Antisite disorder induced spin-glass and exchange bias phenomena in double perovskites

Thesis submitted in partial fulfilment for the Award of Degree
DOCTOR OF PHILOSOPHY

by
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Dedicated to my parents, daughther (DIVA) and the whole family that always encouraged me to follow my dreams.

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Abstract

Complex oxide materials have gained significant interest due to their emerging properties and exceptional applications such as superconductivity, near-room temperature ferromagnetic ordering, magnetodielectric, exchange bias, magnetocaloric, magnetoresistance, half metallicity, and solar cells. These properties are corroborated with distinct lattice, charge, spin, orbital ordering and phase transitions. Based on the atomic distributions, these complex oxides have multiple different structures such as perovskite, spinel, garnet, and pyrochlore. Perovskites (ABO_3) and double perovskites ($A_2BB^{'}O_6$) can be differentiated on the basis of octahedral arrangement and the presence of two different B-site cations (B/B$^{'}$). Double perovskites are a special class of doped perovskites with 50 % doping at the B-sites that theoretically doubles the unit cell in a regular periodic approach. The fascinating features of double perovskites are mostly due to the two different kinds of octahedral configurations that resulted in ordered and disordered phases. The ordering of octahedra may be possible in three different types: rock salt, layered, and columnar. Antisites disorder (ASD) and antiphase boundary (APB) are common types of structural disorder features in double perovskite materials that consist of two different B/B$^{'}$-site cations, which modify the properties by altering B/B$^{'}$-sites.

Among the family of double perovskites, the La_2NiMnO_6 (LNMO) compound has attracted significant interest due to its various underlying properties and applications. In the case of ordered LNMO compound, the reported ferromagnetism phase is explained through the Goodenough-Kanamori (GK) rule for 180° ferromagnetic superexchange interaction between multiple oxidation states of Ni/Mn cations. Ordered LNMO is a ferromagnetic semiconductor having T_c = 280 K with various distinct magnetic properties across T_c. On the other hand, partially disordered LNMO shows exceptional magnetodielectric coupling, magnetoresistance, and magnetocapacitance that strongly influence by competing Ni^{2+} -O^{2-} -Mn^{4+} exchange interactions. LNMO also manifest the Griffith phase and additional low-temperature magnetic anomalies. The lower temperatures transition has been attributed to the combined influence of antisites disorders and Ni^{3+} -O^{2-} -Mn^{3+} ferromagnetic ordering. The multiple oxidation states of B/B$^{'}$ give rise to competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions that stabilized a magnetic frustrated state below the critical temperature. Previous studies have shown changes in T_c by varying the degree of ASD and APB through doping at the A-site and modifying the synthesis procedure of double perovskites. Few earlier studies have also observed the exchange bias in LNMO mediated by APB formed by the accumulation of ASD.

Herein, this thesis explores the phase evolution and microstructural morphologies of LNMO polycrystalline compounds using the size effect on various crystallites. Magnetization variation with temperature M-T and applied external magnetic field M-H loops are utilized to investigate magnetic transitions caused by the presence of multiple exchange interactions and antisite disorders. X-ray photoelectron spectroscopy (XPS) is utilized to probe the charge transfers in the LNMO crystallites. The XPS investigation verifies the existence of various valence states of cations with Ni^{3+} and Mn^{3+} contributing significantly to the stabilization of secondary ferromagnetic transitions. The thesis also provide the details of the theoretical calculation of the saturation magnetization (M_s) assuming different possible valence states. The core-shell structures are explained using transmission electron microscopy (TEM). The magnetization relaxation dynamics of the spin-glass (SG) phase that are derived from coexisting FM and AFM exchange interactions are explained within the framework of the power law, Vogel-Fulcher law, and Cole-Cole formalism that determine the nature of spin relaxation.

The present thesis also attempts to address the interesting aspects of the influence of ASD and APB upon the A-sites doping. Sm-substitution influences the structural characteristics of bond angle and bond length as well as magnetization. Present thesis emphasized SG state, spin dynamics, and exchange bias effect in these oxide compounds. Measurements of the continuous successive M-H loop and field reversal magnetization further support the observation of exchange bias phenomena. The Raman spectra are used to understand how the degree of ASD and APB influence through Sm-doping. This thesis highlights various modelling techniques to examine the nature of the SG state and its properties. The addition of Sm transforms the SG state into a cluster glass (CG) state. The determination of the Mydosh parameter, magnetization decay, magnetic memory, and rejuvenation effects has been utilized to elaborate on the SG state characteristics. In the proximity of CG transition a modified g-value ranging from 2.050 to 2.037 were reported utilizing electron spin resonance (ESR) techniques. The line width of the ESR signals increases across the transition due to spin freezing that is further examined by temperature-dependent ac-magnetic susceptibilities $\chi(\omega,T)$. To illustrate the magnetic memory and dynamics properties, two different complementary methods, namely the droplet and hierarchical models, are employed. Arrot's plot and mean-field theory are used to describe the order of magnetic phase transitions in this thesis. The density functional theory (DFT) explains spin state density and supports the presence of antisites. The DFT reveals that the Sm position in the unit cell has limited effect on the characteristics and that the antisites identify the various spin configurations. In a broad way, this thesis focuses on the magnetic characteristics of various protocols and models-based analysis.

This thesis systematically highlights the synthesis of $La_{2-x}Sm_xNiMnO_6$ (x = 0, 0.1, 0.2) compounds through the *sol-gel* process using all aqueous precursors. The physical characteristics of $La_{2-x}Sm_xNiMnO_6$ were probed using X-ray diffraction (XRD), Raman spectroscopy, magnetization, and susceptibilities measurements. The impact of site substitution on intrinsic behaviours and magnetic properties has been studied. The experimental studies suggest that the structural phase stability of $La_{2-x}Sm_xNiMnO_6$ improves significantly with Sm proportion as evident from the transformation of the compound from a biphasic (monoclinic + rhombohedral) structure into an aphasic (monoclinic, space group: $P2_1/n$). Sm-addition mediates variation in exchange interactions and ordering of Ni^{2+}-O^{2-}-Mn^{4+} that further suppress (284 K $\rightarrow$ 245 K) the T_c. Lower T_c and higher saturation magnetization (M_s) resulted from the reduced degree of antisites disorder. Along with T_c, a massive shift (45.5 K $\rightarrow$ 72.9 K) in glass transition temperature is also reported. Field-cooled magnetization M-H loops confirm the evidence of exchange bias in Ni^{2+}-O^{2-}-Mn^{4+} that reduces (120 Oe $\rightarrow$ 28 Oe) with Sm proportion. The measurements of temperature-dependent magnetization M-T curves and frequency-dependent ac-susceptibility $\chi(\omega$,T) were utilized to characterize the antisites-driven SG phase, magnetization relaxation dynamics, magnetic memory, and rejuvenation effect. The phase stability, lower T_c, tuneable M_s, and exchange bias make $La_{2-x}Sm_xNiMnO_6$ a potential candidate for its applications in energy-efficient devices.

In contrast, the $La_{1.5}Sm_{0.5}NiMnO_6$ compound shows the presence of antisites disorder in double perovskites and manifests various intriguing properties like SG state, exchange bias, and memory effect. The results suggest that the compound crystallizes in a monoclinic ($P2_1/n$) structure. The oxidation state of Ni(Mn) cations induces competing ferromagnetic and antiferromagnetic exchange interactions that originate from a heterogeneous spin frustrated state, as evident from reported magnetic anomalies in temperature-dependent magnetization measurements. SG state is evolved that manifests a exchange bias phenomenon (153 Oe) below T_{SG} (65.1 K). The strength of the exchange bias is reduced after successive magnetization reversal cycles that are performed at 5 K. The reported magnetic training effect is explained within the frameworks of meta-stable magnetic disorder across frozen antiphase boundaries in the frustrated SG state. Measurements of frequency-dependent ac-susceptibility suggest critical slowing dynamics and memory effect in the proximity of T_{SG}, which is described using a critical slowing model resulting in relaxation exponent $z\nu = 1.99 \pm 0.04$ and $\tau_0 = 8.91$ X 10^{-7} s. Employing DFT calculations, we report the insulating ferromagnetic ground state of $La_{1.5}Sm_{0.5}NiMnO_6$ in the ordered phase where Ni (Mn) appears to be in a 2+ (4+) state. The presence of antisites disorder eventually results in lower magnetic moments per formula unit that is

well matched with experimental observations. Our findings provide a pathway to control the induced exchange bias by manipulating the degree of ASD in such heterogeneous systems that have potential applications in designing magnetic sensors. Sm is known to have excellent thermal and optical characteristics; in the future, it would be interesting to investigate the thermal and optical characteristics and influence on Sm addition in LNMO compound.

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List of Abbreviations

DP	Double perovskite
LNMO	La_2NiMnO_6
LSNMO	$La_{2-x}Sm_xNiMnO_6$
XRD	X- ray Diffraction
ASD	Antisite Disorder
APB	Antiphase Boundary
JCPDS	Joint committee on powder diffraction standards
ICDD	International Centre for Diffraction Data
TEM	Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
ESR	Electron Spin Resonance
XPS	X-ray Photoelectron Spectroscopy
MPMS	Magnetic Property Measurement System
SQUID	Superconducting Quantum Interfaces Devices
VSM	Vibrating-Sample Magnetometer
FM	Ferromagnetic
AF	Antiferromagnetic
EDX	Energy Dispersive X-ray spectroscopy
FWHM	Full Width Half Maximum
BSC	Backscattering Coefficient

ac	Alternating Current
dc	Direct Current
ZFC	Zero Field Cooling
FC	Field Cooling
NN	Nearest Neighbour
NNN	Next Nearest Neighbour
EB	Exchange Bias
SG	Spin-glass
CG	Cluster glass
SPM	Superparamagnetic
TRM	Thermoremanent Magnetization
SOC	Spin-Orbital Coupling
DFT	Density Functional Theory

List of Symbols

S	Total spin angular momentum
β	Angle (Lattice Parameter)
θ	Bragg's angle
L	Total orbital angular momentum
J	Total angular momentum
μ	Magnetic permeability
μ_B	Bohr magneton
μ_{eff}	Effective magnetic moment
H	Magnetic field intensity
H_c	Coercivity
M	Magnetization
M_r	Remanent magnetization
T	Temperature
H_{EB}	Strength of exchange bias
χ	Magnetic susceptibility
χ_{dc}	dc magnetic susceptibility
χ_{ac}	ac magnetic susceptibility
$\chi^{''}$	The imaginary part of magnetic susceptibility
$\chi^{'}$	The real part of magnetic susceptibility
μ_0	The magnetic permeability of free space
T_{SG}	Spin glass transition temperature
T_c	Curie temperature

T_f	Freezing temperature
τ	Relaxation time
θ_P	Curie-Weiss temperature
Ω	Mydosh parameter
ω	Ac frequency
ΔX	Peak to peak line width
X_{RES}	Resonance field
$\mathbf{c}$	Speed of light
λ	Wavelength
θ_i	Incidence or local incidence angle
$\mathbf{r}$	Ionic radii
K	Kelvin
(hkl)	Miller index
d	Lattice spacing
a, b, c	Lattice parameters

Preface

Complex oxide materials have attended immense interest due to their exceptional characteristics and applications such as superconductivity, magnetoresistance, magnetodielectric, and electronic properties. These characteristics are related to structure, charge, spin, orbital ordering, and transitions. These complex oxides have various structures based on their atomic distribution and arrangement such as perovskites, spinel, garnet, and pyrochlore. Perovskites and double perovskites can be distinguished by their octahedral organization and the presence of two distinct B(B$^{'}$)-site cations. Double perovskite is a kind of doped perovskite with 50% doping at the B(B$^{'}$)-sites that theoretically doubles the unit cell in a regular periodic method. These two forms of octahedral configurations that generate ordered and disordered phases are important contributors to the interesting features of double perovskites. Octahedra can be ordered in three ways: rock salt, stacked, and columnar. ASD and APB are two frequent forms of disorders.

The LNMO compound has attracted significant interest in the family of double perovskites due to its multiple promising applications. Ferromagnetism in ordered LNMO is explained by the Goodenough-Kanamori rule for 180° ferromagnetic superexchange interactions. Ordered LNMO is a ferromagnetic semiconductor with T_c = 280 K, displaying various distinct magnetic properties across T_c. On another side, partially disordered LNMO shows exceptional magneto-dielectric coupling. Physical behaviours like magnetoresistance and magnetocapacitance in such compounds strongly depend on Ni^{2+}-O^{2-}-Mn^{4+} exchange interactions. Previous investigations suggest that different fascinating features and variations in Curie temperature by altering ASD and APB via doping at the A-site and modifying the synthesis procedure and conditions. Because of the underlying intrinsic strain, bi-phasic studies are more fascinating. In the case of thin film, a heterostructure is generated by an alternative layer of $LaNiO_3$ and $LaMnO_3$ and discovered charge transfer at the bilayer interface. There are very less reports on exchange bias in LNMO explained by APB formed by the accumulation of ASD. This thesis is divided into various chapters that are described below.

Chapter 1 presents a literature review about double perovskite, especially LNMO due to its useful properties and characterizations. This chapter explains the difference between perovskite & double perovskites and list out the major advantages of double perovskites. An overview of the synthesis process and doping affects the cation ordering and disordering, which affects the properties of double perovskite. The literature review about the different possible structures of LNMO with varying synthesis routes and conditions is also explained.

Chapter 2 describes the synthesis process used to prepare the LNMO nanocrystallites. As the literature implies that structure changes with synthesis conditions, we used two alternative ways namely the solid-state and sol-gel approaches to synthesize LNMO crystallites. The discussion of surface topology by SEM & TEM, and magnetization measurement techniques using a SQUID, MPMS in a distinct protocol. X-ray diffraction and Raman spectra corroborate the structural phase. The presence of multiple valences is identified by X-ray photoelectron spectroscopy. The electron spin resonance implies the resonance field and Lande g-factor.

Chapter 3 of the present thesis briefly investigates the phase development and microstructural study of LNMO using several synthesis techniques. The impact of millings on the microstructure and surface morphology of various lattice planes and crystallites. M-T curves and M-H loops are used to probe the various magnetic anomalies across T_c caused by multiple spin ordering. X-ray photoelectron spectroscopy (XPS) explains charge transfers found in nanocrystallites. The XPS investigation verifies the occurrence of various valance states of charge cations, with Ni^{3+} and Mn^{3+} contributing significantly to the stabilization of secondary ferromagnetic transitions. The thesis also deals with the theoretical calculation of the saturation magnetization assuming different possible valance states and comparing it with experiment data. The core-shell structures are imaged using TEM. The relaxation dynamics are explained by a power law, Vogel-Fulcher law, and also Cole-Cole formalism defines the nature of spin relaxation. The saturation magnetization assumes different possible valance states and compares.

Chapter 4 deals with the influence of ASD and APB on magnetic properties. Because of its premixture magnetic band structure, high spin-orbital coupling (SOC), and other properties, Sm is employed for doping at A-site. This chapter describes the Sm doping in $La_{2-x}Sm_xNiMnO_6$ (where $x = 0, 0.1, 0.2$) and their structure, size and shape, Raman spectroscopy, and magnetic properties. Sm doping has an effect on structural characteristics that is confirmed by the Rietveld refinement. Sm doping alters the biphasic (monoclinic + rhombohedral) structure into the aphasic monoclinic phase. The surface morphology analysis confirms particles are agglomerated and cations distributed homogenous and quantification within the nominal fraction. Our thesis primarily concerned with magnetic

characteristics. This thesis is concerned with spin glass dynamics and exchange bias. The SG state confirms with frequency-dependent cusp shift and power law fitting. The SG state nature further characterizes by the hierarchical modeling and magnetization decay measurement. The exchange bias confirms by the field reversal field cooling M-H loop measurement. The Raman spectra also illustrate how ASD and APB interact with Sm doping. The chapter has a brief discussion about antisites disorder with varying the properties such as exchange bias magnetic memory effect.

Chapter 5 highlights the synthesis and magnetic properties of $La_{1.5}Sm_{0.5}NiMnO_6$ crystallites. An increase in the Sm doping fraction transforms the typical spin glass into a cluster glass. The Mydosh parameter, magnetization decay, and memory and rejuvenation all explain the spin glass properties. To illustrate the dynamics, and Arrot's plot & mean field theory are used to describe the order of magnetic phase transitions in this thesis. The exchange bias confirms different field hysteresis loop measurements and magnetic training effects. The density functional theory (DFT) explains spin state density and supports the presence of antisites. The DFT reveals that the Sm position in the unit cell has little or no effect on the properties via consider different positions Sm atom in the unit cell. The antisites disorder are also confirmed by considering various spin configurations and antisites positions to analyse saturation magnetization.

Chapter 6 concludes the thesis with the novel findings. In a broad way, this thesis focuses on the magnetic characteristics of various protocols and models-based analysis. In this chapter, concluding remarks are presented on the basis of the experimental results and theoretical interpretation obtained in all the nano crystallite samples that are addressed in the thesis.

Chapter 7 describes the summary and conclusion of this work and also provides suggestions for the future prospect of current studies. The system with SG state and an exchange bias caused by ASD. Because Sm has good thermal and optical qualities, there is room to investigate the thermal and optical features.