

**STRUCTURAL, MAGNETIC, ELECTRONIC, AND
TRANSPORT PROPERTIES OF COBALT BASED
COMPLEX OXIDES**

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COMPLEX OXIDES**

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by

RISHABH SHUKLA

(2016PHZ8215)

under the supervision of

Prof. Rajendra Singh Dhaka



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DECLARATION BY THE CANDIDATE

I, Rishabh Shukla, declare that the work in this thesis entitled “*Structural, Magnetic, Electronic and Transport Properties of Cobalt based Complex Oxides*”, 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 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 _____

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CERTIFICATE OF THE SUPERVISOR

This is to certify that the thesis entitled “*Structural, Magnetic, Electronic and Transport Properties of Cobalt based Complex Oxides*”, being submitted by **Rishabh Shukla** (2016PHZ8215) 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 _____

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Rishabh Shukla

ABSTRACT

In the present era of technological advances and the development of materials with desirable applications, a fundamental understanding of their physical properties and their tunability to external perturbations is essential. In this aspect, the perovskite oxides, a general chemical formula of ABO_3 , have emerged as a promising candidate because of their robust physical properties, which can be greatly tailored in a systematic manner with external perturbations like temperature, mechanical pressure, cationic substitution (chemical pressure), magnetic field, electric field, light, epitaxial strain, etc. This control on the perovskite oxides makes them suitable for a wide range of applications such as electrodes for solid oxide fuel cells, electrodes for batteries, magnetic storage devices, solar cells, sensors, superconductors, flexible electronics, etc. In the family of perovskite oxides, cobaltites have their unique place because of an additional degree of freedom of spin-state transition for different valence states of Co-ions. An in-depth understanding to tailor these properties with cationic substitution greatly depends on the crystal field strength of BO_6 octahedra and Hund's exchange energy coupling. Therefore, a complete understanding to tune the physical properties for fundamental understanding and their controlled technological application make this study vital for future endeavors.

The principle theme of this thesis work is to understand the effect of cationic substitution and epitaxial strain on the structural, magnetic, transport, and electronic properties of $La_{1-x}Sr_xCo_{1-y}Nb_yO_3$. The substitution of Sr^{2+} in place of La^{3+} induces the transformation of Co^{3+} into Co^{4+} and stabilizes the ferromagnetic metallic state for $x \geq 0.18$, while in contrast, the substitution of Nb^{5+} in place of Co^{3+} transforms them to Co^{2+} favors the stabilization of an insulating paramagnetic state. Therefore, the co-substitution of Sr^{2+} and Nb^{5+} ions in a ratio of 2:1 preserve the Co^{3+} state and rhombohedral structure similar to $LaCoO_3$. Substitution induces modification in the Co-O bond length and the Co-O-Co bond angle enhances the net magnetization and a cluster spin-glass behavior is induced. Further, the x-ray absorption manifests that Co^{3+} ions are Jahn-Teller active similar to $LaCoO_3$, while this effect is suppressed with the emergence of Co^{2+} ions. Further, a monotonous substitution of Nb^{5+} in ferromagnetic metal $La_{0.5}Sr_{0.5}CoO_3$ dilutes the magnetic order and double exchange interaction suppresses and superexchange interaction dominated with x and a spin-glass behavior is observed for $x > 0.1$. Further, the metallic behavior is modified with Nb^{5+} , and a metal-to-insulating transition is observed for $x \leq 0.05$, which propagates to a semiconducting behavior for $x > 0.05$.

Interestingly, a competitive FM and AFM interaction due to the microscopic magnetoelectronic phase separation is induced in the created interface of AFM and cluster spin glass in $x = 0.15$, which leads to a giant negative exchange bias (NEB) of $H_{EB} = -7.4$ kOe for a cooling field of 50 kOe at 5 K, useful for several technological applications.

This giant NEB is tunable with the cooling field, temperature, and measuring field, such that, for increasing the cooling field NEB first increases up to a cooling field of 50 kOe and then decreases. Further, for increasing the temperature NEB decreases and a higher measuring field of >50 kOe also leads to the decrease in the NEB. This unconventional NEB appears because of the intrinsic interface effect, where a higher applied magnetic field increases the Zeeman energy of FM regions and reduces the pinning effect at the interface, leading to the diminishing of NEB.

Further, the strain-controlled structural, transport and vibrational properties of the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Nb}_y\text{O}_3$ thin films on the single-crystalline perovskite oxides manifest the cube-on-cube growth of pure phase epitaxial thin films having compressive and tensile strain. The vibrational spectra of epitaxial thin films confirm the strain-induced ordering of the $(\text{Co/Nb})\text{O}_6$ octahedra, and the dc-transport of these thin films manifest an enhancement in the density of states near the Fermi level with the compressive strain and reduction in the activation energy. Therefore, the strain-induced control of the structural, and transport properties make these Co-based perovskite oxides vital to study.

Thus, the effect of cationic substitution and epitaxial strain on the structural, magnetic, transport, and electronic properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Nb}_y\text{O}_3$ has been established using the x-ray and neutron diffraction, dc- and ac-magnetization, x-ray absorption, specific heat, x-ray photoemission, dc-transport, and Raman spectroscopy. The controlled tunability of the oxidation and spin-states of the Co ions with the cationic substitution has been discussed and that will lead to a better understanding of the Co-based perovskite oxides. Moreover, the modification of the conductivity, magnetization, giant exchange bias, and electronic structure of these materials will make them useful for technological applications in the area of solid oxide fuel cells, magnetic memory devices, electronic devices, etc.

सार

तकनीकी प्रगति और पदार्थों के विकास एवं उनके वांछनीय अनुप्रयोगों के वर्तमान युग में उनके भौतिक गुणों की मौलिक समझ एवं बाहरी विक्षोभों के प्रति उनकी परिवर्तनीयता की समझ आवश्यक है। इस पहलू में पेरोव्स्काइट ऑक्साइड, जिनका सामान्य रासायनिक सूत्र ABO_3 है, एक आशाजनक उम्मीदवार के रूप में उभरा है, उनके मजबूत भौतिक गुण, जिन्हें सुव्यवस्थित तरीके से बाहरी विक्षोभों, उदाहरणार्थ, तापमान, यांत्रिक दबाव, धनायनिक प्रतिस्थापन (रासायनिक दबाव), चुंबकीय क्षेत्र, विद्युत क्षेत्र, प्रकाश, अधिरोहण जनित तनाव, आदि द्वारा काफी हद तक परिवर्तित किया जा सकता है। पेरोव्स्काइट ऑक्साइड पर यह नियंत्रण उन्हें अनुप्रयोगों की एक विस्तृत श्रृंखला के लिए उपयुक्त बनाता है, जैसे कि ठोस ऑक्साइड ईंधन सेल के लिए इलेक्ट्रोड, बैटरी के लिए इलेक्ट्रोड, चुंबकीय भंडारण उपकरण, सौर सेल, सेंसर, अतिचालकता, लचीले इलेक्ट्रॉनिक्स आदि। पेरोव्स्काइट ऑक्साइड के परिवार में कोबाल्टाइट्स का अपना विशिष्ट स्थान है, क्योंकि इन यौगिकों में कोबाल्ट आयनों की विभिन्न संयोजकताएँ के साथ स्पिन-अवस्था संक्रमण स्वतंत्रता का एक अतिरिक्त विकल्प प्रदान करता है। धनायनित प्रतिस्थापन के साथ इन गुणों को अनुकूलित करने की गहन समझ काफी हद तक BO_6 अष्टफलक के क्रिस्टल क्षेत्र की ताकत और हुंड के विनिमय ऊर्जा युग्मन की ताकत पर निर्भर करती है। इसलिए, मौलिक समझ के लिए भौतिक गुणों को समायोजित करने की पूरी समझ और उनके नियंत्रित तकनीकी अनुप्रयोग इस अध्ययन को भविष्य के प्रयासों के लिए महत्वपूर्ण बनाते हैं।

इस थीसिस कार्य का मुख्य विषय $La_{1-x}Sr_xCo_{1-y}Nb_yO_3$ के संरचनात्मक, चुंबकीय, परिवहन और इलेक्ट्रॉनिक गुणों पर धनायनित प्रतिस्थापन और अधिरोहण जनित तनाव के प्रभाव को समझना है। La^{3+} के स्थान पर Sr^{2+} का प्रतिस्थापन Co^{3+} के Co^{4+} में परिवर्तन को प्रेरित करता है और $x \geq 0.18$ के लिए लौहचुंबकीय धात्विक अवस्था को स्थिर करता है, जबकि इसके विपरीत, Co^{3+} के स्थान पर Nb^{5+} का प्रतिस्थापन उन्हें Co^{2+} में बदल देता है, जो एक इन्सुलेटिंग पैरामैग्नेटिक अवस्था के स्थिरीकरण को बढ़ावा देता है। इसलिए 2:1 के अनुपात में Sr^{2+} और Nb^{5+} आयनों का सह-प्रतिस्थापन $LaCoO_3$ के समान Co^{3+} अवस्था और त्रिसमनताक्ष संरचना को संरक्षित करता है। प्रतिस्थापन $Co-O$ आबन्ध लम्बाई में संशोधन प्रेरित करता है और $Co-O-Co$ आबन्ध कोण शुद्ध चुंबकीयकरण को बढ़ाता है और क्लस्टर स्पिन-ग्लास व्यवहार को प्रेरित करता है। इसके अलावा, एक्स-रे अवशोषण से पता चलता है कि Co^{3+} आयन $LaCoO_3$ के समान जान टेलर सक्रिय हैं, जबकि Co^{2+} आयनों के उभरने से यह प्रभाव क्षीण हो जाता है। इसके अलावा, लौहचुंबकीय धातु $La_{0.5}Sr_{0.5}CoO_3$ में Nb^{5+} का एकविध प्रतिस्थापन चुंबकीय क्रम को क्षीण करता है और डबल एक्सचेंज इंटरैक्शन को अवरोधित करता है और x के साथ सुपरएक्सचेंज इंटरैक्शन हावी हो जाता है और $x > 0.1$ के लिए एक स्पिन-ग्लास आचरण देखा जाता है।

दिलचस्प बात यह है कि एक प्रतिस्पर्धी लौहचुंबकीय और प्रतिलौहचुंबकीय इंटरैक्शन, सूक्ष्म मैग्नेटोइलेक्ट्रॉनिक अवस्था पृथक्करण को प्रतिलौहचुंबकीय और क्लस्टर ग्लास ($x = 0.15$) के निर्मित अंतराफलक पर प्रेरित करता है, जो 50 kOe के शीतलन क्षेत्र के लिए 5 K पर $H_{EB} = -$

7.4 kOe के एक विशाल नकारात्मक विनिमय झुकाव की ओर ले जाता है एवं कई तकनीकी अनुप्रयोगों आगे लिए उपयोगी है। यह विशाल नकारात्मक विनिमय झुकाव शीतलन क्षेत्र, तापमान और मापक क्षेत्र आदि के साथ इस तरह परिवर्तन योग्य है कि, पहले शीतलन क्षेत्र को 50 kOe तक बढ़ाने पर नकारात्मक विनिमय झुकाव बढ़ता है और शीतलन क्षेत्र को 50 kOe के आगे तक बढ़ाने पर फिर घट जाता है। इसके साथ ही तापमान बढ़ाने पर नकारात्मक विनिमय झुकाव घटता है और मापक क्षेत्र 50 kOe से अधिक बढ़ाने पर भी नकारात्मक विनिमय झुकाव में कमी आती है। यह अपरंपरागत नकारात्मक विनिमय झुकाव आंतरिक अंतराफलक प्रभाव के कारण प्रकट होता है, जहां एक उच्च चुंबकीय क्षेत्र लौहचुंबकीय क्षेत्रों की ज़ीमैन ऊर्जा को बढ़ाती है और इसलिए अंतराफलक पर पिनिंग प्रभाव को कम करती है, जो नकारात्मक विनिमय झुकाव को हास की ओर ले जाता है।

इसके साथ ही तनाव नियंत्रित संरचनात्मक, परिवहन और कंपन संबंधी गुण, एकल-क्रिस्टलीय पेरोव्स्काइट ऑक्साइड पर $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Nb}_y\text{O}_3$ की शुद्ध अवस्था एपीटैक्सियल पतली परतों की घन पर घन वृद्धि को दिखाता है जिनमें संपीडित और तन्य तनाव प्रेरित किया जाता है। एपीटैक्सियल पतली परतों का कंपन स्पेक्ट्रा तनाव प्रेरण की $(\text{Co/Nb})\text{O}_6$ ऑक्टाहेड्रा के क्रम में पुष्टि करता है, और इन पतली फिल्मों का डीसी-परिवहन संपीडन के साथ फर्मी स्तर के पास अवस्थाओं के घनत्व में वृद्धि और सक्रियण ऊर्जा में कमी को दर्शाता है। इसलिए संरचनात्मक और परिवहन गुणों पर तनाव-प्रेरित नियंत्रण इन कोबाल्ट आधारित पेरोव्स्काइट ऑक्साइड को महत्वपूर्ण बनाते हैं।

इस प्रकार धनायनित प्रतिस्थापन और अधिरोहण जनित तनाव के प्रभाव को $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Nb}_y\text{O}_3$ के संरचनात्मक, चुंबकीय, परिवहन और इलेक्ट्रॉनिक गुणों पर एक्स-रे और न्यूट्रॉन विवर्तन, डीसी और एसी-चुंबकत्व, एक्स-रे अवशोषण, विशिष्ट ताप, एक्स-रे फोटोउत्सर्जन, डीसी-परिवहन, और रमन स्पेक्ट्रोस्कोपी द्वारा स्थापित किया गया है। धनायनित प्रतिस्थापन के साथ सह आयनों की विभिन्न संयोजकताएँ के साथ स्पिन-अवस्था संक्रमण के नियंत्रित परिवर्तन की चर्चा की गई है और इससे कोबाल्ट आधारित पेरोव्स्काइट ऑक्साइड की बेहतर समझ पैदा होगी। इसके अलावा, चालकता, चुंबकत्व, विशाल नकारात्मक विनिमय झुकाव का संशोधन और इलेक्ट्रॉनिक संरचना में परिवर्तन उन्हें तकनीक के लिए उपयोगी बनाता है, उदाहरणार्थ, ठोस ऑक्साइड ईंधन सेल, चुंबकीय भंडारण उपकरण, इलेक्ट्रॉनिक उपकरणों, आदि के क्षेत्र में।

Contents

Declaration by the Candidate	i
Certificate of the Supervisor	ii
Acknowledgement	iii
Abstract	vi
List of Figures	xii
List of Tables	xxiv
1 Introduction	1
1.1 Crystal Structure	2
1.1.1 Disorders in Perovskite Crystal Structure	3
1.2 Crystal-Field Splitting	5
1.2.1 Jahn-Teller Effect	5
1.3 Electron-Electron Interaction in Strongly Correlated Transition Metal Oxides	8
1.3.1 Exchange Interaction in Charge-Transfer Insulator	12
1.3.2 Magnetic Exchange Interactions	14
1.3.2.1 Superexchange Interaction	14
1.3.2.2 Double Exchange Interaction	17
1.4 Motivation of This Work: Enigmatic case of LaCoO_3	19
1.5 Tuning the Material Properties in Lower Dimensions: Thin Films	22
1.6 Organization of the Thesis Chapters	24
2 Experimental Details	36
2.1 Sample Preparation Techniques	37
2.1.1 Solid State Reaction Route	37
2.1.1.1 Mixing and Sintering	37
2.1.1.2 Uniaxial Pressing	38
2.1.1.3 Advantages of Solid State Reaction Method	38
2.1.1.4 Disadvantages of Solid State Reaction Method	38
2.1.2 Pulsed laser deposition (PLD) technique	40

2.1.2.1	Working of the Pulsed Laser Deposition	41
2.1.2.2	Advantages of Pulsed Laser Deposition	43
2.1.2.3	Disadvantages of Pulsed Laser Deposition	44
2.2	Characterization techniques	44
2.2.1	X-ray Diffraction	44
2.2.1.1	Generation of x-rays	45
2.2.1.2	Theoretical Background of Diffraction	46
2.2.1.3	Instrumentation	49
	Bragg-Brentano Arrangement	49
	Grazing incidence x-ray diffraction	50
	X-ray reflectivity (XRR)	51
2.2.1.4	High-resolution x-ray diffraction	52
	Rocking curve	52
	ϕ -scan	53
	Reciprocal space mapping	54
2.2.1.5	Limitations of the x-ray diffraction	55
2.2.2	Neutron Powder Diffraction	55
2.2.2.1	Instrumentation	57
2.2.2.2	Basic Theory of Neutron Diffraction	57
2.2.2.3	Limitations of the powder neutron diffraction	59
2.2.3	Polarized neutron spectroscopy	59
2.2.4	Atomic force microscopy	63
2.2.4.1	Short-Range Forces	63
2.2.4.2	Van der Waals Forces	63
2.2.4.3	Electrostatic Forces	63
2.2.4.4	Capillary Forces	64
2.2.4.5	Operation Modes	65
	Static Contact Mode	65
	Dynamic Non-Contact Mode	66
	Tapping mode	67
2.2.5	Raman Spectroscopy	67
2.2.5.1	What is Raman Spectroscopy	67
2.2.5.2	Filters used in Raman Spectroscopy	68
2.2.5.3	Effect of different parameters on the Raman Signal	69
2.2.5.4	Use of Confocal Microscopy in Raman Spectroscopy	72
2.2.5.5	Advantages of Raman Spectroscopy	73
2.2.5.6	Disadvantages of Raman Spectroscopy	74
2.2.6	Physical Property Measurement System	74
2.2.6.1	Vibrating Sample Magnetometer	75
2.2.6.2	AC-Susceptibility Measurements	76
2.2.6.3	Heat capacity measurements	77
2.2.6.4	dc-Resistivity measurements	79
2.2.7	Superconducting Quantum Interference Device	79
2.2.8	X-ray absorption spectroscopy	80
2.2.8.1	Instrumentation	81
2.2.8.2	X-ray absorption near edge structure	82
2.2.8.3	Extended x-ray absorption fine structure	83

2.2.8.4	Analysis of Extended x-ray absorption fine structure . . .	84
2.2.9	X-ray photoelectron spectroscopy	85
2.2.9.1	Working Principle	86
2.2.9.2	Intstrumentation	87
2.2.9.3	Advantages of the X-ray Photoelectron Spectroscopy . .	87
2.2.9.4	Disadvantages of the X-ray Photoelectron Spectroscopy .	88
3	Structural, Magnetic, Transport, and Electronic Properties of	
	$\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$	93
3.1	Introduction	94
3.2	Experimental Details	97
3.3	Results and Discussion	99
3.3.1	Room Temperature X-ray and Neutron Diffraction	99
3.3.2	DC-Magnetization and Magnetic Susceptibility	104
3.3.3	AC-Magnetic Susceptibility	109
3.3.4	Low Temperature Neutron Diffraction	115
3.3.5	Temperature-dependent Resistivity	115
3.3.6	X-ray Photoelectron Spectroscopy	117
3.3.7	X-ray Absorption Study	120
3.3.7.1	XANES Analysis	120
3.3.7.2	EXAFS Analysis	126
3.4	Conclusion	133
4	Evolution of Complex Magnetic Phases and Metal-Insulator Transition	
	through Nb Substitution in $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Nb}_x\text{O}_3$	147
4.1	Introduction	148
4.2	Experimental Details	149
4.3	Results and Discussion	150
4.3.1	X-ray Diffraction	150
4.3.2	DC-Magnetic Susceptibility	152
4.3.3	Magnetic Isotherms	157
4.3.4	Temperature-dependent Resistivity	158
4.3.5	X-ray Photoemission Spectroscopy	166
4.4	Conclusion	168
5	Investigation of Tunable Unconventional Giant Negative Exchange	
	Bias in Polycrystalline $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$	178
5.1	Introduction	179
5.2	Experimental Details	180
5.3	Results and Discussion	182
5.3.1	DC-Magnetic Susceptibility	182
5.3.2	AC-Magnetic Susceptibility	184
5.3.3	Specific Heat	189
5.3.4	Magnetic Isotherms and Exchange Bias	192
5.3.5	Origin of Exchange Bias	197
5.4	Conclusion	200

6 Structural, Vibrational, and Transport Properties of $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ Thin Films	209
6.1 Introduction	210
6.2 Experimental	211
6.3 Results and Discussion	213
6.3.1 X-ray Diffraction	213
6.3.2 Atomic Force Microscopy	216
6.3.3 Raman Spectroscopy	217
6.3.4 Transport Measurements	220
6.4 Conclusion	223
7 Conclusion and Future Scope of the Work	230
A Investigation of Lattice Dynamics, Magnetism, and Electronic Transport in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$	234
A.1 Introduction	235
A.2 Experimental Details	236
A.3 Results and Discussion	237
A.3.1 X-ray Diffraction	237
A.3.2 Temperature-dependent Raman Measurements	240
A.3.3 Spin-Phonon Analysis	248
A.3.4 Magnetic and Transport Measurements	249
A.3.5 X-ray Photoemission and Absorption Measurements	254
A.4 Conclusion	256
Publications	264
Conferences and Presentations	266
Biodata	268

List of Figures

1.1	A schematic crystal structure of ideal perovskite structure ABO_3 (left panel), where B atom is surrounded by six oxygen atoms forming an octahedron (upper right panel), and A atom is surrounded by the twelve oxygen atoms forming a polyhedron (lower right panel). These images are created with Vesta [24].	3
1.2	The effect of cation sizes at A and B-sites on the structural distortions of perovskite oxides structure. This image is taken from ref. [25].	4
1.3	A schematic presentation of two adjacent layers of an octahedron, where the + and - sign manifest the tilt of the octahedron relative to one axis. The idea of this image is taken from ref. [26].	5
1.4	(a) A schematic showing a transition metal ion in an octahedral crystal field surrounded by the oxygen anions, (b) splitting of the d -orbital into two degenerate groups (t_{2g} and e_g) due to the octahedral crystal field with a separation of $10Dq$	6
1.5	A schematic diagram showing the electron densities in the typical shapes of the d -orbitals, where (a, b) are the e_g orbitals and (c-e) is the t_{2g} orbitals. This image is taken from ref. [29].	7
1.6	The splitting of the d -levels for lifting the degeneracy of the unstable states because of the tetragonal distortion of the BO_6 octahedra, for the tetragonal elongation (a, b) and tetragonal compression (c, d). This image is taken from ref. [29].	9
1.7	A schematic energy level diagram illustrates the position of p and d -levels and depicts the charge-transfer gap for (a) d^0 , and (b) d^1 shells. This image is taken from ref. [29].	10
1.8	A schematic diagram showing the process of hopping of the d -electron from one TM site to another TM site via an intermediate oxygen ion. This image is taken from ref. [29].	10
1.9	A schematic diagram showing the possibilities of the $d - p$ overlap of t_{2g} electrons, where (a) the d_{xy} orbital is orthogonal to the p_x orbital and (b) the finite overlap of d_{xy} orbital with the p_y orbital. This image is taken from ref. [29].	11
1.10	A schematic diagram showing the mechanism of exchange interaction which involves the oxygen ion and the p -orbitals in an apparent way. This image is taken from ref. [29].	13
1.11	A schematic diagram to summarize the exchange interaction via the $d - d$ hopping of the electron from one TM site to another TM site in (a) a strong antiferromagnetic interaction, (b) a weak ferromagnetic interaction. This image is taken from ref. [29].	15

1.12	A schematic diagram to show the three different possibilities of the superexchange interaction where exchange happens via p -orbital of the ligand, here (a) shows the strong antiferromagnetic interaction, (b) a weak ferromagnetic interaction, and (c) also depicts a weak ferromagnetic interaction. This image is taken from ref. [29].	16
1.13	A schematic showing the summary of the superexchange interaction based on the GKA rules, here TM sites are expected to have at least one unpaired electron and two oxygens are needed for the oxygen octet, therefore four electrons are participating in this interaction. The spin configuration shows (a) a ground state having an antiferromagnetic interaction, (b) a ferromagnetic ground state, and (c) the lowest excited state. For the ferromagnetic ground state (d) there is no equivalent low energy state, and (f) state is forbidden by the Pauli exclusion principle. This image is taken from ref. [40].	17
1.14	(a–c) A schematic showing the mechanism of the double exchange interaction in a doped Mott-Hubbard insulator with the intrinsic electrons, and (d) this canted magnetic state shows the double exchange interaction for the low-doped systems. This image is taken from ref. [29].	18
1.15	The double exchange interaction between the two valence states of Mn (Mn^{3+} and Mn^{4+}) in $La_{1-x}Sr_xMnO_3$ and Fe (Fe^{2+} and Fe^{3+}) in Fe_3O_4 . This indirect exchange bonds to the $3d^{n+1}$ and $3d^n$ through an O atom. This image is taken from ref. [40].	19
1.16	A schematic diagram showing the electronic structure of transition metal oxides, where U, W, and Δ manifest the Mott-Hubbard splitting, bandwidth, and charge transfer energy, respectively. The idea of this image is taken from ref. [68].	21
1.17	A schematic showing the possibilities of the different mechanisms at a heteroepitaxial interface which leads to the novel properties in the thin films that are not found in their respective counterparts. This image is taken from ref. [87].	22
2.1	Typical steps used to synthesize $La_{1-y}Sr_yCo_{1-x}Nb_xO_3$ samples using solid state route.	39
2.2	The schematic illustrates the stepwise evolution of the pulsed laser deposition process over time. The idea for the image is taken from ref. [3].	41
2.3	(a) Ultra-high vacuum compatible pulsed laser deposition setup in Novel Materials and Interface Physics Laboratory at Department of Physics, IIT Delhi, (b) formation of the plume during the deposition of complex oxides, (c) metal sample holder for fixing the substrate, and (d) formation of the step by partially shadowing the Si[100] substrate.	43
2.4	A Schematic of the x-ray tube structure describes the generation of the x-rays by the high-speed electrons subjected to the high potential difference between the cathode (filament) and anode (metal target).	45
2.5	(a) Schematic energy level diagram showing the generation of x-rays, and (b) Characteristic x-rays along with the continuous Bremsstrahlung electromagnetic radiation. The image (b) is taken from ref. [5].	47
2.6	A Schematic to show the diffraction by the crystal planes. The path difference of the incident (1 and 2) and diffracted (1' and 2') x-ray beams is given by the $SQ+QT = 2PQ\sin\theta$. The idea of the image is taken from refs. [4,5].	48

2.7	(a) Real image of the PANalytical X'pert ³ Powder x-ray diffractometer at Department of Physics, IIT Delhi, (b) x-ray source (highlighted with the red outline) and detector (highlighted with the blue outline) used in the Bragg-Brentano geometry to measure the out-of-plane XRD of the samples, the red arrow points the pressure probe to adjust the height of the samples for maximum intensity, and (c) x-ray source (highlighted with the red outline) and detector (highlighted with the blue outline) used in the grazing incidence XRD, XRR and out-of-plane (Gonio-mode) XRD of the thin-film samples, black arrow points the sample stage used to keep the sample on a flat surface for the different XRD measurements.	50
2.8	A schematic diagram for the grazing incidence x-ray diffraction, where θ is the Bragg angle, ϕ is the angle of incidence, ϕ' is the exit angle of the diffracted beam, and ω is the angle of rotation about the surface normal.	51
2.9	(a) Real image of the PANalytical Emperean X'pert Pro high-resolution x-ray diffractometer at Central Research Facility, IIT Delhi, (b) x-ray source (highlighted with red outline) and point-detector (highlighted with blue outline) used to record the high-resolution of XRD of different types of samples, the sample stage is marked with a red arrow, which has the freedom to rotate in the ω , χ , and ϕ -planes precisely, and (c) shows (from left to right) the beam attenuator made up of copper foil (to reduce the intensity of the x-ray beam), anti-scatter/receiving slit (to improve the signal-to-noise ratio on the detector side by reducing the background), x-ray mask to control the width of the x-ray beam, divergence slit to control the linewidth of the x-ray beam, and soller slit used to improve the resolution and peak shape of the diffraction patterns by controlling asymmetry and axial acceptance.	53
2.10	A schematic highlighting the misalignment of the tilt-axis in the rocking curve (ω -scan). The image is taken from ref. [8].	54
2.11	A schematic showing the principle of operation of neutron powder diffractometer at (a) Poder Diffractometer(PD)-I and (b) PD-II at the Dhruva reactor, Bhabha Atomic Research Center, Trombay, Mumbai in India. These images are taken from ref. [12].	56
2.12	A schematic showing the interaction of the sample with the polarized neutron beam and having two different contributions from the nuclear and magnetic interactions. The image is taken from ref. [13].	60
2.13	Effect of magnetic field on neutron magnetic moment and Larmor precession shows the conservation of the angular momentum and energy. The idea of the image is taken from ref. [19].	60
2.14	A schematic showing the interaction of the sample with the polarized neutron beam and having two different contributions from the nuclear and magnetic interactions. The idea of the image is taken from ref. [19].	61
2.15	Schematic diagram of the neutron depolarization measurement set-up at Dhruva reactor in Mumbai, India. The image is taken from refs. [12,20].	62
2.16	A schematic of the atomic force microscopy showing its different components, cantilever, photodetector, laser source, and tip. The image is taken from ref. [21].	64
2.17	A schematic showing the working of the static contact mode where different forces are acting on the cantilever due to the contact to the sample surface. The idea of this image is taken from the ref. [22].	65

2.18	A schematic showing the working of the non-contact mode in which the shift of the cantilever frequency is utilized in the feedback loop to obtain the surface topography. The idea of this image is taken from ref. [23]. . .	66
2.19	A schematic showing the working of the tapping mode for the constant amplitude of oscillations. The idea of this image is taken from ref. [23]. . .	66
2.20	A schematic diagram showing the principals of the Raman and Rayleigh Scattering. Energy levels marked with numbers 0, 1, and 2 show the vibrational energy levels and transitions a+b, a+c, and d+e manifest the Rayleigh scattering, Stokes Raman Scattering, and anti-Stokes Raman scattering, respectively.	68
2.21	A schematic diagram showing the principal of the Confocal microscopy. . .	72
2.22	(a) Real image of Horiba Confocal Raman microscope at Department of Physics, IIT Delhi, (b) Real image showing the smart sample stage, (c) real image of different lasers used as the excitation source for the Raman measurement, and (d) a typical raw Raman spectrum observed in wire software.	73
2.23	(a) Physical property measurement system (PPMS), Evercool-II, (b) Magnetic property measurement system (MPMS)-3: SQUID Magnetometer, and (c) Magnetic property measurement system (MPMS) from the Quantum Design USA. Images in (a) and (b) are taken from ref. [26] and (c) is the real image of the system at Central Research Facility, IIT Delhi. . .	75
2.24	(a) Different sample mounting rods used for the magnetic measurements, (b) VSM assembly head used for the magnetic measurements in PPMS Evercool-II and SQUID-VSM, (c) A schematic diagram of the PPMS probe used for the VSM assembly which has the metallic baffles, sample coil, connections for the computer, (d) a schematic of the sample probe used for the dc-magnetic measurements, and (e) a schematic used for the dynamic/ac magnetic measurements. These schematics are taken from the ref. [26].	76
2.25	(a) dc-resistivity puck used for the temperature-dependent and magneto-transport measurements, (b) schematic of the dc-resistivity puck showing the key, pin, and solder pads, and (c) a schematic for the connection pad used for making the contacts for the resistivity measurements. These images are taken from ref. [26].	78
2.26	A schematic setup showing the SQUID magnetometer along with the 2 nd order gradiometer. Inset shows the voltage response with the sample position. The image is taken from ref. [35].	80
2.27	A schematic energy level diagram showing the absorption process of the (a) K-edge and (b) L-edge for an element. Here the energy levels are not drawn to scale.	81
2.28	(a) An assembly of three ionization chambers aligned in a row to measure the x-ray absorption spectra in the transmission mode, (b) a beamline view of the BL-09 at RRCAT, Indore, India showing the double crystal monochromator, and (c) the beamline layout used to record the x-ray absorption spectra for a range of materials, where several components in the beamline are highlighted. These images are taken from the ref. [42]. . .	83

2.29	(a) A energy level diagram showing the ejection of the photoelectron from the K-shell when an x-ray photon is incident on the sample, and (b) a schematic showing the different components of the x-ray photoemission spectrometer. The image (b) is taken from ref. [44].	86
3.1	Rietveld refined powder x-ray diffraction patterns of $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples, (a) $x = 0.025$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.15$. The experimental data, Rietveld refinement profiles, Bragg peak positions, and the residual are shown in open red circles, black solid lines, green vertical bars, and solid blue lines, respectively.	99
3.2	Rietveld refined neutron powder diffraction patterns for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples, (a) $x = 0.025$, (b) $x = 0.05$, and (c) $x = 0.15$, measured at room temperature. The Rietveld refinement profiles, the fitted Bragg peak positions, and the residual are shown in black solid lines, short vertical bars, and blue lines at the bottom of each panel, respectively.	101
3.3	Isothermal magnetization (M-H) for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples, (a) $x = 0.025$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.15$, measured at 5 K, inset in each panel shows the magnetic behavior near the origin.	104
3.4	Temperature dependent ZFC-FC curves for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples, (a) $x = 0.025$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.15$, measured at 500 Oe field. (e) The temperature-dependent χ^{-1} (FC mode) plots, and (f) the variation of χT (ZFC mode) with temperature for $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples.	106
3.5	(a, b) The virgin curves (M-H) and (c, d) Arrott plots (M^2 vs H/M) of $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples at different temperatures across the transition, for (a, c) $x = 0.05$, and (b, d) $x = 0.1$	108
3.6	Temperature dependent ac-susceptibility measurements (a, c) real part, and (b, d) imaginary part of the $x = 0.05$ and 0.1 samples, respectively, inset in (a) shows the shift in the peak position with the change in the frequency and inset in (c) shows that the susceptibility decreases after the freezing temperature T_f	110
3.7	(a) Frequency sensitivity of the freezing temperature is plotted in terms of $\log_{10}(\nu)$ versus $\log_{10}\left(\frac{T_f - T_{SG}}{T_{SG}}\right)$, where $\nu = 1/\tau$, the solid line shows the fit to the power law, (b) Excitation frequency dependence of freezing temperature is plotted as T_f versus $1/\ln(\nu_0/\nu)$, solid line is fit to Vogel-Fulcher law, (c) frequency dependence of T_f plotted as $\ln(\nu)$ versus $1/(T_f - T_0)$ along with a fit to the Vogel Fulcher law, and (d) temperature dependent Ogielski plot for the $x = 0.05$ sample (inset shows the power law fit of extracted frequency independent values), (e) Critical slowing down analysis of the imaginary part of the ac- χ data at different frequencies, and (f) a linear scaling plot of $\chi''(\omega, T)/\omega^{\beta/z\nu'}$ plotted with $\epsilon/\omega^{1/z\nu'}$ using $\chi''(T)$ data, for the $x = 0.05$ sample.	112
3.8	The Rietveld refined neutron powder diffraction data for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples, (a) $x = 0.025$, (b) $x = 0.05$, and (c) $x = 0.15$, measured at 3 K. (d) and (e) show the temperature variation of the flipping ratio (R) for $x = 0.05$ and 0.15 , respectively.	116

3.9	Temperature dependent resistivity data for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples (a) $x = 0.025$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.15$, inset shows the fitting in different temperature ranges, and (e) the comparison of resistivity values for all the samples in logarithmic scale.	118
3.10	The La $3d$ (a, b) and Co $2p$ (c, d) core level photoemission spectra of $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$; $x = 0.05$ and 0.1) samples along with fitting components.	119
3.11	The core level photoemission spectra of substituted elements, Sr $3d$ (a, b) and Nb $3d$ (c, d) in $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$; $x = 0.05$ and 0.1) samples along with fitting components.	119
3.12	The normalized Co K-edge XANES spectra of the bulk $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ samples at room temperature (a) LSCNO and (e) LCNO ($x = 0-0.15$), where different features are marked with eight alphabets (A-H). The insets in (a, e) show the variation in the first-order differential around the edge jump to highlight the change in the valence state of Co ions. The deconvoluted and fitted XANES spectra with four components and one step function for the (b-d) LSCNO and (f-h) LCNO samples.	121
3.13	The normalized La L_3 -edge XANES spectra of the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ samples (a) LSCNO ($y = 2x$), and (e) LCNO ($x = 0-0.15$); insets in (a, e) panels show the change in the FWHM of the white line with x ; fitted XANES spectra with one main peak and a step function for the selected (b-d) LSCNO and (f-h) LCNO samples.	124
3.14	A comparison of the Fourier transform (FT) of the EXAFS spectra ($k^2\chi(k)$) measured at Co K-edge as a function of radial distance R for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ samples (a) LSCNO ($y = 2x$), and (b) LCNO, respectively. The FT of the EXAFS spectra is simulated with the (c) 6-model and (d) 2+4-model for LSCNO samples. The simulated FT of the EXAFS spectra with the (e) 6-model and (b) 2+4 model for the LCNO ($x = 0.025$ and 0.05) samples, all the spectra are shifted vertically with a constant factor of 0.6 for better presentation.	126
3.15	A comparison of the Fourier transform (FT) of the EXAFS spectra ($k^2\chi(k)$) of experimentally recorded data at the La L_3 -edge as a function of radial distance R for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ samples (a) LSCNO and (b) LCNO. (c, d) The experimental and simulated FT of $k^2\chi(k)$ for the LSCNO and LCNO samples, respectively, each spectrum is shifted vertically by a constant factor of 0.35 for better presentation.	129
3.16	The normalized experimental Sr K-edge absorption spectra of the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ samples ($x = 0.1$ and 0.15 ; $y = 2x$) samples, vertically shifted by a constant factor of 0.2 for clear presentation. The left and right insets present the simulated and experimental Fourier transform of the EXAFS spectra and first-order differential near inflection around the edge jump.	132

- 4.1 (a–h) The Rietveld refined x-ray diffraction patterns of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0.025\text{--}0.25$) samples; where open red circles, solid black and blue line represent the experimental, refined, and the difference between experimental and refined patterns, while green vertical markers manifest the Bragg positions corresponding to the $R\bar{3}c$ space group. (i, j) The Rietveld refined unit cell parameters plotted as a function of x 151
- 4.2 A comparison of the temperature-dependent zero-field-cooled (ZFC) and field-cooled (FC) dc-magnetic susceptibility recorded at 100 Oe and 1000 Oe applied magnetic field: (a) $x = 0.025$, (b) $x = 0.05$, (c) $x = 0.075$, (d) $x = 0.1$, and (e) $x = 0.125$, and in (f) for the $x = 0.15$ (100 Oe and 1000 Oe), $x = 0.2$ (100 Oe), and $x = 0.25$ (100 Oe) samples. 153
- 4.3 A linear fit (solid black lines) of the inverse susceptibility data (recorded at 100 Oe and/or 1000 Oe) manifests the Curie-Weiss law in the paramagnetic region of (a) 260–320 K for the $x = 0.025$ and 0.05 samples, (b) 260–320 K for the $x = 0.075$ and 0.1 samples, (c) 230–320 K for the $x = 0.125\text{--}0.25$ samples. (d) The thermomagnetic irreversibility, ΔM , for 100 Oe (solid red circles) and 1000 Oe (solid black rhombus) on a semilogarithmic left-axis, and peak/freezing (T_f) temperature from the ZFC magnetization (open blue rhombus) on right-axis as a function of x , and (e) the Curie-Weiss temperature, θ_{CW} , for 100 Oe (open magenta triangles) and 1000 Oe (open black rhombus) along with the average cobalt valence, n [open green rectangles (calculated) and solid blue rhombus (experimentally obtained using XPS)], and (f) a comparison of experimentally determined values of effective magnetic moments for susceptibility data recorded at 100 Oe and 1000 Oe magnetic fields and theoretically calculated values considering different possible spin-states of the Co ions. 154
- 4.4 The isothermal M-H loops recorded at 5 K within the applied magnetic field of ± 70 kOe for the $x = 0.125$, 0.15, and 0.25 samples; the inset highlights the variation of magnetization near the zero-magnetic field. . . 158
- 4.5 (a) A comparison of the temperature-dependent resistivity of the $x = 0.025$ and 0.05 samples at zero magnetic field, (b) the variation in resistivity with the applied magnetic field (0, 7, and 14 T) for the $x = 0.05$ sample, experimental and fitted data are shown in the open symbols and solid lines, respectively. The inset in (b) highlights the decrease in the resistivity minimum (T_{min}) with the magnetic field. (c) The variation of the low-temperature (below 100 K) fitting parameters using equation (1), σ_0 (left-axis) and a_1 (right-axis), and (d) the variation in fitting parameters in 120–200 K range using equation (3), A (first-left-axis), ρ_0 (second-left-axis), and power law-exponent (n) with the magnetic field (for the $x = 0.05$ sample) and for both the $x = 0.025$ and 0.05 samples at the zero-magnetic field. 159

- 4.6 (a) A comparison of the temperature-dependent resistivity variation of $x = 0.075$ – 0.25 samples on the semi-logarithmic scale, (b) the low-temperature resistivity fitted with the 3D-VRH model, and (c) the high-temperature resistivity data fitted with the Arrhenius model; a solid-black line presents the fit for the corresponding model and the dotted lines mark the range where the experimental curve deviates from the respective fits, and (d) the activation energy (E_a) extracted from the Arrhenius model on a linear scale and density of states near the Fermi level [$N(E_F)$] extracted from the 3D-VRH model on a semi-logarithmic scale. 164
- 4.7 The core-level x-ray photoemission spectra and the deconvoluted components of (a–c) La $3d$, (d–f) Co $2p$, (g–i) Sr $3d$, (j–l) Nb $3d$, and (m–o) O $1s$ for the $x = 0.1$, 0.15 and 0.25 samples. 167
- 4.8 The first order derivatives of the dc-magnetic susceptibility of (a) $x = 0.025$, 0.05 , and (b) $x = 0.075$, 0.1 samples measured at 100 Oe to highlight the magnetic ordering temperature (T_{MO}). 176
- 4.9 A linear fit of the inverse susceptibility data manifests the Curie-Weiss fit in the paramagnetic region of 320–260 K (solid black line) for the (a, b) $x = 0.025$ and 0.05 , (c, d) $x = 0.075$ and 0.1 samples, and the (e, f) $x = 0.125$ and 0.15 samples. The dc -susceptibility data are recorded at applied magnetic fields of 100 Oe and 1000 Oe for the $x = 0.025$ – 0.15 samples. 176
- 4.10 (a) The virgin curves for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0.125$, 0.15 and 0.25) samples at 5 K. In the virgin curves of (b) $x = 0.125$ and (c) $x = 0.15$ samples, the magnetic fields H_{m1} and H_{m2} are marked to highlight the different metamagnetic transition fields and corresponding deviations from the linear behavior, similar to ref. [64]. 177
- 4.11 A closer view of the fit of experimental resistivity data using the three dimensional (3D) weak localization (WL) and renormalized electron-electron interaction (REEI) for the (a) $x = 0.025$ and (b) $x = 0.05$ samples in the 3D limit; (c, d) temperature-dependent variation of the $\Delta\rho$ (%) = $[(\rho_{fit}(T) - \rho(T)) / \rho(T)] \times 100\%$ for the 3D and two dimensional (2D) limits of the WL and REEI combinations. 177
- 5.1 Temperature-dependent zero-field cooled (ZFC) and field-cooled (FC) magnetization data for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$ sample recorded at an applied magnetic field of (a) $H = 100$ Oe, (b) $H = 1$ kOe, and (c) $H = 10$ kOe, insets (a1, a2, and a3) highlight the freezing/peak temperature (T_f/T_p) in the ZFC curve, and insets (b1, b2, and b3) mark the irreversibility temperature (T_{irr}) in the ZFC-FC curve; (d) a linear fit (black solid line) of T_f/T_p and T_{irr} with $H^{2/3}$ using the Almeida-Thouless relation, and (e) a Curie-Weiss fit (black solid lines) in the χ^{-1} (ZFC) vs T plots for the different fields in the paramagnetic temperature range of 290–390 K. 181
- 5.2 Temperature-induced memory effect in the (a) zero-field cooled (ZFC) magnetization and (b) field-cooled (FC) magnetization at an applied magnetic field of $H = 100$ Oe; inset in each figure highlights the region which manifests the memory effect. Halts at 20 K and 100 K for 2 hrs were employed during the measurement. 183

- 5.3 Temperature variation of (a) real, and (b) imaginary components of ac-magnetic susceptibility of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$ sample at different excitation frequencies between 192.8 to 9984 Hz at an excitation field of $H_{ac} = 3$ Oe, (c) real, (d) imaginary part of ac-magnetic susceptibility recorded in the 55-62 K temperature range with 0.1 K step for better analysis. 185
- 5.4 (a) Dependence of spin relaxation time τ on the freezing temperature (T_f) with an exponential fit using the dynamical scaling law, and (b) inverse of T_f is plotted with the inverse of spin relaxation time τ along with the linear fit using the Arrhenius law, (c) dependence of freezing temperature T_f on $1/\ln(\tau/\tau_0)$ with a linear fit using another form of Vogel-Fulcher law, (d) linear power scaling graph of the χ'' data at different frequencies, and (e,f) power law scaling plots of χ'' in the log-log scale. 186
- 5.5 Measurement of aging effect for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$ at 5 K under an applied magnetic field of 1000 Oe for different waiting times (t_w) of 10^2 , 10^3 , and 10^4 sec along with the fit (solid black line) using the exponential model. Curves are shifted vertically for better presentation with a value of 0.5 emu/mole. 189
- 5.6 (a) The specific-heat data best fitted in the temperature range of 30–300 K (black solid line) using a combination of Debye and Einstein models; blue solid line presents the specific heat value regarding the Dulong-Petit law ($3nR$), inset in the graph highlights the specific heat in the spin-glass region (50–70 K), and (b) The low-temperature data of C_P/T fitted with the electronic (γT) and lattice (βT^3) effects and with an additional magnetic term ($\delta T^{3/2}$), inset presents the dependence of C_P/T with T^2 in the low-temperature regime (2–8 K). 190
- 5.7 Isothermal MH loops recorded (a) under the ZFC protocol at 5 K, 10 K, 30 K, and 50 K; under the FC protocol (b) with a cooling field of 70 kOe at 5 K, 10 K, 30 K, and 50 K, (c) with a cooling field of 50 kOe at 2 K, 10 K, 15 K, 20 K, 30 K, and 50 K, and (d) with a cooling field of 90 kOe at 5 K, 10 K, and 30 K, and; insets in each graph highlight the behavior of MH loops near zero-field. 193
- 5.8 (a) Eight cycles ($n = 1-8$) of isothermal MH loops for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$ recorded within ± 90 kOe applied magnetic field at 5 K to observe the magnetic training effect under the field cooled protocol with +50 kOe magnetic field, inset highlights the decay in the H_{EB} with the subsequent loops, (b) training effect in the exchange bias field (H_{EB}) with the number of cycles/loop index (n); the fits with the equations (5.15) and (5.17) are presented with blue dotted and black solid lines, respectively, (c) variation of the TE (%) with the number of cycles/loop index (n). 196

5.9	Temperature dependence of the exchange bias (a) field (H_{EB}) and (b) magnetization (M_{EB}) for the isothermal MH loops recorded under the 90 kOe, 70 kOe, and 50 kOe cooling fields between 2–50 K along with a fit using the exponential functions (solid black line), temperature-dependent variation of (c) coercivity (H_C) and (d) retentivity (M_r) values in the isothermal MH loops recorded with the cooling fields of 90 kOe, 70 kOe and 50 kOe between 2–50 K, and the cooling field dependence of (e) exchange bias field (H_{EB}) at 5 K with a best fit (solid black line) of the experimental data using the interface intrinsic model, and (f) exchange bias magnetization (M_{EB}) parameters at 5 K.	198
5.10	Isothermal MH loops recorded under the FC protocol with the cooling fields of ± 70 kOe at (a) 5 K, (b) 10 K, (c) 30 K, and (d) 50 K.	207
5.11	Isothermal MH loops recorded under the FC protocol (a) for a cooling field of 70 kOe loops are measured in ± 90 and 70 kOe, (b) for a cooling field of 60 kOe loops are measured in ± 90 and 60 kOe, (c) for a cooling field of 50 kOe loops are measured in ± 90 and 50 kOe, (d) for a cooling field of 40 kOe loops are measured in ± 90 and 40 kOe, (e) for a cooling field of 30 kOe loops are measured in ± 90 and 30 kOe, and (f) for a cooling field of 10 kOe loops are measured in ± 90 and 10 kOe.	208
5.12	Isothermal MH loops recorded under the FC protocol at (a) 2 K, (b) 10 K, (c) 15 K, (d) 20 K, (e) 30 K, and (f) 50 K with the different cooling and measuring fields.	208
6.1	A schematic diagram of the ultra-high vacuum compatible pulsed laser deposition setup equipped with an excimer laser of wavelength 248 nm.	212
6.2	High-resolution room temperature x-ray diffraction: (a, b) out of plane θ - 2θ patterns of LSCNO and LCNO thin films on LAO[001] substrate, respectively, (c–e) the slow scans for the LSCNO films near the (002) reflection for the LAO, LSAT, and STO substrates recorded in the triple axis mode, (f, g) reciprocal space mapping of the LSCNO and LCNO thin films on the LAO substrate along the asymmetric (220) peak, (h–j) ϕ -scans of the LSCNO and LCNO films on LAO along with the bare LAO substrate about an asymmetric (220) plane, (k–m) the slow scans for the LCNO films near the (002) reflection for the LAO, LSAT, and STO substrates recorded in the triple axis mode, respectively.	214
6.3	Atomic force microscopy images of the surface of the LSCNO and LCNO films on the (a, d) LAO, (b, e) LSAT, and (c, f) STO substrates, respectively.	217
6.4	Lorentzian peak shape fitted room temperature Raman spectra of the deposited LSCNO thin films on (a) STO, (b) LSAT, and (c) LAO substrates using an excitation wavelength of 514.5 nm.	218
6.5	De-convoluted room temperature Raman spectra of LCNO thin films on (a) STO, (b) LSAT, and (c) LAO substrates using an excitation wavelength of 514.5 nm are fitted with a Lorentzian function.	219

- 6.6 Temperature dependent resistivity of LSCNO thin films grown on (a) LAO, (b) LSAT, and (c) STO substrates, (d) logarithmic comparison of resistivity for all LSCNO and LCNO films on different substrates, and resistivity of LCNO thin films on (e) LAO, and (f) STO substrate. The insets in (a-c, e, f) exhibit fitting with the Arrhenius model in the high-temperature region and 3D variable range hopping (VRH) in the low-temperature region, and the inset in (d) shows the strain dependence of activation energy (E_a) and density of states near the Fermi level $N(E_F)$ of grown films. 221
- A.1 (a) The Rietveld refinement of the XRD pattern of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ sample. (b) A schematic of the crystal structure projected in the ac -plane (cyan color for Na; blue, magenta, and black polyhedra are formed around the V1, V2, and V3 sites, at different symmetry positions, and the red color represents the oxygen atoms), (c) the VO_6 octahedron and distribution of neighboring oxygen atoms manifests three groups of bonds as shown by grey (apical), red (basal), and magenta (farthest) colors. 238
- A.2 The temperature-dependent Raman spectra of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$, measured with (a) 514.53 nm, and (b) 632.82 nm laser wavelengths. The red dotted arrows in each graph represent the sequential measurement protocol and each curve is shifted vertically just for clarity in presentation. 241
- A.3 Raman spectrum of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ at selected temperatures measured with (a-e) 632.82 nm, and (f-j) 514.53 nm excitation wavelengths. The solid lines present the fitted individual modes using the Voigt function and a solid thick black line presents the total fit. All the Raman modes are marked with the S0-S11 notation according to their position and their assignment is presented in Table A.3. 244
- A.4 The temperature dependence of the (a-f) phonon frequency and (g-l) full-width half maximum (FWHM) of the Stokes lines (S2, S3, S4, S7, S8, and S9) in the range of 13-673 K. The green open circles and blue open triangles represent the experimentally determined values of the peak positions and FWHM, respectively. The solid black lines are the fit of an anharmonic phonon decay using equations (2) and (3), and the solid red lines represent the fit corresponding to the spin-phonon interaction using equations (4) and (5). (m) The plot between $\Delta\omega_{s-ph}$ and $[\text{M}(\text{T})/\text{M}_{max}]^2$ at ≤ 70 K for selected Raman modes and solid lines show the linear fit. . . . 246
- A.5 (a) Temperature-dependent ZFC-FC curves of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ with an applied field of 10 kOe, inset shows the Curie-Weiss fit of the FC data, (b) isothermal M-H loop recorded at 5 K, and the magnetic behavior near the origin is presented in the inset, (c) the Arrott's plot (M^2 versus H/M) from the virgin data at 5 K, and (d) the temperature-dependent resistivity data, with the fitting for the three different ranges: (e) low temperature 50-140 K using the 3D-variable range hopping model, high-temperature range of (f) 260-190 K with the nearest-neighbor hopping model, and (g) 290-370 K using an Arrhenius model. The solid black line in (e-g) manifests the fitting of the experimental data and the dotted red lines exhibit the range where the experimental data deviate from the respective models. 251

- A.6 (a) The O 1s and V 2p, and (b) Na 1s core-levels, (c) the XANES curves compared (vertically shifted for the clarity in presentation) with the references V₂O₅ and VOSO₄ samples for the 5+ and 4+ oxidation states, respectively; this comparison is further highlighted in the inset, (d) the linear combination fitting of the XANES spectra using the standard samples for 5+ and 4+ oxidation states, and (e) the Fourier transformed EXAFS curve of the β -Na_{0.33}V₂O₅ sample at the V K-edge where the open circles present the experimental data and the solid black lines are the best fits to the data. 253

List of Tables

1.1	A complete list of the different tilt systems in perovskites [26].	6
2.1	Characteristic x-rays of different metal targets used as anode in the x-ray tube [4].	46
3.1	The Rietveld refined parameters of $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples; the lattice parameters and unit cell volume obtained from the Rietveld refinement of x-ray diffraction patterns, and the bond lengths and bond-angles are obtained from the Rietveld refinement of neutron powder diffraction patterns measured at 300 K.	100
3.2	The strain parameter is $e_t = (c_{pc}-a_{pc})/(c_{pc}+a_{pc})$. c_{pc} and a_{pc} are the pseudocubic lattice constants given by $c/\sqrt{12}$ and $a/\sqrt{2}$. The distortion parameter Δ_d for the La-O polyhedra. The ϕ_1 is the tilting angle about the z-axis for BO_6 octahedra. The average bond valence sum (BVS) for the B and A sites are v_B and v_A , respectively.	103
3.3	Experimentally determined fitting parameters (from FC inverse susceptibility data), Curie constant (C) in $\text{emu}\cdot\text{K}\cdot\text{mole}^{-1}$, effective magnetic moment (μ_B) and calculated average spin (S_{av}) for $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples.	107
3.4	Calculated values of density of states $N(E_F)$ by VRH model fitting and activation energy E_a by Arrhenius equation fitting, and other fitting parameters for $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($y = 2x$) samples.	117
3.5	The fitting parameters of EXAFS curves for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ (LSCNO, $y = 2x$) samples obtained using the two different models at the Co K-edge.	127
3.6	The EXAFS curve fitting parameters, bond-length (\AA), DW factor ($\times 10^{-3}\text{\AA}^2$) for the $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ samples (LSCNO; $y = 2x$ and LCNO; $y = 0$) measured at the La L_3 -edge.	130
4.1	The Rietveld refined parameters obtained for the $x = 0.025$ – 0.25 samples with $R\bar{3}c$ space group using the hexagonal setting with their rhombohedral equivalents.	152
4.2	Experimentally estimated values of ZFC peak/freezing temperature (T_f), magnetic ordering temperature (T_{MO}), Curie-Weiss temperature θ_{CW} , experimentally determined $\mu_{\text{eff}}^{\text{expt.}}$ with theoretically calculated $\mu_{\text{eff}}^{\text{calc.}}$ for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0$ – 0.25) samples.	157
4.3	A comparison of the fitting parameters of the temperature-dependent resistivity data in the low, intermediate, and high-temperature regions for the $x = 0.025$ and 0.05 samples.	162

4.4	Experimentally determined values of the density of states at Fermi level, $N(E_F)$ from 3D-VRH model and thermal activation energy (E_a) from the Arrhenius model for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0.075\text{--}0.25$) samples. The mean hopping distance (R_H) and mean hopping energy (W_H) are calculated for the 3D-VRH model.	165
5.1	Parameters obtained from the fitting of stretched exponential function with magnetic relaxation.	188
5.2	Experimentally estimated values of exchange bias for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$ from the measurements performed under the 0 kOe, +90 kOe cooling field and under the ± 70 kOe and +50 kOe cooling field.	194
5.3	Fitting parameters obtained from the exponential fitting of H_{EB} and M_{EB} at different cooling fields for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$	199
5.4	Fitting parameters obtained from the intrinsic interface effect of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.85}\text{Nb}_{0.15}\text{O}_3$	199
6.1	Lattice mismatch induced strain and fitted parameters from the temperature-dependent resistance data of LSCNO films grown on different single crystal substrates.	215
A.1	Wyckoff Positions and atomic parameters of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ compound obtained from the Rietveld refinement of powder x-ray diffraction pattern using space group $C2/m$	239
A.2	The multiplicity and bond-lengths of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ sample obtained from the Rietveld refinement of room temperature powder x-ray diffraction pattern for different V-sites, namely, V1, V2, and V3.	239
A.3	The experimentally observed frequencies (ω_{obs}) of the Raman modes in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ (NVO) at room temperature are compared with polycrystalline [8], and single-crystalline [28] NVO samples. The assignment as well as the origin of individual modes are summarized according to the published room temperature data on single-crystalline AV_2O_5 ($A = \text{Na}, \text{Ca}, \text{Mg}, \text{Cs}$) [40] and NaV_2O_5 [41] samples.	243
A.4	Anharmonic fit parameters determined for the phonon frequency (ω_0 , A) and full-width at half-maximum (Γ_0 , B) of the individual Raman modes of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$	247
A.5	The EXAFS fitting parameters from the V K-edge of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ sample; path degeneracy, effective bond lengths (R_{eff}), scattering paths, and the D-W factor.	255