

STUDY OF THE EFFECT OF DOPED CADMIUM ON THE ELECTRONIC AND STRUCTURAL PROPERTIES OF ZINC SELENIDE CRYSTALS USING DENSITY FUNCTIONAL THEORY

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Abstract

Zinc Selenide (ZnSe) is a semiconductor materials for fabrication of light emitting devices, such as blue green laser diodes, infrared laser gain medium, X-ray and gamma ray detectors, and other photoelectronic devices. Zn-3d resides close to the valence band. Empirical pseudopotential band calculations with band structure do not explicitly include this level in ZnSe. In this work overcome such drawback. Exchange correlations were treated using Perdew Burke Ernzerhoff (PBE)-Generalized Gradient Approximation (GGA) as implemented in the Quantum Espresso package. Band structure and electronic properties of ZnSe and ZnSe doped with Cd have been investigated based on Density Functional Theory (DFT). Cd doped with ZnSecan improve its properties and further be used for the application of optoelectronic and also fill the gap of the literature. Spherical charge density was observed in the ZnSe and Oval charge density were observed in the ZnSe: Cd, the energy of the projected density of state of ZnSe and ZnSe: Cd were observed to be -8eV and -8eV respectively, ZnSe: Cd have smaller value of energy band gap than the ZnSe. Furthermore ZnSe and ZnSe: Cd indicated direct band gap with 1.0eV and 0.9eV respectively.

Keywords: Band structure, Cadmium, Density functional theory (DFT), Perdew Burke Ernzerhoff- Generalized Gradient Approximation (PBE-GGA), ZnSe.

1.0 INTRODUCTION

Zinc Selenide (ZnSe) semiconductors have received considerable attentions due to its great technological importance. Zinc Selenide (ZnSe) is a light yellow, solid compound comprising with zinc (Zn) and selenium (Se). ZnSe it is among II–VI semiconducting materials, ZnSe is a potentially good material for short wavelength lasers and other photoelectronic devices. In addition ZnSe is of special interest as exhibits tunable ultraviolet (UV) luminescence via quantum confinement effects [1].

ZnSe is a one of the promising materials for fabrication of light emitting device, such as blue green laser diodes, infrared laser gain medium, Xray and gamma ray detectors, and tunable mid-IR laser sources for remote sensing applications. ZnSe rarely occurs in nature, and is found in the mineral that was named after Hans Stille called “Stilleite”. ZnSe can be made in both hexagonal (Wurtzite) and cubic (zincblende) crystal structure. It is insoluble in water, but it reacts with acid hydrogen selenide gas. It can be deposited as a thin film by chemical vapour deposition techniques including metarlorganicvapour phase epitaxy (MOVPE) and vacuum evaporation [2]. Zinc is a metallic element with the atomic number 30 and chemical symbol Zn. It is found in nature most often as mineral sphalerite, while Selenium is a non-metal element with atomic number 34 and chemical symbol Se. Selenium rarely occurs in its elemental state in nature and is usually found in sulfide ores such as pyrite, partially replacing the sulphur in the ore matrix.

Cadmium is a chemical element with symbol Cd and atomic number 48. Cadmium is a soft, malleable, ductile, bluish white divalent metal. It is similar in many respects to Zinc (Zn) but forms complex compounds, such as Cadmium Sulfide, Cadmium Selenide, and Cadmium Telluride, used for light detection and Solar cell [3].

Hexagonal (Wurtzite) structure of ZnSe of material mp-380 with space group of P63mc (186) and formation energy of -0.707eV used in this work, the structure comprised of four number of atoms as shows in Figure2.

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The purpose of this work is to obtain the optimized parameter, and to calculate the band structure and electronic properties of ZnSe semiconductor compound before and after doping of Cadmium (Cd) using density functional theory as implemented in the quantum espresso package.

2. THEORETICAL BACKGROUND

2.1 Density Functional Theory

DFT is a simple method of obtaining approximate solution to the many-body Schrodinger equation. In DFT, without loss of rigour one can work with the electron density $n(\vec{r})$ as the basic variable, instead of the wave function $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$.

The electron density $n(\vec{r})$ is a three-dimensional single-particle density and the quantum theory for ground state can be put in terms of it. The restriction of DFT to ground state is what makes it possible, with the minimum energy variation principle playing a vital role [4].

The time independent Schrodinger equation is given as

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \tag{1}$$

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i \neq j} v(i, j) \tag{2}$$

where $h(i)$ is a single particles operator and $v(i, j) = v(j, i)$ is the two particles interaction.

For solving eqn (1) is to formulate the electron density in terms of ψ as

$$n(\vec{r}) = N \int \dots \int |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N \tag{3}$$

and satisfies the normalization condition

$$N = \int n(\vec{r}) d\vec{r} \tag{4}$$

In 1927 Thomas-Fermi Model shows the distribution of electron and be able to calculate the energy of an atom using kinetic energy functional [5].

$$E_{TF} = C_F \int n^{5/3}(\vec{r}) d\vec{r} - Z \int \frac{n(\vec{r})}{r} d\vec{r} + \frac{1}{2} \iint \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \tag{5}$$

where E_{TF} is the Thomas-Fermi energy, Z is the nuclear charge.

Hohenberg-Kohn (1964) proves two important theorems which lead to the development of DFT. The first theorem treats electron density $n(r)$ as a function of energy given as;

$$E[n(r)] = \langle \psi | T + U + V | \psi \rangle \tag{6}$$

$$\text{where } T = \frac{-\hbar^2}{2me} \sum_i \nabla_i^2 \tag{7}$$

T is the kinetic energy of the system

$$V = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \tag{8}$$

V is the coulomb potential

The second theorem provide the variational principle [6], which given by;

$$E_0 = E[n_0] \leq E[n] \tag{9}$$

Kohn-Sham in 1965 reformulated the problem in a more familiar form having the same ground state charge density $n(r)$.

$$n(r) = 2 \sum_i |\phi_i(r)|^2 \tag{10}$$

and the Kohn-Sham orbital are the solution to the Schrodinger equation given as;

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}\right) \phi_r(r) = \epsilon_i \phi_i(r) \tag{11}$$

Where (m is the electron mass) obeying orthogonality constraints;

$$\int \phi_i^*(r) \phi_j(r) dr = \delta_{ij} \tag{12}$$

2.2 Equation of State

The equations of state consist of mathematical relationship between two or more state functions such as temperature, pressure and volume. In order to determine the energy–volume relationship which allows us to obtain the equilibrium lattice parameter, we adopt the method proposed by [7] to fit the data generated by energy–volume calculations;

$$\Delta E(V) = E - E_0 = BV_0 \left[\left(\frac{V_n}{B} \right) + \left(\frac{1}{1-B} \right) + \left(\frac{V_n}{B'(B'-1)} \right) \right] \quad (13)$$

3. MATERIAL AND METHOD

3.1 Quantum Espresso

Quantum espresso stands for Quantum open-Source Package for Research in Electronic Structure, Simulation, and Optimization. Quantum ESPRESSO is an integrated suite of software for atomistic calculations based on electronic structure, using density functional

Theory, a plane-wave basis set, pseudopotentials. Freely available under the terms of the GNU General Public License [8].

3.2 Method

3.2.1 Building the Structure

The hexagonal structure of ZnSe with space group of $p6mc$ (186) were build using material project [9] and viewed with Xcrysden shown in Fig1. The figure shows the Hexagonal structure of ZnSe and ZnSe:Cd.

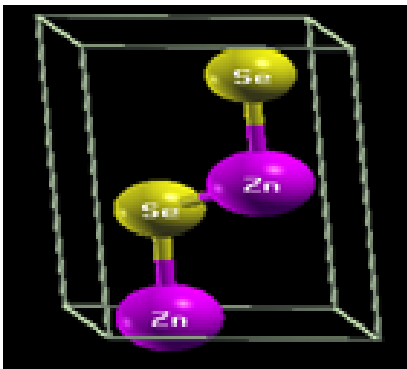


Fig 1a. Hexagonal Structure of ZnSe.

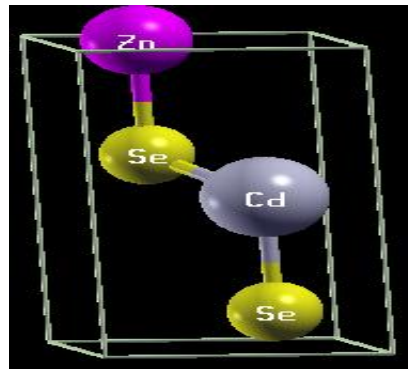


Fig 1b Hexagonal Structure of ZnSe:Cd.

3.2.2 Optimization of the structure

The optimization were carried out using the script file and the calculation were done with the command “./run_ZnSe_eos” until the calculation achieved and print out the result of the optimized parameter vs total energy. The optimized parameters are viz: lattice parameter (alat), cut off energy (ecut), degauss (deg), and kpoints (nks).

3.2.3 Structure Relaxation

The minimal energy selected from the each of the optimized parameter were set into the input file and calculation in the control of the input file was set to ‘relax’, calculation was done with the command ‘pw.x’ until the final geometry coordinate were achieved in the output file.

3.2.4 Computational procedure

In this work, all the calculations after optimization were based on first-principles pseudopotential method within DFT with pw as basis set implemented in the quantum espresso. The calculation of the electronic band structure was carried out by calculating the self-consistent (scf) after which non self-consistent were performed. However in the calculations of density of state, the occupancy of the bands is determined using tetrahedral with an automatic kpoint generations. Phonon frequency calculation were done in two step procedure employed in the phonon frequencies calculations by finding the ground state configurations and followed the used of density functional theory [8]. The equilibrium lattice parameter, bulk modulus and pressure derivatives of the bulk modulus of ZnSe and ZnSe:Cd was carried out by the standard procedure at computing the total energy for different lattice constant and fitted these to Murnaghan’s equations of states[7][8].

4 RESULTS AND DISCUSSION

4.1 Optimization result

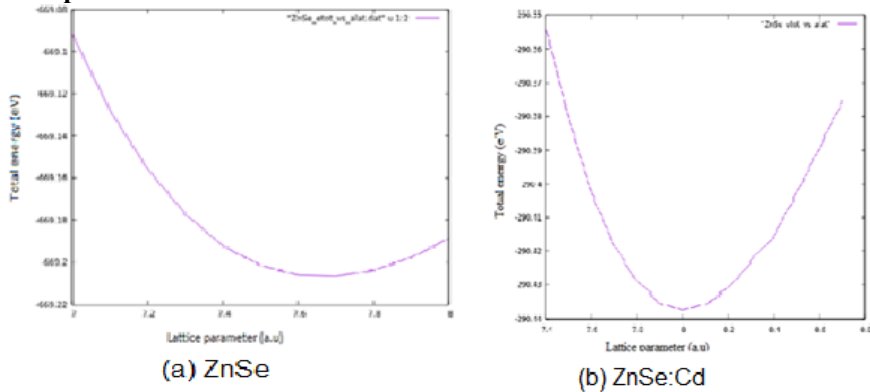


Fig 2 Total energy (eV) variation with Lattice parameter (a.u) using PBE GGA.

Fig(2a)above shows the lattice parameter (a.u) variation with total energy (eV) calculated for the ZnSe while fig (2b) shows the lattice parameter (a.u) variation with total energy (eV) calculated for the ZnSe doped with Cd. From(fig 2a) and b the result shows that the minimal energy of the lattice parameter of ZnSe and ZnSe:Cd were found to be 7.6 a.u and 8.0 a.u respectively which was used for the calculation of band structure and electronic properties.

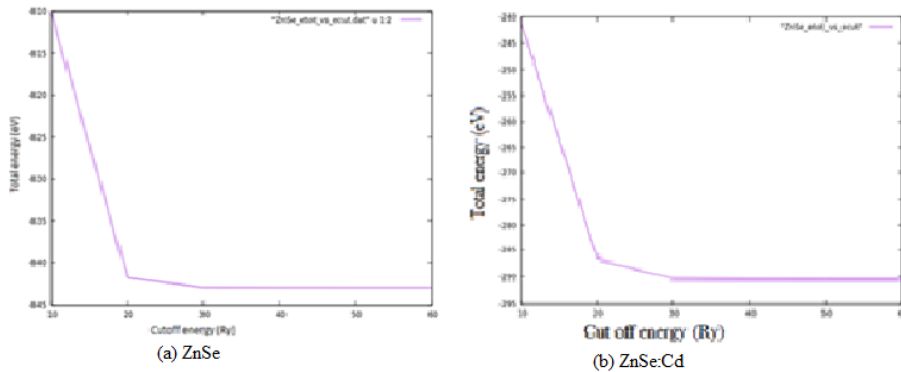


Fig 3 Total energy (eV) variation with cut off (Ry) using PBE GGA.

Fig 3a shows the cutoff energy (Ry) variation with the total energy (eV) calculated for the ZnSe while Fig 3b shows the cutoff (Ry) variation with total energy (eV) calculated for the ZnSe doped with Cd. From Fig 3a and b the result shows that the cutoff energy of ZnSe and ZnSe:Cdwere found to be 30 Ry and 30 Ry respectively, both the structure has the same cut off energy which later used for the this work.

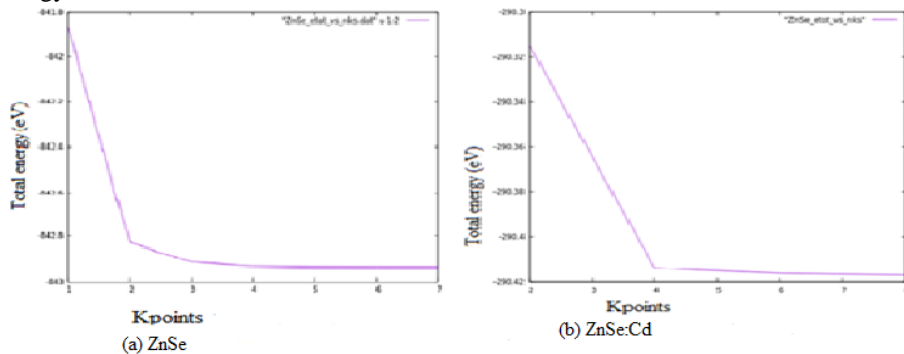


Fig 4 Total energy (eV) variation with Kpoints using PBE GGA.

Fig(4a) above shows the number of kpoints variation with total energy (eV) calculated for the ZnSe while Fig (4b) shows the number of kpoints variation with total energy (eV) calculated for the ZnSe doped with Cd. From Fig (4a) and b the result shows that the optimized kpoints of ZnSe and ZnSe:Cd were found to be 4 4 4 and 4 4 4 respectively which were used for the calculation of remaining properties.

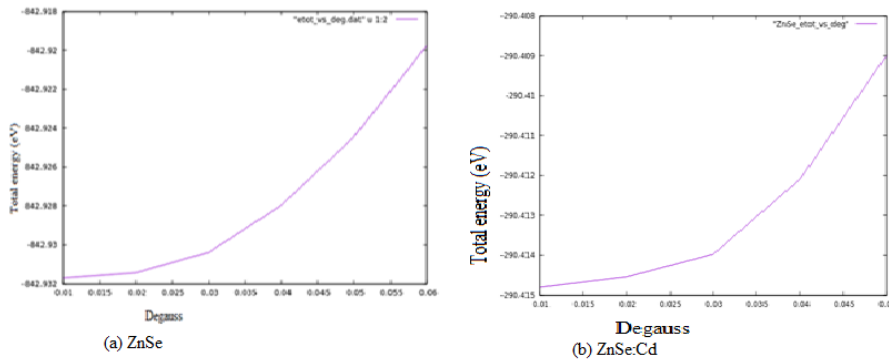


Fig 5 Total energy (eV) variation with Degauss using PBE GGA.

Fig (5a) above shows the degauss variation with the total energy (eV) calculated for the ZnSe while **Fig (5b)** shows the degauss variation with total energy (eV) calculated for the ZnSe doped with Cd. From the **Fig (5a)** and b the result shows the minimal energy of degauss of ZnSe and ZnSe: Cd to be 0.02 and 0.03 respectively which was used for calculation of band structure and electronic properties of ZnSe and ZnSe doped with Cd.

4.2 Structural Properties

The geometrical relaxations of ZnSe in hexagonal crystal structure before and after doping of Cd were performed to avoid an error for accurate analysis of other properties, such as band structure within the framework of DFT calculations. The fitting of murnaghan equations of state to the total energy versus lattice parameter to obtain the result of lattice constant (a_0), bulk modulus (B_0), and the pressure derivatives of the bulk modulus (B') [7]. In Table 1 summarized our calculated structure properties (lattice constant, bulk modulus, and its pressure derivatives) of ZnSe before doping of Cd and after doping of Cd. The result shows an agreement in the bulk modulus with some previous work, lattice constant and pressure derivatives of bulk modulus under estimate the result due to the use of GGA approximation [10]. Furthermore, the present result of structure before and after doping has an agreement on the result of each of the parameters calculated.

Table 1: Lattice constant (a_0), bulk modulus (B_0), and the pressure derivatives of the bulk modulus (B').

Material	Parameters	Present result	Previous result
ZnSe	a_0 (a.u)	3.9205	5.578, 5.820, 5.669
	B_0 (GPa)	72.60	71.84, 52.92, 67.60
	B'	15.00	4.599, 3.81, 4.670
ZnSe: Cd	a_0 (a.u)	3.8131	
	B_0 (GPa)	72.20	
	B'	15.00	

4.3 Electronic Properties

The calculation of electronic band structure is very important for describing the optoelectronic behaviour of materials. Here we performed an analysis of band structure, density (DOS) and partial density of state (PDOS) of ZnSe before and after doping of Cd. The electronic band structure of ZnSe were computed within PBE approximation based on DFT. Fermi energy level scale at 0eV represented by dash line shown in **Fig (6a)** and **(6b)**. From the band structure calculations the differences in energy between bottom of conduction band and top of valence band were found to occur at Γ indicating that ZnSe before and after doping of Cd is a direct band gap of 1.0eV and 0.9eV respectively and these values shows an agreement with experimental value from the material project. It can be observed from those two band structure that ZnSe before doping is greater than the ZnSe after doping with 0.1eV energy band gap.

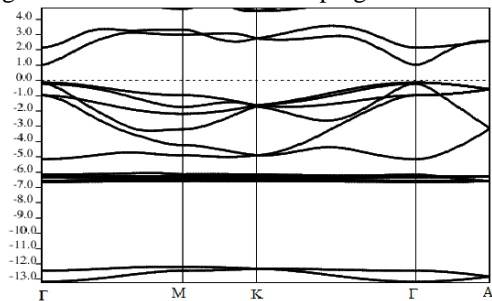


Fig 6a Band structure of hexagonal ZnSe

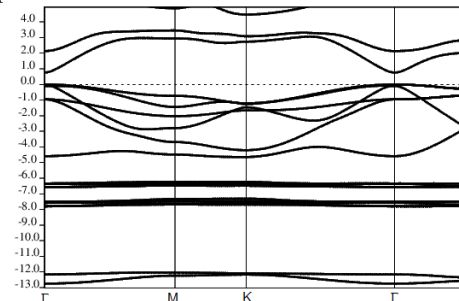


Fig 6b Band structure of hexagonal ZnSe: Cd

Charge density

The charge density is one of the ground state energy property of a crystal which is important for an understanding the structure and chemical bond in crystalline materials. It is also a complementary way of understanding the electronic structure of crystals [11]. The calculated charge density distribution is shown in **Fig 7a** for ZnSe. This highlights the visual nature of chemical bond in ZnSe before doping. The result shows spherical charge densities with a distance between any two charges around the Zinc ions, but a small band charge inside the Selenium ion which is an effect of hybridization due to charge sharing by Zinc and Selenium sp orbitals. While **Fig 7b** highlights the visual nature of ZnSe doped with Cd, the result shows oval charge density around the Zinc and Cadmium ions with small band charge inside the Selenium ion which is an effect of hybridization due to the charge sharing by Zinc, Cadmium and Selenium orbitals.

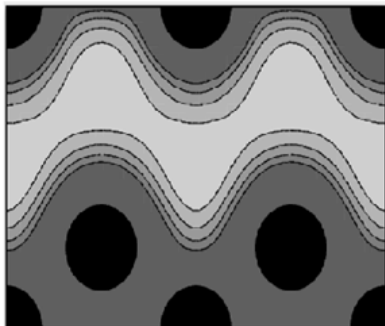


Fig 7a Charge density of ZnSe

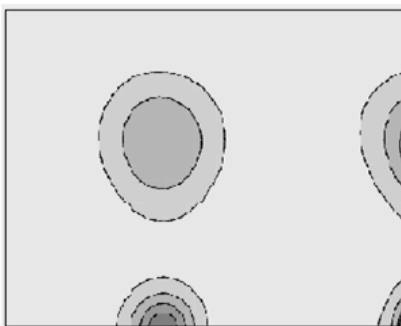


Fig 7b Charge density of ZnSe:Cd

Density of state (DOS)

The Density of state of a system describes the number of states per an interval of energy at each energy level available to be occupied. DOS calculated result from **Fig (8a)** shows the energy in the range of -9eV to 17eV with a dominant structure having a peak of energy level. **Fig (8b)** shows the energy is in the range of -9eV to 17eV, with a dominant structure having a peak of energy level. It was observed one long peak from **Fig (8a)** due to Zn-3d in the valence electrons of the Zn. Also it was observed that two long peaks from **Fig 8b** due to the Zn-3d and Cd-3d in their valence electrons of Zn and Cd.

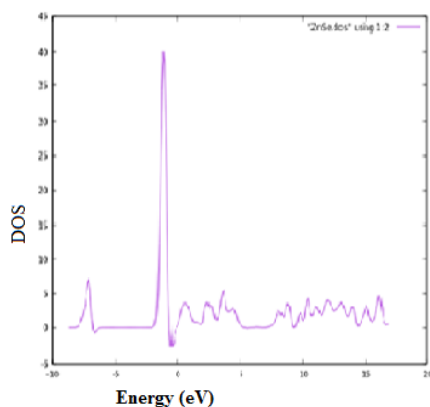


Fig 8a Density of State of ZnSe

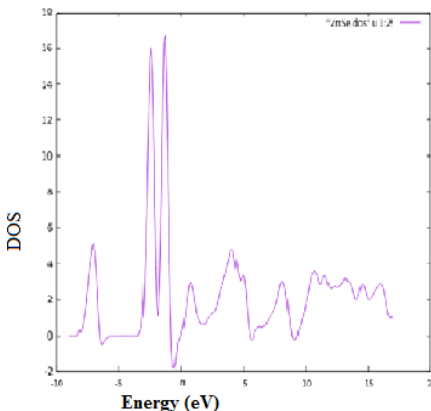


Fig 8b Density of State of ZnSe:Cd

Projected Density of State

The projected density of state gives a clearer definition of elemental contributions to the electronic structure of materials. From **Fig 9(a, b)** shows the PDOS structure of ZnSe and ZnSe doped with Cd computed based on the dispersion relation and the pseudo-wave functions of the eigen state of the KS equation. The results from **Fig 9a** shows that the energy level was found to be -8eV. It was observed from the result Zn-3d has higher PDOS between -2eV and -1.5eV, Se-4s, and Se-4p orbitals have pre-peaks. However in the energy range Zn-3d, Se-4s, and Se-4p were range from negatives to positive side of the energy level. Also Zn-3d and Zn-4s has little depression. The peaks between the Fermi level and 18eV were due to the Zn-4s and Se-4p orbitals both Zn-4s and Se-4p states contribute more to conduction band. From **Fig 9b** result shows that the energy level was found to be -8eV. It was also observed that from the result Zn-3d and Cd-3d has the higher PDOS is computed value between -2.5eV and -1.0eV and -3.5eV and -1.5eV respectively. Se-4s and Se-4p orbitals have pre-peaks. However, the energy level of Zn-3d, Cd-3d, Se-4s, and Cd-2s were ranged from negative to positive side of the energy level. Zn-3d, Cd-3d, and Se-4s have little depression. The peaks between the Fermi level and 18eV are due to the Zn-1s, Cd-2s, and Se-4p orbital both Zn-1s, Cd-2s, and Se-4p states contribute more to the conduction band.

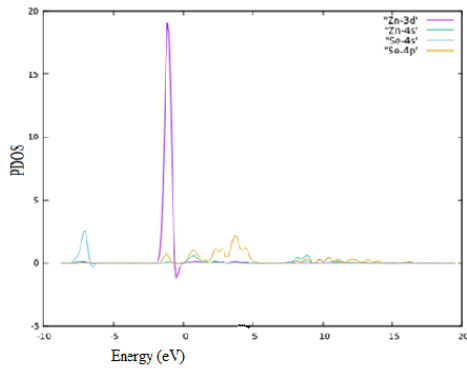


Fig 9a Projected density of State of ZnSe

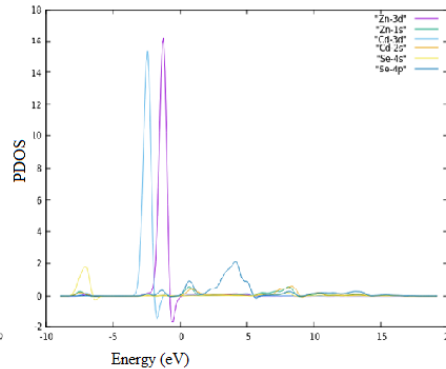


Fig 9b Projected density of State of ZnSe:Cd

Phonon frequency

Phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, like solids and some liquids. The study of phonon is important in condensed matter Physics. Phonons play an important role in many of physical properties of condensed matter, like thermal conductivity and electric conductivity. Phonon frequencies were calculated in the first Brillouin zone. Along some high symmetry points, phonon dispersion curves for ZnSe and ZnSe:Cd were computed. Our calculation of ZnSe before doping is in good agreement with the phonon dispersion curves from the material project while the calculated of ZnSe after doping of Cd has a little different as compared with the material project one. The present result of **Fig (10a)** shows that from Γ points at around 50Thz, along the high symmetry Γ there is two branches of dispersion curves, also at high symmetries of A/L/H dispersion curves has two branches which later split into four branches. Furthermore at A/L/H one of the dispersion curve of the optical mode interact with the acoustic mode branches. The result of **Fig (10b)** shows that from Γ points at 0.0Thz, along the high symmetry Γ there is four branches of dispersion curves. The result also has no interaction between the optical mode and the acoustic mode branches as observed from **Fig (10b)**.

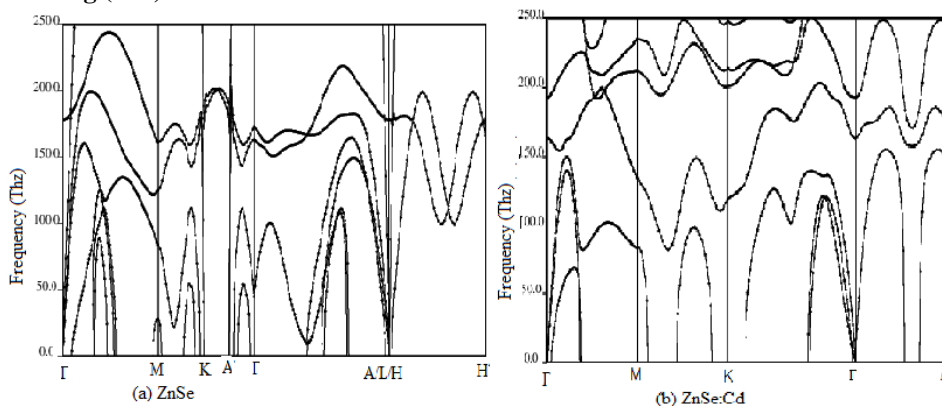


Fig 10 Phonon dispersion frequencies along high symmetry Brillouin Zone

Conclusion

Generalized gradient approximation (GGA)-Perdew burke ernzerhof (PBE) method was used to study the band structure and electronic properties of ZnSe and ZnSe:Cd in hexagonal structure. The band structure shows the direct band gap for both the structure before and after doping. In comparison with the previous work, the bulk modulus shows good agreement while lattice constant and derivatives of bulk modulus were underestimated the result with previous works of ZnSe in zinc blend structure but shows an agreement with the experimental data found from the material project for the structure of ZnSe and ZnSe:Cd. Finally, the charge density and phonon dispersion shows an agreement with the experimental data for ZnSe and ZnSe:Cd doped with Cd has little change, which is due to the effect of doping Cd. To our knowledge there are no earlier studies of hexagonal structure of ZnSe with doping of Cd, so our calculations can be used to cover this lack of data for this compound.

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