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

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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 $ZnO_{1-x}S_x$ (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 (FPLAPW + *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 mengubahsuai bahan ini supaya spektrum tenaga jurang jalur penuh (daripada cahaya nampak ke UV) dapat diliputi oleh bahan ini. Pengaloian 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 terimbuh ditambah orbitan tempatan (FPLAPW + *l*o) dalam teori kefungsian 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.

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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 *et al*.
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
ν_s	-	Saturation velocity
E_B	-	Breakdown field
μ	-	Electron mobility

LIST OF SYMBOLS

Å	-	Angstrom
ψ	-	Wave function
eV	-	Electron volt
h	-	Plank's constant
ħ	-	Reduced Plank's constant
∇	-	Gradient operator
Γ	-	Gamma
E	-	Energy
$\rho\,(\boldsymbol{r})\ \ \rho_0(\boldsymbol{r})$	-	Electron density
$E_{XC}[\{\psi_i\}]$	-	Ground state electron density
$-\frac{\hbar}{2m}\nabla^2$	-	Exchange-correlation functional
	-	Kinetic energy operator
$V_{ext}(\boldsymbol{r})$	-	External potential
$V_H(\boldsymbol{r})$	-	Hartree potential
$V_{XC}(\boldsymbol{r})$	-	Exchange-correlation potential
ϵ_{xc}	-	Exchange-correlation energy
$V_{x,\sigma}^{BR}(\boldsymbol{r})$	-	Becke-Roussel potential
$t_\sigma(\boldsymbol{r})$	-	Kinetic-energy density
$\rho_\sigma(\boldsymbol{r})$	-	Spin dependent density of states
$e^{i\boldsymbol{k}.\boldsymbol{r}}$	-	Plane wave
$\varepsilon_1(\omega)$	-	Real part of dielectric function
$\varepsilon_2(\omega)$	-	Imaginary part of dielectric function
ε_0	-	Static dielectric constant
α (ω)	-	Absorption coefficient
R (ω)	-	Reflectivity
σ (ω)	-	Optical conductivity
n (ω)	-	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, $Cd_xZn_{1-x}O$, $Be_xZn_{1-x}O$ and $Mg_xZn_{1-x}O$ [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.

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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.2 02 0.164285. (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 $ZnO_{1-x}S_x$ (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 $ZnO_{1-x}S_x$ 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.