

FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY BASED ELECTRONIC
STRUCTURE CALCULATIONS OF SOME ZINC-OXIDE AND ZINC-
SULPHIDE POLYMORPHS

SAIRA SHABBIR

UNIVERSITI TEKNOLOGI MALAYSIA

FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY BASED ELECTRONIC
STRUCTURE CALCULATIONS OF SOME ZINC-OXIDE AND ZINC-
SULPHIDE POLYMORPHS

SAIRA SHABBIR

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

Faculty of Science
Universiti Teknologi Malaysia

FEBRUARY 2021

ACKNOWLEDGEMENT

By the grace of Almighty ALLAH, the most beneficent and merciful, it has been possible for me to complete my Ph.D. research work. All my respects for the Holy Prophet Muhammad (PBUH), the foundation of knowledge, whose life is like a beacon for us in every aspect.

First of all, I would like to express my sincerest appreciation and gratitude to my research supervisor Dr. Amiruddin Bin Shaari, co-supervisor Dr. Rashid Ahmed and external supervisor Dr. Bakhtiar Ul Haq for their valuable support, guidance, encouragement, and patient throughout this research period. Their technical expertise proved to be the key element for the successful completion of my doctoral research.

I am exceedingly thankful to Dr. Maqsood Ahmed, Centre for High Energy Physics, University of the Punjab, Lahore-PAKISTAN for their encouragement, technical guidance, and continuous support throughout the research work. I would like to extend my thanks to Dr. Sib Krishna Ghoshal for his continuous guidance. Special thanks to Mr. Ng Ying Xuan from whom I have learnt a lot. I am highly thankful to my lab colleagues; Dr. Arshad Hussain, Dr. Abdullahi Lawal Kubau, Mr. Summanuwa Timothy Ahams, Mr. M.C. Idris, and Dr. Afiq Radzwan for their support and cooperation. Lastly, and above all, I find no words to express my deepest gratitude to my loving parents, sisters and brothers for their selfless prayers and support for my success.

ABSTRACT

Recently, zinc oxide (ZnO) and zinc sulfide (ZnS) have drawn a resurgent attention in the research community due to their interesting properties with diverse potential applications. Wide bandgap, large exciton binding energy at room temperature, and small effective electron mass and piezoelectricity make ZnO a potential candidate for a variety of electronic and optoelectronic devices. ZnS possesses a direct bandgap of 3.6 eV at room temperature and appears to be a promising candidate for a broad range of technological applications including transparent conductors, visual displays and high-density optical memories. However, in order to realize the efficient utilization of ZnO and ZnS in blue, green and ultraviolet (UV) emitters with high efficiency, it is very important to modify these materials so that the full bandgap energy spectrum (from visible to UV) may be covered by the materials. Alloying of ZnO with sulfur (S) chalcogen reveals vivid changes in its electronic and optical properties due to the dramatic restructuring of electronic structure. In this thesis, the structural, electronic and optical properties of pure ZnO and $\text{ZnO}_{1-x}\text{S}_x$ ($x = 0, 0.25, 0.50, 0.75$ and 1) alloys in wurtzite (WZ), sphalerite type, germanium phosphide (GeP) type, 5-5 type, nickel arsenide (NiAs) type, β -beryllium oxide (BeO) type, and cesium chloride (CsCl) type are studied by using full-potential linearized augmented plane wave plus local orbital (FP-LAPW + l_o) method within density functional theory (DFT). The structural properties of pure ZnO and S-doped ZnO in seven crystal structures were calculated by using Perdew-Burke-Ernzerhof – generalized gradient approximation (PBE – GGA) exchange correlation whereas the calculations for electronic and optical properties were carried out by adding the mBJ potential to the PBE-GGA exchange correlation. The structural properties of S-doped ZnO in seven polymorphs reveal a small deviation from Vegard's law which is consistent with the findings from previous literature. It was found that the replacement of the oxygen (O) atom by S produces interesting effects on the band structures of ZnOS alloys. The electronic bandgaps of ZnOS alloys in WZ structure, sphalerite type and BeO type were enhanced from 2.65 eV to 3.68 eV, 2.50 eV to 3.60 eV and 2.85 eV to 3.75 eV, respectively. The bandgap of 5-5 type ZnOS alloys decreases from 3.12 eV to 2.63 eV and the band structures of GeP type and NiAs type ZnOS alloys show different variations with different concentrations. On the other hand, CsCl type ZnOS alloys exhibit a metallic nature. The static dielectric constants of the seven considered polymorphs reveal that the polarization of the S doped ZnO increases by increasing the S concentration. The CsCl type ZnOS alloys with metallic character were found to have the highest value of static dielectric constant. The results for optical properties show that the incorporation of S atoms moves the maximum absorption, reflectivity and conductivity peaks towards low photon energies which reveal the potential of S doped ZnO. The static refractive indices of all considered ZnOS alloys were found to be increased by increasing the S content. The analysis of the absorption spectra shows that WZ structure, sphalerite type and BeO type ZnOS alloys are the promising candidates for visible and UV photoelectronic devices. The 5-5 type and NiAs type ZnOS ZnOS alloys were found suitable for visible light regime applications. On the other hand, GeP type ZnOS alloys are best for the applications corresponding to infrared to visible region.

ABSTRAK

Baru-baru ini, zink oksida (ZnO) dan zink sulfida (ZnS) telah menarik perhatian semula dalam komuniti penyelidik disebabkan sifatnya yang menarik dengan pelbagai potensi aplikasi. Jurang jalur yang lebar, tenaga pengikat eksiton yang tinggi pada suhu bilik, dan jisim elektron berkesan dan kepiezoelektrikan yang kecil menjadikan ZnO sebagai calon yang berpotensi untuk pelbagai peranti elektronik dan optoelektronik. ZnS memiliki jurang jalur terus 3.6 eV pada suhu bilik dan muncul sebagai calon yang berpotensi untuk pelbagai aplikasi berteknologi termasuk pengkonduksi lutsinar, paparan visual dan memori optik berketumpatan tinggi. Walau bagaimanapun, bagi merealisasikan penggunaan ZnO dan ZnS secara cekap dalam pemancar biru, hijau dan ultraungu (UV) dengan kecekapan yang tinggi, adalah penting untuk mengubahsui bahan ini supaya spektrum tenaga jurang jalur penuh (daripada cahaya nampak ke UV) dapat diliputi oleh bahan ini. Pengaloiian ZnO dengan kalkogen sulfur (S) menunjukkan perubahan yang nyata pada sifat-sifat elektronik dan optiknya kerana penstrukturan semula struktur elektronik secara dramatik. Dalam tesis ini, sifat-sifat struktur, elektronik dan optik ZnO tulen dan aloi $ZnO_{1-x}S_x$ ($x = 0, 0.25, 0.50, 0.75$ dan 1) dalam wurtzite (WZ), jenis sfalerit, jenis germanium fosfida (GeP), jenis 5-5, jenis nikel arsenida (NiAs), jenis β -berilium oksida (BeO) dan jenis sesium klorida (CsCl) telah dikaji dengan menggunakan kaedah keupayaan-penuh terlinear gelombang satah terimbuhan ditambah orbital tempatan (FP-LAPW + l_o) dalam teori kefungsi ketumpatan (DFT). Sifat struktur ZnO tulen dan ZnO terdop-S dalam tujuh struktur hablur dikira dengan menggunakan korelasi pertukaran Perdew-Burke-Ernzerhof – penghampiran kecerunan teritlak (PBE – GGA) manakala pengiraan untuk sifat-sifat elektronik dan optik dilakukan dengan menambahkan keupayaan mBJ kepada korelasi pertukaran PBE-GGA. Sifat struktur ZnO terdop-S dalam tujuh polimorf menunjukkan penyimpangan kecil daripada hukum Vegard yang konsisten dengan dapatan daripada literatur sebelum ini. Didapati bahawa penggantian atom oksigen (O) oleh S menghasilkan kesan menarik terhadap struktur jalur aloi ZnOS. Jurang jalur elektronik aloi ZnOS dalam struktur WZ, jenis sfalerit dan jenis BeO didapati meningkat masing-masing daripada 2.65 eV kepada 3.68 eV, 2.50 eV kepada 3.60 eV dan 2.85 eV kepada 3.75 eV. Jurang jalur aloi ZnOS jenis 5-5 menurun daripada 3.12 eV kepada 2.63 eV dan struktur jalur aloi ZnOS jenis GeP dan NiAs menunjukkan variasi yang berbeza dengan kepekatan yang berbeza. Sebaliknya, aloi ZnOS jenis CsCl menunjukkan sifat logam. Pemalar dielektrik statik daripada tujuh polimorf yang dipertimbang menunjukkan bahawa pengutuban ZnO terdop-S meningkat dengan peningkatan kepekatan S. Aloi ZnOS jenis CsCl yang bercirikan logam didapati memiliki nilai pemalar dielektrik statik tertinggi. Hasil sifat optik menunjukkan bahawa penggabungan atom S menggerakkan puncak penyerapan, keterpantulan dan kekonduksian maksimum ke arah tenaga foton yang rendah yang mendedahkan potensi ZnO terdop-S. Indeks biasan statik semua aloi ZnOS yang dipertimbang didapati meningkat dengan peningkatan kandungan S. Analisis spektrum penyerapan menunjukkan bahawa aloi ZnOS dalam struktur WZ, jenis sfalerit dan jenis BeO adalah calon yang berpotensi untuk peranti fotoelektronik cahaya nampak dan UV. Aloi ZnOS jenis 5-5 dan jenis NiAs didapati sesuai untuk aplikasi dalam rejim cahaya nampak. Sebaliknya, aloi ZnOS jenis GeP adalah terbaik untuk aplikasi berpadanan dengan rantau inframerah hingga kepada cahaya nampak.

TABLE OF CONTENTS

TITLE	PAGE
DECLARATION	iii
DEDICATION	iv
ACKNOWLEDGEMENT	v
ABSTRACT	vi
ABSTRAK	vii
LIST OF TABLES	xv
LIST OF FIGURES	xvii
LIST OF ABBREVIATIONS	xxvii
LIST OF SYMBOLS	xxix
CHAPTER 1 INTRODUCTION	1
1.1 Background of the Study	1
1.2 Problem Statement	3
1.3 Objectives of the Study	4
1.4 Scope of the Study	4
1.5 Significance of the Study	5
1.6 Thesis Organisation	6
CHAPTER 2 LITERATURE REVIEW	9
2.1 Group II-VI Compounds: Wide Bandgap Semiconductors	9
2.2 Applications of Wide Bandgap Semiconductors	10
2.3 Structural Properties of ZnO	11
2.4 Structural Properties of ZnS	13
2.5 Band Structure and Density of States of Materials	14
2.5.1 Electronic Structure Properties of ZnO	15
2.5.2 Electronic Structure Properties of ZnS	16
2.6 Optical Properties of Materials	17
2.6.1 Optical Properties of ZnO	18
2.6.2 Optical Properties of ZnS	19

2.7	Bandgap Engineering	19
2.8	Sulfur Doped Zinc Oxide	19
2.9	Fitting Equation for Structural Properties of ZnOS Alloys	20
2.10	Some Properties of ZnO and ZnS	20
2.11	The Many-Particle Problem in Solids	24
2.12	The Born-Oppenheimer Approximation	24
2.13	Density Functional Theory (DFT)	25
2.14	Hartree Approximation	25
2.15	Hohenberg-Kohn Theorems	26
	2.15.1 First Hohenberg-Kohn Theorem	27
	2.15.2 Second Hohenberg-Kohn Theorem	27
2.16	The Energy Functional	27
2.17	The Kohn-Sham Scheme	28
2.18	Exchange-Correlation Functional	29
	2.18.1 Local Density Approximation (LDA)	29
	2.18.2 Generalized Gradient Approximation (GGA)	30
	2.18.3 Modified Becke-Johnson (mBJ) Potential	30
2.19	Bulk Systems and Finite Systems	31
2.20	Bloch's Theorem for Bulk Systems	31
2.21	Pseudopotential Method and Full-Potential Method	32
2.22	k-points	34
2.23	Volume Optimization	34
2.24	Comparative Literature Summary	35
CHAPTER 3	METHODOLOGY	37
3.1	Introduction	37
3.2	Flow Chart of Solving Kohn-Sham Equation in WIEN2k	37
3.3	Steps to Run the Simulations Using WIEN2k	39
	3.3.1 Generating the Structure	39
	3.3.2 Initialization of the Calculations	40
	3.3.3 The Self Consistent Field (SCF) Calculations	41

3.3.4	Convergence Test	44
3.3.5	Volume Optimization	45
3.3.6	Band Structure	45
3.3.7	Density of States (DOS)	46
3.3.8	Optical Properties	47
3.4	Computational Details	48
CHAPTER 4	RESULTS AND DISCUSSION	51
4.1	Introduction	51
4.2	Optimized Values of k-points and RKmax	51
4.3	Structural Properties of Seven Polymorphs of ZnO	53
4.4	Band Structure and Density of States of Seven Polymorphs of ZnO	57
4.5	Optical Properties of ZnO Polymorphs	64
4.5.1	Imaginary Part of Dielectric Function	64
4.5.2	Real Part of Dielectric Function	67
4.5.3	Reflectivity	70
4.5.4	Absorption Coefficient	73
4.5.5	Conductivity	74
4.5.6	Refractive Index	76
4.6	Band Structure, Density of States, Optical and Structural Properties of S Doped ZnO in WZ Structure	78
4.6.1	Structural Properties of S Doped ZnO in WZ Structure	78
4.6.2	Band Structure of S Doped ZnO in WZ Structure	82
4.6.3	Density of States of S Doped ZnO in WZ Structure	84
4.6.4	Optical Properties of S Doped ZnO in WZ Structure	86
4.6.4.1	Imaginary Part of Dielectric Function	86
4.6.4.2	Real Part of Dielectric Function	88
4.6.4.3	Reflectivity	89

	4.6.4.4	Absorption Coefficient	90
	4.6.4.5	Conductivity	91
	4.6.4.6	Refractive Index	92
4.7		Band Structure, Density of States, Optical and Structural Properties of S Doped ZnO in Sphalerite Type	95
	4.7.1	Structural Properties of S Doped ZnO in Sphalerite Type	95
	4.7.2	Band Structure of S Doped ZnO in Sphalerite Type	99
	4.7.3	Density of States of S Doped ZnO in Sphalerite Type	100
	4.7.4	Optical Properties of S Doped ZnO in Sphalerite Type	102
	4.7.4.1	Imaginary Part of Dielectric Function	103
	4.7.4.2	Real Part of Dielectric Function	104
	4.7.4.3	Reflectivity	105
	4.7.4.4	Absorption Coefficient	106
	4.7.4.5	Conductivity	107
	4.7.4.6	Refractive Index	108
4.8		Band Structure, Density of States, Optical and Structural Properties of S Doped ZnO in GeP Type	111
	4.8.1	Structural Properties of S Doped ZnO in GeP Type	111
	4.8.2	Band Structure of S Doped ZnO in GeP Type	115
	4.8.3	Density of States of S Doped ZnO in GeP Type	117
	4.8.4	Optical Properties of S Doped ZnO in GeP Type	119
	4.8.4.1	Imaginary Part of Dielectric Function	119
	4.8.4.2	Real Part of Dielectric Function	121
	4.8.4.3	Reflectivity	122
	4.8.4.4	Absorption Coefficient	123
	4.8.4.5	Conductivity	124

	4.8.4.6	Refractive Index	125
4.9		Band Structure, Density of States, Optical and Structural properties of S Doped ZnO in 5-5 Type	127
	4.9.1	Structural Properties of S Doped ZnO in 5-5 Type	127
	4.9.2	Band Structure of S Doped ZnO in 5-5 Type	131
	4.9.3	Density of States of S Doped ZnO in 5-5 Type	133
	4.9.4	Optical Properties of S Doped ZnO in 5-5 Type	135
	4.9.4.1	Imaginary Part of Dielectric Function	136
	4.9.4.2	Real Part of Dielectric Function	137
	4.9.4.3	Reflectivity	138
	4.9.4.4	Absorption Coefficient	139
	4.9.4.5	Conductivity	140
	4.9.4.6	Refractive Index	141
4.10		Band Structure, Density of States, Optical and Structural Properties of S Doped ZnO in NiAs Type	144
	4.10.1	Structural Properties of S Doped ZnO in NiAs Type	144
	4.10.2	Band Structure of S Doped ZnO in NiAs Type	149
	4.10.3	Density of States of S Doped ZnO in NiAs Type	150
	4.10.4	Optical Properties of S Doped ZnO in NiAs Type	152
	4.10.4.1	Imaginary Part of Dielectric Function	153
	4.10.4.2	Real Part of Dielectric Function	154
	4.10.4.3	Reflectivity	155
	4.10.4.4	Absorption Coefficient	156
	4.10.4.5	Conductivity	157
	4.10.4.6	Refractive Index	158
4.11		Band Structure, Density of States, Optical and Structural Properties of S Doped ZnO in BeO Type	160

4.11.1	Structural Properties of S Doped ZnO in BeO Type	160
4.11.2	Band Structure of S Doped ZnO in BeO Type	164
4.11.3	Density of States of S Doped ZnO in BeO Type	166
4.11.4	Optical Properties of S Doped ZnO in BeO Type	168
4.11.4.1	Imaginary Part of Dielectric Function	169
4.11.4.2	Real Part of Dielectric Function	170
4.11.4.3	Reflectivity	171
4.11.4.4	Absorption Coefficient	172
4.11.4.5	Conductivity	173
4.11.4.6	Refractive Index	174
4.12	Band Structure, Density of States, Optical and Structural Properties of S Doped ZnO in CsCl Type	176
4.12.1	Structural Properties of S Doped ZnO in CsCl Type	176
4.12.2	Band Structure of S Doped ZnO in CsCl Type	180
4.12.3	Density of States of S Doped ZnO in CsCl Type	181
4.12.4	Optical Properties of S Doped ZnO in CsCl Type	183
4.12.4.1	Imaginary Part of Dielectric Function	183
4.12.4.2	Real Part of Dielectric Function	185
4.12.4.3	Reflectivity	186
4.12.4.4	Absorption Coefficient	187
4.12.4.5	Conductivity	188
4.12.4.6	Refractive Index	189
4.13	Comparative Evaluation	192
CHAPTER 5	CONCLUSION AND FURTHER OUTLOOK	195
5.1	Conclusion	195
5.2	Further Outlook	197

REFERENCES	199
LIST OF PUBLICATIONS	209
APPENDICES A-C	211

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 2.1	Comparison of the material properties of some semiconductors at room temperature. Data is taken from the work of Pavlidis et al. [17].	10
Table 2.2	Recent findings by the researchers on the different structure types of ZnO and ZnOS.	35
Table 3.1	Input parameters of WZ, sphalerite type, GeP type, 5-5 type, NiAs type, BeO type, and CsCl type polymorphs of ZnO.	39
Table 3.2	The values of muffin tin radii for Zn, O and S used in the present work.	49
Table 4.1	Optimized lattice parameters of seven polymorphs of pure ZnO.	56
Table 4.2	Calculated E_g values for ZnO polymorphs.	60
Table 4.3	The optical bandgaps, ϵ_o and E_p values of seven polymorphs of ZnO along the x- and z-directions.	70
Table 4.4	Calculated values of lattice constants (a , c), B_0 , E_g , ϵ_o , E_p and $n(0)$ of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	94
Table 4.5	Calculated values of lattice constants ($a = b = c$), B_0 , E_g , ϵ_o , E_p and $n(0)$ of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	110
Table 4.6	Calculated values of lattice constants (a , c), B_0 , E_g , ϵ_o , E_p and $n(0)$ of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	126
Table 4.7	Calculated values of lattice constants (a , c), B_0 , E_g , ϵ_o , E_p and $n(0)$ of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys for various S doping concentrations (x).	143
Table 4.8	Calculated values of lattice constants (a , c), B_0 , E_g , ϵ_o , E_p and $n(0)$ of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	159

Table 4.9	Calculated values of lattice constants (a , c), B_0 , E_g , ϵ_0 , E_p and $n(0)$ of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentration (x).	175
Table 4.10	Calculated values of lattice constants ($a = b = c$), B_0 , E_g , ϵ_0 , E_p and $n(0)$ of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	191
Table 4.11	Comparison of the calculated E_g of pure ZnO with previous theoretical and experimental reports.	193
Table 4.12	Variation in E_g values of ZnOS alloys and their enhanced capabilities for various regions of the electromagnetic spectrum.	194

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 2.1	Crystal structures of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO. Grey atoms are Zn and red atoms are O [10].	13
Figure 2.2	Crystal structures of (a) ZB and (b) WZ forms of ZnS [26].	14
Figure 2.3	Electronic band structure of WZ ZnO using LDA with self-interaction correction [31].	15
Figure 2.4	Electronic band structures of (a) sphalerite type (b) GeP type (c) NiAs type and (d) BeO type of ZnO calculated with mBJ potential [23].	16
Figure 2.5	Electronic band structures of (a) ZB and (b) WZ ZnS calculated by using GGA [32].	16
Figure 2.6	Electron as a point charge in the field of other electrons.	26
Figure 2.7	Illustration of the pseudopotential method [70].	33
Figure 2.8	Partitioning of the unit cell into atomic spheres (I) and interstitial region (II) [71].	33
Figure 3.1	Pictorial representation of solving the Kohn-Sham equation in WIEN2k code [78].	38
Figure 3.2	Flow chart of initialize calculations and self-consistent field (SCF) cycle in WIEN2k code [29].	43
Figure 3.3	Band structure graphs for pure (a) ZnO and (b) ZnS [1, 53].	46
Figure 3.4	DOS plots for pure (a) ZnO and (b) ZnS [83, 84].	47
Figure 4.1	Optimized values of (a) k-points and (b) RKmax for ZnO in stable WZ structure.	52
Figure 4.2	Crystal structures of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO generated in the WIEN2k code. Purple and red spheres are Zn and O atoms respectively.	53

Figure 4.3	Energy versus volumes curves of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	55
Figure 4.4	The first Brillouin Zone diagrams of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	58
Figure 4.5	The calculated electronic band structures of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	59
Figure 4.6	Total density of states of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	62
Figure 4.7	Partial density of states of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	64
Figure 4.8	Imaginary part of dielectric function of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	66
Figure 4.9	Real part of dielectric function of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	68
Figure 4.10	Reflectivity of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO. Green and orange spheres represent E_p of x- and z-components respectively.	72
Figure 4.11	Absorption coefficient of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	74
Figure 4.12	Conductivity of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	76
Figure 4.13	Refractive indices of (a) WZ, (b) sphalerite type, (c) GeP type, (d) 5-5 type, (e) NiAs type, (f) BeO type and (g) CsCl type polymorphs of ZnO.	77
Figure 4.14	A schematic representation of a unit cell and an 8-atom supercell constructed for WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	78
Figure 4.15	Total energy versus volume curves of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	80

Figure 4.16	Optimized (a) lattice parameters and (b) bulk modulus of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys plotted versus S doping concentrations (x). Dotted lines are representing the Vegard's law.	81
Figure 4.17	Electronic band structures of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$. The red bands in the electronic structure represent VB and CB. Yellow spheres denote VBM whereas green spheres represent the CBM.	83
Figure 4.18	Variation in the energy bandgaps of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines are representing Vegard's law.	84
Figure 4.19	Total and partial density of states of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	85
Figure 4.20	The imaginary part of the dielectric function of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph represents that the onset of $\epsilon_2(\omega)$ is experiencing a blue shift by adding the S atom.	87
Figure 4.21	The real part of the dielectric function of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	88
Figure 4.22	The reflectivity of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). Cyan, grey, yellow, brown, and green spheres represent the plasmon energies for $x = 0, 0.25, 0.50, 0.75,$ and 1 respectively.	89
Figure 4.23	Absorption coefficient of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). Cyan colored spheres with vertical dotted lines in the inset of graph denote the electronic bandgaps of ZnOS alloys. The inset of the graph shows that the absorption edges are blue-shifted with S concentration.	91
Figure 4.24	The conductivity of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the onset of optical conductivities is equivalent to their energy bandgaps.	92
Figure 4.25	Refractive indices of WZ $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the static refractive index is increasing with S concentration.	93
Figure 4.26	A schematic representation of a unit cell and an 8-atom supercell constructed for sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	95

Figure 4.27	Total energy versus volume curves of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	96
Figure 4.28	Optimized (a) lattice parameters and (b) bulk modulus of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys plotted versus S doping concentration (x). Dotted lines are representing the Vegard's law.	98
Figure 4.29	Electronic band structures of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$. The red bands in the electronic structure represent VB and CB. Yellow spheres denote VBM whereas green spheres represent the CBM.	99
Figure 4.30	Variation in the energy bandgaps of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentration (x). Dotted lines are representing Vegard's law.	100
Figure 4.31	Total and partial density of states of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	101
Figure 4.32	The imaginary part of the dielectric function of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph represents a blue shift in the onset of $\epsilon_2(\omega)$ with an increase in S atom.	103
Figure 4.33	The real part of the dielectric function of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	104
Figure 4.34	The reflectivity of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). Cyan, grey, yellow, brown, and green spheres represent the plasmon energies for $x = 0, 0.25, 0.50, 0.75$, and 1 respectively.	105
Figure 4.35	Absorption coefficient of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). Cyan colored spheres with vertical dotted lines in insets of graphs denote the electronic bandgaps of ZnOS alloys. The inset of the graph shows that the absorption edges are blue-shifted with S concentrations.	106
Figure 4.36	The conductivity of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the onset of optical conductivities is equivalent to their energy bandgaps and are blue shifted.	107
Figure 4.37	Refractive indices of sphalerite type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the static refractive index is increasing with S concentration.	108

Figure 4.38	A schematic representation of a unit cell and an 8-atom supercell constructed for GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	112
Figure 4.39	Total energy versus volume curves of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	113
Figure 4.40	Optimized (a) lattice parameters and (b) bulk modulus of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys plotted versus S doping concentrations (x). Dotted lines are representing Vegard's law.	114
Figure 4.41	Electronic band structures of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$. The red bands in the electronic structure represent VB and CB. Yellow spheres denote VBM whereas green spheres represent the CBM.	116
Figure 4.42	Variation in the energy bandgaps of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines are representing Vegard's law.	117
Figure 4.43	Total and partial density of states of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	118
Figure 4.44	The imaginary part of the dielectric function of the GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph represents the first major structures of $\epsilon_2(\omega)$ which are varying according to their energy bandgaps.	120
Figure 4.45	The real part of the dielectric function of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The vertical dotted lines represent the plasmon energy of GeP type ZnOS alloys.	121
Figure 4.46	The reflectivity of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). Cyan, grey, yellow, brown, and green spheres represent the plasmon energies for $x = 0, 0.25, 0.50, 0.75$, and 1 respectively.	122
Figure 4.47	Absorption coefficient of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys for various S doping concentrations (x). The inset of the graph shows that the onset of the absorption spectrum is varying according to their energy bandgaps.	123
Figure 4.48	The conductivity of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the onset of optical conductivities is equivalent to their energy bandgaps.	124

Figure 4.49	Refractive indices of GeP type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the static refractive index is increasing with S concentrations.	125
Figure 4.50	A schematic representation of a unit cell and an 8-atom supercell constructed for 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	128
Figure 4.51	Total energy versus volume curves of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	129
Figure 4.52	Optimized (a) lattice parameters and (b) bulk modulus of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines are representing the Vegard's law.	130
Figure 4.53	Electronic band structures of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$. The red bands in the electronic structure represent VB and CB. Yellow spheres denote VBM whereas green spheres represent the CBM.	132
Figure 4.54	Variation in the energy bandgaps of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentration (x). Dotted lines represent the Vegard's law.	133
Figure 4.55	Total and partial density of states of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	134
Figure 4.56	The imaginary part of the dielectric function of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with S doping concentrations (x). The inset of the graph represents a redshift in the onset of ϵ_2 (ω) with an increase in S atom.	136
Figure 4.57	The real part of the dielectric function of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The vertical dotted lines represent the plasmon energy of 5-5 type ZnOS alloys.	137
Figure 4.58	The reflectivity of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentration (x). Cyan, grey, yellow, brown, and green spheres are representing the plasmon energies for $x = 0, 0.25, 0.50, 0.75$, and 1 respectively.	138
Figure 4.59	Absorption coefficient of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentration (x). Colored spheres with vertical solid lines in the inset of graph denote the electronic bandgaps of 5-5 type ZnOS alloys. The inset of the graph shows that the absorption edges are red-shifted	

	with S concentration due to decrement in the energy bandgaps.	139
Figure 4.60	The conductivity of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentration (x). The inset of the graph shows that the onset of optical conductivities of 5-5 type ZnOS alloys is almost equivalent to their electronic bandgaps and is showing redshift.	140
Figure 4.61	Refractive indices of 5-5 type $\text{ZnO}_{1-x}\text{S}_x$ alloy with various S doping concentration (x). The inset of the graph shows that the static refractive index is increasing with S concentration.	141
Figure 4.62	A schematic representation of a unit cell and an 8-atom supercell constructed for NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	145
Figure 4.63	Total energy versus volume curves of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	146
Figure 4.64	Optimized (a) lattice parameters and (b) bulk modulus of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines are representing the Vegard's law.	148
Figure 4.65	Electronic band structures of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$. The red bands in the electronic structure represent VB and CB. Yellow spheres denote VBM whereas green spheres represent the CBM.	149
Figure 4.66	Variation in the energy bandgaps of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines are representing the Vegard's law.	150
Figure 4.67	Total and partial density of states of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	151
Figure 4.68	The imaginary part of the dielectric function of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x).	153
Figure 4.69	The real part of the dielectric function of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The vertical dotted lines represent the plasmon energy of NiAs type ZnOS alloys.	154
Figure 4.70	The reflectivity of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys for various S doping concentrations (x). Cyan, grey, yellow, brown, and green spheres are representing the plasmon energies of	

	NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys for $x = 0, 0.25, 0.50, 0.75,$ and 1 respectively.	155
Figure 4.71	Absorption coefficient of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the absorption edges are varying according to the variation in their energy bandgaps.	156
Figure 4.72	The conductivity of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the onset of optical conductivities is varying according to their energy bandgaps.	157
Figure 4.73	Refractive indices of NiAs type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the static refractive index is increasing with S concentration.	158
Figure 4.74	A schematic representation of a unit cell and an 8-atom supercell constructed for BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0,$ (b) $x = 0.25,$ (c) $x = 0.50,$ (d) $x = 0.75$ and (e) $x = 1.$	161
Figure 4.75	Total energy versus volume curves of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0,$ (b) $x = 0.25,$ (c) $x = 0.50,$ (d) $x = 0.75$ and (e) $x = 1.$	162
Figure 4.76	Variation in the (a) lattice parameters and (b) bulk modulus of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines are representing the Vegard's law.	163
Figure 4.77	Electronic band structures of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0,$ (b) $x = 0.25,$ (c) $x = 0.50,$ (d) $x = 0.75$ and (e) $x = 1.$ The red bands in the electronic structure represent VB and CB. Yellow spheres denote VBM whereas green spheres represent the CBM.	165
Figure 4.78	Variation in the energy bandgaps of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines represent the Vegard's law.	166
Figure 4.79	Total and partial density of states of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0,$ (b) $x = 0.25,$ (c) $x = 0.50,$ (d) $x = 0.75$ and (e) $x = 1.$	167
Figure 4.80	The imaginary part of the dielectric function of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph represents a blue shift in the onset of $\epsilon_2(\omega)$ with an increase in sulfur atom.	169
Figure 4.81	The real part of dielectric function of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The	

	vertical dotted lines represent the plasmon energy of BeO type ZnOS alloys.	170
Figure 4.82	The reflectivity of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentration (x). Cyan, grey, yellow, brown and green spheres are representing the plasmon energies for $x = 0, 0.25, 0.50, 0.75$ and 1 respectively.	171
Figure 4.83	Absorption coefficient of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentration (x). Colored spheres with vertical solid lines in the inset of graph denote the electronic bandgaps of BeO type ZnOS alloys. The inset of the graph shows that the absorption edges are blue-shifted with S concentration.	172
Figure 4.84	The conductivity of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentration (x). The inset of the graph shows that the onset of optical conductivities is equivalent to their electronic bandgaps and showing a blue shift.	173
Figure 4.85	Refractive indices of BeO type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows that the static refractive index is increasing with S concentration.	174
Figure 4.86	A schematic representation of a unit cell and an 8-atom supercell constructed for CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	177
Figure 4.87	Total energy versus volume curves of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	178
Figure 4.88	Variation in the (a) lattice parameters and (b) bulk modulus of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys as a function of S doping concentrations (x). Dotted lines are representing the Vegard's law.	179
Figure 4.89	Electronic band structures of CsCl type ZnOS $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$. The red and pink bands in the electronic structure are representing VB and CB. Yellow spheres denote VBM whereas green spheres represent the CBM.	180
Figure 4.90	Total and partial density of states of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.	182
Figure 4.91	The imaginary part of the dielectric function of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows the onset of $\epsilon_2(\omega)$.	184

Figure 4.92	The real part of the dielectric function of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The vertical dotted lines represent the plasmon energy.	185
Figure 4.93	The reflectivity of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). Cyan, grey, yellow, brown, and green spheres are representing the plasmon energies for $x = 0, 0.25, 0.50, 0.75,$ and 1 respectively.	186
Figure 4.94	Absorption coefficient of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows the onset of the absorption spectra.	187
Figure 4.95	The conductivity of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows the onset of optical conductivities.	189
Figure 4.96	Refractive indices of CsCl type $\text{ZnO}_{1-x}\text{S}_x$ alloys with various S doping concentrations (x). The inset of the graph shows the static refractive index versus sulfur doping concentration.	190

LIST OF ABBREVIATIONS

Zn	-	Zinc
Cd	-	Cadmium
Hg	-	Mercury
O	-	Oxygen
S	-	Sulfur
Se	-	Selenium
Te	-	Tellurium
ZnO	-	Zinc oxide
ZnS	-	Zinc sulfide
ZnTe	-	Zinc telluride
CdO	-	Cadmium oxide
CdS	-	Cadmium sulfide
CdTe	-	Cadmium telluride
Si	-	Silicon
GaAs	-	Gallium arsenide
SiC	-	Silicon carbide
GaN	-	Gallium nitride
ZnOS		Sulfur doped ZnO
WZ	-	Wurtzite
GeP	-	Germanium phosphide
BeO	-	Beryllium oxide
NiAs	-	Nickel arsenide
CsCl	-	Cesium chloride
APW	-	Augmented Plane Wave
DFT	-	Density Functional Theory
FP-LAPW	-	Full Potential Linearized Augmented Plane Wave
LAPW	-	Linearized Augmented Plane Wave
LDA	-	Local Density Approximations
GGA-PBE	-	Generalized gradient approximations by Perdew <i>et al.</i>
mBJ	-	Modified Becke-Johnson

BZ	-	Brillouin Zone
CBM	-	Conduction band minimum
VBM	-	Valence band maximum
E_g	-	Bandgap
DOS	-	Density of states
SCF	-	Self-consistent field
UV	-	Ultraviolet
LEDs	-	Light-emitting diodes
v_s	-	Saturation velocity
E_B	-	Breakdown field
μ	-	Electron mobility

LIST OF SYMBOLS

\AA	-	Angstrom
ψ	-	Wave function
eV	-	Electron volt
h	-	Plank's constant
\hbar	-	Reduced Plank's constant
∇	-	Gradient operator
Γ	-	Gamma
E	-	Energy
$\rho(\mathbf{r})$ $\rho_0(\mathbf{r})$	-	Electron density
$E_{XC}[\{\psi_i\}]$	-	Ground state electron density
$-\frac{\hbar}{2m}\nabla^2$	-	Exchange-correlation functional
	-	Kinetic energy operator
$V_{ext}(\mathbf{r})$	-	External potential
$V_H(\mathbf{r})$	-	Hartree potential
$V_{XC}(\mathbf{r})$	-	Exchange-correlation potential
ϵ_{xc}	-	Exchange-correlation energy
$V_{x,\sigma}^{BR}(\mathbf{r})$	-	Becke-Roussel potential
$t_\sigma(\mathbf{r})$	-	Kinetic-energy density
$\rho_\sigma(\mathbf{r})$	-	Spin dependent density of states
$e^{ik.r}$	-	Plane wave
$\epsilon_1(\omega)$	-	Real part of dielectric function
$\epsilon_2(\omega)$	-	Imaginary part of dielectric function
ϵ_0	-	Static dielectric constant
$\alpha(\omega)$	-	Absorption coefficient
$R(\omega)$	-	Reflectivity
$\sigma(\omega)$	-	Optical conductivity
$n(\omega)$	-	Refractive index
$n(0)$	-	Static refractive index

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The quest of finding the wide bandgap semiconductors with enhanced and modified properties for various optoelectronic applications are never ending. Wide bandgap semiconductors from the group II-VI family are the most appealing members for their great potential to be used in electronic and optoelectronic devices, chemical sensors, catalysts, light-emitting diodes, and so forth [1].

ZnO is one of the most demanding compounds from the above-mentioned family and it has gained considerable attention in the research community due to its wide bandgap (3.44 eV), large exciton binding energy (60 meV) at room temperature, small effective electron mass and piezoelectricity [2]. Therefore, ZnO has remarkable potential applications for a variety of electronic and optoelectronic devices. It is used in heat mirrors, bioimaging and an additive material in the ultraviolet absorber, pigment, gas sensor, and rubber production, etc. ZnO is also a promising candidate for transparent ohmic contacts, optical devices, transducers, light-emitting diodes, and transparent thin-film transistors. ZnO powder is used in different materials such as ceramics, glasses, and food, etc. [3].

Another well-known wide bandgap semiconductor from the II-VI family is ZnS. ZnS possesses a direct bandgap of 3.6 eV at room temperature and appears to be a promising candidate for a broad range of technological applications including transparent conductors, visual displays and high-density optical memories, etc. ZnS is widely used in electronic, optical, and photonic devices as well [4].

Due to the remarkable features of ZnO and ZnS, they are extensively used in various optoelectronic devices. However, in order to produce ZnO and ZnS based

sensors and blue, green and UV emitters with high efficiency, it is very important to modify these materials so that the full bandgap energy spectrum (from visible to UV) may be covered by the materials [5]. It is reported that this type of spectrum can be established by the substitution of the isoelectronic cations or anions in ZnO. As compared to the anion-substituted ZnO alloys, a numerous work on the theoretical and experimental study of the ZnO alloys with cations substitution is presented by different researchers, for instance, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, $\text{Be}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ [6-8]. Due to the large difference in the electronegativities and the size of O and S, the incorporation of S atoms in ZnO can produce a remarkable change in the physical properties of ZnOS alloys [9].

As it is well known that in nature, ZnO possesses the wurtzite structure which is stable at room temperature; however, it is reported that different modified (metastable) structures of ZnO are also possible. One of them is known as sphalerite type ZnO which can be obtained by growing the ZnO on cubic substrates. It is also reported that during the global optimization at different negative pressures, various metastable modifications of ZnO compound can be achieved such as 5-5 type, germanium phosphide (GeP) type, nickel arsenide (NiAs) type, cesium chloride (CsCl) type and β -beryllium oxide (BeO) type [10].

Presently, a few studies on the new structures of pure ZnO are available which are mostly related to their structure stability and the band structures calculations. Due to this fact, this research was conducted to perform the detailed discussions on the structural, electronic and optical properties of pure ZnO and the anion-substituted S doped ZnO alloys in the newly discovered polymorphs of ZnO along with the stable (WZ) structure. Furthermore, the selection of the suitable method and the proper exchange correlation functional to obtain the accurate energy bandgaps especially for the strong correlated systems is always a challenging task. The conventional exchange correlation functional such as LDA and GGA cannot provide the accurate bandgaps. Therefore, in this thesis, the calculations of the electronic band structures are carried out by using the mBJ potential which has the ability to provide the bandgaps close to the experimental results.

1.2 Problem Statement

Group II-VI semiconductors presenting the wide bandgaps are considered to have great potential for a broad range of optoelectronic applications. Two most demanding materials from the above mentioned group are ZnO and ZnS which are suitable for many technological applications. However, pure ZnO and ZnS cannot achieve the various wavelength ranges (from visible to ultraviolet) which is the disadvantage for the devices such as sensors and blue, green and ultraviolet emitters. Modifying the band structures of pure ZnO and ZnS to achieve the various ranges of wavelengths is the key issue.

Consequently, the idea for the incorporation of S atoms in ZnO or O atoms in ZnS is introduced in which the energy bandgaps cover the desired wavelength ranges [5]. The effect of the S atoms on the structural properties of ZnO in the newly discovered polymorphs (sphalerite type, GeP type, 5-5 type, NiAs type, BeO type, and CsCl type) is not studied yet. Detail studies on the electronic structures of S doped ZnO alloys are still lacking. The small energy bandgaps by using the LDA and GGA being the main limitation for the strong correlated systems must be overcome.

The evolution in the different optical parameters such as real and imaginary part of dielectric function, absorption coefficient, reflectivity, conductivity and refractive index of S doped ZnO alloys in the considered metastable structures is not reported yet. Therefore, the main focus of the current study is to examine the influence of S atoms on the structural, electronic and optical properties of ZnO in wurtzite, sphalerite type, GeP type, 5-5 type, NiAs type, BeO type, and CsCl type. The aim is to relate the significant enhancement of the electronic bandgaps with the most suitable exchange correlation potential (mBJ) used in the present study.

1.3 Objectives of the Study

The main goal of this research is to design cheap and non-toxic zinc oxide and zinc sulfide based binary and ternary compounds in seven polymorphs for optoelectronic devices. The objectives of this research can be summarized as follow:

1. To determine the structure and morphology of pure ZnO and ZnO_{1-x}S_x alloys with the various S doping concentrations ($x = 0, 0.25, 0.50, 0.75$ and 1) in seven polymorphs including wurtzite, sphalerite type, GeP type, 5-5 type, NiAs type, BeO type and CsCl type within the framework of DFT.
2. To analyze the electronic band structures of pure ZnO and ZnO_{1-x}S_x alloys with the various S doping concentrations ($x = 0, 0.25, 0.50, 0.75,$ and 1) in seven structural geometries.
3. To determine the optical properties such as real and imaginary part of dielectric function, conductivity, reflectivity, absorption coefficient and refractive index of the seven polymorphs of pure ZnO and ZnO_{1-x}S_x alloys with various S doping concentrations ($x = 0, 0.25, 0.50, 0.75,$ and 1) for applications in photovoltaic and other optoelectronic devices.

1.4 Scope of the Study

Using the DFT-based full potential linearized augmented plane wave (FP-L(APW+*l*o)) method with different exchange correlations and potential; the structural, electronic and optical properties of seven polymorphs (wurtzite, sphalerite type, GeP type, 5-5 type, NiAs type, BeO type, and CsCl type) of ZnO are carried out. The incorporation of the S atoms in seven polymorphs of ZnO with various S doping concentrations such as 0, 0.25, 0.50, 0.75, and 1 were taken into account by using the supercell approach.

The structural properties (lattice constants and bulk modulus) of pure ZnO in seven structures were calculated by using the PBE-GGA exchange correlation. The

effect of sulfur on the structural properties of the considered seven polymorphs of ZnO was investigated by the replacement of oxygen atoms with sulfur atoms.

Investigations of the electronic properties (band structure and density of states) of pure ZnO in seven polymorphs were carried out by using TB-mBJ potential in which PBE-GGA was used as exchange correlation. The effect of S atoms with various doping concentrations on the nature of the electronic band structures of considered polymorphs of ZnO was also observed.

Calculations of the optical properties (real and imaginary parts of the dielectric function, reflectivity, conductivity, absorption coefficient, and refractive indices) of pure ZnO in the seven considered structures were carried out by using TB-mBJ potential along with PBE-GGA as exchange correlation. Moreover, the change in the absorption spectra, conductivity, dielectric constant, reflectivity and the refractive index of S doped ZnO in wurtzite, sphalerite type, GeP type, 5-5 type, NiAs type, BeO type, and CsCl type is also examined.

1.5 Significance of the Study

The quest for finding the non-toxic wide bandgap materials with large energy ranges for optoelectronic devices is never-ending. The study concerning the wide bandgap materials with broad ranges of applications is crucial due to the increasing demands of the advanced optical and electronic devices. The remarkable potential exhibited by ZnO and ZnS as wide bandgap semiconductors need to explore the different features such as electronic, structural and optical properties to be used in the future. In this study, the S doped ZnO alloys in the newly discovered polymorphs along with the stable WZ structure of ZnO are appeared as the promising candidates for various optical devices in the different ranges of wavelengths. The understanding of the electronic structures of ZnO doped with five concentrations of the S atoms provided better control to achieve the desirable energy ranges. Moreover, new structures of the ZnO are found to have the interesting features which can be used for the future optical devices. In the current study, the detailed discussion on the

structural, electronic and optical properties of seven structures of ZnO and ZnOS alloys will lead to extent of knowledge in the exploration of the materials with superior optical properties for diverse applications in the optoelectronic devices.

1.6 Thesis Organisation

This thesis describes the detail discussion on the different physical properties of pure ZnO as well as S doped ZnO alloys in WZ, sphalerite type, GeP type, 5-5 type, NiAs type, BeO type and CsCl type. PBE-GGA exchange correlation is applied to optimize the structures. In addition, mBJ potential is used to improve the energy bandgaps.

Chapter 1 offers a brief discussion on the background of the current problem, the problem statement is underscored to find the research gap to fill, objectives, scope of the study, the significance of the study and thesis organisation are also highlighted in this chapter.

Chapter 2 describes the literature review which is based on the brief discussion on the wide bandgap semiconductors. This chapter further provides the detailed discussion on the different physical properties of the materials studied in this thesis. Moreover, many fundamental aspects such as DFT used for the present study and knowledge of different exchange correlation functional are also discussed in this chapter.

Chapter 3 explains the methodology with a brief introduction to the WIEN2k code which is used for the simulation in the present study and the steps to perform the calculations in WIEN2k code. This chapter further explains the computational details.

In Chapter 4, a comparative study of the structural, electronic, and optical properties of seven polymorphs including WZ, sphalerite type, GeP type, 5-5 type, NiAs type, BeO type, and CsCl type of pure ZnO are carried out. Chapter 4 further

explains the structural, electronic, and optical properties of S doped ZnO alloys in the above discussed seven polymorphs. The different concentrations (x) such as 0%, 25%, 50%, 75%, and 100% of S atom are used to perform the structural, electronic, and optical properties of ZnOS alloys in above discussed polymorphs of ZnO.

Chapter 5 concludes the entire research that was carried out to fulfil the stated objectives. Many other areas in this emerging field are regarded as the future directions. At the end, references and the list of publications are given. The effect of O and S occupancy on the structural properties of ZnOS alloys in sphalerite type, graphs on the linear fitting of the absorption coefficient and the explanation about the high dielectric constant of CsCl type with metallic nature are affixed in the appendices.

REFERENCES

1. Sarkar, B., A. Verma, S. Sharma, and S. Kundu, First-principles calculations of the structural, phonon and thermal properties of ZnX (X= S, Se, Te) chalcogenides. *Physica Scripta*, 2014. **89**(7): p. 075704.
2. Ikhmayies, S., Introduction to II-VI Compounds. 2014. p. 1-24.
3. Kumari, V., A. Mittal, J. Jindal, S. Yadav, and N. Kumar, S-, N-and C-doped ZnO as semiconductor photocatalysts: A review. *Frontiers of Materials Science*, 2019. **13**(1): p. 1-22.
4. Yu, Y., J. Zhou, H. Han, C. Zhang, T. Cai, C. Song, and T. Gao, Ab initio study of structural, dielectric, and dynamical properties of zinc-blende ZnX (X= O, S, Se, Te). *Journal of Alloys and Compounds*, 2009. **471**(1-2): p. 492-497.
5. Fan, X., Z. Shen, Y. Lu, and J.-L. Kuo, A theoretical study of thermal stability and electronic properties of wurtzite and zincblende ZnO_xS_{1-x}. *New Journal of Physics*, 2009. **11**(9): p. 093008.
6. De Almeida, J. and R. Ahuja, Tuning the structural, electronic, and optical properties of Be_xZn_{1-x}Te alloys. *Applied Physics Letters*, 2006. **89**(6): p. 061913.
7. Ohtomo, A., M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda, and Y. Segawa, Mg_xZn_{1-x}O as a II-VI widegap semiconductor alloy. *Applied Physics Letters*, 1998. **72**(19): p. 2466-2468.
8. Ishihara, J., A. Nakamura, S. Shigemori, T. Aoki, and J. Temmyo, Zn_{1-x}Cd_xO systems with visible band gaps. *Applied Physics Letters*, 2006. **89**(9): p. 091914.
9. Khan, I. and I. Ahmad, Theoretical studies of the band structure and optoelectronic properties of ZnO_xS_{1-x}. *International Journal of Quantum Chemistry*, 2013. **113**(9): p. 1285-1292.
10. Zagorac, D., J. Schön, J. Zagorac, and M. Jansen, Prediction of structure candidates for zinc oxide as a function of pressure and investigation of their electronic properties. *Physical Review B*, 2014. **89**(7): p. 075201.

11. Owens, A. and A. Peacock, Compound Semiconductor Radiation Detectors. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 2004. **531**(1-2): p. 18-37.
12. Barlow, D., Predicting the temperature for the solid–solid phase transition in II–VI semiconductor alloys. *Journal of Physics and Chemistry of Solids*, 2013. **74**(3): p. 406-409.
13. Akimov, V., M. Frolov, Y. Korostelin, V. Kozlovsky, A. Landman, Y. Podmar'kov, and Y. Skasyrsky, Vapor growth of CdSe: Cr and CdS: Cr single crystals for mid-infrared lasers. *Optical Materials*, 2009. **31**(12): p. 1888-1890.
14. Razykov, T., S.Z. Karazhanov, A.Y. Leiderman, N. Khusainova, and K. Kouchkarov, Effect of the grain boundaries on the conductivity and current transport in II–VI films. *Solar Energy Materials and Solar Cells*, 2006. **90**(15): p. 2255-2262.
15. Afzaal, M. and P. O'Brien, Recent developments in II–VI and III–VI semiconductors and their applications in solar cells. *Journal of Materials Chemistry*, 2006. **16**(17): p. 1597-1602.
16. Chu, T.L. and S.S. Chu, Thin film II–VI photovoltaics. *Solid-State Electronics*, 1995. **38**(3): p. 533-549.
17. Pavlidis, S., Investigation of wide band gap semiconductors: InGaZnO TFTs for chemical sensing and hybrid GaN/organic high-frequency packaging and circuits, in School of Electrical and Computer Engineering Georgia Institute of Technology. 2016.
18. Yang, M., Wide Bandgap Semiconductors for Energy Efficiency and Renewable Energy Applications. 2014, University Of California, San Diego.
19. Benali, M.K.M., First-Principles study of Structural, Elastic and Electronic Properties of AlN and GaN Semiconductors under Pressure Effect and Magnetism in AlN:Mn and GaN:Mn systems, in *Faculty Of Sciences – Physics Department*. 2004, Abou-Bakr Belkaid University - Tlemcen.
20. Segawa, Y., A. Ohtomo, M. Kawasaki, H. Koinuma, Z. Tang, P. Yu, and G. Wong, Growth of ZnO thin film by laser MBE: lasing of exciton at room temperature. *Physica Status Solidi (B)*, 1997. **202**(2): p. 669-672.

21. Ashrafi, A. and C. Jagadish, Review of zincblende ZnO: Stability of metastable ZnO phases. *Journal of Applied Physics*, 2007. **102**(7): p. 4.
22. Stefaniuk, I., B. Cieniek, I. Rogalska, I. Virt, and A. Kosciak, Magnetic Properties of ZnO:Co Layers Obtained by Pulsed Laser Deposition Method. *Materials Science-Poland*, 2017. **36**.
23. Haq, B.U., S. Al Faify, and R. Ahmed, An Insight into the Electronic and Optical Properties of Various Polymorphs of ZnO. *Current Nanomaterials*, 2018. **3**(1): p. 26-31.
24. Khamala, B., L. Franklin, Y. Malozovsky, A. Stewart, H. Saleem, and D. Bagayoko, Calculated electronic, transport, and bulk properties of zincblende zinc sulphide (zb-ZnS). *Computational Condensed Matter*, 2016. **6**: p. 18-23.
25. Kaur, N., S. Kaur, J. Singh, and M. Rawat, A review on zinc sulphide nanoparticles: from synthesis, properties to applications. *J Bioelectron Nanotechnol*, 2016. **1**(1): p. 1-5.
26. Labiadh, H. and S. Hidouri, ZnS quantum dots and their derivatives: Overview on identity, synthesis and challenge into surface modifications for restricted applications. *Journal of King Saud University - Science*, 2017. **29**(4): p. 444-450.
27. Coh, S., Electronic structure theory: applications and geometrical aspects. 2011, Rutgers University-Graduate School-New Brunswick.
28. Callister, W. and D. Rethwisch, Materials science and engineering, vol. 5 New York. NY: John Wiley & Sons, 2011.
29. Blaha, P., K. Schwarz, G.K. Madsen, D. Kvasnicka, and J. Luitz, wien2k. 2018.
30. K. Schwarz, P.B., G.K.H. Madsen, Electronic structure calculations of solids using the WIEN2k package for material sciences. *Computer Physics Communications*, 2002.
31. Pasquarelli, R.M., D.S. Ginley, and R. O'Hayre, Solution processing of transparent conductors: from flask to film. *Chemical Society Reviews*, 2011. **40**(11): p. 5406-5441.
32. Tustison, J.S.M.R.W., Physics and Chemistry of ZnS, in Chemical Vapor Deposited Zinc Sulfide. 2013. p. 192.

33. Hao, A., X. Yang, X. Wang, Y. Zhu, X. Liu, and R. Liu, First-principles investigations on electronic, elastic and optical properties of XC (X= Si, Ge, and Sn) under high pressure. *Journal of Applied Physics*, 2010. **108**(6): p. 063531.
34. King-Smith, R. and D. Vanderbilt, Theory of polarization of crystalline solids. *Physical Review B*, 1993. **47**(3): p. 1651.
35. Rehman, S.U., F.K. Butt, Z. Tariq, B.U. Haq, G. Lin, and C. Li, Cubic Germanium monochalcogenides (π -GeS and π -GeSe): Emerging materials for optoelectronic and energy harvesting devices. *Solar Energy*, 2019. **185**: p. 211-221.
36. Wang, Q., T. Li, H. Wang, H. Li, Y. Miao, Q. Chen, M. Wan, L. Chen, J. Sun, and K. He, The thermodynamic, electronic and optical properties of GeP type ZnO under pressure calculated by Debye model and hybrid function. *Materials Chemistry and Physics*, 2018. **211**: p. 206-213.
37. Rasul, M.N., A. Anam, M.A. Sattar, A. Manzoor, and A. Hussain, DFT based structural, electronic and optical properties of B1-xInxP (x= 0.0, 0.25, 0.5, 0.75, 1.0) compounds: PBE-GGA vs. mBJ-approaches. *Chinese Journal of Physics*, 2018. **56**(6): p. 2659-2672.
38. Hussain, A., S. Aryal, P. Rulis, M.A. Choudhry, J. Chen, and W. Ching, Ab initio electronic structure calculations and optical properties of ordered and disordered Ni₃Al. *Journal of Alloys and Compounds*, 2011. **509**(17): p. 5230-5237.
39. Reshak, A., I. Kityk, J. Ebothe, A. Fedorchuk, M. Fedyna, H. Kamarudin, and S. Auluck, Crystallochemical affinity and optical functions of ZrGa₂ and ZrGa₃ compounds. *Journal of Alloys and Compounds*, 2013. **546**: p. 14-19.
40. LAWAL, A., Theoretical study of structural, electronic and optical properties of bismuth-selenide, bismuth-telluride and antimony-telluride/graphene heterostructure for broadband photodetector, in *Faculty of Science 2018*, Universiti Teknologi Malaysia. p. 177.
41. Kumar, V., M. Sharmam, J. Gaur, and T. Sharmam, Polycrystalline ZnS thin films by screen printing method and its characterization. *Chalcogenide Letters*, 2008. **5**(11): p. 289-295.

42. Cheng, J., D. Fan, H. Wang, B. Liu, Y. Zhang, and H. Yan, Chemical bath deposition of crystalline ZnS thin films. *Semiconductor Science and Technology*, 2003. **18**(7): p. 676.
43. Capasso, F., Band-gap engineering: from physics and materials to new semiconductor devices. *Science*, 1987. **235**(4785): p. 172-176.
44. Bhattacharjee, R. and S. Chattopadhyaya, Effects of barium (Ba) doping on structural, electronic and optical properties of binary strontium chalcogenide semiconductor compounds-A theoretical investigation using DFT based FP-LAPW approach. *Materials Chemistry and Physics*, 2017. **199**: p. 295-312.
45. Shen, G., J.H. Cho, J.K. Yoo, G.-C. Yi, and C.J. Lee, Synthesis and optical properties of S-doped ZnO nanostructures: nanonails and nanowires. *The Journal of Physical Chemistry B*, 2005. **109**(12): p. 5491-5496.
46. Ohno, T., M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, and M. Matsumura, Preparation of S-doped TiO₂ photocatalysts and their photocatalytic activities under visible light. *Applied Catalysis A: General*, 2004. **265**(1): p. 115-121.
47. Chen, L.C., Y.J. Tu, Y.S. Wang, R.S. Kan, and C.M. Huang, Characterization and photoreactivity of N-, S-, and C-doped ZnO under UV and visible light illumination. *Journal of Photochemistry and Photobiology A: Chemistry*, 2008. **199**(2-3): p. 170-178.
48. Vegard, L., The constitution of the mixed crystals and the filling of space of the atoms. *Zeitschrift Fur Physik*, 1921. **5**: p. 17-26.
49. Hümmer, K., Interband magnetoreflexion of ZnO. *Physica Status Solidi (B)*, 1973. **56**(1): p. 249-260.
50. Charifi, Z., H. Baaziz, and A. Hussain Reshak, Ab-initio investigation of structural, electronic and optical properties for three phases of ZnO compound. *Physica Status Solidi (B)*, 2007. **244**(9): p. 3154-3167.
51. Tran, F. and P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. *Physical Review Letters*, 2009. **102**(22): p. 226401.
52. Khuili, M., N. Fazouan, and H.A. El Makarim. DFT study of physical properties of wurtzite, zinc blende, and rocksalt phases of zinc oxide using GGA and TB-mBJ potential. 2015 3rd International Renewable and Sustainable Energy Conference (IRSEC). 2015. IEEE.

53. John, R. and S. Padmavathi, Ab initio calculations on structural, electronic and optical properties of ZnO in wurtzite phase. *Crystal Structure Theory and Applications*, 2016. **5**(02): p. 24.
54. Rozale, H., L. Beldi, B. Bouhafs, and P. Ruterana, A theoretical investigation of ZnO_x S_{1-x} alloy band structure. *Physica Status Solidi (B)*, 2007. **244**(5): p. 1560-1566.
55. Baldissera, G. and C. Persson, Understanding the optical properties of ZnO_{1-x} S_x and ZnO_{1-x} Se_x alloys. *Journal of Applied Physics*, 2016. **119**(4): p. 045704.
56. Wang, Y., F. Tian, D. Li, D. Duan, H. Xie, B. Liu, Q. Zhou, and T. Cui, First principle studies of ZnO_{1-x}S_x alloys under high pressure. *Journal of Alloys and Compounds*, 2019.
57. Sargolzaei, M., N. Lotfizadeh, and R. Hayn, First principles study on magnetic properties of Zn vacancies in ZnO doped with single chalcogen X (X= S, Se, and Te). *Journal of Applied Physics*, 2011. **109**(7): p. 073705.
58. Zafar, M., S. Ahmed, M. Shakil, and M. Choudhary, First-principles calculations of structural, electronic, and thermodynamic properties of ZnO_{1-x}S_x alloys. *Chinese Physics B*, 2014. **23**(10): p. 106108.
59. Zagorac, D., J.C. Schön, and M. Jansen, Energy landscape investigations using the prescribed path method in the ZnO system. *The Journal of Physical Chemistry C*, 2012. **116**(31): p. 16726-16739.
60. Cottenier, S., Density Functional Theory and the family of (L) APW-methods: a step-by-step introduction. Instituut voor Kern-en Stralingsfysica, KU Leuven, Belgium, 2002.
61. Schwarz, K., DFT calculations of solids with LAPW and WIEN2k. *Journal of Solid State Chemistry*, 2003. **176**(2): p. 319-328.
62. Hohenberg, P. and W. Kohn, Inhomogeneous electron gas. *Physical Review*, 1964. **136**(3B): p. B864.
63. Kohn, W. and L.J. Sham, Self-consistent equations including exchange and correlation effects. *Physical Review*, 1965. **140**(4A): p. A1133.
64. Kohn, W., W. Kohn and LJ Sham, Phys. Rev. 140, A1133 (1965). *Phys. Rev.*, 1965. **140**: p. A1133.
65. Harrison, N., An introduction to density functional theory. *Nato Science Series Sub Series III Computer And Systems Sciences*, 2003. **187**: p. 45-70.

66. Tran, F., P. Blaha, and K. Schwarz, Band gap calculations with Becke–Johnson exchange potential. *Journal of Physics: Condensed Matter*, 2007. **19**(19): p. 196208.
67. Camargo-Martínez, J. and R. Baquero, Performance of the modified Becke–Johnson potential for semiconductors. *Physical Review B*, 2012. **86**(19): p. 195106.
68. Ahluwalia, G.K., Applications of chalcogenides: S, Se, and Te. 2016: Springer.
69. Vanhoof, V., Density Functional Theory Studies for Transition Metals: Small (Fe,Co)-clusters in fcc Ag, and the Spin Density Wave in bcc Chromium. 2006.
70. Råsander, M., A Theoretical Perspective on the Chemical Bonding and Structure of Transition Metal Carbides and Multilayers. 2010.
71. Blaha, P., K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k. 2011.
72. Kiejna, A., G. Kresse, J. Rogal, A. De Sarkar, K. Reuter, and M. Scheffler, Comparison of the full-potential and frozen-core approximation approaches to density-functional calculations of surfaces. *Physical Review B*, 2006. **73**(3): p. 035404.
73. Monkhorst, H.J. and J.D. Pack, Special points for Brillouin-zone integrations. *Physical Review B*, 1976. **13**(12): p. 5188.
74. Murnaghan, F., *FD Murnaghan*, Proc. Natl. Acad. Sci. USA 50, 697 (1944). *Proc. Natl. Acad. Sci. USA*, 1944. **50**: p. 697.
75. Kuang, F.G., X.Y. Kuang, S.Y. Kang, M.M. Zhong, and X.W. Sun, Ab initio study on physical properties of wurtzite, zincblende, and rocksalt structures of zinc oxide using revised functionals. *Materials Science in Semiconductor Processing*, 2015. **31**: p. 700-708.
76. Alberto Flores-Hidalgo, M., D. Barraza-Jiménez, and D. Glossman-Mitnik, Effects of Moderate Amounts of Sulfur Substitutional Impurities on ZnO Using Density Functional Theory. *The Open Nanoscience Journal*, 2011. **5**(1).
77. Wang, X., K. Chen, Y. Zhang, J. Wan, O.L. Warren, J. Oh, J. Li, E. Ma, and Z. Shan, Growth conditions control the elastic and electrical properties of ZnO nanowires. *Nano Letters*, 2015. **15**(12): p. 7886-7892.

78. [Thesis Chapter] [cited 2020 29 July]; Available from: http://shodhganga.inflibnet.ac.in/bitstream/10603/50463/4/04_chapter%203.pdf.
79. Blaha, P., K. Schwarz, G.K. Madsen, D. Kvasnicka, and J. Luitz, wien2k. An augmented plane wave+ local orbitals program for calculating crystal properties, 2001.
80. Blaha, P., K. Schwarz, G.K. Madsen, D. Kvasnicka, and J. Luitz, wien2k. 2015.
81. Blaha, P., K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, wien2k. An augmented plane wave+ local orbitals program for calculating crystal properties, 2001.
82. Jackson, A.J., J.M. Skelton, C.H. Hendon, K.T. Butler, and A. Walsh, Crystal structure optimisation using an auxiliary equation of state. *The Journal of Chemical Physics*, 2015. **143**(18): p. 184101.
83. Honglin, L., Y.B. Lu, L. Jinzhu, and Y. Ke, First-principles study of p-type conductivity of N-Al/Ga/In co-doped ZnO. *Physica Scripta*, 2015. **90**.
84. Abideen, Z. and F. Teng, Enhanced photochemical activity and stability of ZnS by a simple alkaline treatment approach. *Cryst. Eng. Comm.*, 2018. **20**.
85. Mohammadi, A.S., S.M. Baizae, and H. Salehi, Density functional approach to study electronic structure of ZnO single crystal. 2011.
86. Schleife, A., F. Fuchs, J. Furthmüller, and F. Bechstedt, First-principles study of ground-and excited-state properties of MgO, ZnO, and CdO polymorphs. *Physical Review B*, 2006. **73**(24): p. 245212.
87. Jaffe, J.E., J.A. Snyder, Z. Lin, and A.C. Hess, LDA and GGA calculations for high-pressure phase transitions in ZnO and MgO. *Physical Review B*, 2000. **62**(3): p. 1660.
88. Decremps, F., F. Datchi, A. Saitta, A. Polian, S. Pascarelli, A. Di Cicco, J. Itié, and F. Baudelet, Local structure of condensed zinc oxide. *Physical Review B*, 2003. **68**(10): p. 104101.
89. Amrani, B., I. Chiboub, S. Hiadsi, T. Benmessabih, and N. Hamdadou, Structural and electronic properties of ZnO under high pressures. *Solid State Communications*, 2006. **137**(7): p. 395-399.

90. Xu, C., G. Xu, Y. Liu, and G. Wang, A simple and novel route for the preparation of ZnO nanorods. *Solid State Communications*, 2002. **122**(3-4): p. 175-179.
91. Mang, A. and K. Reimann, Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure. *Solid State Communications*, 1995. **94**(4): p. 251-254.
92. Berrezoug, H., A. Merad, A. Zerga, and Z.S. Hassoun, Simulation and modeling of structural stability, electronic structure and optical properties of ZnO. *Energy Procedia*, 2015. **74**: p. 1517-1524.
93. Hellwege, K. and O. Madelung, Landolt-Bornstein (Eds.), Semiconductors Physics of Group IV Elements and III–V Compounds, New Series, Group III, vol. 17. 1982, Springer, Berlin.
94. Debbichi, M., T. Sakhraoui, L. Debbichi, and M. Said, Hybrid functional study of structural, electronic and magnetic properties of S-doped ZnO with and without neutral vacancy. *Journal of Alloys and Compounds*, 2013. **578**: p. 602-608.
95. Koller, D., F. Tran, and P. Blaha, Merits and limits of the modified Becke-Johnson exchange potential. *Physical Review B*, 2011. **83**(19): p. 195134.
96. Zouaneb, A., F. Benhamied, and A. Rouabhia. First Principles Calculations of Structural, Electronic and Optical Properties of Ternary ZnO Alloys: Te Doped. in International Conference in Artificial Intelligence in Renewable Energetic Systems. 2017. Springer.
97. Hu, C.E., L.L. Sun, Z.Y. Zeng, and X.R. Chen, Pressure and temperature induced phase transition of ZnS from first-principles calculations. *Chinese Physics Letters*, 2008. **25**(2): p. 675-678.
98. Desgreniers, S., L. Beaulieu, and I. Lepage, Pressure-induced structural changes in ZnS. *Physical Review B*, 2000. **61**(13): p. 8726.
99. Zagorac, D., J. Zagorac, J.C. Schön, N. Stojanović, and B. Matović, ZnO/ZnS (hetero) structures: ab initio investigations of polytypic behavior of mixed ZnO and ZnS compounds. Acta Crystallographica Section B: Structural Science, *Crystal Engineering and Materials*, 2018. **74**(6).
100. Bakhtiar, U.H., R. Ahmed, R. Khenata, M. Ahmed, and R. Hussain, A first-principles comparative study of exchange and correlation potentials for ZnO. *Materials Science in Semiconductor Processing*, 2013. **16**(4): p. 1162-1169.

101. Rashid, M., N. Noor, B. Sabir, S. Ali, M. Sajjad, F. Hussain, N. Khan, B. Amin, and R. Khenata, Ab-initio study of fundamental properties of ternary ZnO_{1-x}S_x alloys by using special quasi-random structures. *Computational Materials Science*, 2014. **91**: p. 285-291.
102. Haq, B.U., R. Ahmed, A. Shaari, F.E.H. Hassan, M.B. Kanoun, and S. Goumri-Said, Study of wurtzite and zincblende GaN/InN based solar cells alloys: First-principles investigation within the improved modified Becke–Johnson potential. *Solar Energy*, 2014. **107**: p. 543-552.
103. Lokman Ali, Zahidur Rahaman, Atikur Rahman, Afjalur Rahman, First principles investigation of structural, electronic and optical properties of MgRh intermetallic compound. *Cond-Mat.Mtrl-Sci*, 2015.
104. Ali, M.L., M.Z. Rahaman, and M.A. Rahman, The structural, elastic and optical properties of ScM (M = Rh, Cu, Ag, Hg) intermetallic compounds under pressure by ab initio simulations. *International Journal of Computational Materials Science and Engineering*, 2016. **05**(04): p. 1650024.

LIST OF PUBLICATIONS

1. Saira Shabbir, A. Shaari, Bakhtiar Ul Haq, R. Ahmed, M. Ahmed. “Investigations of novel polymorphs of ZnO for optoelectronic applications”. Optik, Volume 206, March 2020, 164285. Status: Published, <https://doi.org/10.1016/j.ijleo.2020.164285>. (IF: 1.914, Q2)
2. Saira Shabbir, Amiruddin Shaari, Bakhtiar ul Haq, Rashid Ahmed, Salem ALFAIFY, M. Ahmed, amel laref. “First-principles investigations of electronic structures and optical spectra of wurtzite and sphalerite types of $\text{ZnO}_{1-x}\text{S}_x$ ($x = 0, 0.25, 0.50, 0.75$ & 1) alloys”. Materials Science in Semiconductor Processing. Status: Published. (IF: 3.085, Q2)
3. Saira Shabbir, Amiruddin Shaari, Bakhtiar ul Haq, Rashid Ahmed, Salem ALFAIFY, Maqsood Ahmed. “First-principles investigations of structural parameters, electronic structures and optical spectra of 5-5- and BeO- type of $\text{ZnO}_{1-x}\text{S}_x$ alloys”. Materials Science and Engineering B. Status: Published. (IF: 4.7, Q1)
4. Saira Shabbir, A. Shaari, Bakhtiar Ul Haq, S. AlFaify, R. Ahmed, M. Ahmed. “Exploring thermoelectric response of novel polymorphs of ZnO for renewable energy applications using first-principles approaches”. ECS Journal of Solid State Science and Technology. Status: Revision submitted.