Light Matter Interactions in Metal Chalcogenides Investigated By Optical Spectroscopy

A Thesis

submitted by

Juhi Pandey (Roll No. D14020)

for the award of the degree

of

Doctor of Philosophy

School of Basic Sciences,

Indian Institute of Technology Mandi,

Mandi, Himachal Pradesh, India

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Dedicated

To

My Parents

Declaration of Research Scholar

I hereby declare that the entire work embodied in this thesis entitled **"Light Matter Interactions in Metal Chalcogenides Investigated By Optical Spectroscopy"** is the result of investigations carried out by me in the School of Basics Sciences, Indian Institute of Technology Mandi, India, under the supervision of **Dr. Ajay Soni**, and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on the finding of other investigators.

Place :- IIT Mandi Signature

Date :- 23.07.2020 Name: **Juhi Pandey**

Declaration by the Research Advisor

I hereby certify that the entire work in the Thesis **"Light Matter Interactions in Metal Chalcogenides Investigated By Optical Spectroscopy"** has been carried out by **Juhi Pandey** under my supervision in the School of Basic Sciences, Indian Institute of Technology Mandi, and no part of it has been submitted elsewhere for any Degree or Diploma.

Name of the Guide: **Dr. Ajay Soni**

Date: 23.07.2020

Acknowledgments

I take this opportunity to expresses my gratitude to all those people who have supported in the successful completion of this doctoral thesis work at IIT Mandi. My tenure as a scholar is full of delightful memories of learning to approach several professional and personal challenges with a positive attitude. First, I would like to express my gratitude to my PhD supervisor, Dr. Ajay Soni for his persistence guidance and support throughout the duration to bring the best out of me. I owe my especial thanks to him for spending his precious time, motivational encouragements and giving freedom to plan and execute research work. Through him, I learnt about team work, proper utilization of available resources to perform high quality research. His everlasting passion and enthusiasm for research also taught not only me but all the group members about right attitude to solve scientific research problems. I feel fortunate that he gave me the opportunity to work with Raman and Photoluminescence spectroscopy to study vast variety of materials system relevant not only for the present thesis but also beyond the thesis.

I wish to thank my doctoral committee members Dr. Kaustav Mukherjee, Dr. Chandra Shekhar Yadav, Dr. Pradeep Kumar and Dr. Sudhir Kumar Pandey for their invaluable advices, discussions and support throughout the PhD tenure. I owe especial thanks to Dr. Chayan Kant Nandi for teaching a course on group theory which helped me to understand and analyse Raman data. I also thank the faculty members in the School of Basic Sciences for teaching me various interesting courses.

I express my sincere gratitude to Prof. Timothy Gonsalves, Director, IIT Mandi for providing all the facilities and funding to support the research work. I am also grateful to the IIT Mandi administration and AMRC staff members for administrative and academic support in my research journey.

I am grateful to Prof. Arghya Taraphdar (IIT Kharagpur), Prof. Nikhil Koratkar (RPI, USA), Prof. Kanishka Biswas and Prof. Umesh Waghmare (JNCASR, Bangalore), Dr. Satinder Sharma and Dr. Viswanath Balakrishnan (IIT Mandi), Prof. Ramesh Chandra Mallik (IISC Bangalore), Dr. Dibyendu Dey (Arizona State University, USA), Dr. Tushar Gupta (RPI, USA), Mr. Debjit Ghoshal (RPI, USA) and Dr. Shriparna Mukherjee (IISC Bangalore) for the collaborative research work and valuable discussions. Special thanks are due for Dr. Surajit Saha from IISER Bhopal for providing his valuable support in technical discussion and clarification of various concepts.

My research life is full of positive and joyful experience because of my seniors, colleagues and friends. I wish to thank my research group members Dr. Somnath, Dr. Mohit, Dr. Surender and Dr. Mahesh, for technical discussions, motivation, and exchange of their experiences. I express my gratitude to friends Niraj, Ankit, Kewal, Divya, Kavita, Sheetal, Sonu, Shailja, Sonika, Gurpreet, Karan, Deepu, Ankita Mathur, Dr. Navneet and Dr. Pawan Kumar for their timely help on various aspects of the research work.

I take this opportunity to thank many of my friends Dr. Swati, Dr. Shaifu, Pratibha, Priyanka, Tulika, Shewta and Jagriti for providing friendly atmosphere and emotional support. I also wish to thank Mrs. Preeti Soni and Nitigya for their love and affection in giving me homely atmosphere as a family member away from home.

Finally, I express my heartfelt gratitude to my parents for standing-by me for all my decisions and providing me the best support and environment to chase my dreams at every stage of life. I am very much thankful to them for all the sacrifices they have made for my happiness. Further, I am also thankful to my grandmother, brother and sister-in law, aunts and uncles for their love, care and all kind of support whenever needed.

Preface

Recent technological advancements have opened up new directions for studying light matter interactions for energy harvesting through photovoltaics, light emitting diodes, phase change materials, optoelectronic and solar-thermoelectric devices in addition to probing numerous multi-body interactions for fundamental studies. The extent of light-matter interaction strongly depends upon several intrinsic properties of the material such as refractive index, polarizability, dielectric constant, susceptibility, absorption and extinction coefficient. With the development of nanoscience and nanotechnology, varieties of novel one-dimensional and two-dimensional materials are designed to explore different possibilities of light matter interactions through enhanced surface to volume ratio and confinement effects. The interactions involving electron-electron, electron-phonon, plasmon-phonon, electron-hole and phonon-phonon interactions are established strongly upon the interplay of light with matter. The fundamental understandings of such multi-body phenomena are important to enrich the current scientific understanding for development of advanced technologies.

The family of transition metal chalcogenides, in this regard, is an ideal material system to explore these interesting phenomena owing to its rich library of physical properties such as metallic, semiconducting, superconducting, insulating nature. For technological advancements, the materials systems have been studied for applications like thermoelectricity, superconductivity, topological insulators, photovoltaics, phase change memory, nanoelectronics and optoelectronic devices. Most of the transition metal chalcogenides, such as MoS_2, WS_2, VSe_2, $NbSe_2$, $TaSe_2$, $TiSe_2$, are layered materials with a weak van der Waals interactions between the stacked layers, thus can be exfoliated as ultra-thin flakes of thickness down to single layer. The freedom of exfoliation from three-dimensional bulk material to two-dimensional sheets results in emergence of remarkably modified properties due to quantum confinement effect. For instance, bulk MoS_2, WS_2 and WSe_2 are indirect band gap materials whereas monolayer of these compounds possesses direct band gap properties. Further, different polytypes and polymorphs are also exhibited by such compounds. The electronic and optical properties of transition metal chalcogenides are also varied by the arrangement of atoms in the unit cell of the same compound. By employing top down and bottom up approaches of material synthesis, novel two-dimensional transition metal chalcogenides can be prepared for desirable physical

properties, on demand. Thus, transition metal chalcogenides are important material systems to explore their exotic physical properties.

Multi-body interactions in transition metal chalcogenides are strongly modulated by their structural arrangement, electronic band structure, dielectric screening, carrier concentration and Coulomb interactions. Semiconducting transition metal chalcogenides are among the few materials which have demonstrated to have exciton at room temperature owing to strong Coulomb interaction between electron and hole pair. Monolayer of MoS_2, WS_2 and WSe_2 exhibits neutral and charged excitons along with excitonic complexes depending upon the spin-orbit splitting of the valence band, doping and substrate effect. Further, excitons also show their excited states which can be fundamentally understood from the analogy to the hydrogen atom model. Recently, excited states of exciton are being examined in several semiconducting transition metal chalcogenides by studying the dielectric screening effect, enhancement of spin-orbit splitting through external magnetic field, modulation of carrier concentration through gated source-drain current measurements and by employing various sophisticated non-linear spectroscopic techniques. Excitonic transitions in these materials are important for studying many-body interactions, valleytronics and optoelectronics. In the current thesis, monolayer of MoS_2, exfoliated on SiO_2/Si substrate, is identified by simplistic optical contrast model and Raman spectroscopy. Neutral excitons such as A and B excitons along with negatively charged A^- trion is observed at room temperature in the photoluminescence spectra. Further, by using the temperature and laser power dependent photoluminescence study, the first excited state of A exciton (A_{2s}) is realized at cryogenic temperature (4 K) along with sulfur vacancy bound defect exciton and biexciton.

Another unique phenomenon of multi-body interaction that can be probed through light-matter interaction is the formation of charge density wave in metallic systems, which has not been explored in literature, extensively. The major reason is high reflectivity of metallic systems, which limits the interactions to be observed by optical tools, especially for charge density wave. Generally, for one-dimensional system the driving mechanism of charge density wave is understood through Fermi surface nesting, however for the case of higher dimensional systems, the involvement of electron-phonon coupling is also being considered. Several quasi two-dimensional transition metal chalcogenides such as 2H-$NbSe_2$, 1T-$TaSe_2$, 1T-VSe_2, 2H-$TaSe_2$

shows the formation of charge density wave at low temperature. Interestingly, the involvement of electron-phonon coupling can be probed through Raman spectroscopy and aid in the fundamental understanding of charge density wave phenomena. In the above context, the emergence of incommensurate and commensurate charge density wave in 1T-VSe_2 is studied in the present thesis by using temperature dependent Raman spectroscopy. The manifestation of electron-phonon interaction is estimated in the variation of Raman signal intensity with charge density wave formation at low temperatures.

The current era of research demands for ferroelectric semiconductor to achieve high photovoltaic conversion efficiency through intrinsic charge separation via inherent polarization. Various transition metal oxide-perovskite and organic-inorganic halide-perovskites are ferroelectric in nature, but with the high band gap of oxides while instability of organic-inorganic halides limit their application as photovoltaic. Thus, a system of novel transition metal chalcogenides perovskite has been investigated, theoretically and experimentally, as an alternative photovoltaic material, which are environmentally stable, non-toxic, direct band gap materials with intrinsic ferroelectric polarization. To address the challenge of ferroelectric semiconductor, we have grown a thin film of anti-ferroelectric polycrystalline $BaZrS_3$ and studied the physical properties with optical spectroscopy. Thin film has showed a localized ferroelectric polarization, below 100 K, in the Raman spectroscopy owing to the loss of inversion symmetry via localized oxygen impurities. Interestingly $BaZrS_3$ is a non-toxic and environmentally stable material with optimum band gap ranging from 1.7 to 1.85 eV, thus the localized ferroelectric polarization hosts $BaZrS_3$ thin film as a potential ferroelectric photovoltaic.

The present thesis also addresses other important aspects of light matter interaction in chalcogenide materials for thermoelectric applications. For this, the optical properties of superionic copper telluride is studied in detail. Copper telluride is a p-type semiconductor with carrier concentration ~ 10^{22} cm^{-3}, emerging as a potential material for thermoelectricity, photovoltaic, photonics and plasmonic devices. The materials system belongs to the class of phonon-liquid-electron-crystal because the cation is loosely bonded with the rigid sub-lattice of tellurium. A precise understanding of the vibrational and optical properties of such system is challenging due to non-stoichiometry and complex crystal structure which thus, limits the

development of smart devices using copper telluride. Therefore, in this work, structural phases, structural transitions, vibrational properties as well as strong plasmon-phonon coupling with carrier concentration is studied via temperature dependent Raman spectroscopy. Thermal conductivity of different stoichiometric compounds is determined by estimation of phonon lifetime for thermoelectric application.

In summary, the present thesis elaborates on the exploration of less understood multi-body interactions such as (i) excitonic complexes and excitonic excited states in non-centrosymmetric direct band gap monolayer MoS_2; (ii) charge density wave in metallic 1T-VSe_2; (iii) emergence of local ferroelectricity in anti-ferroelectric direct band gap semiconducting $BaZrS_3$ thin film; and (iv) plasmon-phonon coupling and vibrational properties of copper telluride. A brief summary of all the chapters of the thesis are elaborated in the following section.

The present thesis is divided into eight chapters. The brief outline of the chapters is discussed below:

Chapter 1: Introduction

This chapter contains the background of the research problem, thesis objectives and a brief description of physical properties such as structure, electronic, vibrational properties of typical transition metal chalcogenides material systems investigated in the thesis.

Chapter 2: Experimental Techniques

The chapter describes about several techniques used in the present thesis to synthesize and characterize transition metal chalcogenides. For instance, chemical vapor transport to grow single crystalline bulk VSe_2 and chemical vapor deposition to prepare $BaZrS_3$ thin film are discussed. Mechanical exfoliation method to achieve two-dimensional sheets down to monolayer from bulk MoS_2 is described. Characterization techniques, such as X-ray diffraction, field emission scanning electron microscopy, UV-visible absorbance spectroscopy, Raman spectroscopy, photoluminescence spectroscopy, physical property measurement system and magnetic property measurement system are employed to assess the crystal quality, composition, surface morphology, structural, optical, vibrational, electronic and magnetic properties, are presented.

Chapter 3: Optical Methods for Thickness Identification of Atomically Thin 2D Layers over Substrate

Prior to the investigation of physical properties of two-dimensional materials, the key challenge is the visibility and determination of thickness of nanosheets grown/transferred over desired substrate. Optical microscopy is commonly employed for visualization and identification of two-dimensional sheets by perceiving optical contrast between nanosheets of different thickness and the substrate upon illumination with incident light. The chapter describes about theoretical calculation of optical contrast based on Fresnel equations for flakes of several layered transition metal chalcogenides such as MoS_2, WS_2, WSe_2 and $NbSe_2$ to achieve maximum visibility for monolayer deposited over SiO_2/Si substrate. Two different methods namely Weber contrast and Michelson contrast are compared with the experimentally estimated contrast values for graphene monolayer over SiO_2/Si substrate to determine the best theoretical method. Weber contrast provided better theoretical estimation of optical contrast and suggested that ~ 90 nm as well as ~ 285 ± 5 nm thick SiO_2 layer over Si substrate gives maximum optical contrast upon illumination with light of wavelength ranging from 500 – 700 nm for MoS_2, WS_2, WSe_2 and $NbSe_2$.

Chapter 4: Excitonic Complexes and Excited States in Monolayer MoS_2

The fourth chapter provides an experimental investigation of excitons, complexes of excitons such as trion, biexciton and defect bound exciton along with the observation of first excited state of A exciton (A_{2s}) in monolayer MoS_2 mechanically exfoliated over SiO_2(290 nm)/Si substrate. Temperature dependent micro-Photoluminescence spectroscopy from 4 K to 300 K and laser power dependent photoluminescence at 4 K is used to determine the origin of several optical transitions. The study suggest that the defect bound excitons are observed at low temperature due to low binding energy however free excitons, trion and biexciton can exist up to 300 K because of binding energy higher than thermal energy. Further, unlike several reports where Rydberg states on A exciton of monolayer MoS_2, WS_2 and WSe_2 is observed using several sophisticated non-linear optical techniques, we present the our observation of A_{2s} state for monolayer MoS_2 using photoluminescence spectroscopy at 4 K.

Chapter 5: Charge Density Wave in Single Crystalline VSe_2

Charge density wave is a low temperature ordered phase arising due to periodic modulation of conduction electron density accompanied by structural modulation. The phenomenon is realized in two-dimensional metallic layered transition metal chalcogenides such as 1T-$TaSe_2$, 1T-$TiSe_2$, 2H-$NbSe_2$. Generally, charge density wave is understood in the perspective of Fermi surface nesting where periodic modulation of conduction electron opens up a gap at Fermi level. However, several recent studies suggest that Fermi surface nesting is insufficient to understand charge density wave phenomenon especially for two and higher dimensions. It has been observed that electron-phonon coupling and Fermi surface nesting together can provide a better understanding for the mechanism of charge density wave. 1T-VSe_2 is an interesting material which undergoes incommensurate and commensurate charge density wave below 110 K. The present chapter demonstrates the involvement of electron-phonon coupling with incommensurate and commensurate charge density wave transitions in 1T-VSe_2 using temperature dependent Raman study from 300 K to 10 K.

Chapter 6: Emergence of Localized Polarization in Anti-ferroelectric $BaZrS_3$ Thin Film

This chapter discusses on the observation of localized ferroelectric polarization in chemical vapor deposition grown $BaZrS_3$ film through temperature dependent Raman study and supported by first principles calculations. The presence of localized ferroelectric phases is understood by the anomalous behavior of Raman modes in temperature dependent Raman study. Localized oxygen impurities break the center of inversion symmetry of ZrS_6 octahedra of $BaZrS_3$ and thus develop ferroelectric polarization. Existence of rotational mode of ZrS_6 octahedra with temperature and phonon band structure calculations suggested the stability of *Pnma* crystal structure of $BaZrS_3$. Electronic band structure calculations and optical spectroscopic studies showed that oxygen impurities did not modulate the nature and the band gap of $BaZrS_3$. Thus, localized ferroelectric polarization provides intrinsic charge separation that can enhance the efficiency of photovoltaic materials.

Chapter 7: Plasmon-Phonon Coupling and Vibrational Properties of $Cu_{2-x}Te$ Thermoelectric Material

The chapter summarizes the investigations on optical and vibrational properties of $Cu_{2-x}Te$ as *p*-type thermoelectric material. The interesting compound belongs to the class of Phonon-Liquid-Electron-Crystal of thermoelectric materials which provides a new pathway of achieving ultra-low thermal conductivity due to loosely bounded metal cation in the rigid sub-lattice of chalcogens. Due to the complex crystal structure, presence of polymorphic phases and various structural transitions vibrational properties of $Cu_{2-x}Te$ compounds are not well understood yet. In this chapter, vibrational properties and plasmon-phonon coupling with carrier concentration have been studied for $Cu_{1.25}Te$, $Cu_{1.6}Te$, and Cu_2Te using temperature and laser power dependent Raman studies in the temperature range of 300-773 K. Thermal conductivity of the three compounds are qualitatively estimated from phonon lifetime estimation through Raman spectroscopy.

Chapter 8: Conclusions and Future Scope

This chapter briefly summarizes the major highlights and outcomes of the thesis with the proposal for further studies and scope for future directions in the field.

Appendix 1: Matlab Simulation Codes for Optical Contrast Calculations

In appendix-1, the Matlab programming codes used to simulate optical contrast calculations for visibility of the transition metal dichalcogenides thin layers on SiO_2/Si substrate are documented. With the help of literature and understanding of the optical contrast, the codes have been written for Michelson and Weber contrast for thin film thickness identification. By taking example of graphene, the simulations helped in identifying the most appropriate thickness of SiO_2 layer on degenerately doped silicon substrates for specific wavelength of incident light using research grade microscope.

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