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Irradiation induced oxygen vacancy and strain effects in $LaMn_{1-x}Co_xO_3$ thin films: Insights from XAS, XPS, and Raman spectroscopy

Jan Asifa [a], F.H. Bhat [a], G. Anjum [b], Shah Faisal [a], R. Meena [c]

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Highlights

- $LaMn_{1-x}Co_xO_3$ thin films are irradiated with 100MeV Ag^{+8} swift heavy ions (SHI) $\times^2$ and comprehensively characterized. .
- SHI irradiation induced oxygen vacancies and associated structural disorder/strain modifies the electronic structure of the films.
- XAS and XPS results reveal that SHI irradiation leads to the formation of oxygen vacancies.
- Raman spectroscopy indicates substantial changes in vibrational/phonon modes upon SHI irradiation.
- Magnetic measurements reveal degraded ferromagnetic interactions due to SHI induced oxygen vacancies.

Abstract

In this study, $LaMn_{1-x}Co_xO_3$ (x=0.0, 0.2, 0.4, 0.5, 0.7) thin films were deposited on $LaAlO_3$ (100) substrates via pulsed laser deposition technique and subsequently irradiated with swift heavy ions (SHI). X-ray diffraction was utilized to investigate the structural properties, while elemental composition was verified using Energy Dispersive Analysis of X-rays. To have insight of underlying physics through the electronic structure, X-ray absorption spectroscopy measurements at the Mn $L_{2,3}$-, O K-, and La $M_{4,5}$-edges, along with X-ray photoelectron spectroscopy at the O 1s core level was done. These measurements indicate that SHI irradiation induces the oxygen vacancy formation and introduces structural disorder and strain, thereby altering the Mn/Co 3d and O 2p orbital hybridization. Further, Raman spectroscopy measurements revealed Co-induced strain and Jahn-Teller distortion in pristine films, while SHI led to mode suppression and broadening due to oxygen vacancy formation. Magnetic measurements suggested weakening of ferromagnetism in irradiated samples.

Introduction

Perovskite materials have been observed to exhibit intriguing features like colossal magneto-resistance (CMR), ferromagnetism/anti-ferromagnetism, and tunable electrical conductivity; thus are considered to have prospective applications in catalysis, magnetic memory devices, sensors, refrigeration, bio-medical area, etc. Due to these facets and applications, perovskites have received a lot of attention and have been studied extensively for application as well as fundamental approach [[1], [2], [3], [4], [5]]. Among these, mixed valence manganites have been particularly well studied in different physical forms including single crystal, polycrystalline bulk, nanostructure, thin film interface, device, etc. [6]. $LaMnO_3$ (LMO), a prototypical perovskite manganite, exhibits diverse physical properties in both stoichiometric and non-stoichiometric phases [7]. Stoichiometric bulk LMO, characterized by an orthorhombic perovskite crystal structure, is an A-type antiferromagnetic insulator with Mn spins aligned ferromagnetically within each plane and alternating (001) planes aligned antiferromagnetically [8]. On the other hand, $LaMnO_{3\pm\delta}$ (non-stoichiometric phase) show properties similar to doped LMO systems [7,9]. Thus, the physical/functional properties of manganite systems can be modified by various ways like changing oxygen Stoichiometry, substituting A and B site ions, or preparing them in thin film forms.

An additional and powerful experimental tool for tuning material properties is Swift Heavy Ion (SHI) irradiation, which induces artificial defects in films and facilitates material modification [10]. This technique involves traversing of highly energetic ions (generally in the MeV range) through the target material, resulting in energy losses viz. nuclear energy loss through elastic collisions with target nuclei and electronic energy loss through inelastic collisions with electrons in the target material. This can induce various types of defects including point defects, columnar defects, or amorphization, thereby altering physical properties. Further, SHI irradiation can cause structural strain modifications in thin films enabling the tuning of their physical properties [11]. Strong electronic excitations and/or ionization processes induced due to SHI irradiation are also known to be effective in creating deep-level defects such as oxygen vacancies. Among the various effects induced by ion irradiation, the formation of oxygen vacancies in manganite thin films is of particular importance due to their potential for enabling multifunctional device applications [[12], [13], [14]]. Oxygen vacancies can significantly alter the structural properties of these materials as they migrate through the lattice. In transition metal oxides, the creation of vacancy defects often leads to substoichiometry at either the metal or oxygen lattice sites [14,15].

In mixed-valence manganites, structural, transport, electronic, and magnetic properties are largely governed by double exchange (DE) and superexchange (SE) mechanisms. In the DE process, the conduction electrons at Mn (Mn^{3+}/Mn^{4+}) sites hop via oxygen bridges (O^{2-}). The disruption of the Mn-O-Mn network due to oxygen vacancies weakens the DE interaction, resulting in fragile Mn-O hybridization and degrades the magnetic and transport properties. Furthermore, oxygen vacancy formation can lead to a reduction in the Mn valence state from Mn^{4+} to Mn^{3+}/Mn^{2+}, thereby suppressing the DE interaction between Mn^{3+} and Mn^{4+} ions. This degradation can drive a transition from metallic or semiconducting behaviour to an insulating state [14,16], as also observed in our study. In the case of semiconducting $LaMn_{1-x}Co_xO_3$ (LMCO) thin films [17], SHI irradiation induced oxygen vacancies (discussed in later section) led to a dramatic increase in resistivity (beyond the measurable range of our instrumentation) indicating an insulator-like behaviour.

It is well established that the electrical and magnetic properties of lanthanum manganites are generally described in terms of Jahn-Teller (JT) distortion, DE, and SE interactions [18,19]. Several studies reveal the presence of strong electron-phonon (e-ph) interactions (driven by JT distortion) in these systems, which have a significant impact on their charge transport mechanism [20]. For instance, our previous study on LMCO thin films demonstrated strong e-ph interactions, which were attributed to the interplay between JT distortion, crystallite size, and strain [17]. Raman spectroscopy is a widely used technique to explore phonon modes and characterize the JT distortion. Since the latter lowers the crystal symmetry, the signatures of JT phonons reflect this symmetry reduction [21]. Therefore, analysing the symmetry of JT phonons is crucial for characterizing JT distortion in thin films. Further, Raman spectroscopy has been widely used to study heavy ion induced radiation damage [22]. Thus, in this study, we explored the phonon modes of LMCO thin films by employing the Raman spectroscopy and analysed the impact of 100 MeV Ag ion irradiation on these phonon modes. Structural modifications, variations in vibrational/phonon modes, and changes in the electronic structure and magnetic properties due to ion-induced oxygen vacancies have been systematically explored.

Oxygen-deficient manganites are known to exhibit resistive switching behaviour, which is of great interest for non-volatile memory and memristive applications [11,12]. Given the established role of oxygen vacancies in enabling such functionalities in similar oxides (e.g., $La_{2/3}Sr_{1/3}MnO_3$, $YMnO_3$, etc.) [11,12,23], our defect-engineered LMCO thin films may also hold potential for future device applications. The present findings, thus lay the groundwork for further studies focused on tuning functional responses in these materials through controlled defect engineering. Moreover, our results highlight a viable strategy for tailoring the magnetic and transport properties of oxide thin films through precise control of oxygen vacancy concentrations, offering potential for next-generation spintronic device applications.

Section snippets

Experimental details

The $LaMn_{1-x}Co_xO_3$ (x=0.0, LMO; 0.2, LMCO2; 0.4, LMCO4; 0.5, LMCO5; and 0.7, LMCO7) thin films were deposited on (100) oriented $LaAlO_3$ (LAO) substrates by pulsed laser deposition (PLD) technique, with detailed experimental procedures already outlined in previous study [17]. To induce the defects, the above mentioned thin films (~$5 \times 5\,mm^2$ in size) were irradiated with 100 MeV Ag^{+8} ions at a fluence of 5×10^{12} ions/cm^2. This SHI irradiation was carried out using 15UD Tandem Accelerator facility …

XRD study

The XRD diffraction patterns of SHI irradiated thin films (LMO-IRR, LMCO2-IRR, LMCO4-IRR, LMCO5-IRR, and LMCO7-IRR) are depicted in Fig. 1. Since SHI induced electronic excitations can modify peak positions [10], a slight shift in peak positions towards lower angles is observed for the irradiated LMCO thin films compared to their pristine counterparts (see Fig. 2), suggesting an increase in the out-of-plane lattice constant. This out-of-plane parameter elongation indicates the presence of …

Conclusion

Swift heavy ion (SHI) irradiation induced significant modifications in the magnetic properties and local electronic structure of $LaMn_{1-x}Co_xO_3$ (x=0.0, 0.2, 0.4, 0.5, 0.7) thin films. XRD, XAS, XPS, and Raman spectroscopy analysis provide clear evidence for the creation of oxygen vacancies and the associated structural disorder/strain, which critically affect the hybridization between Mn/Co 3d and O 2p orbitals. Magnetic studies revealed reduction in both magnetization and T_c in irradiated …

CRediT authorship contribution statement

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

Novelty statement

This study uniquely demonstrates the impact of swift heavy ion (SHI) irradiation on the structural, magnetic, and electronic properties of $LaMn_{1-x}Co_xO_3$ thin films deposited on $LaAlO_3$ substrates. By employing a comprehensive set of advanced characterization techniques including X-ray diffraction (XRD), Raman spectroscopy, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and SQUID, the work reveals the direct correlation among SHI-induced oxygen vacancy formation, …

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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