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 $\tau_0 = 8.91 \times 10^{-7}$ 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.

List of Publications

International Journals

1. **R. Hissariya**, S. Babu, S. Ram, and S. K. Mishra 2021,"Spin-up conversion, exchange-interactions, and tailored magnetic properties in core-shell La_2NiMnO_6 of small crystallites ", *Nanotechnology 32 (43), 435702*

2. P. K. Ojha, R. Sharma, **R. Hissariya**, S. Babu, E. Ketkar, S. Singh, S. Neema, A. Rana, N. Pal, V. G. Sathe, and S. K. Mishra, 2021,"Observation of V–V dimers softening and distinct length scales in nanostructured VO_2 thin films ", *Journal of Physics and Chemistry of Solids, 110564*

3. **R. Hissariya**, V. G. Sathe, and S. K. Mishra, 2023, "Antisite disorder mediated exchange bias effect and spin-glass state in $La_{2-x}Sm_xNiMnO_6$ ", *Journal of Magnetism and Magnetic Materials, 170769*

4. **R. Hissariya**, R. Sharma, and S. K. Mishra, 2023, "Antisites disorder mediated magnetization relaxation and polydispersity in La_2NiMnO_6 crystallites. ", *Journal of Physics and Chemistry of Solids, 111549*

Comunicated articles

1. **R. Hissariya**, N. Tripathi, Vivekanand Shukla, Tommas Brumme, and S. K. Mishra, 2023, "Antisite disorder induced exchange bias effect and spin-glass state in $La_{1.5}Sm_{0.5}NiMnO_6$. (under Review)

Proceedings

1. **R. Hissariya**, and S. K. Mishra, 2021, "Antisites driven magnetic transition study in La_2NiMnO_6 ", *Journal of Physics: Conference Series 2070 (1), 012060*

Seminar and Symposium

1. WWSTMS-2018, Winter School on Synchrotron Techniques in Materials Science, S. N. Bose National Centre for Basic Sciences, Kolkata, India, October 25-31, 2018 (**Winter School**).

2. ICMAGMA-2018, International conference on Magnetic Materials and Applications Dept. of Physics, NISER, Bhubaneswar, December 09-13, 2018 (**Poster Presentation**).

3. ICFNM-2019, International Conference on Functional Nanomaterials at Department of Physics, IIT-(BHU), Varanasi, India, February 22-25, 2019 (**Poster Presentation**).

4. SMST-2020, International Conference on Smart Material for Sustainable Technology at Bogmallo Beach Resort, Goa Conference is jointly organized by Society of Interdisciplinary Research in Materials and Biology (SIRMB), IIT (BHU) Varanasi, IIT-Delhi, IIT-Goa, and SINP-Kolkata IIT-(BHU), Varanasi, India, February 22-25, 2020 (**Poster Presentation**).

5. Expert/tranier lecture to ceramic engginеer student through video conferencing during COVID-19 emergency which held during 4^{th} May- 20^{th} June, 2020.

6. AMBT-2021, International Conference on Advances Materials for Better Tomorrow, jointly organized by Society of Interdisciplinary Research in Materials and Biology (SIRMB), IIT (BHU) Varanasi, July 13-17, 2021 (**flash talk Presentation**).

7. ICAPSM-2021, International Conference on Advances in Physical Sciences and Materials at Coimbatore, Tamil Nadu, India, August 12-13, 2021 (**Paper Presentation**).