO. This rightward shift of the diffraction peaks of LMCO thin films is attributed to the different ionic …

Conclusion

The EDAX study carried out on $LaMn_{1-x}Co_xO_3$ (x=0.0, 0.2, 0.7) thin film samples confirms the uniformity and the presence of only known elements in the samples. The semiconducting properties of $LaMn_{1-x}Co_xO_3$ (x=0.2, 0.5, 0.7) thin films and the existence of negative MR in $LaMn_{0.8}Co_{0.2}O_3$ were studied using different models i.e. band conduction, NNH, Mott-VRH, and SPH. It was observed that the samples follow band conduction and SPH model at higher temperatures, NNH in the intermediate …

CRediT authorship contribution statement

Jan Asifa: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis. **F.H. Bhat:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **G. Anjum:** Writing – review & editing, Visualization, Supervision, Methodology, Funding acquisition, Formal analysis, Data curation. **R.J. Choudhary:** Writing – review & editing, Methodology, Investigation, Data …

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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