

**FIRST-PRINCIPLES INVESTIGATIONS ON OPTICAL AND
THERMOELECTRIC PROPERTIES IN STATE-OF-THE-ART
MATERIALS**

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**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



**DEPARTMENT OF PHYSICS
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March 2024**

To my father

CERTIFICATE

This is to certify that the thesis entitled **First-principles Investigations on Optical and Thermoelectric Properties in State-of-the-art Materials** submitted by **Chandan Kumar Vishwakarma** to the Indian Institute of Technology Delhi, for the award of the degree **Doctor of Philosophy** in Physics is a record of bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the requisite standard.

The material contained in the thesis has not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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Chandan Kumar Vishwakarma

ABSTRACT

Amidst the growing demand for novel materials showing multifunctional properties, first-principle calculations are recognized as an essential tool in the condensed matter theory. With limited resources and remarkable precision, these calculations can be crucial in examining state-of-the-art materials. Examining materials with diverse and fascinating properties and understanding their interactions with external perturbations like electromagnetic fields and heat is essential. Motivated by these considerations, we have investigated two exciting phenomena of materials – the first part involves the interaction between electrons and photons in the well-established ferroelectric material sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT), and based alloys; And the second part of the study is specifically focused on investigating the impact of the applied heat gradient by examining the thermoelectric properties of Zintl phases and double half-Heusler alloys.

In the first part of the thesis, we have completed two projects focusing on the electrical, optical, and magneto-optical properties of NBT-based alloys. The first project delved into the effect of rare-earth (Nd and Er) substitution on the physical properties of NBT. While rare-earth-substituted NBT has been extensively examined for its significance in luminescence applications, the emergence of a magnetic degree of freedom due to rare-earth substitution remained unexplored. Through first-principle calculations, we reported the emergence of ferromagnetism in these systems. Our calculations predicted the magnetic moments of 1.47 and 1.49 $\mu_B/f.u.$ for Nd and Er NBT, respectively, for the highest concentration of 25%. The mechanism for nonzero magnetic moments in (Nd/Er)-NBT is traced to the presence of unpaired f -electrons. Additionally, we investigated the optical properties of these materials and explored the coupling of the magnetic degree of freedom with the dielectric behavior of Nd and Er NBT. Our simulations on magneto-optic effects revealed a significant Kerr signal of 0.7° in both materials. This suggests rare-earth substituted NBT as potential candidates for magneto-optical applications

and motivates more theoretical and experimental works in this direction. In a similar study, we considered transition metals (Ni and Fe) substitution in NBT. Our calculations predicted the emergence of half-metallic ferromagnetism in TM-substituted NBT. A significant magnetic moment of 1.5 and 1.9 $\mu_B/f.u.$ for 25% Ni and Fe substituted NBT, respectively, suggest the strong coupling between the magnetic degree of freedom and the dielectric behavior of these materials. Additionally, we explored the ferroelectric properties of Ni and Fe-substituted NBT. As expected, our calculations predict a reduced spontaneous polarization in Ni/Fe-substituted NBT. Our study confirmed the multifunctionality of transition metal-substituted NBT, highlighting their significance in various potential applications such as spintronics, magneto-optic devices, and multiferroics.

The other part of the thesis is dedicated to the investigation of electronic and transport properties of Zintl phases and double half-Heusler alloys. Within this segment, we completed three major projects. The first two projects delved into the study of two categories, X_2YZ and XYZ , of Zintl phases for their potential applications in thermoelectrics. In the first category, we chose Na_2AuBi and Na_2AuSb as the subjects of our study. Our simulations predict remarkably low room temperature lattice thermal conductivity (κ_L) of 0.46 and 0.73 $Wm^{-1}K^{-1}$ for Na_2AuBi and Na_2AuSb , respectively. We attribute such low κ_L values to low phonon group velocities in the acoustic region, significant atomic displacement parameter, and lattice anharmonicity. We further predict a high figure of merit, *i.e.*, $ZT \sim 1$ at 300 K for *p*-type Na_2AuBi . The value is significantly improved for Na_2AuBi with spin-orbit coupling, *i.e.*, $ZT \sim 1.8$. In another study, we selected $NaSrSb$ and $NaBaSb$ as thermoelectric prospects in the second category of XYZ type Zintl phases. Similar to their intrinsic characteristics, these materials exhibit exceptionally low lattice thermal conductivity (κ_L) ranging from 1.9 to 0.6 and 1.4 to 0.3 $Wm^{-1}K^{-1}$, respectively, in the temperature range of 300 to 900 K. We associate such low values with small phonon group velocities arising from the less dispersed phonon bands, short phonon lifetimes, and considerable lattice anharmonicity. Further, we found a large power factor of 28.2 $\mu Wcm^{-1}K^{-2}$ for $NaSrSb$, arising from its anomalously large electrical conductivity. Taken together, we obtained a figure of merit $ZT \sim 2.0$ at 900 K for *n*-type $NaSrSb$, whereas the figure of merit surpasses unity in the case of $NaBaSb$.

In the last study, for the thermoelectric material, we considered two double half-Heusler alloys, $NbFe_{0.5}Ni_{0.5}Sn$ and $TaFe_{0.5}Ni_{0.5}Sn$. From our simulations, we find that both systems optimize in $P4\bar{m}2$ symmetry and possess a band gap of 0.1 eV. The phonon dispersion of these

materials suggests the dynamical stability of these systems and, interestingly, the absence of characteristic gaps in acoustic and optical phonons, which imparts high lattice thermal conductivity to half-Heusler alloys. Our simulations predict a significantly low lattice thermal conductivity in both these materials in comparison to TiCoSb, a well-known thermoelectric Heusler material. We attribute this reduced lattice thermal conductivity to the short phonon lifetime of NbFe_{0.5}Ni_{0.5}Sn and TaFe_{0.5}Ni_{0.5}Sn, arising from the interaction among acoustic and low-lying optical modes. Our simulations on electrical transport properties suggest that these materials are best suited in temperature range 400-600 K and in the carrier concentration range less than 10²¹ carriers cm⁻³, showing ~ 35% and 17% enhancement in the ZT value for NbFe_{0.5}Ni_{0.5}Sn and TaFe_{0.5}Ni_{0.5}Sn, respectively, as compared to TiCoSb.



सार

नवीन पदार्थों की बढ़ती मांगों के बीच, जो विभिन्न गुणधर्म प्रदर्शित करते हैं, प्रथम-सिद्धांत गणनाओं को संकुचित पदार्थ सिद्धांत में एक महत्वपूर्ण औजार के रूप में माना जाता है। सीमित संसाधनों और अत्यधिक सटीकता के साथ, ये गणनाएँ नवीनतम पदार्थों की जांच में महत्वपूर्ण हो सकती हैं। विभिन्न और रोचक गुणधर्मों वाले पदार्थों की जांच और बाह्य उत्तेजनाओं जैसे विद्युतचुंबकीय क्षेत्रों और ऊष्मा के साथ उनके प्रभावों को समझना आवश्यक है। इन विचारों से प्रेरित होकर, हमने पदार्थों की दो रोमांचक प्रक्रियाओं की जाँच की है-पहले भाग में, हमने अच्छी तरह से ज्ञात लोहवैधुतीय पदार्थ सोडियम बिस्मथ टाइटेनेट, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) और उस पर आधारित मिश्र धातुओं में इलेक्ट्रॉनों और फोटॉनों के बीच अन्तर्क्रिया का अध्ययन किया है और दूसरे भाग में, हमने विशेष रूप से प्रयुक्त तापीय प्रवाहन के प्रभाव की जाँच पर केंद्रित होकर जिंटल अवस्थाओं और दोहरा अर्ध-ह्यूस्लर मिश्र धातुओं के तापवैधुतीय गुणधर्मों का अध्ययन किया।

शोध प्रबंध के प्रथम भाग में हमने NBT पर आधारित मिश्र धातुओं की वैद्युतीय, प्रकाशिकीय और चुम्बक-प्रकाशिकीय गुणों को ध्यान में रखते हुए दो परियोजनाएं समाप्त की। प्रथम परियोजना में दुर्लभ-मृदा धातुएं प्रतिस्थापन से NBT के भौतिक गुणों में हुए प्रभाव का विस्तृत अध्ययन किया गया है। प्रकाशगमिता अनुप्रयोगों में दुर्लभ-मृदा धातु प्रतिस्थापित NBT के महत्व की बड़े पैमाने पर जांच की गई है, किन्तु दुर्लभ-मृदा धातु के प्रतिस्थापन के कारण उत्पन्न चुम्बकीय स्वतंत्रता की कोटि का अध्ययन अभी अज्ञात है। प्रथम-सिद्धांत गणनाओं के माध्यम से हमने इन प्रणालियों में लौहचुम्बकत्व के उद्भव की पुष्टि की। हमारी गणनाओं ने 25% की उच्चतम सांद्रता के लिए Nd और Er प्रतिस्थापित NBT में क्रमशः 1.47 और 1.49 $\mu\text{B}/\text{f.u}$ चुंबकीय आघूर्ण की भविष्यवाणी की। (Nd/Er)-NBT में अशून्य चुंबकीय आघूर्ण का पता अयुग्मित f-इलेक्ट्रॉनों की उपस्थिति से लगाया जाता है। इसके अतिरिक्त, हमने इन तंत्रों के प्रकाशिकीय गुणों की जांच की और (Nd/Er)-NBT के परावैद्युत व्यवहार का चुम्बकीय स्वतंत्रता की कोटि के साथ युग्मन का पता लगाया। इन दोनों तंत्रों के चुम्बक-प्रकाशिकीय गुणों का सैद्धांतिक प्रतिरूपण करने पर 0.7 \circ के महत्वपूर्ण केर सिग्नल का पता चला। यह चुम्बक-प्रकाशिकीय अनुप्रयोगों के लिए संभावित उम्मीदवारों के रूप में दुर्लभ-मृदा धातु प्रतिस्थापित NBT का सुझाव देता है और इस दिशा में अधिक सैद्धांतिक और प्रयोगात्मक कार्यों को प्रेरित करता है। इसी तरह के एक अध्ययन में, हमने NBT में संक्रमण धातुओं (Ni और Fe) के प्रतिस्थापन पर विचार किया। हमारी गणनाओं ने संक्रमण धातु-प्रतिस्थापित NBT में अर्ध-धातु लौहचुम्बकत्व के उद्भव की भविष्यवाणी की। Ni और Fe प्रतिस्थापित NBT की 25% की सांद्रता के लिए एक महत्वपूर्ण चुंबकीय आघूर्ण 1.5 और 1.9 $\mu\text{B}/\text{f.u}$, इन तंत्रों के चुम्बकीय स्वतंत्रता की कोटि और परावैद्युत व्यवहार के मध्य मजबूत युग्मन को दर्शाता है। इसके अतिरिक्त, हमने Ni और Fe-प्रतिस्थापित NBT के फेरोइलेक्ट्रिक गुणों का पता लगाया। जैसा कि अपेक्षित था, हमारी गणनाएँ Ni और Fe- प्रतिस्थापित NBT में स्वतः ध्रुवीकरण में कमी की भविष्यवाणी करती है। हमारे अध्ययन ने संक्रमण धातु-प्रतिस्थापित NBT की बहुक्रियाशीलता की पुष्टि की, जिसमें स्पिंट्रॉनिक्स, मैग्नेटो-ऑप्टिक उपकरण, और मल्टीफ़ेरोइक्स जैसे विभिन्न संभावित अनुप्रयोगों में उनके महत्व पर प्रकाश डाला गया।

शोध प्रबंध का दूसरा भाग ज़िंटल चरणों और दोहरा अर्ध-ह्यूस्लर मिश्र धातुओं के वैद्युतीय और परिवहन गुणों की जांच के लिए समर्पित है। इस खंड के भीतर, हमने तीन प्रमुख परियोजनाओं को पूरा किया। पहली दो परियोजनाओं में ज़िंटल चरणों की दो श्रेणियों, X_2YZ और XYZ का तापवैद्युतिकी में उनके संभावित अनुप्रयोगों के लिए अध्ययन किया गया। पहली श्रेणी में हमने हमारे अध्ययन के विषयों के रूप में Na_2AuBi और Na_2AuSb को चुना। हमारे सैद्धांतिक प्रतिरूपण, Na_2AuBi और Na_2AuSb के लिए क्रमशः 0.46 और $0.73 \text{ Wm}^{-1}\text{K}^{-1}$ कम कक्ष ताप जालक ऊष्मा चालकता (κ_L) की उल्लेखनीय रूप से भविष्यवाणी करते हैं। हम ऐसे निम्न κ_L मानों का श्रेय ध्वनिक क्षेत्र में निम्न फोनॉन समूह वेगों, महत्वपूर्ण परमाणु विस्थापन मापदंड और चालक असंगति को देते हैं। हम 300 K पर p - प्रकार के Na_2AuBi के लिए योग्यता का आंकड़ा अर्थात्, $ZT \sim 1$ की भी उम्मीद करते हैं। इस मान को विशेष रूप से Na_2AuBi के लिए प्रचक्रण-कक्षण युग्मन को सम्मिलित कर के सुधारा गया है, अर्थात्, $ZT \sim 1.8$ । एक और अध्ययन में, हमने दूसरे श्रेणी के XYZ प्रकार के ज़िंटल चरणों में तापवैद्युत गुणों की संभावना के रूप में $NaSrSb$ और $NaBaSb$ का चयन किया। इनकी स्वाभाविक विशेषताओं की तरह, इन तंत्रों की जालक उष्मीय चालकता (κ_L) 300 से 900 K तक के तापमान में 1.9 से 0.6 और 1.4 से $0.3 \text{ Wm}^{-1}\text{K}^{-1}$ तक है जो की असाधारण रूप से कम है। हम इस प्रकार के कम मानों को छोटे फोनॉन समूह की गतियों से उत्पन्न होने वाली कम विस्तृत फोनॉन बैंड्स, छोटे फोनॉन जीवनकाल, और महत्वपूर्ण जालक असमयता से जोड़ते हैं। इसके अतिरिक्त, हमने $NaSrSb$ के लिए $28.2 \mu\text{Wcm}^{-1}\text{K}^{-2}$ का विशाल शक्ति कारक पाया, जो इसके असामान्य बड़ी विद्युत चालकता से उत्पन्न होता है। यह सब मिलाकर, हमने n-प्रकार के $NaSrSb$ के लिए 900 K ताप पर योग्यता का आंकड़ा $ZT \sim 2.0$ प्राप्त किया है, जबकि $NaBaSb$ के मामले में यह एक को पार करता है।

अंतिम अध्ययन में, तापवैद्युत पदार्थ लिए हमने दो दोहरा अर्ध-ह्यूस्लर मिश्र धातु $NbFe_{0.5}Ni_{0.5}Sn$ और $TaFe_{0.5}Ni_{0.5}Sn$ पर विचार किया। हमारे सैद्धांतिक प्रतिरूपण से हम पाते हैं कि दोनों तंत्र $P4m2$ सममिति में अनुकूलित होते हैं और इनमें 0.1 इलेक्ट्रॉन वोल्ट का ऊर्जा अंतराल है। इन तंत्रों का फोनॉन परिक्षेपण हमें इनका गतिकीय स्थायित्व दर्शाता है, और दिलचस्प रूप से, ध्वनिक और प्रकाशीय फोनॉनों में विशेष अंतराल की अनुपस्थिति, जो हाफ-ह्यूस्लर आलाय को उच्च चालकता प्रदान करती है। इन तंत्रों का फोनॉन परिक्षेपण उनकी गतिक स्थिरता को सुझाव देता है, और रोचक रूप से, ध्वनिक और प्रकाशीय फोनॉनों में अंतराल की अनुपस्थिति अर्ध-ह्यूस्लर मिश्र धातुओं को उच्च जालकीय तापीय चालकता प्रदान करती है। हमारा सैद्धांतिक प्रतिरूपण, $TiCoSb$ जो एक प्रसिद्ध तापवैद्युत ह्यूस्लर तंत्र है, की तुलना में दोनों तंत्रों में तापीय जाल चालकता कम होने का पूर्वानुमान करता है। $NbFe_{0.5}Ni_{0.5}Sn$ और $TaFe_{0.5}Ni_{0.5}Sn$ में कम हुए जालक उष्मीय चालकता का कारण फोनॉन का अल्प जीवन काल है, जिसका उद्गम ध्वनिक और निम्न स्थितिकीय प्रकाशीय विधाओं के बीच अंतर्क्रिया है। विद्युत परिवहन गुणों पर हमारे सैद्धांतिक प्रतिरूपण से पता चलता है कि ये तंत्र 400-600 K तापमान रेंज और 10^{21} सेमी⁻³ से कम वाहक सांद्रता रेंज में सबसे उपयुक्त हैं जो कि $NbFe_{0.5}Ni_{0.5}Sn$ और $TaFe_{0.5}Ni_{0.5}Sn$ के लिए ZT मान में $TiCoSb$ की तुलना में क्रमशः $\sim 35\%$ और 17% की वृद्धि दर्शाता है।

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