INVESTIGATION OF THE STRUCTURAL, MAGNETIC, ELECTRONIC, AND TRANSPORT PROPERTIES OF DOUBLE PEROVSKITES Sr2-xLaxCoNbO6

AJAY KUMAR

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI (IITD)
HAUZ KHAS, NEW DELHI

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AJAY KUMAR
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under the supervision of

Prof. Rajendra Singh Dhaka

Novel Materials and Interface Physics Laboratory

Department of Physics

Indian Institute of Technology Delhi (IITD)
Hauz Khas, New Delhi–110016, India

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DECLARATION BY THE CANDIDATE

I, Ajay Kumar, declare that the work in this thesis entitled *"Investigation of the Structural, Magnetic, Electronic, and Transport Properties of Double Perovskites* $Sr_{2-x}La_xCoNbO_6$*"*, is my own work conducted under the supervision of Prof. Rajendra S. Dhaka and approved by student research committee (SRC) at Department of Physics, Indian Institute of Technology Delhi, New Delhi, India.

I further declare that this work is not submitted and will not be submitted to any other institute/university for any degree or diploma. I confirm to the norms and guidelines given in the ethical code of conduct of the institute. Moreover, I have given appropriate credit to all materials, theoretical analysis, data, figures, and text used from other sources, by citing them in the text of the thesis.

Signature __________________________
Name of the candidate: Ajay Kumar
Entry Number: 2016PHZ8393
Department of Physics
Indian Institute of Technology Delhi
Hauz Khas, New Delhi – 110016, India.
Date:

CERTIFICATE OF THE SUPERVISOR

This is to certify that the thesis entitled *"Investigation of the Structural, Magnetic, Electronic, and Transport Properties of Double Perovskites $Sr_{2-x}La_xCoNbO_6$"*, being submitted by **Ajay Kumar** (2016PHZ8393) to the Department of Physics, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide work carried out by her. He has worked under my supervision and guidance and has fulfilled the requirements for the submission of this thesis, which in my opinion has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree/diploma.

Signature__________________________

Prof. Rajendra S. Dhaka
Associate Professor
Department of Physics
Indian Institute of Technology Delhi
Hauz Khas, New Delhi – 110016, India.
Date:

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Ajay Kumar

ABSTRACT

Understanding the various functional properties of the materials is necessary to engineer suitable candidates for different technological applications such as energy storage devices, memory devices, superconductors, solar cells, etc. In this context, the perovskite oxides provide the most suitable platform due to their robust crystal structure, which can be perturbed in a controlled manner using external parameters like temperature, mechanical pressure, chemical pressure, magnetic field, substrate-induced strain in the thin films, etc. Particularly, the cobalt-based perovkite oxides show intriguing physical properties due to the small energy difference between the various valence states of Co viz. Co^{2+}, Co^{3+}, and Co^{4+}. More interestingly, Co^{3+} in the perovskite matrix (octahedral environment) can exist in the various spin-states, depending on the relative strength of the Hund's exchange energy and the crystal field splitting, which can be systematically tuned for the desired applications. Thus, a coherent understanding of the influence of the various valence and spin state transitions on the structural, electronic, transport, and magnetic properties of Co-based perovskite is the need for hours. Furthermore, the degree of B-site ordering in the case of double perovskite oxides can alter the nearest as well as next-nearest neighbor interactions and hence provide an additional degree of freedom to tune these properties.

The main focus of this thesis is to understand the evolution of the structural, magnetic, transport, and electronic properties of $Sr_{2-x}La_xCoNbO_6$ (x =0–1) double perovskites with the La substitution. The substitution of non-magnetic La^{3+} ions at Sr^{2+} site transforms Co from 3+ (in x =0) to 2+ (in x =1) state, which systematically enhances the alternating ordering of the corner shared NbO_6 and CoO_6 octahedra due to increase in the valence mismatch between Co and Nb^{5+} ions ($\Delta V=2\rightarrow 3$). The disordered structure in the lower La substituted samples provide the additional Co–O–Co exchange paths along with the Co–O–Nb–O–Co channels in the ordered configuration and hence the resulting competing exchange interactions give rise to the low-temperature cluster glass behavior in $x \leqslant 0.4$ samples, where spin-spin correlation, as well as intercluster interaction strength, decreases with x. However, a sharp antiferromagnetic (AFM) transition with a systematic enhancement in the Néel temperature has been observed with further increase in the La substitution for the $x \geqslant 0.6$ samples due to the dominance of Co^{2+}–O–Nb^{5+}–O–Co^{2+} AFM superexchange interactions. Interestingly, the magnetization measurements show the large unquenched orbital magnetic moment in the case of Co^{2+}, which indicates the degenerate orbital states in the La-rich samples. This is further supported by the specific heat measurements, which evident the presence of free Co^{2+}-like Kramers doublet ground state in the x =1 sample. Further, the detailed electronic and local structure of these samples has been investigated using x-ray absorption spectroscopy (XAS) and neutron diffraction measurements. Both the measurements show a decrease in the local distortion around B-site (Co and Nb) and an increase around A-site (La and Sr) cations with the La substitution. A strong correlation between the degree of octahedral distortion and the intensity of the white line feature in the XANES spectra of the transition metals has been established and the possible reasons for the same are discussed. Moreover, all these samples show the giant dielectric constant in the low frequency and the high-temperature regime, which is attributed to the grain boundaries/ interfacial polarization of the charge carriers and the on-set of the electronic conduction, respectively. The combined dielectric and polarization measurements on these samples indicate their possible use as a high dielectric material in the various microelectronic and charge storage devices.

The inelastic light scattering (Raman spectroscopy) shows the anomalous renormalization of the self-energy parameters (frequency and line width) of the Raman modes below around 60 K in case of the $x = 1$ sample, which is attributed to the spin-phonon coupling, indicating the presence of short-range magnetic correlations in the sample deep into the paramagnetic region. This spin-phonon coupling also causes a small but notable change in the bond distances and the corresponding Debye-Walles factors around Co atoms below ~70-100 K for the x =1 sample. Finally, we report the structural, electronic, and transport properties of the thin films of the x =0 sample, epitaxially grown on the various substrates ranging from tensile to the different degrees of the compressive strain using pulsed laser deposition. A systematic enhancement (reduction) in the electronic conductivity has been observed with an increase in the compressive (tensile) strain due to a change in the covalency character and oxygen non-stoichiometry in the thin film sample. Moreover, the complex exchange coupling at the FM-AFM interface of $La_{0.67}Sr_{0.33}MnO_3$/ $LaSrCoNbO_6$ and La_2CoMnO_6/ $LaSrCoNbO_6$ heterostructures, epitaxially grown on the $SrTiO_3$(100) substrate, have been also briefly reported.

Overall, a systematic correlation between the structural, magnetic, electronic, and transport properties of $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) double perovskites have been established using the x-ray and neutron diffraction, magnetization, specific heat, x-ray absorption, dielectric, and Raman spectroscopy measurements. The correlation between the various valence and spin-states of Co with the underlined physical properties is expected to provide a pathway for a better understanding of the different functional properties of the Co-based perovskite oxides. Further, the systematic investigation of the nature of Co–O bonding and various low-lying energy states in these samples can be useful to engineer suitable candidates for solid oxide fuel cells, memory devices, microelectronics, energy storage devices, etc.

सार

वस्तुओं के विभिन्न कार्यात्मक गुणों को समझना, विभिन्न प्रौद्योगिकीय अनुप्रयोगों जैसे ऊर्जा संग्रह उपकरण, स्मृति उपकरण, सुपरकंडक्टर, सौर सेल आदि के लिए उपयुक्त उम्मीदवारों को इंजीनियर करने के लिए आवश्यक है। इस संदर्भ में, पेरोव्स्काइट ऑक्साइड्स अपनी मजबूत क्रिस्टल संरचना के कारण सबसे उपयुक्त मंच प्रदान करते हैं, जिस पर तापमान, यांत्रिक दबाव, रासायनिक दबाव, चुंबकीय क्षेत्र, पतली फिल्मों में उत्पन्न तनाव, आदि जैसे बाह्य पैरामीटरों को नियंत्रण करके संचालित ढंग से काबू पाया जा सकता है। विशेष रूप से, कोबाल्ट पर आधारित पेरोव्स्काइट ऑक्साइड्स रोमांचक भौतिक गुण प्रदर्शित करते हैं क्योंकि कोबाल्ट के विभिन्न ऑक्सीकरण अवस्थाओ (Co^{2+}, Co^{3+}, और Co^{4+}) के बीच ऊर्जा का अंतर बहुत कम होता है। महत्वपूर्ण बात यह है कि पेरोव्स्काइट मैट्रिक्स (अष्टधिक्षीय पर्यावरण) में Co^{3+} विभिन्न स्पिन अवस्थाओ में मौजूद हो सकता है, जो हुंड की विनिमय ऊर्जा और क्रिस्टल क्षेत्र विपाटन की ताकत के अनुपात पर निर्भर करता है, जिसे इच्छित अनुप्रयोगों के लिए व्यवस्थित रूप से समायोजित किया जा सकता है। इस प्रकार, Co पर आधारित पेरोव्स्काइट की संरचनात्मक, इलेक्ट्रॉनिक, ट्रांसपोर्ट, और चुंबकीय गुणों पर विभिन्न वैलेंस और स्पिन स्थिति के परिवर्तनों के प्रभाव की सुसंगत समझ इस समय की आवश्यकता है। इसके अलावा, डबल पेरोव्स्काइट ऑक्साइड्स के मामले में बी-स्थान के परमाणुओं की क्रमबद्धता पहले और दूसरे निकटतम परमाणुओं के साथ अन्योन्य क्रिया बदल सकती हैं और इस प्रकार इन गुणों को समायोजित करने के लिए एक अतिरिक्त स्वतंत्रता प्रदान कर सकती हैं।

इस थीसिस का मुख्य ध्यान $Sr_{2-x}La_xCoNbO_6$ ($x = 0–1$) डबल पेरोव्स्काइट्स में La के स्थानांतरण के कारण संरचनात्मक, चुंबकीय, ट्रांसपोर्ट और इलेक्ट्रॉनिक गुणों के विकास को समझने पर है। Sr^{2+} के स्थान पर गैर-चुंबकीय La^{3+} आयनों का स्थानांतरण Co को 3+ (x =0 में) से 2+ (x =1 में) की स्थिति में परिवर्तित करता है, जो संरचित ढंग से Co और Nb^{5+} आयनों के बीच मौल्य विसंगति में वृद्धि ($\Delta V=2\rightarrow 3$) के कारण कॉर्नर साझी NbO_6 और CoO_6 अष्टधिक्षीयों के आपसी क्रम में सुधार करता है। नियमित विन्यास में अव्यवक्त संरचना के निम्नतर La प्रतिस्थापन वाले नमूनों में Co–O–Nb–O–Co चैनलों के अतिरिक्त Co–O–Co आदान-प्रदान मार्ग प्रदान करती है, और इसलिए परिणामस्वरूप प्रतिस्पर्धी आदान-प्रदान संवेदनाएं $x \leq 0.4$ नमूनों में निम्न तापमान पर क्लस्टर ग्लास व्यवहार को उत्पन्न करती है, जहां स्पिन-स्पिन सहसंबंध, साथ ही इंटरक्लस्टर परस्पर क्रिया की ताकत x के साथ कम होती है। हालांकि, La प्रतिस्थापन के बढ़ते साथ $x \geq 0.6$ नमूनों के लिए तीव्र विलोमचुंबकीय (AFM) परावर्तन तथा नील तापमान में एक योजनात्मक वृद्धि देखी गई है, जो Co^{2+}– O–Nb^{5+}–O–Co^{2+} AFM सुपरएक्सचेंज संवेदनाओं की प्रभुत्वता के कारण होती है। रोचक तथ्य यह हैं कि, चुंबकीय अवेशन मापनों में Co^{2+} के मामले में असंतृप्त आवर्तीय चुंबकीय क्षण दीखता है, जो La-धनी नमूनों में अपचयित आवर्तीय स्थितियों की ओर संकेत करता है। आगे विशेष ऊष्मा मापनों द्वारा $x = 1$ नमूने में स्वतंत्र Co^{2+} जैसी Kramers डबलेट ग्राउंड स्थिति की मौजूदगी का प्रमाण इस बात का समर्थन करता है। इसके अलावा, इन नमूनों की विस्तृत इलेक्ट्रॉनिक और स्थानीय संरचना का अध्ययन x-रे शोध स्त्राव (XAS) और न्यूट्रॉन प्रक्षेपण मापों का उपयोग करके किया गया है। दोनों मापनों में La प्रतिस्थापन के साथ बी-स्थान (Co और Nb) के आसपास स्थानीय विकर्ण में कमी और A-स्थान (La और Sr) के आसपास वृद्धि दिखाई दी है। XANES स्पेक्ट्रा में सफेद रेखा की तीव्रता और अष्टधिक्षीय विकर्ण के बीच एक मजबूत

संबंध स्थापित किया गया है और इसके संभावित कारणों पर चर्चा की गई है। इसके अलावा, इन सभी नमूनों में निम्नतर आवृत्ति और उच्च-तापमान क्षेत्र में विशाल विद्युत धारात्मक का संकेत दिखाई देता है, जो क्रमशः आवरण सीमाओं/अंतरवालीय धारात्मकता के कार्यात्मक विधुत और इलेक्ट्रॉनिक संवहन के प्रारंभ के आधार से किया जाता है। इन नमूनों पर संयुक्त आवेशविद्युत और धारणा मापनों के आधार पर संकेत मिलता है कि इन्हें विभिन्न माइक्रोइलेक्ट्रॉनिक और चार्ज संचयन उपकरणों में उच्च आवेशीय पदार्थ के रूप में संभवतः उपयोग किया जा सकता है।

अप्रत्यास्थ प्रकाश प्रकीर्णन (रमन स्पेक्ट्रोस्कोपी) में, $x = 1$ नमूने के लिए लगभग 60 K के नीचे, रमन मोड के स्व-ऊर्जा पैरामीटर (आवृत्ति और रेखा की चौड़ाई) में असामान्य पुनर्सामान्यीकरण दिखाई दिया, जो स्पिन-फोनॉन कपलिंग के कारण माना जाता है, और यह संकेत करता कि है नमूने में पैरामैग्नेटिक क्षेत्र में भी नजदीकी चुंबकीय संबंध मौजूद हैं। यह स्पिन-फोनॉन कपलिंग $x = 1$ नमूने के लिए 70-100 K के नीचे बॉन्ड दूरियों और डेबाई वौलर फैक्टर में भी महत्वपूर्ण परिवर्तन का कारण होता है। अंत में हम $x = 0$ नमूने की पतली फिल्मों के संरचनात्मक, इलेक्ट्रॉनिक और ट्रांसपोर्ट गुणधर्मों को रिपोर्ट करते हैं, जो कि टेंसाइल से लेकर अलग-अलग मात्रा के कंप्रेसिव तनाव वाले विभिन्न सबस्ट्रेट पर पल्सड लेजर डिपोजिशन का उपयोग करके प्रज्जित किए गए हैं। नमूने के पतले फिल्म में कोवेलेंसी के स्वरूप में परिवर्तन और ऑक्सीजन गैर-यथापूर्वीकरण के कारण, कंप्रेसिव (टेंसाइल) तनाव के साथ विद्युत चालकता में व्यवस्थित वृद्धि (कमी) का पता चला है। इसके अलावा, $SrTiO_3$(100) सबस्ट्रेट पर प्रज्जित $La_{0.67}Sr_{0.33}MnO_3$/ $LaSrCoNbO_6$ और La_2CoMnO_6/ $LaSrCoNbO_6$ हेटेरोस्ट्रक्चर के FM-AFM इंटरफेस पर जटिल एक्सचेंज कपलिंग को संक्षेप में रिपोर्ट किया गया है।

कुल मिलाकर, x-रे, न्यूट्रॉन विकिरण, चुंबकन, विशिष्ट ऊष्मा, x-रे शोधन, विधुतीय और रमन स्पेक्ट्रोस्कोपी मापनों का उपयोग करके $Sr_{2-x}La_xCoNbO_6$ (x = 0-1) डबल पेरोव्स्काइट के संरचनात्मक, चुंबकीय, इलेक्ट्रॉनिक और ट्रांसपोर्ट गुणधर्मों के बीच एक स्या व्यवस्थित संबंध स्थापित किया गया है। कोबाल्ट पेरोव्स्काइट ऑक्साइड की विभिन्न वैलेंस और स्पिन-अवस्थाओं का भौतिक गुणधर्मों के साथ संबंध स्थापित करना Co पर आधारित पेरोव्स्काइट ऑक्साइड की विभिन्न कार्यात्मक गुणों की बेहतर समझ के लिए एक मार्ग प्रदान कर सकता है। Co-O बॉन्ड की प्रकृति का व्यवस्थित अन्वेषण और इन नमूनों में विभिन्न कम ऊर्जा वाली स्थितियों की प्रणालीगत जांच करना ठोस ऑक्साइड ईंधन सेल, मेमोरी उपकरण, माइक्रोइलेक्ट्रॉनिक्स, ऊर्जा भंडारण उपकरण इत्यादि के लिए उपयुक्त उम्मीदवारों को इंजीनियर करने में सहायक हो सकती है।

Contents

Declaration by the Candidate i

Certificate of the Supervisor ii

Acknowledgement iii

Abstract v

List of Figures xi

List of Tables xxviii

1 Introduction 1
- 1.1 Crystal structure 2
  - 1.1.1 Perovskites 2
  - 1.1.2 Double perovskites 4
    - 1.1.2.1 Types of disorders in double perovskites 5
    - 1.1.2.2 Detection of disorders in double perovskites 6
- 1.2 Magnetic exchange interactions 7
  - 1.2.1 Direct exchange mechanism 7
  - 1.2.2 Super exchange mechanism 8
  - 1.2.3 Double exchange mechanism 8
- 1.3 Behavior of cobalt in the octahedral environment 10
  - 1.3.1 Properties of Co^{2+} in the octahedral environment 11
    - 1.3.1.1 Electronic properties 11
    - 1.3.1.2 Octahedral crystal field 11
    - 1.3.1.3 spin-orbit coupling 13
    - 1.3.1.4 For the weak crystal field 14
    - 1.3.1.5 For the strong crystal field 14
    - 1.3.1.6 Magnetic properties 15
    - 1.3.1.7 Zeeman splitting 15
    - 1.3.1.8 Quenching of the orbital magnetic moment 16
    - 1.3.1.9 Exchange integral 17
    - 1.3.1.10 Van Vleck's equation and Curie-Weiss law 18
  - 1.3.2 Properties of Co^{3+} in the octahedral environment 21

1.3.2.1 Electronic properties 21
1.3.2.2 Weak crystal field 22
1.3.2.3 Strong crystal field 24
1.4 Magnetocaloric effect 24
1.5 Growth of epitaxial thin films 25
1.6 Scope of the work 26
1.7 Organization of Thesis Chapters 29

2 Experimental Details 42
2.1 Sample Preparation Techniques 43
2.1.1 Solid state reaction route 43
2.1.1.1 Advantages 44
2.1.1.2 Disadvantages 44
2.1.2 Pulsed laser deposition (PLD) technique 46
2.2 Characterization techniques 48
2.2.1 Diffraction techniques 48
2.2.1.1 X-ray diffraction 48
2.2.1.2 Bragg-Brentano geometry 50
2.2.1.3 Grazing incidence x-ray diffraction (GIXRD) 51
2.2.1.4 Rocking curve 51
2.2.1.5 Phi(ϕ)-scan 51
2.2.1.6 Reciprocal space mapping (RSM) 51
2.2.1.7 X-ray reflectivity (XRR) 52
2.2.1.8 Limitations of the XRD technique 52
2.2.2 Neutron Powder Diffraction 53
2.2.2.1 Limitations of the neutron diffraction technique 55
2.2.2.2 Rietveld Refinement 55
2.2.3 Polarized neutron spectroscopy 58
2.2.4 Raman Spectroscopy 60
2.2.4.1 Vibrations Raman Spectra 61
2.2.4.2 Rotational Raman Spectra 63
2.2.5 Physical property measurement system (PPMS) 64
2.2.5.1 Vibrating sample magnetometer (VSM) 64
2.2.5.2 ac susceptibility measurements 66
2.2.5.3 Resistivity measurements 67
2.2.5.4 Heat capacity measurements 67
2.2.6 Superconducting quantum interference device (SQUID) 69
2.2.7 X-ray absorption spectroscopy (XAS) 70
2.2.7.1 X-ray absorption near edge structure (XANES) 71
2.2.7.2 Extended x-ray absorption fine structure (EXAFS) . . . 72
2.2.8 X-ray photoelectron spectroscopy (XPS) 77
2.2.9 Ultra violet-visible-near infrared absorption spectroscopy 79
2.2.10 ac impedance spectroscopy 81
2.2.10.1 Dielectric measurement 81
2.2.10.2 Electric Modulus 83
2.2.10.3 P-E loop measurements 84
2.2.11 Atomic force microscopy (AFM) 85

3 Structural, magnetic, and transport properties of $Sr_{2-x}La_xCoNbO_6$ 93
3.1 Introduction . . . 94
3.2 Experimental Details . . . 96
3.3 Results and Discussion . . . 97
  3.3.1 X-ray diffraction . . . 97
  3.3.2 Raman spectroscopy . . . 98
  3.3.3 Magnetic measurements . . . 99
  3.3.4 Magnetocaloric effect (MCE) . . . 106
  3.3.5 Temperature dependent resistivity . . . 111
3.4 Conclusion . . . 114

4 Study of the low lying energy states and cluster-glass behavior in $Sr_{2-x}La_xCoNbO_6$ 123
4.1 Introduction . . . 124
4.2 Experimental Details . . . 126
4.3 Results and Discussion . . . 126
  4.3.1 Temperature and field dependent specific heat [$C_P(H,T)$] . . . 126
  4.3.2 dc magnetic susceptibility . . . 141
  4.3.3 Thermo-remanent magnetization . . . 142
  4.3.4 Aging effect . . . 146
  4.3.5 ac magnetic susceptibility . . . 148
  4.3.6 Exchange bias effect . . . 153
  4.3.7 Phase evolution in $Sr_{2-x}La_xCoNbO_6$ . . . 157
4.4 Conclusion . . . 158

5 Electronic and crystal structural investigation of $Sr_{2-x}La_xCoNbO_6$ using the x-ray absorption and neutron powder diffraction 167
5.1 Introduction . . . 168
5.2 Experimental Details . . . 170
5.3 Results and Discussion . . . 171
  5.3.1 X-ray absorption near edge structure: . . . 171
  5.3.2 Extended x-ray absorption fine structures: . . . 182
  5.3.3 Soft x-ray absorption spectroscopy . . . 193
  5.3.4 Neutron powder diffraction . . . 195
5.4 Conclusion . . . 206

6 Dielectric and ac impedance spectroscopy of $Sr_{2-x}La_xCoNbO_6$ 228
6.1 Introduction . . . 229
6.2 Experimental Details . . . 231
6.3 Results and Discussion . . . 232
6.4 Conclusion . . . 249

7 Temperature dependent Raman spectroscopy of $SrLaCoNbO_6$ 270
7.1 Introduction . . . 271
7.2 Experimental . . . 273
7.3 Results and discussion . . . 274
  7.3.1 Temperature dependent Raman spectroscopy . . . 274
  7.3.2 Temperature dependent x-ray absorption spectroscopy . . . 286

7.3.3 X-ray photoemission spectroscopy . . . 289
7.4 Conclusion . . . 291

8 Growth and physical properties of Sr_2CoNbO_6 thin films and La_2CoMnO_6/ $LaSrCoNbO_6$/ $SrTiO_3$(100) heterostructures 299
8.1 Introduction . . . 300
8.2 Experimental Details . . . 304
8.3 Results and Discussion . . . 306
8.3.1 XRD of Sr_2CoNbO_6 films . . . 306
8.3.2 AFM of Sr_2CoNbO_6 films . . . 308
8.3.3 Resistivity measurement on Sr_2CoNbO_6 films . . . 309
8.3.4 UV-Vis-NIR spectroscopy on Sr_2CoNbO_6 films . . . 311
8.3.5 XPS of Sr_2CoNbO_6 films . . . 312
8.3.6 Raman spectroscopy on Sr_2CoNbO_6 films . . . 316
8.3.7 XRD, XRR, and AFM measurements on LSMO/STO film and LSMO/ LSCNO/ STO heterostructure . . . 318
8.3.8 Magnetic measurements on LSMO/STO film and LSMO/ LSCNO/ STO heterostructure . . . 321
8.3.9 XRD, XRR, and resistivity measurements on LCMO/ LSCNO/ STO heterostructure . . . 323
8.3.10 Magnetic measurements on LCMO/ LSCNO/ STO heterostructure 325
8.4 Conclusion . . . 328

9 Conclusions and Future Scope of the Work 338

Publications 344

Conferences and Presentations 345

Biodata 347

List of Figures

1.1 Ideal cubic perovskite structure ABO_3. 2
1.2 (a) Schematic illustration of an ordered double perovskite $A_2BB'O_6$ structure. Arrows represent the swapping between the two *B*-site cations, resulting in the antisite disorders. (b) Mapping of the several double perovskite oxides in the ordered (solid downward triangles) and disordered (empty upward triangles) as a function of ionic and valence mismatch between the *B*-site cations, taken from Ref. [25]. 6
1.3 Schematic representation of direct exchange(DE) mechanism, where upper and lower panels show the allowed and forbidden DE interactions with the neighboring atoms, respectively. The d_{z^2} orbitals are used just for the representation. 8
1.4 Schematic representation of a typical 180^0 B-O-B′ antiferromagnetic superexchange (SE) path, where upper and lower panels show the electronic distribution in the CF splitted energy states and the different orbitals having the directional character. The d_{z^2} and p_z orbitals are used just for the representation. 9
1.5 Example of the ferromagnetic double exchange mechanism through Mn^{3+}-O^{2-}-Mn^{4+} path. 10
1.6 Energy level splitting scheme of Co^{2+} ion having $3d^7$ configuration with ^4F ground term in the presence of weak octahedral crystal field, spin-orbit coupling, and the Zeeman's splitting, sequentially. Numbers in the parenthesis represent the degeneracy of the corresponding energy levels, see text for more details. 13
1.7 (a) Transformation of $d_{x^2-y^2}$ orbital into the d_{xy} by a 45^0 rotation about the z-axis, (b) transformation of d_{xz} orbital into d_{yz} by a 90^0 rotation about the z-axis. (c) The inability d_{z^2} orbital to transform into any other *d* orbitals, resulting in the zero orbital angular momentum. The image of the *d* orbitals is taken from Ref. [65]. 16
1.8 Energy level splitting scheme of Co^{3+} ion having $3d^6$ configuration with ^5D ground term in the presence of weak distorted octahedral crystal field and spin-orbit coupling. Numbers in the parenthesis represent the degeneracy of the corresponding energy levels. The relative energy separation between different levels has been taken arbitrarily, which can vary with the surrounding environment. Refer to the discussion and Ref. [70] for more details. 22
1.9 The possible electronic distribution within the strong crystal field splitted t_{2g} and e_g states of Co^{3+} ($3d^6$). The low spin (LS) state (t_{2g}^6 e_g^0), intermediate spin (IS) state (t_{2g}^5 e_g^1) and high spin (HS) states (t_{2g}^4 e_g^2) are presented with their respective total unpaired spins (S). 23

1.10 (a) The effect of compressive strain on BO_6 octahedra on (001) and (b) (111) substrate. Green and red lines indicate the reduction and elongation in the B–O bond length. The compressive strain on (001) and (d) (111) substrate by taking the octahedral tilting into account, taken from Ref. [82]. 27

2.1 Typical steps used to synthesize $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) samples using solid state route. 45

2.2 (a) Schematic of PLD set-up taken from Ref. [8], (b) real image of UHV compatible PLD set-up with load lock chamber in our lab at IIT Delhi. (c) Plume formed during the thin film growth, (d) deposited film on Si(100) substrate placed on the substrate holder along with another Si substrate to partially shadow the lower substrate, (e) deposited film with a sharp step used to estimate its thickness using stylus profiler. 47

2.3 (a) Schematics of the diffraction of the x-rays from the crystal planes, (b) real image of the x-ray diffractometer at the physics department of IIT Delhi, (c) inside view of the XRD set-up, where the regions I, II, and III represent the x-ray tube, sample stage, and x-ray detectors, respectively. . 49

2.4 (a) Schematic diagram of the operational principle of neutron powder diffractometer PD-I and (b) PD-II at the Dhruva reactor, Trombay, Mumbai in India, taken from Ref. [20]. 53

2.5 Schematic diagram of the neutron depolarization measurement set-up at Dhruva reactor in Mumbai, India, taken from Ref. [20]. 59

2.6 (a) Energy level diagram representing the mechanism of Raman scattering. (b) Real image of set-up for the Raman spectroscopy at IIT Delhi. . 62

2.7 (a) The Ever Cool- II PPMS set-up from Quantum Design, USA. (b) The different sample holders used for the magnetization measurements. (c) Schematic diagram of the VSM assembly and (d) ac susceptibility measurement coil. (e) Puck for the dc resistivity measurement, (f) test station to check the connections for the transport measurements. The image in (c) is taken from Ref. [36] and all the other images are taken from Ref. [35]. 66

2.8 (a) The schematic representation of the working principle of superconducting quantum interference device (SQUID). (b) Real image of the SQUID set-up at IIT Delhi, India. 69

2.9 (a) The absorption coefficient at Nb K-edge for Sr_2CoNbO_6 sample, representing the XANES and EXAFS region of the spectra. The letters A, B, and C represent the pre-edge, main-edge, and post-edge regions of the XANES spectra. (b) Normalized XAS spectra, (c) $\chi(k)$ spectra, (d) k^3 weighted $\chi(k)$ spectra, (e) magnitude of the Fourier-transformed $k^3\chi(k)$ spectra, and (f) Fitting of the spectra presented in (e) using the combination of different scattering paths. The dashed green line in panel (f) highlights the fitting window from 1.1 to 4 Å. 73

2.10 (a) The schematic representation and (b) real image of the EXAFS beamline, BL-09 at Indus-2 synchrotron source at RRCAT, Indore in India. (c) Three ionization chambers used to detect the flux of incident x-ray, after transmission from the sample and that from the reference metal foil. The sample placed after the first ionization chamber is shown in the inset. The images are taken from Refs. [42] and [43]. 74

2.11 The schematic representation of the various components of x-ray photoelectron spectroscopy set-up, taken from the Ref. [51]. 77

2.12 (a) The schematic diagram of the working principle of the UV-Vis-NIR spectroscopy. (b) Real image of UV-Vis-NIR absorption spectroscopy set-up at IIT Delhi, India. 80

2.13 (a) The schematic diagram for the ac impedance measurements on a pellet sample using a LCR meter. (b) Spring loaded sample holder, (c) low-temperature sample assembly, (d) low-temperature ac impedance and P-E loop measurement set-up, (e) temperature controller, (f) impedance analyzer, and (g) work station for P-E loop measurements at UGC-DAE, Indore in India. 82

2.14 (a) Block diagram of the working principle of atomic force microscopy. Inset shows the real image of the AFM set-up at IIT Delhi, India. 85

3.1 (a–f) The Rietveld refinement of XRD data of $Sr_{2-x}La_xCoNbO_6$ (x = 0–1), where the observed data points, simulated curve, Bragg positions and difference in observed and simulated data are shown by open red circles, continuous black line, vertical green bars and continuous blue line, respectively. Insets of panel (f) show the evolution of the superlattice reflections (101) and (103) with La concentration. 98

3.2 Raman spectra of $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) measured at room temperature using 532 nm excitation wavelength. Red solid line in case of $x = 1$ sample represents the Lorentzian fitting of the data points. The curves have been vertically shifted for the clear presentation. 100

3.3 (a–f) The magnetic susceptibility of x = 0–1 samples measured in both zero field cooled (ZFC) and field cooled (FC) modes from 2 K to 320 K at 500 Oe, inset in each panel shows the magnification of the low temperature region for the clarity of the presentation. 101

3.4 Temperature dependent inverse susceptibility (a) and temperature weighted susceptibility (χT) (b) of $Sr_{2-x}La_xCoNbO_6$ for x = 0–1 respectively in ZFC mode from 2 K to 320 K in the presence of 500 Oe magnetic field. Inset in (b) show the magnification of the lower temperature regime for the clarity. (c) Comparison of the experimentally calculated effective magnetic moment $\mu_{\rm eff}$ (solid black circles) with that reported in the literature, and expected magnetic moment for the various spin-states of Co^{3+} with increase in La content (x), where Co^{2+} is expected and considered to be always in HS state with composition weighted 5.62(1) μ_B contribution in the magnetic moment. The error in the $\mu_{\rm eff}$ values of the present study is less than the size of the symbols. 102

3.5 Field dependent isothermal magnetization curves of $Sr_{2-x}La_xCoNbO_6$ for x = 0–0.4 (a) and 0.6–1 measured at 5 K (b) and 0–1 at 30 K (c). Upper and lower insets in (c) show the coercivity and magnetization at 70 kOe, respectively, at 5 K (red solid circles) and 30 K (blue solid squares). 105

3.6 Virgin magnetization isotherms for the x = 0 (a), 0.2 (b), 0.6 (c and d) and 1 (e and f) samples from 0 to 70 kOe. Insets in (c) and (e) show susceptibility at different applied magnetic fields extracted from the virgin magnetization isotherms for the x = 0.6 and 1 samples, respectively . . . 106

3.7 Arott plots (M^2 versus H/M) for the x = 0 (a), 0.2 (b), 0.6 (c and d) and 1 (e and f) samples. 107

3.8 Temperature dependent magnetic entropy change at different $\mu_0\Delta$H values for $x = 0$ (a), 0.2 (b), 0.6 (c) and 1 (d) samples. Upper and lower insets in (a) and (b) show the low temperature region of the normalized ΔS with respect to ΔS value at 55K at various $\mu_0\Delta$H values for the clear presentation. Insets in (c) and (d) represent the magnetic field evolution of the crossover temperature of ΔS curves for the $x = 0.6$ and 1 samples, respectively. Red solid line indicate the fit to the data points (see the text) and black dotted line represents the extrapolation of the fit. 108

3.9 Temperature and magnetic field dependence of exponent n for the $x = 0$, 0.2, 0.6 and 1 samples. 111

3.10 (a) Temperature dependent electrical resistivity of $Sr_{2-x}La_xCoNbO_6$ for $x = 0$–0.8. (b) Arrhenius plot of ln(ρ) versus 1000/T and (c) VRH plot of ln(ρ) versus $T^{-1/4}$. Continuous black lines show the linear fitting of high (low) temperature data and dashed red line show the extrapolation of the linear fitting in the lower (higher) temperature regime. Inset of (b) and (c) represent the variation in the activation energy and DOS respectively, with La concentration. 112

4.1 (a) The temperature dependent specific heat curves of $Sr_{2-x}La_xCoNbO_6$ ($x = 0$–1) samples measured from 1.8 K to 300 K at zero magnetic field. Insets (a1) and (a2) show the enlarged view of the low temperature region up to 23 K and 7 K, respectively, (a3) shows the C_P/T vs T plot of low temperature specific heat for the $x = 0$–0.4 samples. (b) The best fit of the specific heat data from 30– 300 K using the combination of Einstein and Debye models (black solid lines). The dashed lines in the low temperature region are the extrapolation of high temperature fit. Each curve is vertically shifted cumulatively by 50 J/mole–K for the clear presentaion. 127

4.2 (a) The low temperature specific heat data of the $x = 0$–0.4 samples from 1.8–20 K on the semi-log scale as C_P/T vs T plot. The solid black lines represent the best fit of the data using the lattice, Schottky, and approximated hyperfine contributions. The dashed lines show the individual contributions in the $C_P(T)$ for the $x = 0$ sample. (b) The proposed energy level scheme as a function of x. 131

4.3 (a–c) The temperature dependent specific heat data presented as C_P/T vs T plot measured at different magnetic fields for the $x = 0$–0.4 samples, respectively. The solid black lines represent the best fit with the lattice, Schottky, and hyperfine contributions. Inset in each panel shows the field dependent Zeeman splitting of the zero field excited doublet. 132

4.4 (a–c) The low temperature specific heat data along with the lattice contribution (solid line) from the harmonic lattice model fitted between 20–30 K (marked by vertical green arrows). (d–f) The magnetic specific heat plotted as C_{mag}/T vs T and magnetic entropy (S_{mag}) on left and right scales, respectively, for the $x = 0$–0.4 samples. 134

4.5 (a–c) The temperature dependent specific heat in the low temperature region measured at different magnetic fields for the $x = 0.6$–1 samples. Inset of (a) shows the enlarged view across the magnetic phase transition. Insets of (b) and (c) show the H–T phase diagram extracted from the C_P(H, T) data for the $x = 0.8$ and 1 samples, respectively. The solid red lines represent the best fit using the AFM decay model and dashed black lines are the extrapolation of the fitted curves. 135

4.6 (a–c) The zero-field specific heat data measured in heating and cooling modes across the transition. (d–f) The specific heat data measured with smaller step size and fitted (solid red lines) using the harmonic lattice model in the region indicate by vertical green arrows and its extrapolation down to 1.8 K. (g–i) The magnetic specific heat and magnetic entropy on the left and right scales, respectively for the $x = 0.6$–1 samples. Dashed line in (i) represents the theoretical magnetic entropy expected for the ground state Kramers doublet of Co^{2+} ions in the $x = 1$ sample. 137

4.7 (a–c) The magnetic specific heat data of the $x = 0.6$–1 samples along with the temperature dependence of the spin wave ordering (solid red lines) in the AFM region. (d–f) The zero field specific heat data of the $x = 0.6$–1 samples in the vicinity of the transition temperature along with the best fit (solid red lines) in both AFM and PM regions using the equation 4.5. . 138

4.8 (a–c) The change in the magnetic entropy (ΔS) and (d–f) adiabatic temperature (ΔT_{ad}) extracted from C_P(H, T) data for the $x = 0.6$–1 samples, respectively. The dashed curve in panel (c) represents the ΔS for $\Delta\mu_0$H = 7 T extracted from the magnetization data [M(H, T)] for the comparison.140

4.9 The temperature dependent dc susceptibility in ZFC and FC modes measured at different applied magnetic fields for the $x = 0.4$ sample. The curves recorded at 10^2 and 10^3 Oe are vertically shifted by 17×10^{-3} and 5×10^{-3} emu/mole–Oe, respectively, for clarity in the presentation. 141

4.10 The field cooled thermo-remanent magnetization (TRM) of the $x = 0.4$ sample measured at 2 K for different waiting times ($t_w = 10^2$, 10^3, and 10^4 sec) with the applied magnetic fields of 10^2 Oe (a), 10^3 Oe (b), and 10^4 Oe (c). The solid lines represent the best fit of the data using the stretched exponential behavior. The inset in each panel shows the semilogarithmic plots of the data for $t_w = 10^3$ sec and the solid red line represent the fit using the logarithmic relaxation model. 142

4.11 (a, b) The field cooled thermo-remanent magnetization (TRM) data at 2 K for different waiting times ($t_w = 10^2$ sec, 10^3 sec, and 10^4 sec) with the applied magnetic field of 10^3 Oe for the x =0 and 0.2 samples, respectively. The solid lines indicate the best fit of the data using the stretched exponential behavior. Insets in each panel show the semilogarithmic plots of the data for t_w=10^3 sec and solid red lines are the fit using the logarithmic relaxation model. 144

4.12 The field cooled thermo-remanent magnetization (TRM) for the $x = 1$ sample measured at 2 K for $t_w = 100$ sec with the applied magnetic field of 1000 Oe. 145

4.13 The zero field cooled time dependent isothermal magnetization for the $x = 0.4$ sample measured at 2 K (a) and 8 K (b) for different waiting times (t_w = 100, 1000, and 5000 secs) with 50 Oe magnetic field. 145

4.14 The zero field cooled time dependent isothermal magnetization for the $x = 0$ (a) and 0.2 (b) samples measured at 2 K for different waiting times. The insets show the logarithmic time dependence of the magnetization for $t_w = 5000$ sec. 147

4.15 The temperature dependent real and imaginary part of ac susceptibility measured at different frequencies with 5 Oe magnetic field for the $x = 0$ (a, b), 0.2 (c, d), and 0.4 (e, f) samples. The real part of ac susceptibility for the $x = 0.6$ and 1 samples are shown in (g, h). The insets in (a, c, e) show zoomed view across the transition along with the dashed reference line subtracted for further analysis to be shown in Figs. 11(a–c) for the $x =$ 0–0.4 samples, respectively. 148

4.16 (a–c) The temperature dependent ac susceptibility curves for the $x =$ 0–0.4 samples [see the insets of Figs. 4.15(a, c, e), respectively] presented after linear reference line subtraction. The black dotted lines represent the Gaussian fitting of the data points in the vicinity of the freezing temperature (T_f) to estimate the exact value of T_f. The arrows indicate the shift in T_f to the higher temperature with increase in the excitation frequency. (d–f) The dependence of spin relaxation time, τ on the freezing temperature (T_f) along with the best fit (solid black lines) using the critical slowing down model. (g–i) The dependence of the freezing temperature on the excitation frequency plotted as T_f vs $100/\ln(\omega_0/\omega)$ along with the best fit (solid black lines) using the Vogel-Fulcher law. 150

4.17 Field dependent magnetization curves recorded at 5 K in zero field cooled and field cooled modes for (a) $x = 0$ and (b) 0.2 sample. Insets show the enlarged view of the low field region for the zero field and 20 kOe field cooled modes to clearly demonstrate the field-dependent shift in the MH loops. (c) Cooling field dependent exchange bias field (H_{EB}), (d) coercive field (H_C), (e) exchange bias magnetization (M_{EB}), and magnetic coercivity (M_C) at 5 K for $x =$0 and 0.2 samples. 153

4.18 (a) Virgin magnetization isotherms at 5 K in zero magnetic field cooled and different field cooled states for the (a) $x =$0 and (b) 0.2 sample. (c) Remanent magnetization value for the different field cooled modes, as a function of the cooling field. 155

4.19 The right half of the M-H curves around zero magnetization for the (a) $x =$0 and (b) 0.2 sample, consecutively recorded after cooling the sample in 50 kOe magnetic field. The red circles represent the positive coercivity as a function of number of recorded M-H curves for the (c, d) $x =$0 and (e, f) $x =$0.2 samples, where the solid black lines are the best fit using (c, e) equation 8.4 for $n \geqslant 2$ and (d, f) equation 4.12 for $n =$1-12 (see text for more details). 155

4.20 The phase diagram of $Sr_{2-x}La_xCoNbO_6$ ($x =$ 0–1), where different colors represent the evolution of various magnetic interactions with temperature, magnetic field, and La concentration (x). The ΔS_{max}(J/kg–K) values in the vicinity of T_N are shown in parentheses at $\Delta\mu_0 H$=5 and 9 T fields for the $x \geqslant 0.6$ samples. 157

5.1 (a) The normalized Nb K-edge XANES spectra of $\mathrm{Sr}_{2-x}\mathrm{La}_x\mathrm{CoNbO}_6$ ($x =$ 0–1) samples where 1, 2, 3 represent the main absorption features, and enlarged view of features 2 and 3 are shown in the insets. (b) The first derivative of the experimental absorption spectra of the Nb K-edge along the simulated spectrum for the $x = 0$ and 1 samples and their corresponding $\mathrm{Nb_{abs}}$ d-LDOS in the XANES region. The red dashed ellipse highlight the presence of pre-edge feature in both experimental and simulated spectra, and sharp $\mathrm{Nb_{abs}}$ d-LDOS at this energy. All the experimental spectra have been vertically shifted by fix 0.025 units for the clarity. (c) The comparison of first order derivative of the simulated absorption coefficient of Nb K-edge for dipole, and dipole plus quadrupole transitions for the $x =$ 0 sample. (d, e) The experimental and simulated Nb K-edge absorption spectra along the calculated p-LDOS of absorbing Nb atoms for $x = 0$ and 1 samples. The experimental spectra have been vertically shifted by 0.3 units for the clarity. The black dashed line represent the Fermi level and red dashed lines indicate the shift in the $\mathrm{Nb_{abs}}$ p-LDOS peak corresponding to the feature 3 (shaded region). 171

5.2 (a) The simulated Nb K-edge XANES spectra for the $x = 0$ sample by varying the number of first nearest Sr atoms. Insets (a1) and (a2) represent the enlarged view of the spectra in different energy regimes. (b) The $\mathrm{Nb_{abs}}$ p-LDOS corresponding to the XANES spectra presented in (a), and the inset shows the enlarged view of the highlighted region. (c) The comparison of simulated Nb K-edge spectra of the $x = 0$ sample for all first neighbor A-site atoms as Sr and La (on the left axis) and corresponding $\mathrm{Nb_{abs}}$ p-LDOS (on the right axis), and the inset shows the enlarged view of the highlighted region. (d) The Nb K-edge spectra for the x =1 sample with all eight first neighbor A-site atoms as eight Sr, four each of La and Sr as well as eight La. The insets (d1) and (d2) represent the enlarged view of the highlighted region and the corresponding $\mathrm{Nb_{abs}}$ p-LDOS, respectively. 174

5.3 (a) The normalized Co K-edge XANES spectra of $\mathrm{Sr}_{2-x}\mathrm{La}_x\mathrm{CoNbO}_6$ ($x =$ 0–1) samples. The alphabets A–G represent the absorption features resulting from various electronic transitions (see text for the detail). The red arrow indicate the shift in the rising edge towards the lower energy with the La substitution. The solid black arrow and dashed red line represent the shift and invariance in the white line for x$\leqslant$0.4 and $x \geqslant$0.6 samples, respectively. Inset shows the enlarged view of the A and B (arrow) pre-edge features for the clarity. (b) The average oxidation state of Co (open circles) on left axis and oxygen concentration (open triangles) on the right axis, as a function of x. Dashed red and blue lines represent the ideal behavior for the full transformation of Co from 3+ to 2+ valence state (considering the linear relationship between shift in edge position and oxidation state) and six oxygen atoms per formula unit, respectively. (c) The Co K-edge XANES spectra for the intermediate compositions, i.e., x = 0.2–0.8 samples, where the solid black lines represent the Co valence state weighted linear combination of the $x = 0$ ($\mathrm{Co}^{3.0+}$) and $x =$ 1 ($\mathrm{Co}^{2.25+}$) spectra. Each spectrum is vertically shifted cumulatively by 0.5 units for the clarity. 177

5.4 (a) The normalized Sr K-edge XANES spectra of $\mathrm{Sr_{2-x}La_xCoNbO_6}$ ($x =$ 0–1) samples. The inset (a1) shows the first derivative of the absorption coefficient, where the vertical dashed line represents the invariance in the rising edge position. These curves are vertically shifted for better presentation. The inset (a2) presents the enlarged view of feature II, where arrow shows the shift in the peak position with x. (b) The normalized Sr K- (on top and right axis) and La L_3-edge (on bottom and left axis) spectra for the $x = 1$ sample in 150 eV range in the vicinity of the white line. The dashed line represents the presence of the absorption feature II at the same position with respect to the white line in both the spectra. . . 181

5.5 (a) The magnitude of the Fourier transformed $k^3\chi(k)$ spectra for $\mathrm{Sr_{2-x}La_xCoNbO_6}$ ($x =$ 0–1) in 0–6 Å spectral range, derived from the EXAFS region of the Nb K-edge. The inset shows the comparison of simulated spectra of the $x = 0$ sample for two different Nb–O_e–Co/Nb angles (Nb–O_a–Co/Nb=180^0). (b)–(g) The enlarged view of (a) between 3.75 to 5.75 Å with cumulative increment in x to clearly show the evolution of the new scattering path resulting from the Co/Nb atoms, located diagonally to the absorber, as indicated by the arrows (refer text for more details). (h–m) The fitting of the $|\chi(R)|$ and corresponding $\mathrm{Im}[\chi(R)]$ spectra in the window shown by the dotted green line, each $\mathrm{Im}[\chi(R)]$ spectrum is shifted downward for clarity in presentation. 183

5.6 (a) The magnitude of the Fourier transformed $k^3\chi(k)$ spectra for $\mathrm{Sr_{2-x}La_xCoNbO_6}$ ($x =$ 0–1) in 0–6 Å spectral range, derived from the EXAFS spectra of Co K-edge. (b) The evolution of the intensity of the white line (left axis) and amplitude of the first coordination shell (right axis) with the La substitution for the Co K-edge and (c) Nb K-edge EXAFS spectra. (d–i) The fitting of the $|\chi(R)|$ and corresponding $\mathrm{Im}[\chi(R)]$ spectra in the window shown by the dotted green line, where the $\mathrm{Im}[\chi(R)]$ spectrum in each panel is shifted downward for the clarity in the presentation. 187

5.7 (a) The Nb K-edge XANES spectra simulated for the $x = 0$ sample by varying the degree of distortion in $\mathrm{NbO_6}$ octahedra. The insets (a1) and (a2) represent the enlarged view of the white line and variation of the white line intensity with the distortion parameter, Δ_{Nb}, defined in equation 5.1, respectively. The error bars in the white line intensity in inset (a2) are accounting for the finite step size of the simulated spectra. (b) The corresponding $\mathrm{Nb_{abs}}$ p-LDOS simulated at different values of Δ_{Nb} for the $x = 0$ sample. 189

5.8 (a) The magnitude of the Fourier transformed $k^3\chi(k)$ spectra of Sr K-edge for $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) samples. (b) The enlarged view of the normalized Sr K-edge EXAFS spectra for the $x = 0$ sample, which shows the KN_1 double-electron excitation feature and the resulting spectra after the manual removal of this feature. (c) The k^3 weighted $\chi(k)$ spectra and (d) its Fourier transformation for the $x = 0$ sample before and after the subtraction of the KN_1 excitation feature, where arrows highlight the change in the corresponding features. (e) The ratio of the magnitude of the Sr–Sr/La and Sr–Co/Nb scattering paths as a function of x. (f–k) The fitting of the $|\chi(R)|$ and corresponding Im$[\chi(R)]$ spectra in the window shown by the dotted green line, where the Im$[\chi(R)]$ spectra in each panel are shifted downward for the clarity in the presentation. The asterisk symbol in (f) represent the peak arising from the KN_1 intra-atomic transition. 192

5.9 The Co $L_{2,3}$-edge spectra (vertically offset for clarity) for $Sr_{2-x}La_xCoNbO_6$ samples. The atomic multiplet based simulated spectra for HS Co^{2+} and HS Co^{3+} are compared. 194

5.10 (a–g) The Rietveld refinement of NPD patterns of the $Sr_{2-x}La_xCoNbO_6$ ($x = 0.4$) sample recorded with $\lambda = 1.094$ Å from 6 K to 300 K, shown on the semilogarithmic scale, where the observed data points, simulated curve, and Bragg peak positions ($I4/m$) are shown by open red circles, a continuous black line, and vertical green bars, respectively. 196

5.11 (a) The tetragonal crystal structure of the $x = 0.4$ sample at 300 K as viewed from the a-axis. (b) Two representative octahedra to show the octahedral distortion parameters, Θ and Ω. (c) The temperature evolution of the pseudocubic lattice parameters ($a_{pc}=a/\sqrt{2}=b_{pc}=b/\sqrt{2}$, $c_{pc}=c/2$), and (d) the unit cell volume, extracted from the Rietveld refinement of the NPD patterns of the $x = 0.4$ sample from 6–300 K. The solid black lines show the best fit using the Grüneisen approximation considering the Debye-Einstein model. 198

5.12 (a–f) The Rietveld refinement of NPD patterns of the $Sr_{2-x}La_xCoNbO_6$ ($x = 0.6$) sample measured at λ =1.094 Å from 6 to 300 K. A solid black arrow in panel (f) represent the presence of (101) superlattice reflection, whereas the dashed green arrows indicate the evolution of additional Bragg reflections due to the monoclinic ($P2_1/n$) distortion. The Bragg peak positions for the tetragonal ($I4/m$) symmetry are also presented in panel (f) for the comparison. 200

5.13 The monoclinic crystal structure of $Sr_{2-x}La_xCoNbO_6$ ($x = 0.6$) sample at 300 K as viewed from (a) a-axis and (b) c-axis. (c) The temperature evolution of the pseudocubic lattice parameters [$a_{pc}=a/\sqrt{2}$, $b_{pc}=b/\sqrt{2}$ (on left axis) and $c_{pc}=c/2$ (on right axis)], and (d) the unit cell volume, extracted from the Rietveld refinement of the NPD patterns of the x = 0.6 sample from 6–300 K. The solid black lines represent the best fit using the Grüneisen approximation considering the Debye-Einstein model. . . . 202

5.14 The local distortion parameter (Δ), defined by equation 5.1 around (a) A-site (La/Sr), (b) B-site (Co/Nb), and (c) oxygen atoms for the $Sr_{2-x}La_xCoNbO_6$ (x = 0.4 and 0.6) samples, as a function of temperature.204

5.15 The Rietveld refinement of NPD patterns of $Sr_{2-x}La_xCoNbO_6$ samples (recorded at temperature $\leq$ 2 K with λ = 1.2443 Å) using the (a) tetragonal ($I4/m$) for x = 0.4 and (b) monoclinic ($P2_1/n$) phase for x = 0.6. (c) The temperature dependence of the flipping ratio (R) of the polarized neutron beam for the x = 0.4 sample, measured in the FCW mode at 50 Oe applied magnetic field with λ= 1.205 Å. 205

5.16 (a) The normalized Nb K-edge XANES spectra of $Sr_{2-x}La_xCoNbO_6$ (x = 0-1) samples along the reference Nb_2O_5 sample. (b) First derivative of the absorption coefficient is plotted for all the samples where the vertical solid line represents the invariance in the peak position with the La substitution as compared to the Nb_2O_5. 208

5.17 The normalized (a) Nb, (b) Co, and (c) Sr K-edge EXAFS spectra of $Sr_{2-x}La_xCoNbO_6$ (x = 0-1) samples. The spectra in (a–c) are vertically offset by 0.04 units for the clarity. Insets in (a) and (c) show the enlarged view of the low energy region of Nb and Sr K-edge EXAFS spectra, respectively. 209

5.18 (a) The best fit of (a) Nb, (b) Co, (c) Sr K-edge XANES spectra of $Sr_{2-x}La_xCoNbO_6$ samples using the Gaussian peak shape and an error function accounting for the different absorption features and the edge jump, respectively, shown for the x = 0 sample. Here, spectra in each panel are vertically shifted cumulatively by 0.2 units for the clear presentation. 210

5.19 Simulated Nb K-edge XANES spectra for x =0 sample for different number of first nearest Sr atoms on left axis and Sr p-LDOS on right axis. Inset show the enlarged view of the highlighted region. 210

5.20 The normalized XANES spectrum of Co K-edge for x =1 sample in the pre-edge region along the step function. 211

5.21 (a) The normalized Co K-edge XANES spectra of $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) samples with the $LaCoO_3$ spectrum taken from [40]. (b) The first derivative of the absorption coefficient in the rising edge region for all the samples and reference $LaCoO_3$ sample where the curves are vertically shifted for the clarity. 211

5.22 The normalized Co K-edge absorption spectra of $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) samples where the shaded part above μ =1 illustrate the change in the peak height and broadening with x. 212

5.23 (a, b) The experimental and simulated Co K-edge absorption spectra for the x = 0 and 1 samples. Experimental spectra for both the samples are shifted vertically upward by 0.6 units for the clarity. The p-LDOS are compared for (c) absorbing Co, (d) O, (e) scattering Co, (f) Sr, and (g) Nb for the x = 0 and 1 samples. (h) The La p-LDOS for the x = 1 sample. The vertical dashed lines represent the Fermi level in these panels. 214

5.24 The experimental and simulated Sr K-edge absorption spectra for the (a) x = 0 and (b) x = 1 samples along the calculated Sr and O p-LDOS. A simulated Sr K-edge spectrum of the x = 0 sample with the structural parameters of the x = 1 is compared in (b). The experimental spectra of both the samples are vertically shifted by 0.5 units for clarity. The shaded regions represent the unoccupied Sr p-LDOS corresponding to the feature II. 215

5.25 Comparison of the La L_3-edges spectra of the x =1 sample with the reference La_2O_3 sample. Inset shows the first derivative of both spectra in the rising edge region. 216

5.26 The k^3 weighted Nb K-edge EXAFS spectra for x =0 sample from 0–14 Å^{-1}. 216

5.27 Schematic representation of (a) Nb–O.2 and (b) Nb–O.3 single scattering paths for the Nb K-edge EXAFS spectra of the $x = 0$ sample. The Nb–Nb.2/Co.2 scattering paths in (c) pseudocubic and (d) tetaagonal ($I4/m$) representation. 217

5.28 (a) The O K-edge XAS spectra of $Sr_{2-x}La_xCoNbO_6$ samples where each spectrum is vertically shifted for the clarity. The dotted curve represent the absorption spectrum from the copper sample holder. (b) The simulate spectra for the $x = 0$ and 1 samples using the crystal structure (of $x =$ 1 sample from NPD data in [53]). (c–e) The corresponding s-, p-, and d-LDOS for the selected elements. There is no significant change in the LDOS by La substitution, apart from the evolution of new La states and hence LDOS for the $x = 0$ sample are presented in (c) and (d) for the clarity. 218

6.1 (a–f) Temperature dependent real part of impedance (Z′) for $Sr_{2-x}La_xCoNbO_6$ samples at different frequencies. Arrow in (a) indicate the shift in the peak to the higher temperature with increase in the excitation frequency. (g) Variation in the peak position (T_m) as a function of the excitation frequency estimated from the lorentzian fit of the Z′(T, f) data, plotted as ln f versus 1000/T_m. Dashed lines represent the linear fit to show the deviation from the Arrhenius model. (h) ln f versus $T_m^{-1/4}$ plot, where solid lines represent the best fit using the the VRH model. Inset show the change in DOS with the La substitution. . . 232

6.2 (a–f) The frequency dependent imaginary part of impedance (Z″) for $Sr_{2-x}La_xCoNbO_6$ samples at different temperatures. Solid black and red lines represent the experimental and best fit curves using the equivalent circuit shown in the inset of (f), respectively. Solid arrow in (a) represent the direction of increasing temperature. Dashed arrows in (b) indicate the relaxation peaks originating from the grains and grains boundaries. $T^{-1/4}$ versus (g) ln R_g and (h) ln R_{gb} plots, extracted from the fitting of Z″ (T, f) data. Insets show the change in the respective DOS with the La substitution. 235

6.3 Nyquist plots at the selected temperatures for x=0 sample. (b) Solid black lines represent the best fit of the curves presented in (a), using the equivalent circuit shown in the inset of Fig. 6.2(f). Green dashed curves are the extrapolation of the fitted curves to the lower frequency. Inset show the variation of the resistance (Z′ at Z″=0) with the temperature presented as ln Z'_s versus $T^{-1/4}$. 237

6.4 (a–f) The frequency dependent imaginary part of modulus (M$''$) for $Sr_{2-x}La_xCoNbO_6$ samples at different temperatures. Solid black and red lines represent the experimental and best fit curves using KWW model, respectively. Solid arrow in (a) represent the direction of increasing temperature. (g) ln f versus 1000/T_m plot for the relaxation peak position, estimated from the fitting of M$''$(T, f) data. Dashed lines represent the linear fit to show the deviation from the Arrhenius model. (h) ln f versus $T_m^{-1/4}$ plot, where solid lines represent the linear fit, following the VRH model. Inset show the change in DOS with the La substitution. 239

6.5 The frequency dependent imaginary part of impedance (Z$''$) (on left axis) and electric modulus (M$''$) (on right axis) at the selected temperatures for (a1–a4) $x = 0$, (b1–b4) $x = 0.2$, (c1–c4) $x = 0.4$, (d1–d4) $x = 0.6$, (e1–e4) $x = 0.8$, and (f1–f4) $x = 1$ samples. Vertical dashed lines represent the peak positions for both the spectra. (a5–e5) Temperature dependent difference in the grain relaxation peak position of Z$''(f)$ and M$''(f)$ spectra. 240

6.6 (a–f) The frequency dependent real part of the dielectric constant (ϵ') for $Sr_{2-x}La_xCoNbO_6$ samples at different temperatures. Frequency dependent (g) ϵ', (h) -dϵ'/d(ln f), and (i) -Z$''$ for x =0 sample at 149 K. 241

6.7 (a–f) The frequency dependent imaginary part of the dielectric constant (ϵ'') for $Sr_{2-x}La_xCoNbO_6$ samples at different temperatures. Frequency dependent (g) ϵ'', (h)d(ln ϵ'')/d(ln f), and -Z$''$ for $x = 0$ sample at 149 K. 243

6.8 (a–c) Temperature dependent tanδ loss for x =0, 0.4, and 1 samples at 1 kHz, 100 Hz, and 1 Hz frequencies, respectively. The d(ln ϵ')/dT curve for x =0 sample is compared in (a), where vertical solid line represent the presence of maxima in d(ln ϵ')/dT curve in the decreasing region of tanδ. (d–f) Temperature dependent tanδ loss for x =0, 0.4, and 1 samples, respectively at different frequencies. 244

6.9 (a–d) The frequency dependent real part of the ac conductivity for the x =0–0.6 samples, respectively at the selected temperatures. Black and red solid lines represent the experimental data and best fit using equation 6.9. (e–h) Temperature dependence of frequency exponent S and (i–l) constant A for the x = 0–0.6 samples, respectively. (m) VRH fit of the relaxation time, τ for these samples. 245

6.10 The electric field dependent polarization measurements at the selected temperatures and the excitation frequencies for the x =0.2 sample. . . . 247

6.11 The temperature and field dependent (a, b) coercive field (E_C), (c, d) remanent polarization (P_r), and (e, f) maximum polarization (P_{max}), respectively, for the x =0.2 sample. 248

6.12 Temperature derivative of the coercive field (E_C) and temperature dependent Z$'$ at 100 Hz for (a, b) x =0.2 and (c, d) x =0.8 sample, respectively. 249

6.13 The temperature dependent Z$'$ at 1 Hz for $Sr_{2-x}La_xCoNbO_6$ samples. . . 250

6.14 Temperature dependent real part of the impedance (Z$'$) for $Sr_{2-x}La_xCoNbO_6$ samples at the selected frequencies. The black solid lines represent the Lorentzian fit of the experimental data (red circles). 251

6.15 Frequency dependence of the (a) peak position (T_m), (b) peak area, and (c) FWHM, extracted from the Lorentzian fit of the Z$'$ (T) curves as shown in Fig. 6.14. 251

6.16 The frequency dependent real part of impedance (Z$'$) for $Sr_{2-x}La_xCoNbO_6$ samples at the selected temperatures. The black solid lines are the best fit of the data using equivalent circuit shown in the inset of Fig. 6.2(f) (eq. 6.14). 252

6.17 Temperature dependent (a1–a6) grain (C_g) and grain boundary capacitance (C_{gb}), (b1-b6) grain (R_g) and grain boundary resistance (R_{gb}), and (c) exponent (α) of the constant phase element for $Sr_{2-x}La_xCoNbO_6$ samples extracted by fitting the Nyquist plots at the different temperatures using the equivalent circuit shown in the inset of Fig. 6.2(f). 253

6.18 Frequency dependent imaginary part of impedance (Z$''$) for $Sr_{2-x}La_xCoNbO_6$ samples at the selected temperatures. The black solid lines are the best fit of the data using equivalent circuit shown in the inset of Fig. 6.2(f) (eq. 6.15). 254

6.19 Nyquist plots at the selected temperatures for $Sr_{2-x}La_xCoNbO_6$ samples. The black solid lines represent the best fit of the data using equivalent circuit shown in the inset of Fig. 6.2(f). 255

6.20 Variation of the (a) grain and (b) grain boundary resistance with the temperature plotted as 1000/T versus ln R_g and ln R_{gb}, respectively. Black dashed lines represent the best fit using the Arrhenius model. . . . 256

6.21 (a-f) Temperature dependent Z$''$ for $Sr_{2-x}La_xCoNbO_6$ samples at the different frequencies. Temperature dependent (g) Z$''$, (h) temperature derivative of Z$''$, and (i) Z$'$ for x =0 sample at 1 kHz frequency. 256

6.22 (a-f) Frequency dependent M$'$ for $Sr_{2-x}La_xCoNbO_6$ samples at the different temperatures. The frequency dependent (g) M$'$, (h) dM$'$/d(ln f), (i) M$''$, and Z$''$ for x =0 sample at 149 K. Red vertical dashed line at the higher frequency represent the peak position of dM$'$/d(ln f) and M$''$, whereas the blue dashed line at the lower frequency in (j) represent the peak position of the Z$''$ curve corresponding to the bulk relaxation. 257

6.23 Frequency dependent (a) peak position (f_{max}), maximum value of M$''$ (M''_{max}), and β for $Sr_{2-x}La_xCoNbO_6$ samples extracted by fitting the M$''$(f) curves using eq. 6.6. 258

6.24 The M''/M''_{max} versus ln (f/f_{max}) plots for $Sr_{2-x}La_xCoNbO_6$ samples at different temperatures. 259

6.25 (a-f) Temperature dependent ϵ' for $Sr_{2-x}La_xCoNbO_6$ samples at the different frequencies. The temperature dependent (g) ϵ', (h) d(ln ϵ')/dT, and (i) Z$'$ for x =0 sample at 10 Hz frequency. Red and blue vertical dashed lines at the higher and lower frequencies represent the peak position of d(ln ϵ')/dT and Z$'$ curves, respectively. 260

6.26 (a1–f4) Frequency dependent ϵ' for $Sr_{2-x}La_xCoNbO_6$ samples at the selected temperatures. The black solid lines represent the best fit using Havriliak-Negami (H-N) equation. Temperature dependent (a5–f5) shape parameters β and γ, (a6–f6) ϵ'_s (ϵ' for $f \to 0$) and ϵ'_∞ (ϵ' for $f \to \infty$), and (g) characteristic relaxation time, τ_{HN}, extracted from the above fitting. . 261

6.27 (a1–f5) Frequency dependent tanδ for $Sr_{2-x}La_xCoNbO_6$ samples at the selected temperatures. The red dotted curve in (a3) shows the -Z$''$(Ω)/10^4 on the right axis for x =0 sample at 200 K for the comparison. 262

6.28 The electric field dependent polarization measurements at the selected temperatures and the excitation frequencies for the x =0.8 sample. . . . 262

6.29 The temperature and field dependent (a, b) coercive field (E_C), (c, d) remanent polarization (P_r), and (e, f) maximum polarization (P_{max}), respectively, for the x =0.8 sample. 263

6.30 Fitting of the frequency dependent remanent polarization (P_r) at different temperatures using equation 6.13 for (a1–a5) x =0.2 and (b1–b5) x =0.8 sample. (c, d) Temperature dependent zero frequency remanent polarization, P_{r0}, extracted from this fitting for x =0.2 and 0.8 samples, respectively. 264

7.1 Raman spectra of $SrLaCoNbO_6$ recorded using 514 nm excitation source at (a) 13 K and (b) from 13 to 300 K. Solid black line and green lines in (a) indicate the cumulative and individual fitting of the various Raman modes using the Lorentzian peak shape. Each spectrum in (b) is vertically offset for the clarity. 275

7.2 Temperature evolution of the (a, b) P1 and P2, (c, d) P3, and (e, f) P4 modes in the lower and higher temperature regimes, respectively, at some representative temperatures. The arrows represent the direction of increase in the temperature. Enlarged view of (g) P2, (h) P3, and (i) P4 modes. The vertical red dashed lines are drawn to clarity show the change in the peak position with increase in the temperature. Each spectra in (g–i) has been vertically shifted for the clarity. 276

7.3 Temperature dependence of the (a–d) mode frequency and (e–h) line width for P1–P4 modes, respectively. The solid curves above ∼60 K represent the best fit using the anharmonic decay models. The solid yellow lines in (a–d) below ∼60 K are guide to the eye, which are presented more clearly in their respective insets. The regions for T<15 K, 15 K<T<60 K, and 60 K<T<300 K represent the antiferromagnetic state, short-range magnetic correlations, and paramagnetic behavior of $SrLaCoNbO_6$. (i–l) Deviation of the mode frequency from the anharmonic phonon decay model ($\Delta\omega$) in the low temperature regime. Solid red lines represent the best fit using the eqs. 7.5 and 7.6, accounting for the spin-phonon coupling. 278

7.4 Raman spectra of $SrLaCoNbO_6$ recorded using 633 nm excitation source at (a) 12K and (b) from 12 to 300 K. Solid black line and blue lines in (a) indicate the cumulative and individual fitting of the different Raman modes using the Lorentzian functions. Each spectrum in (b) is vertically shifted for the clarity. 280

7.5 (a-c) Enlarged view of Fig. 7.4(b) (unshifted here) in the low energy regime for different temperature ranges. Arrows represent the increasing direction of the temperature. (d) Temperate evolution of the integrated intensity of the broad continuum from 25 to 60 cm^{-1}. The solid blue lines are the guide to the eye. (e) Temperature dependent Raman response $\chi''(\omega, T)$ extracted from the raw Raman data (see text from more details). (f) The temperature evolution of the dynamic Raman susceptibility (χ^{dyn}; on left axis) and static magnetic susceptibility (on right axis, taken from ref. [33]) for $SrLaCoNbO_6$. The solid red curve represent the best fit of the χ^{dyn} data using canonical Curie-Weiss law from 60 K to 300 K and dashed curve is the extrapolation of fit down to 12 K. 281

7.6 Temperature evolution of the (a, b) S7, S8 and S10 (c, d) S11, and (e, f) S18 and S19 modes in the lower and higher temperature regimes, respectively, at some representative temperatures. Enlarged view of (g) S7, S8 and S10 (h) S11, and (i) S18 and S19 modes. The vertical red dashed lines are drawn to clarity show the change in the peak position with increase in the temperature. Each spectra in (g–i) has been vertically shifted for the clarity. 283

7.7 The temperature dependence of the mode frequencies and linewidths for S7, S8, S10, S11, S12, S15, S18, and S19 modes. Blue circles and red triangles represent experimental values of frequencies and linewidths, respectively. Solid red and blue lines are the fitted curves using the anharmonic decay model. The dashed lines are the extrapolation of the fitted curves down to 12 K and the neon blue curves in the low temperature regime are guide to the eye. 284

7.8 (a) Temperature dependent Raman spectra of $SrLaCoNbO_6$ recorded from 294 K to 973 K using 514 nm excitation source. Insets shows the enlarged view of the P4 mode. Each spectra has been vertically shifted for the clarity. Temperature evolution of the (b) peak position and (c) line width of mode P4. Solid red curves represent the best fit of the data using the anharmonic phonon decay models. 285

7.9 The temperature dependent normalized Co K-edge XANES spectra of the $SrLaCoNbO_6$ sample. Inset (a1) shows the enlarged view of the region highlighted by the red rectangle. Horizontal red dashed line represent the μ=1 and the black dashed curve (300 K_BC) represent the spectra recorded at 300 K before cooling the sample. The inset (a2) present the temperature evolution of the formal valence state of Co during warming and at 300 K before cooling the sample. 287

7.10 (a) The temperature dependent magnitude of the Fourier-transformed $k^3\chi(k)$ data. Each spectra has been shifted vertically upward cumulatively by 6 $Å^{-4}$ with respective to that recorded at 300 K for the clear presentation. Solid black and dashed green lines represent the best fit of the experimental data and the fitting window, respectively. (b, c) Enlarged view of the χ(R) data in the two different spectral regions. (d) Temperature evolution of the different scattering paths and their respective Debye-Waller factors, extracted from the EXAFS fitting of $SrLaCoNbO_6$ sample. 288

7.11 (a) The XPS survey spectra, (b) Sr 3*d*, (c) La 3*d*, (d) Co 2*p*, and (e) O 1*s* core-level spectra of the $SrLaCoNbO_6$. 290

8.1 Pseudocubic lattice parameters of the bulk target material Sr_2CoNbO_6 and different substrates used in this study with their in-plane lattice misfit, where misfit=$(a_{sub}-a_{bulk})/a_{sub}*100(\%)$, a_{sub} and a_{bulk} are in-plane pseudocubic lattice parameters of substrates and bulk. 305

8.2 (a) θ-2θ XRD pattern of Sr_2CoNbO_6/STO film and inset shows the rocking curve about (002) reflection, (b) and (c) show the ϕ-scan of the film and bare substrate, respectively, about (211) asymmetric reflection, (d) reciprocal space mapping (RSM) of Sr_2CoNbO_6/STO film about (211) reflection, (e) (002) reflection of the films on different substrates, asterisk symbol in case of LAO indicates the peak originating from the substrate. (f, g) the step on the substrate surface and thickness measurement across the step from the stylus profilometer. 307

8.3 (a) AFM image of (1x1) μm area of Sr_2CoNbO_6/STO film, (b) 1D scan across the periodic features of the film [white line in (a)], (c–e) the (1x1) μm AFM images of Sr_2CoNbO_6 films deposited on LSAT, LAO and KTO substrates, respectively. (f) Dependence of RMS roughness of the films on the lattice misfit for (1x1) and (10x10) μm scan areas. 308

8.4 (a) The temperature dependent resistivity of Sr_2CoNbO_6 films grown on different substrates. (b, c) The Arrhenius and VRH fitting in higher and lower temperature regimes, respectively. Insets show change in the activation energy and DOS with the lattice misfit, respectively. The red dashed lines indicate the extrapolation of the linear fitting to indicate the deviation from the Arrhenius and VRH models in the lower and higher temperature regimes, respectively. 310

8.5 (a) Room temperature absorption spectra in visible and NIR region for Sr_2CoNbO_6 films grown on various substrates. (b) and (c) the Tauc plots in two different energy regimes and insets show the variation of the band gaps with the lattice misfit, estimated from the respective Tauc plot. . . . 312

8.6 The core-level spectra of Sr $3d$ (a–c) and Nb $3d$ (d–f) for Sr_2CoNbO_6 films grown on STO, LSAT and LAO substrates, respectively. The experimental data points and fitted curve are shown by red circles and black solid lines, respectively along with the deconvoluted spin-orbit components by blue dotted lines. 313

8.7 The Co $2p$ (a–c) and O $1s$ (d-f) core-level spectra of Sr_2CoNbO_6 films deposited on different substrates. 314

8.8 Room temperature unpolarized Raman spectra of Sr_2CoNbO_6 thin films grown on various substrates. 317

8.9 Bulk pseudocubic lattice parameters of various perovskite oxides used to study the magnetic properties of the FM/AFM heterostructures, with their respective magnetic ordering temperatures (T_C/T_N) and in-plane lattice misfit with STO substrate. 319

8.10 (a) Room temperature out-of-plane x-ray diffraction measurement on the five bi-layers of $La_{0.67}Sr_{0.33}MnO_3$/ $LaSrCoNbO_6$ on STO (100) substrate (top), single layer of $La_{0.67}Sr_{0.33}MnO_3$ on STO (100) substrate (middle) and bare STO (100) substrate (bottom). (b) The XRR measurement on the $La_{0.67}Sr_{0.33}MnO_3$/ STO(100) film, where dashed blue and solid black lines represent the best fit without and with the dead layer, respectively. (c) 1×1 μm AFM image of the $[La_{0.67}Sr_{0.33}MnO_3/ LaSrCoNbO_6]_5$/STO(100) sample. (d) The XRR data of the $La_{0.67}Sr_{0.33}MnO_3$/ $LaSrCoNbO_6$/ STO(100) heterostructure. 320

8.11 (a) The temperature-dependent in-plane magnetic susceptibility in the ZFC and FC modes at 1000 Oe magnetic field for LSMO/STO film. (b) The best fit (solid red line) and extrapolation (dashed green line) of the FC curves from 2-110 K using the empirical power law (see text for more details). Inset shows the temperature derivative of the FC curve, where the vertical dashed line and arrow represent the global and local minima, respectively. (c) The in-plane field-dependent magnetization curves measured in the ZFC and 3T FC mode at 2 K. Inset shows the enlarged view of the low-field region. (d) ZFC-FC curves for the five bi-layers of LSMO/ LSCNO on STO substrate. (e) Power law fit of the FC curve. Inset shows the dχ/dT versus T plot of the FC curve. (f) MH curves at 2 K for [LSMO/ LSCNO]$_5$/ STO heterostructure measured in ZFC and FC modes. Inset shows the enlarged view between ±5.5 kOe. 322

8.12 (a) Room temperature out-of-plane x-ray diffraction measurement on three bi-layers of La_2CoMnO_6/ $LaSrCoNbO_6$ grown on STO (100) substrate (top) and bare STO (100) substrate (bottom). (b) Best fitted x-ray reflectivity (XRR) of $LaSrCoNbO_6$ (top) and La_2CoMnO_6 (bottom) films grown on Si(100) substrate. (c) Temperature-dependent resistivity measurement on the three bi-layers of La_2CoMnO_6/ $LaSrCoNbO_6$ on STO (100) substrate. Inset shows the four probe geometry for the resistivity measurement. (d) and (f) Arrhenius and VRH fitting in the high and low-temperature regimes (solid black lines) and their extrapolation in the low and high-temperature regimes (red dashed lines), respectively. 324

8.13 (a) Temperature-dependent in-plane magnetic susceptibility curves measured in ZFC and FC modes at 1000 Oe applied magnetic field for the three bi-layers of La_2CoMnO_6/ $LaSrCoNbO_6$ grown on STO (100) substrate. Inset shows the temperature derivative of the susceptibility curves, where the vertical dashed lines indicate the two transition temperatures, T_{c1} and T_{c2}. (b) Inverse and (c) temperature-weighted magnetic susceptibility for both ZFC and FC curves. (d) Field-dependent magnetization curves measured in the zero field cooled and 3T field cooled modes. Inset shows the enlarged view of the low-field region. (e) Virgin magnetization isotherms measured at 2 K in the in ZFC and FC modes for [La_2CoMnO_6/ $LaSrCoNbO_6$]$_3$/ STO(100) heterostructure. 326

List of Tables

3.1 Rietveld refined order parameter (S), lattice parameters, calculated tolerance factor, selected bond lengths (Å) and bond angles (degree) along with fitting reliability parameters of $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) samples. 99
3.2 Curie-Weiss temperature (T_θ), Curie constant (emu K/mol Oe), paramagnetic effective magnetic moment (μ_B) extracted from the linear fitting of $1/\chi$ versus T plot at the higher temperature, calculated effective moment of Co^{3+} (μ_B) and frustration factor (f) for $Sr_{2-x}La_xCoNbO_6$ for x = 0–1. The numbers in the parentheses represent the errors in the last digit of the extracted parameters. 103

4.1 The extracted parameters from the specific heat data of $Sr_{2-x}La_xCoNbO_6$ by fitting from 30 K to 300 K using the combined Debye and Einstein models with $m = 0.69$. 129
4.2 The fitting parameters extracted from the field dependent Schottky anomaly for $x \leqslant 0.4$ samples (E_0 = 0 K). 133
4.3 The critical exponent along with the other fitting parameters for the x = 0.6–1 samples, extracted from the best fit of data above and below the transition temperature, as shown in Figs. 4.7(d–f), using the equation 4.5. 139
4.4 The fitting parameters for the $x = 0.4$ sample using stretched exponential model for different waiting times and magnetic fields, M_0 and M_{SG} are in emu/mole. 143
4.5 The fitting parameters of the TRM data for the $x = 0$ and 0.2 samples using equation 4.7 measured at 1000 Oe for different waiting times. 146
4.6 The fitting parameters for the $x = 0.4$ sample using stretched exponential model for aging effect at 2 K and 8 K. 147
4.7 The best fit parameters for the aging effect of the $x = 0$ and 0.2 samples using stretched exponential model for different waiting times measured at 500 Oe and 2 K. 148
4.8 The fitting parameters extracted from the frequency dependence of the ac-χ for the x = 0–0.4 samples. 151
4.9 Best fitting parameters extracted from the training effect measurements performed on x =0 and 0.2 samples. 156

5.1 The EXAFS fitting parameters for $Sr_{2-x}La_xCoNbO_6$ samples extracted from the Nb, Co, and Sr K-edge spectra. 185
5.2 The charge transfer (Δe) and charge counts in the s, p, and d states of Nb_{abs} and O atoms extracted from the simulation of the Nb K-edge XANES spectra of the $x = 0$ sample by varying Nb–O bond distances. . . 190

3 The Rietveld refinement parameters for the x = 0.4 and 0.6 samples at 300 K. We use $I4/m$ space group; Nb/Co at $2b(0, 0, \frac{1}{2})$, Co/Nb at $2a$(0, 0, 0), O1 at 4e(0, 0, z) with 0.25 occupancy and O2 at $8h$ (x, y, 0) with 0.5 occupancy for the x = 0.4 sample, and $P2_1/n$ space group; La/Sr, O1, O2, O3 at $4e(x, y, z)$, Nb/Co at $2d(\frac{1}{2}, 0, 0)$ and Co/Nb at $2c(\frac{1}{2}, 0, \frac{1}{2})$ for the x = 0.6 sample. 197

4 The parameters extracted from the Grüneisen approximation of the unit cell parameters in the pseudocubic representation for the x = 0.4 and 0.6 samples, using combined Debye-Einstein model. 199

5 Selected bond lengths, monoclinic angle (β), and fitting reliability parameters extracted from the Rietveld refinement of the NPD data for x =0.4 and 0.6 samples. In addition, the tetragonal strain (e_t), and octahedral distortion parameters ϕ_1 and ϕ_2 are tabulated for the x = 0.4 sample (see text for more details). 201

5.6 The best fit parameters of the Nb K, Co K, and Sr K-edge XANES spectra for $Sr_{2-x}La_xCoNbO_6$ (x = 0–1) samples using Gaussian peak shapes and an error step function. The E_0 and FWHM represent the peak position and full width at half maxima in eV for various components.213

7.1 The Wyckoff positions and the irreducible representations of phonon modes for the different atoms of the monoclinic ($P2_1/n$; space group No. 14) odered double-perovskite $SrLaCoNbO_6$ at the Γ point. R_{Ag} and R_{Bg} represent the Raman tensors for A_g and B_g Raman active phonon modes, respectively. 274

7.2 The temperature range and the fitting parameters for the various Raman modes using the three and four phonon decay model, where temperature is in K, and ω_0 and Γ_0 are in cm^{-1} (see text for more details). 279

8.1 The fitting parameters of O 1s core-level spectra and the extracted surface composition of the different ions of Sr_2CoNbO_6 thin films deposited on various substrates. 315