

A First-Principles Study of Structural, Electronic and Optical Properties of $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ Semiconducting Alloy

U. Paliwal*

Department of Physics, Jai Narain Vyas University, Jodhpur-342011, India

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Abstract

In this work, we report the theoretical study of structural, electronic, and optical properties of $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ semiconducting ternary alloy using the first-principles density functional theory approach. The calculations are performed using the Plane Wave Self Consistent Field (PWSCF) method implemented in the QUANTUM ESPRESSO code. The two approaches are used to calculate the properties of semiconducting alloy: the first is local density approximation, and the other is generalized gradient approximation in the framework of the density functional theory. Among structural properties, the ground state equilibrium lattice constant, bulk modulus, elastic constants, shear modulus, and Poisson ratio are computed for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ semiconducting ternary alloy. The electronic band structure is calculated to characterize the electronic properties, and bandgaps and electronic charge transfer between the cation and anion are evaluated. The optical nature of alloy is characterized by computing the static dielectric constant and refractive index. The computed parameters are compared with the available theoretical calculations due to the absence of experimental work on this system.

Keywords: PWSCF method; II-VI Semiconducting alloy; Structural properties.

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1. Introduction

The II-VI semiconductors and their ternary and quaternary alloys composed of II group (Be, Cd, Zn, and Mg) and VI group (O, S, Se, and Te) atoms have a wide range of applications in various optoelectronic devices like light emitting diodes, light sensors, light detectors, lasers, photo-diodes as well as in the spintronics devices [1,2]. The II-VI semiconductor alloys having Be as a cation are of special interest due to the high ionicity and bonding strength of Be atom due to its small size. Due to these two properties, the beryllium-based semiconductors show higher values of bulk modulus and elasticity. The Zn-based alloys are comparatively less ionic; however, both the Be and Zn-based II-VI semiconductors have a wide bandgap than III-V materials [3-8]. So ternary alloys formed by mixing Be and Zn-based II-VI semiconductor materials could provide a way to tune the elastic strength and electronic behavior of the ternary alloy system.

* Corresponding author: uttamphy@gmail.com

A few workers have previously studied Be and Zn-based II-VI semiconductor materials and alloys. However, the $Be_xZn_{1-x}S$ system is studied less compared to other systems [9-11]. It is difficult to prepare the semiconducting alloy experimentally with the exact amount of importance of mixing. But using theoretical study, a qualitative idea about various characteristics of the material can be guessed. The first-principles study on semiconducting alloys requires high computational costs. Although different workers propose some empirical methods and relations, these are less reliable compared to first-principles methods. The first-principles calculations provide a better understanding To reveal the technologically essential characteristics, like structural, electronic, and mechanical parameters of semiconducting alloy,.

In this work, the structural, electronic, and vibrational properties of $Be_{0.75}Zn_{0.25}S$ semiconducting ternary alloys are computed using density functional theory based *ab-initio* method. The lattice parameters, bulk modulus, elastic constants, electronic band structure, bandgap, static dielectric constant, electronic charge transfer, and refractive index are computed for $Be_{0.75}Zn_{0.25}S$ semiconducting ternary alloy using generalized gradient approximation (GGA) and local density approximation (LDA) approaches.

2. Computational Details

The ternary ordered alloy of $A_xB_{1-x}C$ can be assumed as a mixture of two II-VI type compounds AC and BC, with fractions of x and $(1-x)$, respectively. So to model the ternary ordered $Be_{0.25}Zn_{0.75}S$ semiconducting alloy, we assumed the basic luzonite type structure belonging to the cubic space group $P-43m$ (#215) in which Be, Zn, and S atoms occupy $3c$, $1a$, and $4e$ Wyckoff positions, respectively. This structure is equivalent to the $Be_3Zn_1S_4$ configuration, giving $x=0.75$. The structure is shown in Fig. 1.

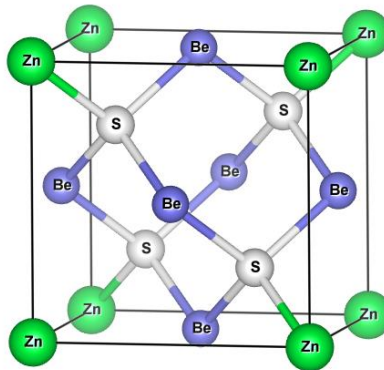


Fig. 1. The ordered $Be_3Zn_1S_4$ configuration for $Be_{0.75}Zn_{0.25}S$ alloy.

We computed the structural, electronic, and vibrational properties of the $Be_{0.25}Zn_{0.75}S$ semiconducting alloy. We applied the *ab-initio* density functional theory (DFT) method using the QUANTUM ESPRESSO package [12], which performs the self-consistent field (SCF) calculations taking plane wave pseudopotential (PW-PP) basis to construct the

wave functions. The ultra-soft pseudopotential optimized for high efficiency and accuracy is used for Be, Zn, and S atoms [13]. To incorporate the exchange and correlation function DFT, we applied two approaches. We used the GGA type functional proposed by Perdew, Burke, and Ernzerhof (PBE) [14] and the LDA type functional proposed by Perdew and Zunger (PZ) [15]. The energy cut-off of 50 Rydberg and charge density cut-off of 400 Rydberg is taken, resulting in about 6000 plane waves. The accuracy of 10^{-8} Rydberg in total energy is taken in SCF cycles is taken, and convergence in energy is achieved in 10 cycles. The dense k point mesh of $9 \times 9 \times 9$ is taken in the first irreducible Brillouin zone considering the special k point integration scheme proposed by Monkhorst-Pack [16].

After computing the total energy (E) at various volumes (V), the Birch-Murnaghan equation of state [17] is fitted to obtain E vs. V data, and the equilibrium lattice parameters, bulk modulus, and pressure derivative of the bulk modulus are computed.

The alloy's elastic constants, shear modulus, and Poisson ratio are computed by applying strain in the ground state structure using quasi-harmonic approximation [12]. The electronic band structure at high symmetry points is computed, and the bandgap is deduced. The static dielectric constant is also computed, and the refractive index is obtained via the relation proposed by Herve and Vandamme [18]. We also performed the Bader charge analysis to quantify the electronic charge distribution at Be, Zn and S [12].

3. Results and Discussion

3.1. Structural properties

The total energy is computed at various volumes, and the obtained E vs. V data are fitted to Murnaghan EOS [17]. The computed E(V) data and the fitted curve are shown in Fig. 2 for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ alloy using PBE-GGA (Red solid line) and PZ-LDA (Blue dashed line). From the Fig., it is clear that GGA predicts lower energy (-163.43 Ryd) than LDA (-162.88 Ryd) for the ground state, and the equilibrium volume corresponding to the minimum energy is less for PZ-LDA than PBE-GGA.

The Murnaghan EOS is fitted to E(V) data, and structural parameters are deduced. The computed lattice constant, bulk modulus, pressure derivative of bulk modulus, elastic constants, shear modulus, and Poisson ratio for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ ternary alloy are presented in Table 1. On analyzing our computed results using PBE-GGA and PZ-LDA, we can see that the lattice constant computed using PBE-GGA is higher than that of PZ-LDA. Thus PZ-LDA predicts strong bonding than PBE-GGA. This is also reflected in the values of bulk modulus and other elastic parameters. The bulk modulus B_0 , elastic constants c_{ij} , and shear modulus G computed using PZ-LDA are higher than that of PBE-GGA. These observations are in agreement with the general overbinding predictions of LDA. However, the Poisson ratio computed by the two approaches is almost the same.

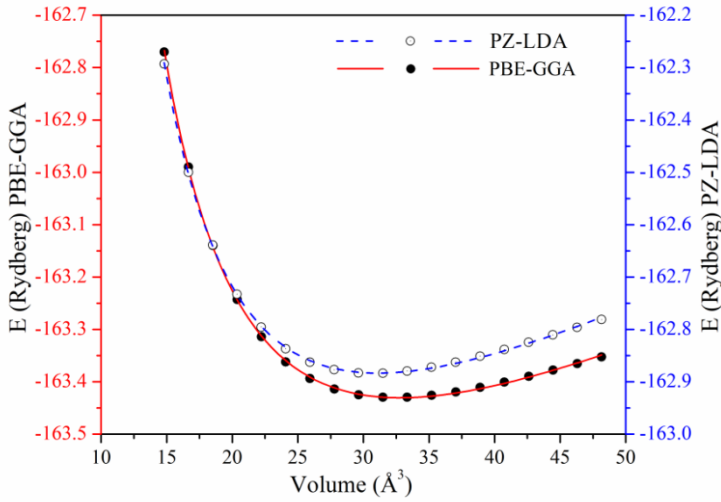


Fig. 2. Variation of total energy with volume for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ alloy.

Table 1. The computed lattice constant (a), bond length (d), bulk modulus (B_0), pressure derivative of bulk modulus (B'), elastic constants (c_{ij}), shear modulus (G), and Poisson ratio (σ) for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ alloy.

	a (Å)	B_0 (GPa)	B'	Elastic constants (GPa)			G (GPa)	σ	
				c_{11}	c_{12}	c_{44}			
This work	GGA	5.08	84.4	3.31	130	57	79	62	0.21
	LDA	4.99	91.6	3.42	142	67	91	64	0.22
Other Calc.	PW-PP [19]	5.01	88.5	--	142	62	73	61	0.29
	FP-LAPW [20]	5.06	86.6	--	--	--	--	--	--
	FP-LMTO [21]	4.98	92.6	4.31	--	--	--	--	--
	FP-LAPW [22]	5.01	92.3	4.34	142	69	84	60	--

In Table 1, we also give the values computed by other workers in the absence of experimental findings for the ternary system. For this system, the Plane Wave Pseudopotential (PW-PP) is applied by Glutekin *et al.* [19], the full-potential linear augmented plane wave (FP-LAPW) method is used by Baziz *et al.* [20], and the full-potential linear muffin-tin orbitals (FP-LMTO) method is applied by Ameri *et al.* [21] to study various properties using GGA. Our computed lattice constant using GGA is nearest to FP-LAPW results [20] and higher than two other calculations [19,21]. The deviation of result from the PW-PP method [19] is due to the fact that the lattice constant is computed by assuming Vegard's law in the reported work while we have computed the lattice constant is computed by fitting the $E(V)$ data to Murnaghan equation of state. The bulk modulus computed in the present work is less than all three other calculations. The elastic constants c_{12} and c_{44} computed in this work using PBE-GGA are in good agreement with the values computed by Glutekin *et al.* [19], while the c_{11} shows some deviation.

3.1. Electronic and optical properties

The computed electronic band structure for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ ternary alloy using PBE-GGA is shown in Figure 3. The figures show that valance bands are divided into two parts lower valance bands (LVB) around -12 eV below the Fermi level and upper valance bands (UVB) ranging from -7 eV to the Fermi level. The figure also depicts that both the valance band maxima and conduction band minima are at Γ point, pointing to the direct bandgap for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$.

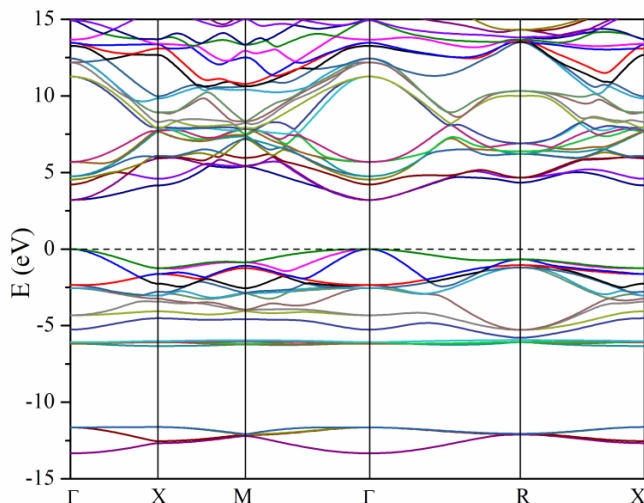


Fig. 3. Electronic band structure for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$ ternary alloy using PBE-GGA.

The computed bandwidths of LVB, UVB, and bandgaps are given in Table 2. We found that both the PBE-GGA and PZ-LDA approaches predict direct bandgap for $\text{Be}_{0.75}\text{Zn}_{0.25}\text{S}$. However, the value of the bandgap predicted by PZ-LDA (2.86 eV) is lower than PBE-GGA (3.21 eV), inconsistent with the usual bandgap underestimation by LDA calculations than PBE. The computed bandgaps at Γ and X points of symmetry using PBE-GGA are in agreement with the previous calculations applying the PW-PP and FP-LAPW methods [19,20]; a small deviation is found with FP-LMTO results predicting bandgaps of 2.94 eV and 3.97 eV at Γ and X points. By calculating bowing parameters, Baziz *et al.* [20] predicted a direct-to-indirect bandgap transition from Γ to X at $x=0.76$. However, our calculations show a large difference of ~ 1 eV between bandgaps at Γ and X points for $x=0.75$.

In Table 2, the static dielectric constants and refractive index are also given. We find that the static dielectric constant (ϵ_0) and refractive index (n) is 5.31 for the alloy using PBE-GGA calculations which is close to 5.38 and 2.32 computed by Gltekin *et al.* [19], the PZ-LDA calculations, however, give the values of 5.56 and 2.32 which are larger than PBE-GGA values.

Table 2. The computed bandgaps at different symmetry points, upper and lower valance bandwidths, static dielectric constant, and refractive index for $Be_{0.75}Zn_{0.25}S$ alloy.

		Bandgaps (eV)		LVB	UVB	ϵ_0	n
		Γ - Γ	Γ -X	(eV)	(eV)		
This work	GGA	3.21	4.16	1.72	6.33	5.31	2.29
	LDA	2.86	3.90	1.91	6.73	5.56	2.39
Other Calc.	PW-PP [19]	3.20	--	--	--	5.38	2.32
	FP-LAPW [20]	3.19	4.15	--	--	--	--
	FP-LMTO [21]	2.94	3.97	--	--	--	--
	FP-LAPW [22]	3.14	3.22	--	--	--	--

The Bader charge analysis for Be, Zn, and S atoms shows that 1.56 e charge is transferred from each Be atom to the S atom while each Zn atom gives 0.86 e charge to the S atom. Thus the Be-S bond is more ionic than the Zn-S bond.

4. Conclusion

The DFT-based calculations of structural, electronic, and optical properties are performed for $Be_{0.75}Zn_{0.25}S$ ternary semiconducting alloy using PBE-GGA and PZ-LDA type exchange-correlation functionals. Our calculations show that PBE-GGA gives a larger value of lattice constant than PZ-LDA. On the contrary, the PZ-LDA predicts larger values of bulk modulus, elastic constants, and shear modulus. The band structure calculations show that $Be_{0.75}Zn_{0.25}S$ is a direct bandgap material and the bandgap predicted by PBE-GGA is more than the PZ-LDA value. The charge density analysis shows that the Be-S bond is more ionic than the Zn-S bond. We also computed the static dielectric constant and refractive index for the alloy. Without any experimental results available for the system, we compared our results with theoretical investigations carried out by other workers wherever available.

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