

THERMOELECTRIC PROPERTIES OF OXIDES AND OTHER NOVEL COMPOUNDS

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THERMOELECTRIC PROPERTIES OF OXIDES AND OTHER NOVEL COMPOUNDS

by

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Submitted

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to the



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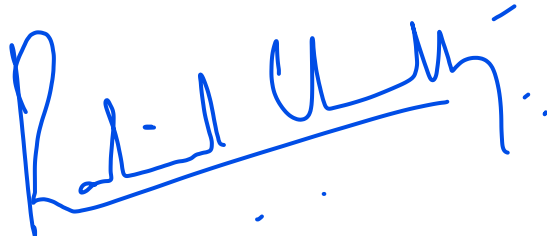
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Dedicated to my Mother

CERTIFICATE

This is to certify that the thesis entitled “**Thermoelectric properties of oxides and other novel compounds**”, which is being submitted by **Mr. Divya Prakash Dubey** to the **Indian Institute of Technology Delhi**, New Delhi, India, for the award of the degree of **Doctor of Philosophy** in Physics, is a record of bonafide research work carried out by him. 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.



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ABSTRACT

The exponentially increasing requirement and usage of energy in our daily life has given rise to a big push to the research in the area of ‘renewable energy’. Among various existing solutions for renewable energy like solar, geo-thermal, wind, ocean etc., use of thermoelectric materials takes the centre-stage. Thermoelectric materials work on the principle of interconversion of heat energy (e.g., industrial waste heat) to electrical energy and thus are seen as efficient source of energy without any adverse effect on climate and human environment. In this field intensive research is ongoing in search of novel materials with large energy conversion efficiency and the ability to replace the existing sources of energy like fossil fuel or coal. The conversion efficiency of the thermoelectric material is decided by a dimensionless parameter called “Figure of Merit” i.e., $ZT = S^2\sigma T/\kappa$; where, S , σ and κ are Seebeck coefficient, electrical conductivity and thermal conductivity respectively. In order to replace the existing energy solutions, the required ZT values are $\sim 4-5$; however, till now the maximum ZT observed is ~ 2.5 to 2.8 for SnSe based compositions. The main impediment in improving the thermoelectric efficiency is the interdependence of the parameters defining the ZT . To have good thermoelectric efficiency, a high value of Seebeck coefficient and electrical conductivity along with a low thermal conductivity is required.

Hence, in this thesis, we have focused our work on the study of oxides and chalcogenides-based compositions for enhancing the thermoelectric efficiency near room temperature. For this, initially we present the results of a comprehensive investigation of electric and thermal transport properties of polycrystalline $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$. We first investigate the lattice modulation effect via heavy element doping within the system. For this a comprehensive investigation of electric and thermal transport properties of polycrystalline Bi substituted $\text{La}_{0.95-x}\text{Bi}_x\text{Sr}_{0.05}\text{CoO}_3$ for (LBSCO-0, 1 & 2) performed. The electrical resistivity reflects the semiconducting nature with n-type to p-type transition $\sim 52\text{K}$ for LBSCO-1 and LBSCO-2 samples. In the low temperature region, the dominant transport mechanism is found to be variable range hopping (VRH), with hopping range decreasing with increasing temperature from 95 to $20 \text{ \AA}$. The substitution of higher atomic weight element Bi at La site drastically affects overall thermal conductivity by reducing the lattice contribution ($\sim 0.12\text{W/m-K}$ at 50K) and also enhancing the Seebeck coefficient ($S \sim 354 \mu\text{V/K}$). The increase in the resistivity and Seebeck coefficient for the Bi-substituted system is related to the decrease in the available

charge carrier concentration ($\sim 5.12 \times 10^{20} \text{ cm}^{-3}$). The overall variation in the Seebeck coefficient depicts a complex nature with a large decreasing trend below 50K followed by an in-depth analysis of the Debye temperature ($\sim 470\text{K}$) and e - ph coupling. These findings suggest the Bi-substituted LBSCO system have phonon mediated charge transport via phonon drag effect below 50K . Notably, we found a large increment in $ZT \sim 0.17$ at RT for LBSCO-2 composition that is 1-order larger than pristine undoped LBSCO-0 and even higher than the other existing cobaltite's-based thermoelectric choice.

In the second part, we analysed the effect on magnetic ion substitution on the thermoelectric properties. For this, a detailed investigations on electrical, magnetic, and thermal transport properties of a series of polycrystalline samples of Cr-substituted $\text{La}_{0.65}\text{Bi}_{0.20}\text{Sr}_{0.15}\text{CoO}_3$ ($x = 0, 0.10, 0.15, 0.20$ and 0.25) have been performed in the view of thermoelectric applications. The optimized composition of $x = 0.25$ has been arrived at by studying the temperature and field dependent properties of samples; where both Co and Cr have mixed valency, that give rise to interesting magnetic ordering, effective at low temperatures. A p-type nature for all compositions observed from Seebeck and Hall coefficient measurements. An in-depth analysis of electrical and thermal transport provides well understanding for the various conduction mechanisms (i.e., small polaron hopping, variable range hopping and phonon drag) involved at different temperature regimes. The Seebeck coefficient increases with Cr-substitution ($S_{\text{max}} \sim 660 \mu\text{V/K}$ for Cr-25 at 115K) while electrical conductivity decreases. This decrease in electrical conductivity is due to decrease in the mobility and charge carrier concentration ($\sim 1.27 \times 10^{21} \text{ cm}^{-3}$ for Cr-25). The value of thermal conductivity is found to be strongly suppressed (6-fold) in Cr-doped compositions $\sim 0.46 \text{ W/m-K}$ for Cr-25. Another important feature is the field dependent Seebeck, electrical and thermal conductivity measurements which show the negative magnetoresistance of the Cr-25 and helps to improve the electrical conductivity and hence thermoelectric efficiency at low temperatures. The field induced increment in thermoelectric efficiency i.e $\Delta ZT \sim 500\%$ observed for 9Tesla at 50K . This provides an effective scheme for magnetically tuned thermoelectricity at low temperatures.

In the third part, we report a detailed investigations of sample dimensionality and correlated electrical and thermal transport behaviour in the view of thermoelectric applications. For this we compared the bulk, thin film and nano ribbon of $\text{La}_{0.75}\text{Bi}_{0.20}\text{Sr}_{0.05}\text{CoO}_3$ composition that have been synthesized using solid state reaction, PLD and electrospinning technique

respectively. Reducing the dimension helps to minimize the scattering processes that affects both the electrical and thermal conductivity. We observed increase in Seebeck coefficient by going from bulk to thin film and then nano ribbons, however, the thermal conductivity gets suppressed significantly. Both these effects help to improve the thermoelectric efficiency of the system. However, with decreasing lattice dimension, the electrical resistivity gets increased from bulk to thin film to nano ribbons by several orders. The overall ZT value is observed to be maximum for thin film i.e., ~ 0.24 , which is highest among the existing bulk/ thin-film literatures of cobaltite system. This study gives a detailed information of various transport mechanism and scattering process activated in different dimensional and temperature regimes of complex oxide system.

The last part of this thesis is focused to investigate the charge density wave property of a chalcogenide system using thermoelectric characterizations. For this, we investigate the CDW characteristics of a highly pure single crystal of Ta_2NiSe_7 through electrical and thermal transport measurements. In addition to the observed $2k_F$ anomaly at $\sim 78.5\text{K}$, we identify an additional feature at around 146K , associated with $4k_F$ CDW modulations within the system. The distinct spiro-step-like feature observed at low temperatures is discussed in terms of phase-slip and quantized conductivity phenomena. We analyse the pinning-depinning behavior of CDW transport through I-V characteristics for both applied DC and AC + DC electric fields. We propose a revised two-band model for this system, introducing the concept of p to n-type carrier inversion for $T < 50\text{K}$. Our examination of Seebeck, thermal conductivity, and specific heat data supports the coexistence of both types of CDW modulations. Furthermore, theoretical calculations using GGA+U validate the presence of both $2k_F$ and $4k_F$ CDW modulations and emphasize the role of the electron pocket at the Fermi surface in the formation of CDW in this system.

Thus, this study provides a comprehensive analysis of thermoelectric properties of oxide i.e., $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$ and a novel compound i.e., Ta_2NiSe_7 along with their correlated electrical and thermal transport behaviour. The focused exploration of these systems underscores the significance findings in the context of potential applications for thermoelectric energy generators.

सारांश

हमारे दैनिक जीवन में ऊर्जा की तेजी से बढ़ती आवश्यकताओं एवं उनके अनुप्रयोग ने 'नवीकरणीय ऊर्जा' के क्षेत्र में अनुसंधान को एक विस्तृत प्रसार प्रदान किया है। सौर, भू-तापीय, पवन, महासागर आदि जैसे नवीकरणीय ऊर्जा के विभिन्न मौजूदा समाधानों में, तापविद्युतीय पदार्थों का उपयोग नवीकरणीय ऊर्जा से सम्बद्ध अनुसंधान के केंद्र-स्थान पर है। तापविद्युतीय पदार्थ उष्मीय ऊर्जा (उदाहरण के लिए, औद्योगिक अपशिष्ट ताप) को विद्युतीय ऊर्जा में परिवर्तित करने के सिद्धांत पर काम करती हैं और इस प्रकार उन्हें जलवायु और मानव पर्यावरण पर किसी भी प्रतिकूल प्रभाव के बिना ऊर्जा के कुशल स्रोत के रूप में देखा जाता है। इस क्षेत्र में बड़ी ऊर्जा रूपांतरण दक्षता और जीवाश्म ईंधन या कोयले जैसे ऊर्जा के मौजूदा स्रोतों को प्रतिस्थापित करने की क्षमता वाली नवीन पदार्थों की खोज के सन्दर्भ में गहन अनुसंधान जारी है। तापविद्युतीय पदार्थों की रूपांतरण दक्षता "फिगर ऑफ मेरिट" ZT नामक एक आयामहीन घटक द्वारा तय की जाती है, अर्थात्, $ZT = (S^2 \sigma T) / \kappa$; जहां, S , σ और κ क्रमशः सीबेक गुणांक, विद्युत चालकता और तापीय चालकता हैं। मौजूदा ऊर्जा समाधानों को बदलने के लिए, आवश्यक ZT मान $\sim 4-5$ हैं; हालाँकि, अब तक देखा गया अधिकतम ZT , SnSe आधारित संयोजनों के लिए ~ 2.5 से 2.8 है। तापविद्युतीय दक्षता में सुधार में मुख्य बाधा ZT को परिभाषित करने वाले मापदंडों की अन्योन्याश्रयता है। एक बेहतर तापविद्युतीय दक्षता के लिए, कम तापीय चालकता के साथ सीबेक गुणांक और विद्युत चालकता के उच्च मूल्य की आवश्यकता होती है।

इसलिए, इस शोध ग्रन्थ में हमने वातावरणीय तापमान के निकट तापविद्युतीय दक्षता को बढ़ाने के लिए ऑक्साइड और चॉल्कोजेनाइड आधारित संयोजनों के अध्ययन पर अपना शोध केंद्रित किया है। इसके लिए, शुरुआत में हम बहु माणभीय $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$ के विद्युतीय और तापीय परिवहनीय गुणों की व्यापक अनुसंधान के परिणाम प्रस्तुत करते हैं। हम पहले इस संयोजन के भीतर भारी तत्वों (Bi) के प्रतिस्थापन के माध्यम से जालकों के प्रादुर्भावित प्रभाव की विवेचना करते हैं। इसके लिए बहु माणभीय $\text{La}_{0.95-x}\text{Bi}_x\text{Sr}_{0.05}\text{CoO}_3$ संयोजनों के विद्युतीय और तापीय परिवहनीय गुणों का तापविद्युतीय दक्षता के प्रभाव की जांच की गई। विद्युत प्रतिरोधकता इस संयोजन के नमूनों के लिए एन-प्रकार से पी-प्रकार विद्युतीय संक्रमण ($\sim 52\text{K}$) के साथ अर्धचालक

प्रकृति को दर्शाती है। कम तापमान वाले क्षेत्र में, प्रमुख परिवहन वैरिएबल रेंज हॉपिंग (VRH) द्वारा प्रेरित होता है, जिसमें तापमान बढ़ने के साथ हॉपिंग रेंज 95 से 20 Å तक कम हो जाती है। La के स्थान पर पर उच्च परमाणु भार तत्व Bi का प्रतिस्थापन जलकीय तापीय चालकता (50K पर $\sim 0.12 \text{ W/m-K}$) को कम करके और सीबेक गुणांक ($S \sim 354 \mu\text{V/K}$) को बढ़ाकर समग्र तापीय चालकता को काफी प्रभावित करता है। द्वि-प्रतिस्थापित प्रणाली के लिए प्रतिरोधकता और सीबेक गुणांक में वृद्धि उपलब्ध आवेश वाहक एकाग्रता ($\sim 5.12 \times 10^{20} \text{ cm}^{-3}$) में कमी से संबंधित है। सीबेक गुणांक में समग्र भिन्नता एक जटिल प्रकृति को दर्शाती है जिसमें 50K से नीचे एक बड़ी घटती प्रवृत्ति के साथ डीबाई तापमान ($\sim 470\text{K}$) और इलेक्ट्रॉन फोनन युग्मन का गहन विश्लेषण किया गया है। इन निष्कर्षों से पता चलता है कि द्वि-प्रतिस्थापित $\text{La}_{0.95-x}\text{Bi}_x\text{Sr}_{0.05}\text{CoO}_3$ प्रणाली में 50K से नीचे फोनन ड्रैग प्रभाव के माध्यम से फोनन मध्यस्थ आवेश परिवहन होता है। विशेष रूप से, हमने 20% Bi संयोजनों के लिए वातावरणीय तापमान पर $ZT \sim 0.17$ में एक बड़ी वृद्धि पाई है जो कि प्राचीन अघोषित संयोजनों से 10 गुना बड़ा है और अन्य मौजूदा कोबाल्टाइट-आधारित तापविद्युतीय विकल्प से भी अधिक है।

दूसरे भाग में, हमने तापविद्युतीय गुणों पर चुंबकीय आयन प्रतिस्थापन के प्रभाव का विश्लेषण किया। इसके लिए, Cr-प्रतिस्थापित $\text{La}_{0.65}\text{Bi}_{0.20}\text{Sr}_{0.15}\text{CoO}_3$ ("x = 0, 0.10, 0.15, 0.20 और 0.25") के बहु माणभीय नमूनों की एक श्रृंखला के विद्युत, चुंबकीय और तापीय परिवहन गुणों पर विस्तृत जांच की गई है। तापविद्युतीय अनुप्रयोगों की दृष्टि से नमूनों के तापमान और चुंबकीयक्षेत्र पर निर्भर गुणों का अध्ययन करके "x = 0.25" की अनुकूलित संरचना प्राप्त की गई है; जहां Co और Cr दोनों में मिश्रित संयोजकताएं होती हैं, जो रोचक चुंबकीय क्रम को जन्म देती हैं, जो कम तापमान पर प्रभावी होती हैं। सीबेक और हॉल गुणांक माप से सभी संयोजनों के लिए पी-प्रकार की विद्युतीय प्रकृति देखी गई। विद्युत और तापीय परिवहन का गहन विश्लेषण विभिन्न तापमान प्रवस्थाओं में शामिल विभिन्न चालन तंत्रों (यानी, छोटे पोलरॉन हॉपिंग, वैरिएबल रेंज हॉपिंग और फोनन ड्रैग) के लिए अच्छी समझ प्रदान करता है। सीबेक गुणांक Cr-प्रतिस्थापन (115K पर Cr-25 के लिए $S_{\text{max}} \sim 660 \mu\text{V/K}$) के साथ बढ़ता है जबकि विद्युत चालकता कम हो जाती है। विद्युत चालकता में यह कमी गतिशीलता और आवेश वाहक एकाग्रता में कमी (Cr-25 के लिए $\sim 1.27 \times 10^{21} \text{ cm}^{-3}$) के कारण है। Cr- प्रतिस्थापित संयोजनों में तापीय चालकता का मान अत्यधिक न्यून (6-गुना कम) पाया गया है जो की Cr-

25 के लिए ~ 0.46 W/m-K है। एक अन्य महत्वपूर्ण विशेषता चुंबकीय क्षेत्र पर निर्भर सीबेक, विद्युत और तापीय चालकता माप है जो Cr-25 के नकारात्मक चुंबकत्व और विद्युत चालकता को दर्शाता है और इसलिए कम तापमान पर तापविद्युतीय दक्षता में सुधार करने में मदद करता है। तापविद्युतीय दक्षता में क्षेत्र प्रेरित वृद्धि यानी $\Delta ZT \sim 500\%$, 50K पर 9T के लिए देखी गई। यह कम तापमान पर चुंबकीय रूप से प्रवर्धित तापविद्युतकीय के लिए एक प्रभावी योजनाविधि प्रदान करता है।

तीसरे भाग में, हम तापविद्युतकीय अनुप्रयोगों के मद्देनजर आयाम और सहसंबद्ध विद्युत और तापीय परिवहन व्यवहार की विस्तृत जांच की रिपोर्ट करते हैं। इसके लिए हमने $\text{La}_{0.75}\text{Bi}_{0.20}\text{Sr}_{0.05}\text{CoO}_3$ संरचना के ठोस, पतली फिल्म और नैनो रिबन की तुलना की, जिन्हें क्रमशः ठोस अवस्था प्रतिक्रिया, PLD और इलेक्ट्रोस्पिनिंग तकनीक का उपयोग करके संश्लेषित किया गया है। आयाम को कम करने से विक्षेपण वाली प्रक्रियाओं को कम करने में मदद मिलती है जो विद्युत और तापीय चालकता दोनों को प्रभावित करती है। हमने ठोस से पतली फिल्म और फिर नैनो रिबन तक जाकर सीबेक गुणांक में वृद्धि देखी, हालांकि, तापीय चालकता काफी कम हो जाती है। ये दोनों प्रभाव संयोजन की तापविद्युतकीय दक्षता को बेहतर बनाने में मदद करते हैं। हालाँकि, आयाम में कमी के साथ, विद्युत प्रतिरोधकता ठोस से पतली फिल्म से लेकर नैनो रिबन तक कई क्रमों तक बढ़ जाती है। समग्र ZT मान पतली फिल्म के लिए अधिकतम यानी ~ 0.24 देखा गया है, जो कोबाल्टाइट प्रणाली के मौजूदा ठोस /पतली-फिल्म साहित्य में सबसे अधिक है। यह अध्ययन जटिल ऑक्साइड प्रणाली के विभिन्न आयामी और तापमान क्षेत्र में सक्रिय विभिन्न परिवहन तंत्र और बिखरने की प्रक्रिया की विस्तृत जानकारी देता है।

इस शोध ग्रन्थ का अंतिम भाग तापविद्युतीय लक्षण के वर्णन का उपयोग करके चॉल्कोजेनाइड संयोजनों की आवेश घनत्व तरंग (CDW) प्रकृति की विवेचना पर केंद्रित है। इसके लिए, हम Ta_2NiSe_7 के अत्यधिक शुद्ध एकल क्रिस्टल की CDW विशेषताओं की जांच विद्युत और तापीय परिवहन माप के माध्यम से करते हैं। लगभग 78.5K पर देखी गई $2k_F$ विसंगति के अलावा, हम लगभग 146K पर एक अतिरिक्त विसंगति की पहचान करते हैं, जो इस संयोजन के भीतर $4k_F$ CDW विक्षोभ से जुड़ी है। कम तापमान पर देखी गई विशिष्ट सीढ़ीनुमा विद्युत चालकता की चर्चा चरणवत प्रतिस्थापित और परिमाणित चालकता के संदर्भ में की जाती है। हम दिष्ट धारा और प्रत्यावर्ती धारा एवं दिष्ट धारा दोनों के लिए विद्युत क्षेत्रों में I-V विशेषताओं के

माध्यम से CDW परिवहन के सम्बद्ध-विमुक्त व्यवहार का विश्लेषण करते हैं। हम इस प्रणाली के लिए एक संशोधित द्विक्षेत्र मॉडल का प्रस्ताव करते हैं, जिसमें $T < 50\text{K}$ के लिए पी से एन-प्रकार के विद्युतीय वाहक व्युत्क्रम की अवधारणा को प्रस्तुत किया गया है। सीबेक, तापीय चालकता और विशिष्ट ऊष्मा की हमारी जांच दोनों प्रकार के CDW विक्षोभ के सह-अस्तित्व का समर्थन करती है। इसके अलावा, GGA+U का उपयोग करते हुए सैद्धांतिक संगणकीय गणना $2k_F$ और $4k_F$ CDW विक्षोभ दोनों की उपस्थिति को मान्य करती है और इस प्रणाली में CDW के निर्माण में फर्मी सतह पर इलेक्ट्रॉन पॉकेट की भूमिका पर जोर देती है।

इस प्रकार, यह अध्ययन ऑक्साइड यानी $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$ और एक नए यौगिक यानी Ta_2NiSe_7 के तापविद्युतीय गुणों के साथ-साथ उनके सहसंबद्ध विद्युतीय और तापीय परिवहन के व्यवहार का व्यापक विश्लेषण प्रदान करता है। इन प्रणालियों पर केंद्रित अन्वेषण तापविद्युतीय ऊर्जा जनित्र के लिए संभावित अनुप्रयोगों के संदर्भ में महत्वपूर्ण निष्कर्षों को रेखांकित करता है।

CONTENT

Certificate.....	i
Acknowledgments.....	ii
Abstract	v
List of Figures	xi
List of Tables	xviii
Chapter 1: Introduction	1
1.1 Fundamentals of Thermoelectricity	2
1.1.1 What is Thermoelectrics ?.....	2
1.1.2 Categorizing the Thermoelectric material.....	3
1.1.3 Review of Thermoelectric materials availabale in literature	4
1.2 Physics of Thermoelectric Module	12
1.3 Working Principle.....	14
1.4 Parameter of interst	18
1.4.1 Electrical concuctivity.....	19
1.4.2 Seebeck coefficient	20
1.4.3 Thermal conductivity	21
1.5 Application of Thermoelectric materials	24
1.6 Background and Motivations	25
1.6.1 Oxides for near room temperature thermoelectric applications	25
1.6.2 Charge density wave properties in novel quasi-1D system.....	28
1.7 Research gaps.....	30
1.8 Objectives of the thesis	31
1.9 Organization of the thesis	31
Chapter 2: Experimental Techniques & Characterization Details	35
2.1 Material synthesis for sample preparation	36
2.2.1 Sample preparation for La-cobaltite.....	36
2.2.1 Sample preparation for single crystal of ternary chalcogenides	37
2.2 Structural, elemental, chemical and morphological charecterizations	37
2.2.1 X-ray diffraction (XRD)	38
2.2.2 Energy Dispersive X-ray Spectroscopy (EDS)	39
2.2.3 Scanning electron microscope (SEM).....	41
2.2.3 X-ray photoelectron spectroscopy (XPS).....	42
2.3 Physical property measurements (PPMS)	46

2.3.1 Vibrating Sample Magnetometry (VSM).....	46
2.3.2 DC & AC electrical conductivity measurements	48
2.3.3 Hall coefficient measurements.....	50
2.3.4 Thermal transport measurements	52
2.3.5 Specific heat measurements	56
Chapter 3: Effect of heavy element (Bi) substitution on thermoelectric properties of La_{0.95}Sr_{0.05}CoO₃.....	57
3.1 Introduction.....	58
3.2 Experimental Details.....	60
3.3 Results and Discussion	59
3.3.1 Structural, morphological and chemical analysis.....	60
3.3.2 Electrical resistivity analysis.....	63
3.3.3 Thermal conductivity analysis	65
3.3.4 Seebeck coefficient analysis	68
3.3.5 Specific heat analysis	70
3.3.6 Thermoelectric efficiency analysis	71
3.4 Conclusions.....	71
Chapter 4: Effect of magnetic ion substitution on thermoelectric properties of La_{0.95}Sr_{0.15}CoO₃.....	72
4.1 Introduction.....	73
4.2 Experimental Details.....	73
4.3 Results.....	75
4.3.1 Structural, morphological and chemical analysis.....	76
4.3.2 Electrical resistivity analysis.....	81
4.3.3 Magnetic analysis.....	85
4.3.4 Thermal conductivity analysis	87
4.3.5 Specific heat analysis	88
4.3.6 Seebeck coefficient analysis	89
4.3.7 Thermoelectric efficiency analysis	90
4.4 Discussions	91
4.5 Conclusions.....	96
Chapter 5: Evidence of incommensurate charge density wave in Ta₂NiSe₇ single crystals using thermoelectric measurements	96
5.1 Introduction.....	97
5.2 Experimental Details.....	97
5.3 Results and Discussion	98

5.3.1 Structural, elemental and morphological analysis	99
5.3.2 Electrical resistivity analysis.....	101
5.3.3 Hall and magneto-transport analysis.....	103
3.3.4 Seebeck coefficient analysis	104
3.3.5 Thermal transport analysis	105
3.3.6 Quantized electrical conductivity analysis.....	106
3.3.6 Dynamic AC & DC conductivity analysis.....	108
3.3.6 Theoretical calculations for CDW analysis.....	109
5.4 Conclusions.....	114
Chapter 6: Summary and Future Perspective	114
6.1 Summary.....	115
6.2 Future Perspective.....	117
References.....	120
APPENDICES	139
APPENDIX-A	156
A.1 Effect of dimensional reduction on thermoelectric properties of $\text{La}_{0.75}\text{Bi}_{0.20}\text{Sr}_{0.05}\text{CoO}_3$	143
APPENDIX-B.....	156
B.1 DFT+Hubbard theory	157
B.2 Calculations parameters	159
Publication in International Journals	160
Mauscript under preparation	160
Other Journal Publications (<i>not part of the thesis</i>)	160
List of International Conferences.....	160
International Fellowship	160
Author's Biography	161

LIST OF FIGURES

Figure no.	Figure caption	Page no.
1.1	Interdependency of different thermoelectric parameters	3
1.2	Development of thermoelectric research from various class of material choices	5
1.3	Chronological development of thermoelectric research for different material choices	9
1.4	Number of articles published on thermoelectric research from different class of material	10
1.5	Number of articles published on Bulk, thin film, nano and single crystals in comparison to all thermoelectric research in the literature	12
1.6	Schematic diagram for thermoelectric material as generator (left) and refrigerator (right)	12
1.7	Schematic diagram for Seebeck effect	13
1.8	Schematic diagram for Peltier effect	14
1.9	Schematic diagram for basic contact	14
1.10	Schematic diagram for contact and associated band diagram	15
1.11	Schematic diagram for contact and associated band diagram for temperature effect	16
1.12	Schematic diagram for Peltier effect and heat current	17
1.13	Different coefficient of current during conduction and its physical relevance	18
1.14	Variation of different parameter with carrier concentration	24
1.15	Oxide thermoelectric materials having their highest ZT value over different temperatures	26
1.16	(a) Magnetic transition and (b) variation of ZT with Sr content in of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$	27
1.17	Band diagram and variation in charge density with modulation in lattice	29
2.1	Schematic diagram showing the different steps of solid-state reaction method	36

2.2	The schematics of: (top) physical vapour transport and (bottom) chemical vapour transport.	37
2.3	Diffraction of X-rays from a set of atomic planes under Bragg's condition.	38
2.4	Schematic diagram showing the working principle of EDS.	40
2.5	Schematic representation of the electron beam in SEM, (b) the electron beam interaction volume	41
2.6	The experimental set-up of SEM (Zeiss EVO 50).	42
2.7	The energy diagram demonstrated photoelectric effect	43
2.8	Schematic diagram for XPS instrument	44
2.9	PPMS instrument (left), probe which is placed inside Dewar (centre), Sample space inside the magnet where VSM coil, and sample puck for transport measurements (right)	46
2.10	Schematic diagram for the operation of PPMS instrument (for CFMS-PPMS Cryogenics Ltd).	47
2.11	Diagram for the internal instrumentation of PPMS (for CFMS-PPMS Cryogenics Ltd).	48
2.12	Schematic diagram for the Resistivity Probe in the PPMS CFMS-PPMS Cryogenics Ltd.	49
2.13	(a) Probe end for the Resistivity Probe front and rear view, (b) Break-out box for the connection arrangements, (c) sample puck attached to the probe-end, (d) the outer assembly at the top of the Resistivity Probe.	50
2.14	The RnX unit for Hall measurement and assigned connection in the software	50
2.15	Schematic for the all-possible connection that is rotated through RnX unit during Hall measurement	51
2.16	Data acquisition through RnX unit for Hall coefficient measurement	52
2.17	Circuit diagram for the TT-Probe end electrical connections	54
2.18	(a) Schematic for the TT-Probe end, (b) heater and thermocouples pins for TT-measurement	54
2.19	Measurement window for the TT-measurement where the thermal conductance and Seebeck coefficient values measured using the slop of curve between heater power and Seebeck voltage vs delta T.	55

2.20	Measurement window for the relaxation heat capacity measurement where the heat capacity is calculated using the time constant by both heating and cooling curve during the ON-current and OFF-current of heat pulse.	56
2.21	Schematic diagram for the probe-end for the Relaxation Heat Capacity measurement	57
3.1	(a) Room temperature powder XRD data for all LBSCO sample, (b) magnified view of the peak around $2\theta \approx 33.5^\circ$ (c) refinement of the LBSCO-0 sample with Bragg diffraction pattern and (d) schematic of crystal structure.	61
3.2	EDX with elemental mapping for LBSCO-2 sample	62
3.3	SEM image for LBSCO-0, 1 and 2 compositions.	62
3.4	(a, b) Core level XPS spectra for Bi and Co for both LBSCO-1, 2 and fitted plot for Bi-4f (c), Co-2p (d) for LBSCO-2.	63
3.5	(a) Electrical resistivity of the LBSCO-0, 1 and 2 samples, inset zoom view around $T \approx 45K$ (b) Hall coefficient and carrier concentration variation with temperature around 45K for LBSCO-2 sample (c) VRH fitting for both LBSCO-1, 2 samples (d) hopping energy and hopping range variation with temperature for LBSCO-2.	64
3.6	(a) The variation of thermal conductivity with temperature for all LBSCO-0, 1, and 2 samples (b) electronic contribution and (c) phononic contribution to the thermal conductivity with temperature for LBSCO-1.	66
3.7	Fitting of $\kappa \propto T^3$ above 70K for all samples.	67
3.8	Variation of Seebeck coefficient with temperature for all compositions.	68
3.9	Variation of Seebeck and thermal conductivity for $T < 80K$ for LBSCO-1 & 2.	69
3.10	Variation of Specific heat with temperature for LBSCO-2 composition.	70
3.11	Variation of ZT with temperature for all compositions and compare the efficiency of this work with available oxide thermoelectric choices (inset).	71
4.1	Room temperature XRD data for all samples with refinement and zoomed plot for the peak around $2\theta \approx 33.5^\circ$ (a-e), schematic of crystal structure (f), variation of lattice parameters a & c and c/a (g).	76

4.2	Variation of bond angle, bond length, porosity, strain and density with Cr-substitution	77
4.3	SEM micrograph for all prepared sample Cr-0, Cr-10, Cr-15, Cr20 and Cr-25 (a-e), EDX spectra of Cr-25 for elemental analysis (f), elemental mapping of all constituent elements La, Sr, Bi, Co, Cr and O (g-l).	79
4.4	Room temperature XPS spectra of Cr-25 for the core level peak of Bi (a), Co (b) and Cr (c) with wide scan spectrum for all constituent elements (d), RAMAN spectra for all compositions recorded at room temperature with 514 nm wavelength (h).	80
4.5	Core level XPS spectra for Sr and La for Cr-25 composition.	80
4.6	Core level XPS spectra for Co-0 and Co-25, Cr-25 composition with relative peak intensity of $\text{Co}^{3+}/\text{Co}^{4+}$ and $\text{Cr}^{3+}/\text{Cr}^{4+}$ respectively.	81
4.7	(a) Variation of electrical resistivity with temperature for all the composition, (b) fitting of resistivity data with VRH, (c) Fitting parameter hopping energy and range variation with temperature for all compositions, (d) SPH fitting of resistivity data, (d) Debye temperature and electron-phonon coupling strength variation with the composition, (f) field dependent resistivity variation for Cr-25.	82
4.8	Variation of W_H , W_D , E_P electron phonon coupling strength (Γ), polaron band width (j), ϕ and debye temperature (θ_D) with different Cr-substitution i.e., Cr-0, Cr-10, Cr-15, Cr-20 and Cr-25.	84
4.9	Variation of resistivity with temperature at 0 and 9 Tesla for Cr-0 and Cr-25.	85
4.10	Magnetization vs temperature in zero field cooled (ZFC) and field cooled (FC) geometry for Cr-25.	85
4.11	Inverse susceptibility (χ^{-1}) and χT vs temperature variations for Cr-25.	86
4.12	Magnetization vs field variations for Cr-25 at different temperatures.	86
4.13	(a) Schematic diagram for measuring setup for Seebeck and thermal conductivity, (b) thermal conductivity variation with temperature for all compositions in the temperature range $50K \leq T \leq 300K$ with its constituent electronic part (c) and phononic part (d), (e) field dependent thermal conductivity at different field for Cr-25, (f) specific heat vs temperature for Cr-25 composition	88

4.14	(a) Seebeck coefficient variation with temperature for all compositions, (b) The fitting of Seebeck coefficient with diffusive, VRH and phonon drag terms, (c) compositional variation of carrier concentration and Hall mobility calculated at room temperature for all compositions, (d) Seebeck coefficient at different magnetic field for Cr-25, (inset) field dependent change in Seebeck coefficient at different field strength for Cr-25.	90
4.15	(a) Variation of ZT for all the compositions, (b) field variation of Cr-25, (c) variation of ΔZT (%) with temperature for different field values.	91
4.16	Variation of resistivity, thermal conductivity, Seebeck and ZT at different fields for Cr-0.	92
4.17	Compositional variation of thermal conductivity and Seebeck coefficient with temperatures.	93
4.18	Variation of resistivity, thermal conductivity, Seebeck and ZT at 0 and 9 Tesla for Cr-0 and Cr-25.	94
4.19	Variation of power factor with temperature (a) and composition (b) for all compositions.	95
4.20	Compositional variation of ZT with temperature for Cr-0, Cr-10, Cr-15, Cr-20 and Cr-25.	96
5.1	(a) Refined XRD pattern for polycrystalline form of Ta_2NiSe_7 , (b) structure of Ta_2NiSe_7 solved by multiple single crystal XRD information.	100
5.2	(a) SEM micrograph of Ta_2NiSe_7 , (b) zoomed view of single strain, (c) EDS spectra for Ta_2NiSe_7 , (d-f) elemental mapping of constituent elements Se, Ta and Ni respectively.	100
5.3	Core level XPS spectra of Ta_2NiSe_7 for its constituent elements Ni, Ta and Se.	101
5.4	(a) Electrical resistivity variation with temperature (heating and cooling) for $2K \leq T \leq 175K$; inset: ρ vs T plot in full temperature regime $2K \leq T \leq 300K$, (b) variation of transition temperature for major charge density wave (T_{CDW}) with RRR value of single crystals taken from the literatures, (c) variation of d^2R/dT^2 with temperature for Ta_2NiSe_7 and (d) plot for $\ln(\rho)$ vs $1/T$ to calculate the activation energy for different scattering involve in the transport.	102
5.5	Charge carrier concentration variation with temperature for Ta_2NiSe_7	103

5.6	(a) Variation of Seebeck with temperature; (b) MR and MS variation for ± 14 Tesla field at 5K	104
5.7	(a) Variation of total thermal conductivity with temperature for Ta ₂ NiSe ₇ at 0 and 14 Tesla, (b) electronic and phononic part thermal conductivity variations with temperature for 0 and 14 Tesla.	105
5.8	Variation of specific heat for Ta ₂ NiSe ₇ at 0 and 14 Tesla.	106
5.9	(a) Fitting of low temperature resistivity data for distinct top and bottom part of quantized resistivity in temperature regime $2K \leq T \leq 55K$, (b) variation of number of steps in the resistivity and the change in conductivity for each conductivity jump	107
5.10	(a) DC I-V plot for Ta ₂ NiSe ₇ , (b) variation of differential resistivity with the applied dc voltage, (c) variation of differential resistivity with the applied dc voltage in presence of enveloping ac voltage.	109
5.11	Crystal structure of Ta ₂ NiSe ₇ . The primitive unit cell is made up of 20 atoms, twice the number of atoms in the formula unit. Ta atoms are depicted in blue, Ni atoms in green and Se ¹⁻ (Se ²⁻) in brown (pink). Ta atoms are surrounded by six Se atoms arranged in rectangular-based pyramid complexes.	110
5.12	Rectangular-based pyramid complexes of Ta ₂ NiSe ₇ (left) and electronic population of Ni d orbitals due to crystal field splitting (right).	110
5.13	Left panel. Linear response DFPT calculation of the Hubbard U parameter for Ni (orange), together with the evolution of the volume of the primitive unit cell with the iterations of the cycle (green). Right panel. Occupation of d orbitals of Ni (orange) and Ta (black) atoms. We obtain the full occupation of 4 d orbitals with pairs of up and down electrons (bold black), which translates into a clear low spin configuration for Ni atoms. Ta atoms are substantially empty, as expected from their 5+ oxidation state suggested from charge balance in the system. Note that the occupation/non occupation of orbitals has been analysed according to the procedure described in Ref. [387].	110
5.14	Left panel. Linear response DFPT calculation of the Hubbard U parameter for Ni (orange) and Ta (azure and blue), together with the evolution of the volume of the primitive unit cell with the iterations of the cycle (green).	111

Right panel. Occupation of d orbitals of Ni (orange) and Ta (azure and blue) atoms. We obtain the full occupation of 4 d orbitals of Ni atoms with pairs of up and down electrons (bold black), which translates into a clear low spin configuration for Ni atoms. Ta atoms are substantially empty, as expected from their 5+ oxidation state suggested from charge balance in the system. The use of Hubbard U values on Ta atoms does not affect the results obtained so far. Note that the occupation/non occupation of orbitals has been analysed according to the procedure described in Ref. [387].

5.14	Electronic band structure and density of states of of Ta ₂ NiSe ₇ computed with DFT+U.	112
5.15	Electronic band structure and density of states of of Ta ₂ NiSe ₇ computed with DFT+U+SOC.	112
5.16	(a) Fermi surface of Ta ₂ NiSe ₇ where the electron (hole) pockets are shown in green (blue), and the projection of the isocontours on the k _{xy} plane. (b) Projection of the isocontours on the k _{yz} plane. (c,d) Nesting of the Fermi surface across 2 adjacent Brillouin Zones where the arrow in red shows the 2k _f transverse nesting and 4k _f longitudinal one.	113

LIST OF TABLES

Table no.	Table caption	Page no.
1.1	Recently reported TE choices and corresponding thermoelectric parameters	6-9
1.2	Scattering mechanism for phonons and their frequency and temperature dependencies for scattering probability, $1/l(\omega)$ and thermal conductivity, $\kappa_l(T)$ respectively.	22
3.1	Extracted lattice parameters, (a,b,c), density (ρ), strain, grain size (D_{FESEM}) and goodness of fitting (χ^2) of all the samples LBSCO-0, 1 and 2 from Refinement considering space group $R\bar{3}C$. The values inside parentheses indicate uncertainty in the last digit.	61
3.2	The fitting parameters for κ vs T using relation $\kappa = AT^3 + B$; in temperature range of $70\text{ K} \leq T \leq 300\text{ K}$ for LBSCO-0, 1 and 2 samples.	67
4.1	The variations of lattice parameters, cell volume, space group wt%, bond length, bond angle, density, strain, porosity and grain size of the samples is calculated from XRD refinement and SEM micrographs.	78
4.2	Fitting parameters extracted from VRH and SPH model of electrical resistivity for all the compositions.	83