CHAPTER 3

Results for ZnS_xSe_{1-x} $(0 \leq x \leq 1)$ from CASTEP

3.1 INTRODUCTION

ZnS (*Eg* = 3.68 eV) [Persson and Zunger, 2003] and *ZnSe* (*Eg* = 2.82 eV) [Huang and Ching, 1993] have received a lot of interest because of their potential applications in optoelectronic devices operating in the visible-light range [Jeon *et al*., 1992; Kawakamin *et al*., 1993] and the possibility of having a vanishingly small conduction band offset [Qteish *et al*., 1995]. Therefore, various research activities have been carried out on the electronic and optical properties of ZnS_xSe_{1-x} alloys and their applications in optoelectronic and microelectronic devices [Lai *et al*., 2003]. The *ZnS* and *ZnSe* compounds have zinc blend (F43m) [Wang and Isshiki, 2007] structure at normal conditions. The electronic and optical properties of *ZnS* and *ZnSe* have been measured experimentally [Walter and Cohen, 1969; Bir *et al*., 1970; Freeouf, 1973; Rossetti *et al*., 1985; Lippens and Lannoo, 1989; Ves *et al*., 1990; Xue and Raj, 1991; Godlewski and Szczerbakow, 2001; Godlewski *et al*., 2001]. However, theoretical treatment of the properties is lagging behind the measurements. In the past years several theoretical studies on *ZnS* and *ZnSe* have been performed [Bernard and Zunger, 1987; Smelyansky and Tse, 1995; Wei and Zunger, 1999; Milman *et al*., 2000; Gabrel'yan *et al*., 2000; Muscat *et al*., 2001; Luo et al., 2002; Fitzer *et al*., 2003; Okoye, 2003; Janetzko and Jug, 2004]. In many early attempts to calculate the band structure of *ZnS* and *ZnSe* compounds, the local density approximation (LDA) [Perdew and Zunger, 1981] was used. Bernard and Zunger [1987] have determined the band gap of $ZnS_{0.5}Se_{0.5}$ and the corresponding optical bowing parameter using a plane wave method at LDA level, whereas Janetzko and Jug [2004] calculated the band gaps for different compositions of ZnS_xSe_{1-x} in a semi-empirical molecular orbital method MSINDO study. Hybrid function formalism was applied for determining band gaps of *ZnS* and other materials [Muscat *et al*., 2001].

Mesri *et al.*, [2007] investigated the lattice parameters and band gap energies for ZnS_xSe_{1-x}. In this investigation the band structure calculations show direct band gaps at Γ point for the whole composition and obtained the downward bowing with the strongest contribution due to the structural relaxation. Bernard and Zunger [1987] calculated electronic structure of zinc blend *ZnS* and *ZnSe* using the electron mixed-basis approach to the density-functional formalism. They used a CuAu I-like structure (space group $P\bar{4}m2$), and analyzed the observed optical bowing, and a structural contribution due to the relaxation of the anion-cation bond lengths in the alloy.

In the following sections we are going to calculate the band structure of ZnS_xSe_{1-x} (x=0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, and 1) using CASTEP simulation.

3.2 COMPUTATIONAL METHOD

The first-principle calculations applied here used the CASTEP computer code [Payne *et al*., 1992], which is based on density functional theory using a plane-wave pseudopotential formalism and aided by the Materials Studio graphical front–end interface [Accelrys Inc., 2001]. Computations have been performed via LDA with ultra-soft pseudopotentials. Ceperley–Alders exchange-correlation potential parametrized by Perdew–Zunger [1981] scheme (CA-PZ) is used. The geometries for all systems are optimized, which uses a conjugated gradient technique in a direct minimization of the Kohn–Sham energy function and employs pseudopotentials to represent core electrons. Plane-wave functions are used as basis sets [Teter, 1989]. A plane-wave cutoff energy of 310 eV has been employed throughout. It has shown that the results are well converged at this cutoff. For the crystal reciprocal-lattices, integrations over the symmetrized Brillouin zone were performed by a sum over special k-points generated from the Monkhorst–Pack scheme [Monkhorst and Pack, 1976]. For calculations, we have sorted the *Zn* ($1s^2 2s^2 2p^6 3s^2 3p^6$), *S* ($1s^2 2s^2 2p^6$), and *Se* ($1s^2 2s^2 2p^6 3s^2 3p^6$) inner-shell electrons were sorted from the valence electrons of *Zn* ($3d^{10} 4s^2$), *S* ($3s^2 3p^4$), and *Se* ($3d^{10} 4s^2 4p^4$) shells.

The LDA method underestimates the band gap in both semiconductors and insulators. To adjust the theoretical band gap to experimental result Tang *et al*., [1998] estimated a multiplicative correction factor of 1.66 applied to the calculated band gaps. In this work the estimation of a multiplicative correction factor of 1.7 will be applied to the calculated band gap and compared with the multiplicative correction factor of 1.66.

The ordered cubic alloys were modelled using Landau– Lifshitz structures [Landau and Lifshitz, 1969; Martins and Zunger, 1986; Mbaye *et al*., 1988]. Mesri *et al*., [2007] reported that the binary compounds are modeled using zinc-blend (ZB) structure AB, AC (F-43m), the ternary alloys at 50% are modeled using the CuAu-I structure (P-4m2) and the chalcopyrite structure (I-42d), the alloys at 75% or 25% are modeled using Luzonite structure (P-43m).

Table 3.1: Calculated equilibrium lattice parameters, internal parameter *u* for ZnS_xSe_{1-x} [Mesri *et al*., 2007]

Compound	Structure	Space Group [Bernard *et al*. 1988]	*a (nm)*	*c/a*	*u*
ZnS	ZB	F-43m	0.53		0.25
$ZnS_{0.25}Se_{0.75}$	LZ	P-43m	0.551		0.247
$ZnS_{0.5}Se_{0.5}$	CuAu-I	P-4m2	0.54	1	0.247
$ZnS_{0.5}Se_{0.5}$	CH	I-42d	0.544	1.99	0.267
$ZnS_{0.75}Se_{0.25}$	LZ	P-43m	0.537		0.260
$ZnSe$	ZB	F-43m	0.557		0.25

Hint: ZB zinc-blend structure, LZ Luzonite structure, CuAu-I structure, CH chalcopyrite structure**.**

The binary compounds have the unit cell vectors given [Bernard and Zunger, 1987] by

$$\begin{aligned} a_1 &= \left(\frac{1}{2},-\frac{1}{2},0\right)a \ , \\ a_2 &= \left(\frac{1}{2},\frac{1}{2},0\right)a \ , \\ a_3 &= \left(0,0,1\right)\eta a \ , \end{aligned} \tag{3.1}$$

and the atomic positions

$$\begin{aligned} \tau_A &= \left(0,0,0\right)a \ , \\ \tau_B &= \left(\frac{1}{2},0,\eta/2\right)a \ , \\ \tau_{C1} &= \left(\frac{1}{4},\frac{1}{4},\eta u\right)a \ , \\ \tau_{C2} &= \left(\frac{3}{4},\frac{1}{4},\eta(1-u)\right)a. \end{aligned} \tag{3.2}$$

where $\eta = c/a$ (=1.00 ± 0.01 at equilibrium) is the tetragonal ratio and u is the internal structure parameter (cation displacement) expressed as

$$u = (R_{AC}^2 - R_{BC}^2)/a^2\eta^2 + \frac{1}{4} \tag{3.3}$$

and R_{AC}^2, R_{BC}^2 represent the two fundamental bonds lengths in the structure which is expressed as [Bernard and Zunger, 1987]

$$\begin{aligned} R_{AC}\left(a,u,\eta\right) &= \left[\frac{1}{8}+\eta^2 u^2\right]^{1/2} a, \\ R_{BC}\left(a,u,\eta\right) &= \left[\frac{1}{8}+\eta^2\left(u-\frac{1}{2}\right)^2\right]^{1/2} a. \end{aligned} \tag{3.4}$$

In the following sections we are going to compute the band gap and density of states for ZnS_xSe_{1-x} (x=0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875 and 1) by applying given parameters from Eqn.(3.1) to Eqn.(3.4) in the CASTEP program.

3.3 COMPUTATIONAL RESULTS

3.3.1 *ZnS* Band Structure Calculation

Figure 3.1 shows the Brillouin zone for *ZnS* unit cell, given G as a center of crystal which is shown in CASTEP, g_1, g_2, and g_3 corresponding to the coordinates x, y, z respectively whereas the other labels were defined in Table 2.1 in chapter 2. The unit cell vectors for *ZnS* are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 $\overset{0}{\mathrm{A}}$, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25, and R_{AC} = R_{BC} = 6.6136 $\overset{0}{\mathrm{A}}$. Lattice constant a = 5.3 $\overset{0}{\mathrm{A}}$ as reported by Mesri *et al.*, [2007] and from CASTEP gives a = 5.4 $\overset{0}{\mathrm{A}}$.

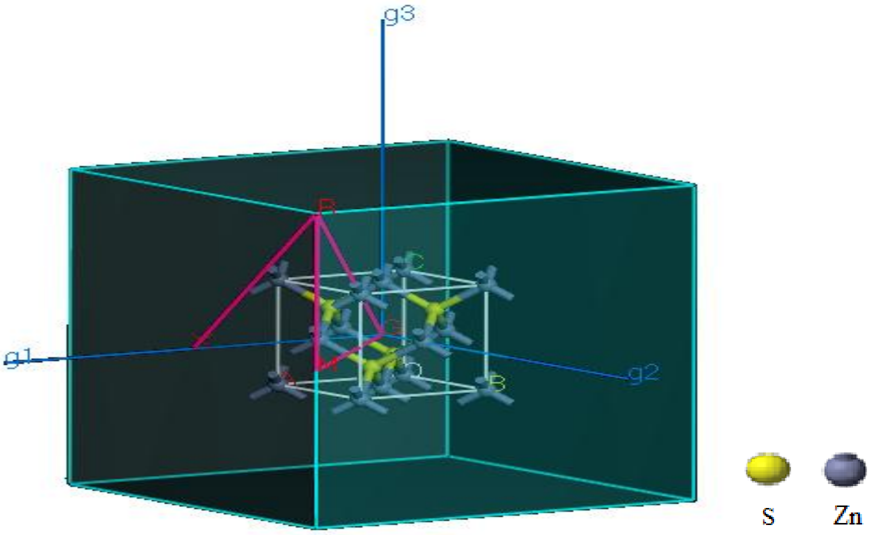

Figure 3.1: Brillouin zone for *ZnS* crystal structure in simple cubic.

With the parameters above the band structure for *ZnS* is shown in Figure 3.2. The band structure of *ZnS* has energetically separated low lying bands, positioned around -13 eV, and is derived from *S* 3s upon comparing with Figure 3.3. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -6.5eV.

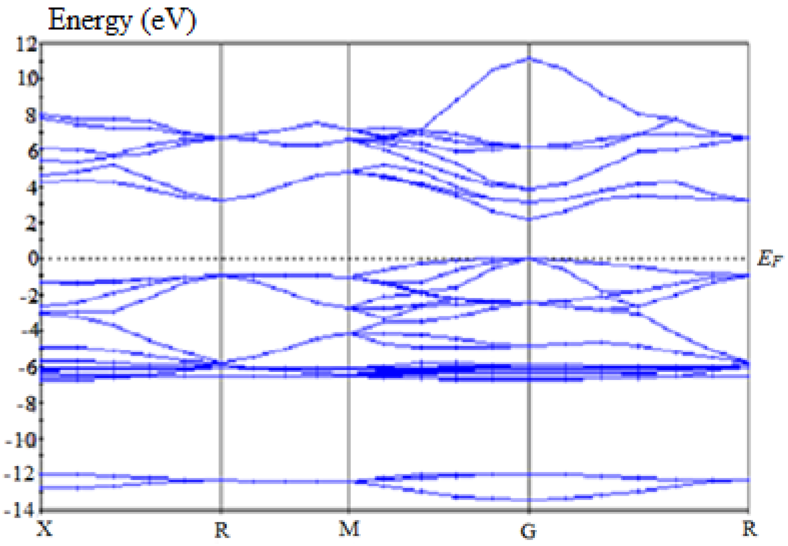

Figure 3.2: The calculated energy band structure for *ZnS*.

At the symmetry G point, the energy gap is 2.2 eV and upon applying the 1.7 correction factor *Eg* is 3.74 eV. This is close to the experimental results given by Ebina *et al*., [1974] which is 3.7 eV, from LCAO [Homann *et al*., 2006], is 3.68 eV and 3.78 eV as reported by Van de Walle [1989]. *Eg* is 3.65 eV upon applying the 1.66 correction factor which is close to the experimental results given by Ebina *et al.*, [1974] which is 3.7 eV, theoretically results LCAO [Homann *et al.*, 2006], which is 3.68 eV, and theoretically results 3.78 eV as reported by Van de Walle.

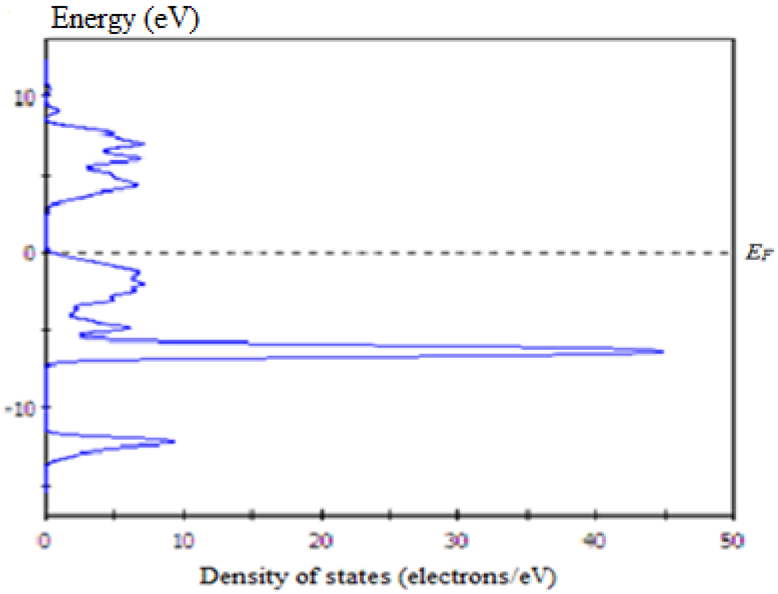

Figure 3.3: Total density of states for *ZnS*.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *S* 3p states. The valence bands are separated from the conduction bands by an energy band gap of 2.196 eV at the symmetry G point.

3.3.2 *ZnSe* Band Structure Calculation

Figure 3.4 shows the Brillouin zone for *ZnSe* unit cell. The unit cell vectors, the atomic positions and the internal structure parameter *u* for *ZnSe* are same as *ZnS*.

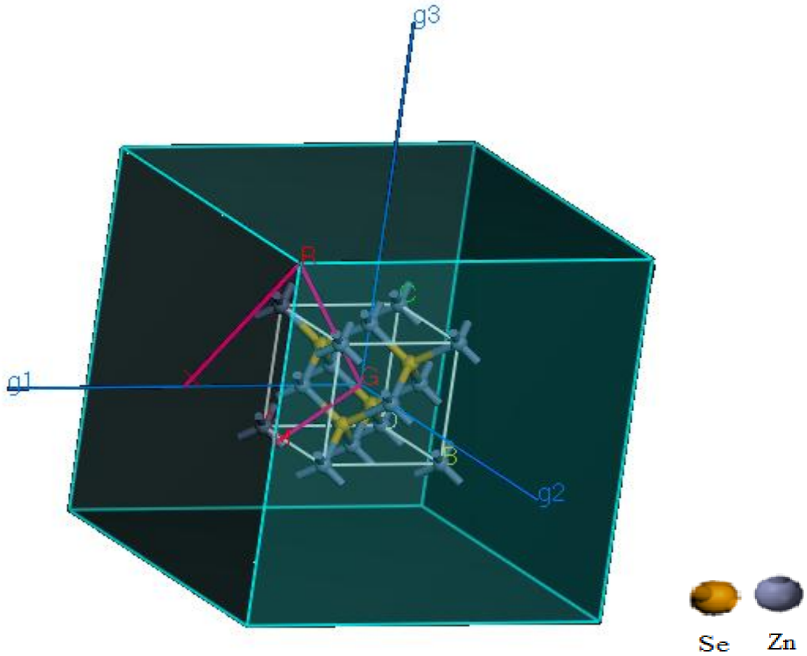

Figure 3.4: Brillouin zone for *ZnSe* crystal structure in simple cubic.

Figure 3.5 shows the band structure for *ZnSe*. The band structure of *ZnSe* has energetically separated low lying bands, positioned around -13 eV, are derived from *Se* 4s comparing with Figure 3.6. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -6.5 eV.

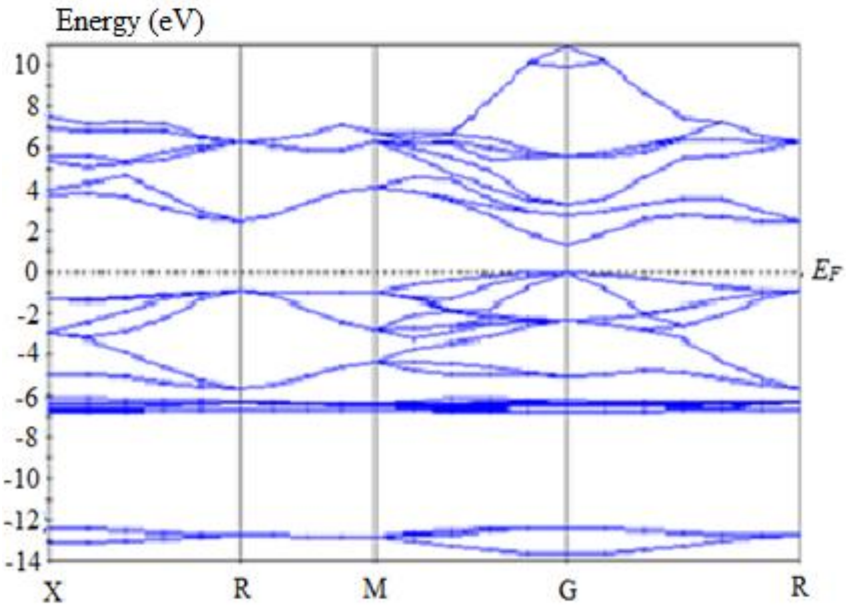

Figure 3.5: The calculated energy band structure for *ZnSe*.

At the symmetry G point, the energy gap is 1.26 eV and upon applying the 1.7 correction factor *Eg* is 2.14 eV. This is different from the experimental results given by Homann *et al*., [2006], which is 2.58 eV and different from experimental results given by Ebina et al. [1974] which is 2.72 eV and theoretical results reported in the literature. *Eg* is 2.1 upon applying the 1.66 correction factor which is different from the experimental results given by Homann *et al*. [2006], Ebina *et al*. [1974], and theoretical results reported in the literature.

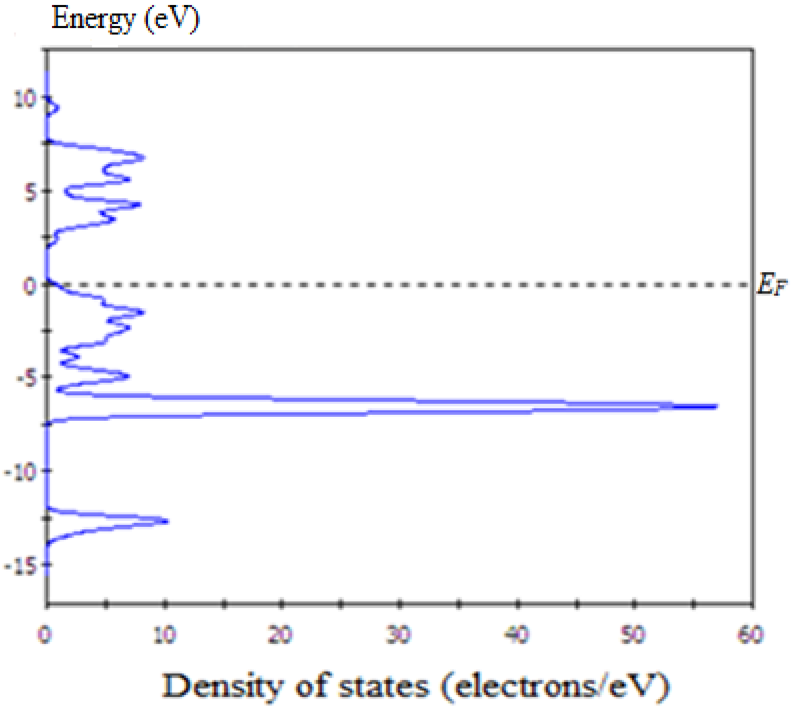

Figure 3.6: Total density of states for *ZnSe*.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.263 eV at the symmetry G point.

3.3.3 $ZnS_{0.125}Se_{0.875}$ Band Structure Calculation

Figure 3.7 shows the Brillouin zone for $ZnS_{0.125}Se_{0.875}$ supercell, where Z, F, B are centers of faces and Q denote to the center of edge. The unit cell vectors for $ZnS_{0.125}Se_{0.875}$ are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 $\overset{0}{A}$, c = 10.8186 $\overset{0}{A}$, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25 and $R_{AC} = R_{BC}$ = 6.6136 A^0 with face centered (0,0,0), (0,1/2,1), (1/2,0,1), (1/2,1/2,0).

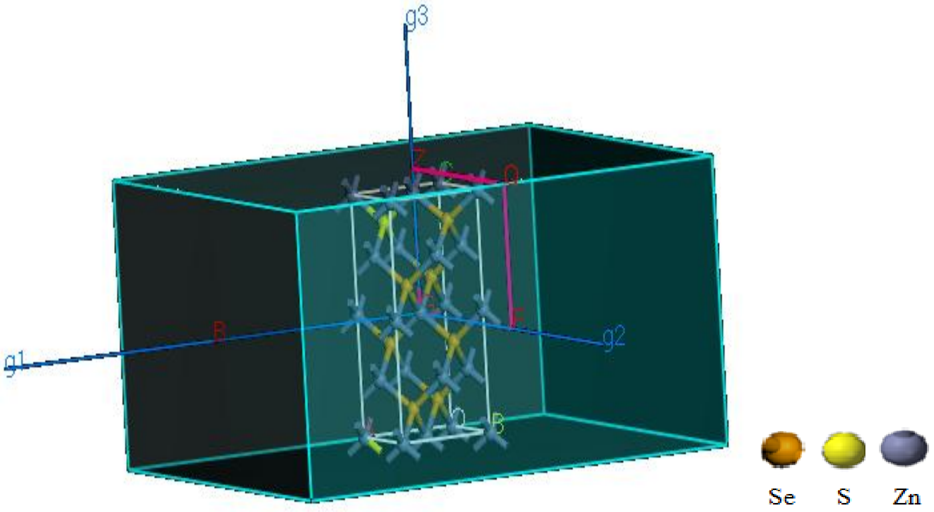

Figure 3.7: Brillouin zone for $ZnS_{0.125}Se_{0.875}$ crystal structure.

Figure 3.8 shows the band structure for $ZnS_{0.125}Se_{0.875}$. The band structure of $ZnS_{0.125}Se_{0.875}$ has energetically separated low lying bands, positioned around -14 eV, are derived from *Se* 4s and shown in Figure 3.9 at the G point symmetry. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -7eV.

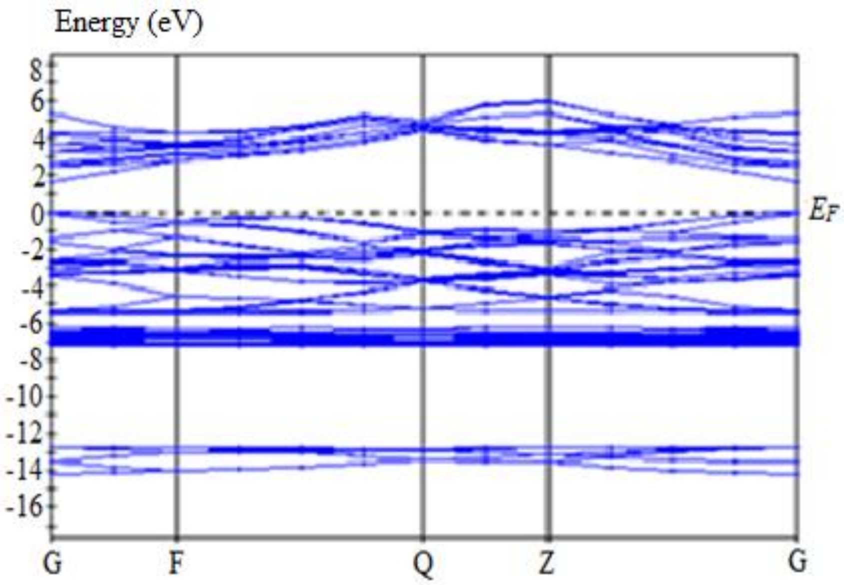

Figure 3.8: The calculated energy band structure for $ZnS_{0.125}Se_{0.875}$.

At the symmetry G point, the energy gap is 1.67 eV and upon applying the 1.7 correction factor *Eg* is 2.84 eV. This is close to the experimental results given by Larach *et al*., [1957] which is 2.78 eV and 2.85 eV as reported by Abo Hassan *et al*., [2005a]. *Eg* is 2.77 eV upon applying 1.66 correction factor which is close to the experimental results given by Larach *et al*. [1975] which is 2.75 eV and 2.85 eV as reported by Abo Hassan *et al*. [2005a].

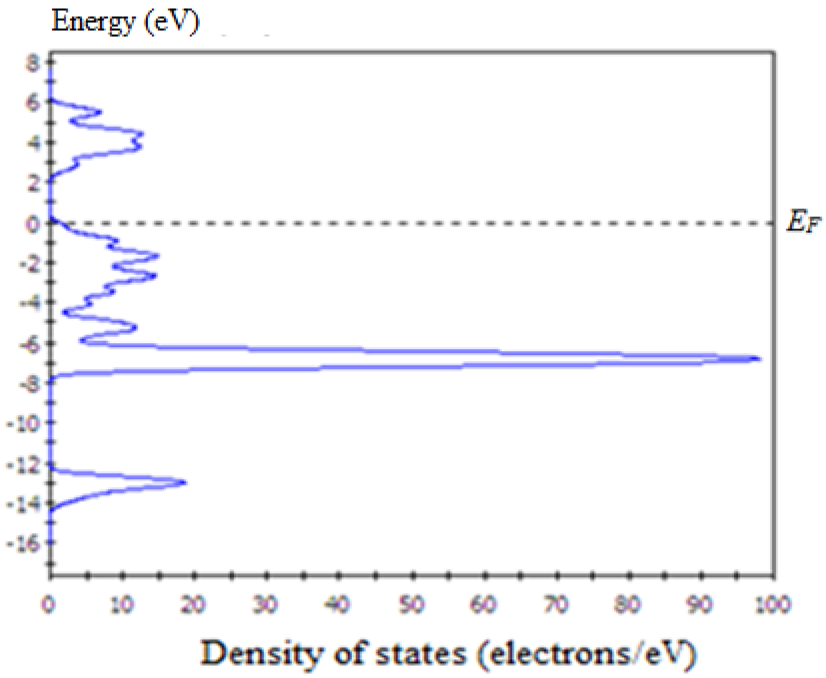

Figure 3.9: Total density of states for $ZnS_{0.125}Se_{0.875}$.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.656eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 2.83 eV.

3.3.4 $ZnS_{0.25}Se_{0.75}$ Band Structure Calculation

Figure 3.10 shows the Brillouin zone for $ZnS_{0.25}Se_{0.75}$ supercell. The atomic vectors for $ZnS_{0.25}Se_{0.75}$ are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 $\overset{0}{\mathrm{A}}$, c = 10.8186 $\overset{0}{\mathrm{A}}$, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25 and R_{AC} = R_{BC} = 6.6136 $\overset{0}{\mathrm{A}}$ with face centered (0,0,0), (0,1/2,1), (1/2,0,1), (1/2,1/2,0). The internal structure parameter u from CASTEP computation is 0.25 whereas given u = 0.247 as reported by Mesri *et al*., [2007].

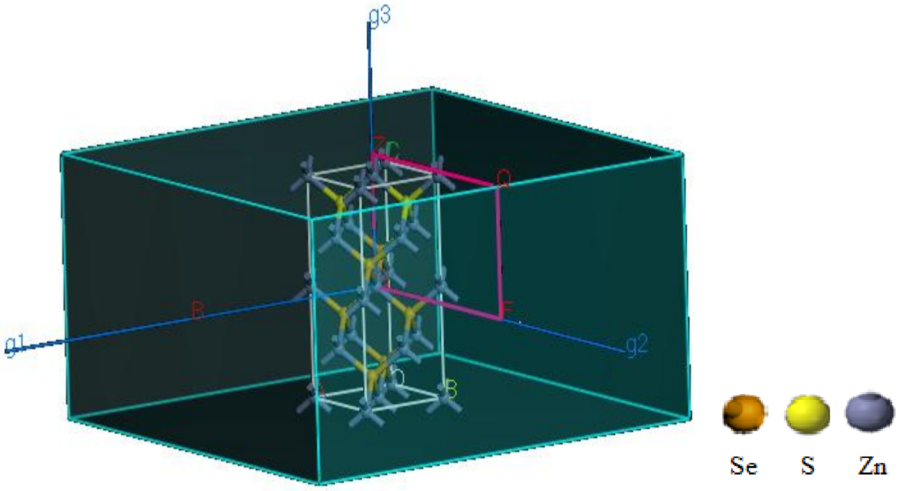

Figure 3.10: Brillouin zone for $ZnS_{0.25}Se_{0.75}$ crystal structure.

Figure 3.11 shows the band structure for $ZnS_{0.25}Se_{0.75}$. The band structure of $ZnS_{0.25}Se_{0.75}$ has energetically separated low lying bands, positioned around -14 eV, are derived from *Se* 4s comparing with Figure 3.12. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -7eV.

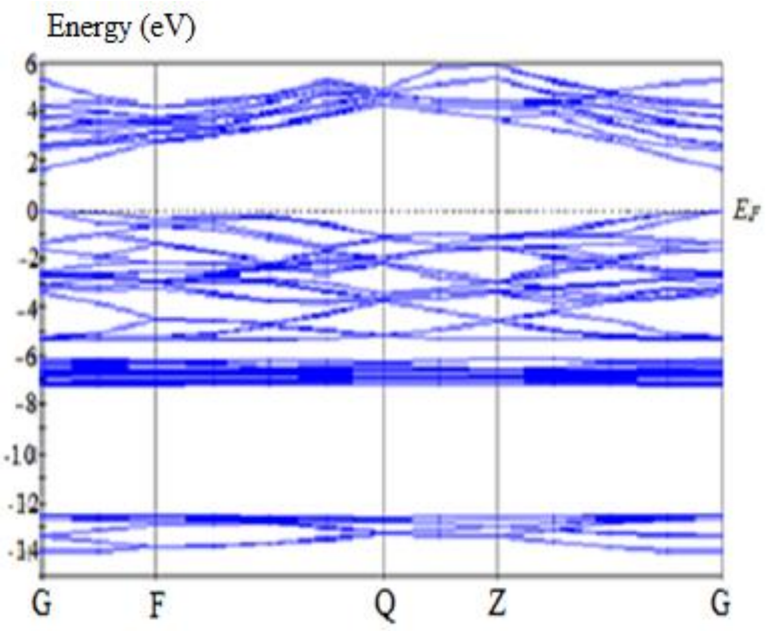

Figure 3.11: The calculated energy band structure for $ZnS_{0.25}Se_{0.75}$.

At the symmetry G point, the energy gap is 1.65 eV and upon applying the 1.7 correction factor *Eg* is 2.81 eV. This is close to the experimental results given by Larach *et al.*, [1957] which is 2.78 eV and 2.85 eV as reported by Abo Hassan *et al.*, [2005a].

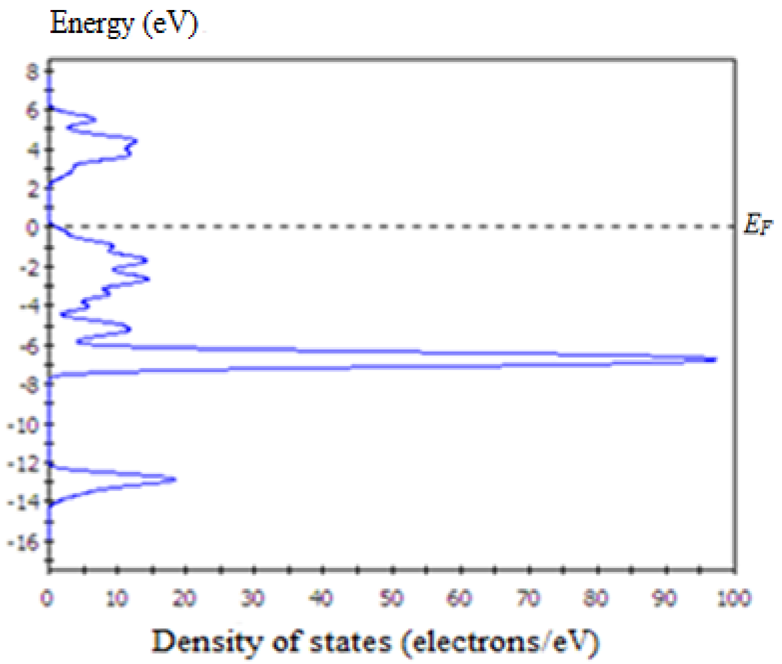

Figure 3.12: Total density of states for $ZnS_{0.25}Se_{0.75}$.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.645 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 2.81 eV. We note here that the correction energy gap is less than the energy gap where x = 0.125 by 0.034 that is may be because of LDA approximation.

3.3.5 $ZnS_{0.375}Se_{0.625}$ Band Structure Calculation

Figure 3.13 shows the Brillouin zone for supercell. The atomic vectors for $ZnS_{0.375}Se_{0.625}$ are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 $\overset{0}{A}$, c = 10.8186 A^0, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25 and R_{AC} = R_{BC} = 6.6136 A^0.

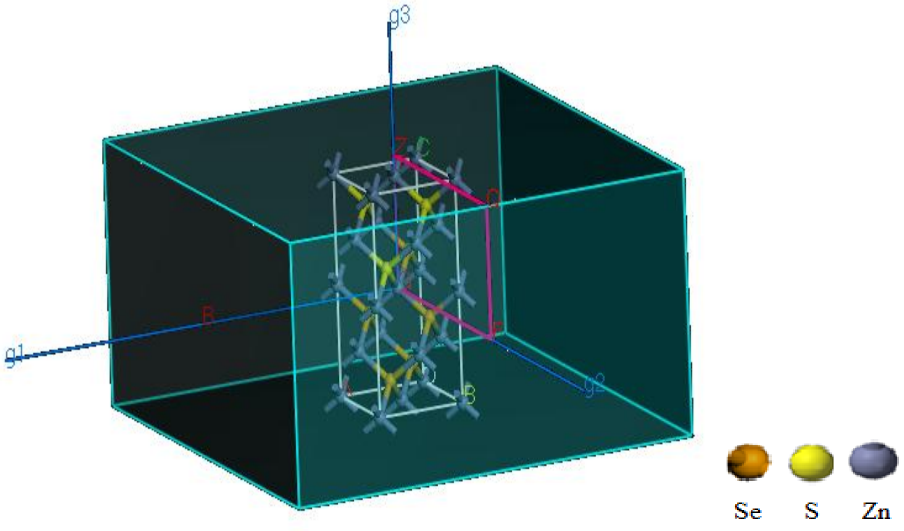

Figure 3.13: Brillouin zone for $ZnS_{0.375}Se_{0.625}$ crystal structure.

Figure 3.14 shows the band structure for $ZnS_{0.375}Se_{0.625}$. The band structure of $ZnS_{0.375}Se_{0.625}$ has energetically separated low lying bands, positioned around -14 eV, are derived from *Se* 4s comparing with Figure 3.15. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -7eV.

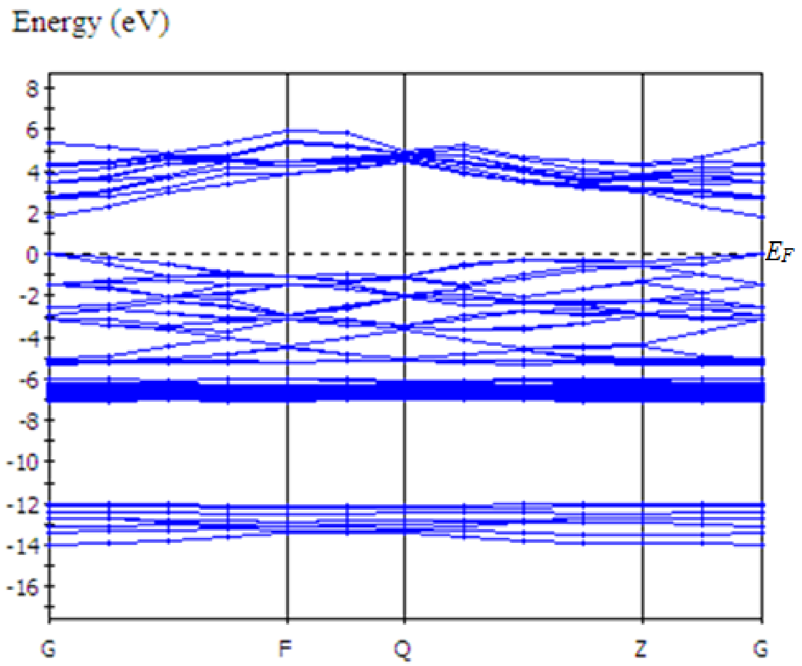

Figure 3.14: The calculated energy band structure for $ZnS_{0.375}Se_{0.625}$.

At the symmetry G point, the energy gap is 1.75 eV and upon applying the 1.7 correction factor *Eg* is 2.97 eV. This is close to the experimental results given by Larach *et al*., [1957] which is 3.01 eV and 2.96 eV as reported by Abo Hassan *et al*., [2005a]. *Eg* is 2.9 eV upon applying the 1.66 correction factor which is near to the experimental results given by Larach *et al*. [1975] and Abo Hassan *et al*. [2005a].

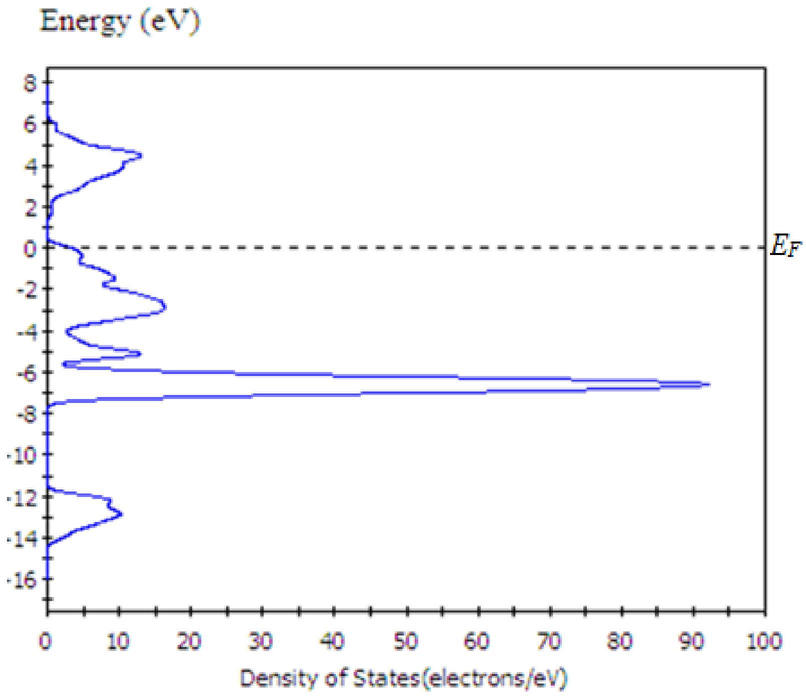

Figure 3.15: Total density of states for $ZnS_{0.375}Se_{0.625}$.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.75 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.15 eV.

3.3.6 ***ZnS*$_{0.5}$*Se*$_{0.5}$ Band Structure Calculation**

Figure 3.16 shows the Brillouin zone for $ZnS_{0.5}Se_{0.5}$ supercell. The atomic position are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 $\overset{0}{A}$, c = 10.8186 $\overset{0}{A}$, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25 and $R_{AC} = R_{BC}$ = 6.6136 A^0.

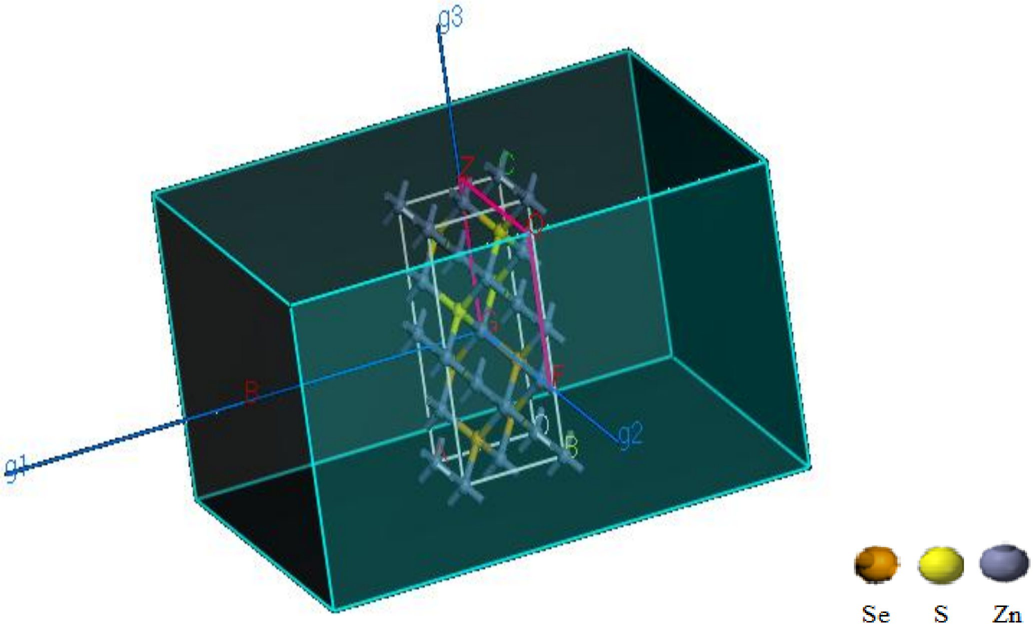

Figure 3.16: Brillouin zone for *ZnS*$_{0.5}$*Se*$_{0.5}$ crystal structure.

Figure 3.17 and Figure 3.18 shows the band structure and the density of states for $ZnS_{0.5}Se_{0.5}$ respectively. The band structure of $ZnS_{0.5}Se_{0.5}$ has energetically separated low lying bands, positioned around -14 eV, and is derived from *Se* 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -6.8eV.

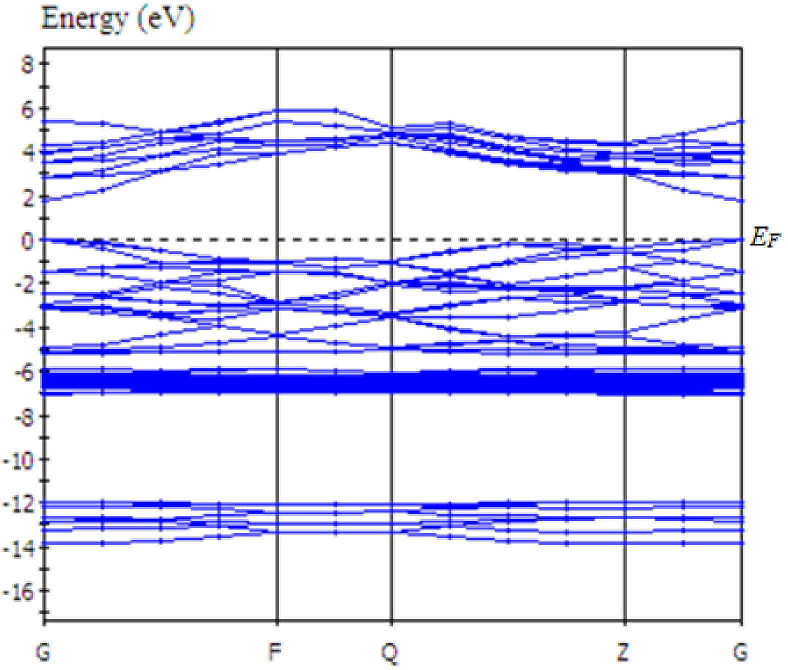

Figure 3.17: The calculated energy band structure for $ZnS_{0.5}Se_{0.5}$.

At the symmetry G point, the energy gap is 1.77 eV and upon applying the 1.7 correction factor *Eg* is 3.00 eV. This is close to the experimental results given by Homann *et al*. [2006] which is 2.92 eV and near to the experimental results which is 3.08 eV as reported by Ebina *et al*. [1974], and close to theoretical results given by Swarnkar *et al*. [2009] which is 3.21 eV and using LCAO [Homann *et al*., 2006] which is 3.29 eV. Eg is 2.94 eV upon applying the 1.66 correction factor which is close to the experimental results given by Homann *et al*. [2006] which is 2.92 eV and different from experimental results given by Ebina *et al*. [1974], and theoretical results reported in the literature.

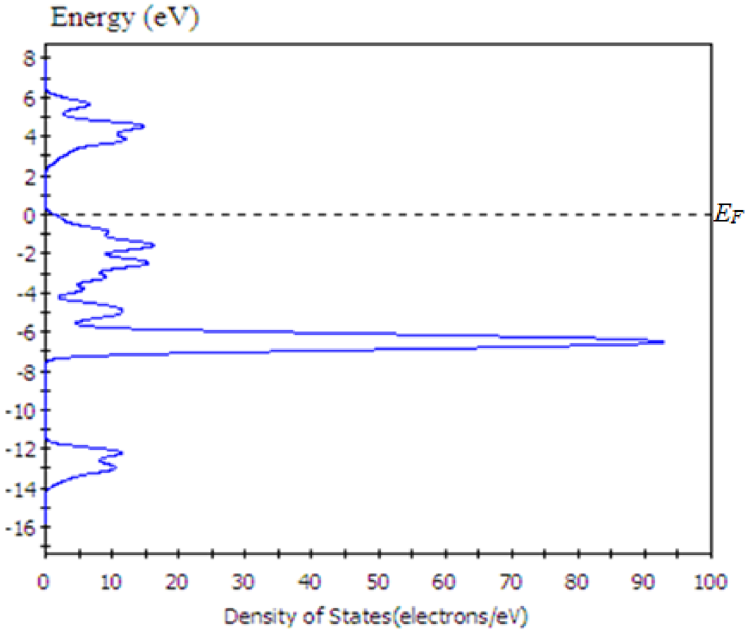

Figure 3.18: Total density of states for $ZnS_{0.5}Se_{0.5}$.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.77 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.19 eV.

3.3.7 $ZnS_{0.625}Se_{0.375}$ Band Structure Calculation

Figure 3.19 shows the Brillouin zone for $ZnS_{0.625}Se_{0.375}$ supercell. The atomic position are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 $\overset{0}{A}$, c = 10.8186 $\overset{0}{A}$, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25 and $R_{AC} = R_{BC}$ = 6.6136 $\overset{0}{A}$.

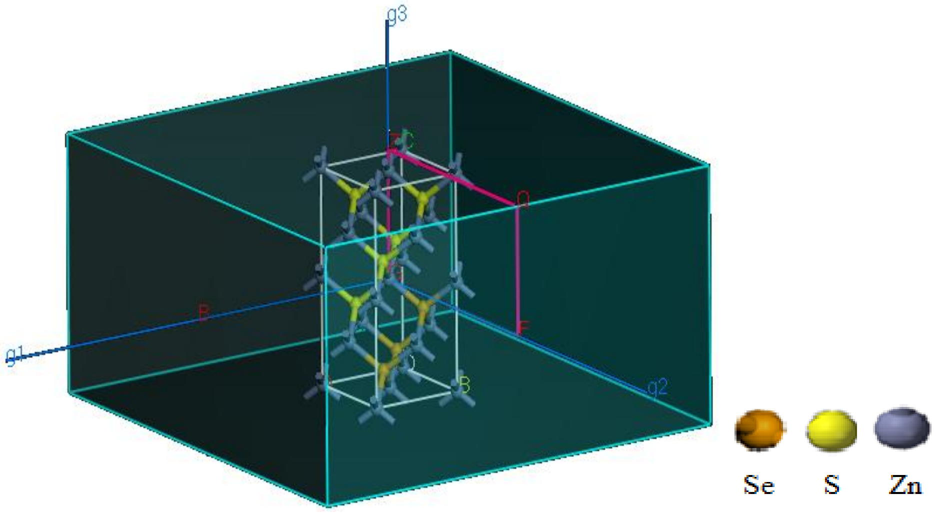

Figure 3.19: Brillouin zone for $ZnS_{0.625}Se_{0.375}$ crystal structure (with space group CMM2 (C2V-11)).

Figure 3.20 and Figure 3.21 show the band structure and the density of states for $ZnS_{0.625}Se_{0.375}$ respectively. The band structure of $ZnS_{0.625}Se_{0.375}$ has energetically separated low lying bands, positioned around -13eV, are derived from *Se* 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -6.5eV.

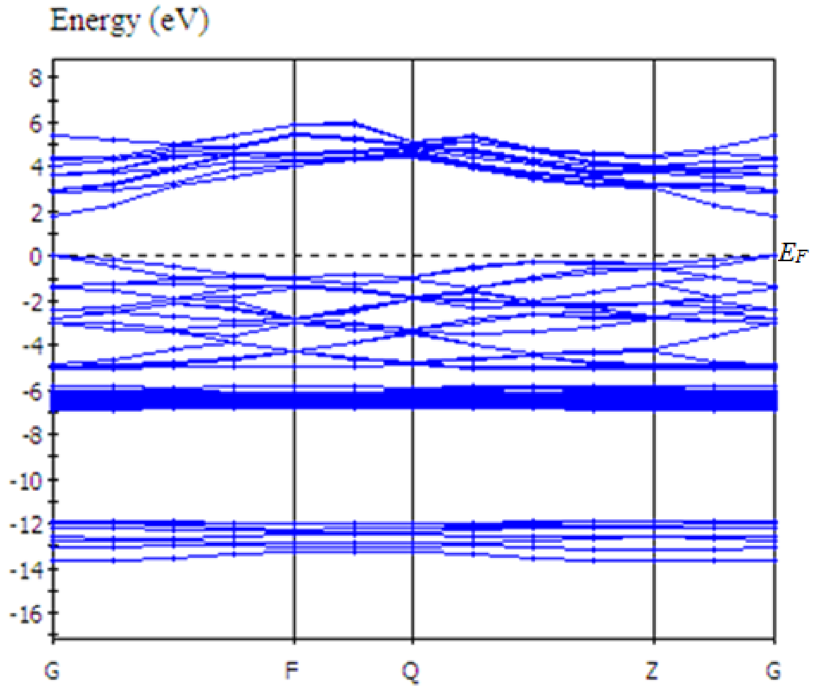

Figure 3.20: The calculated energy band structure for $ZnS_{0.625}Se_{0.375}$.

At the symmetry G point, the energy gap is 1.83 eV and upon applying the 1.7 correction factor *Eg* is 3.11 eV. There is no theoretical and experimental results reported for this concentration. *Eg* is 3.04 eV upon applying the 1.66 correction factor.

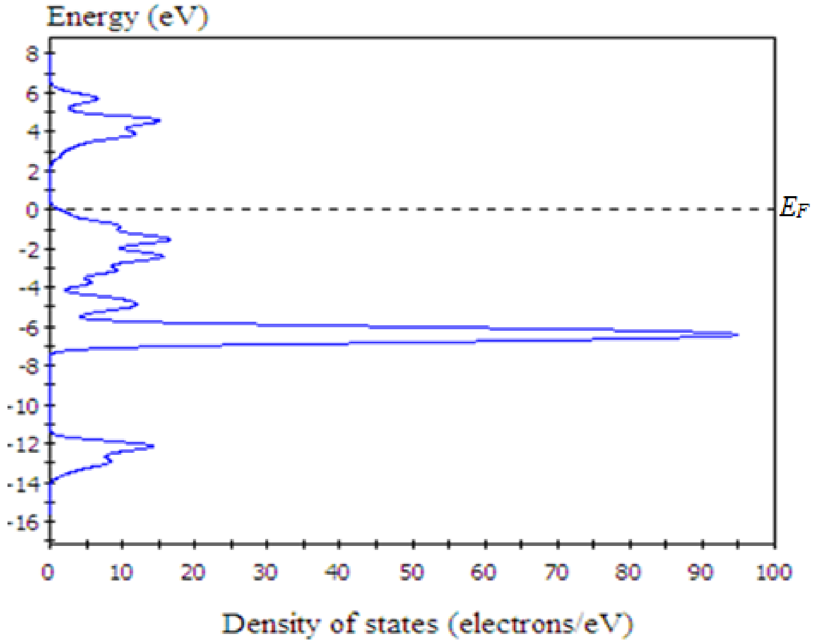

Figure 3.21: Total density of states for $ZnS_{0.625}Se_{0.375}$.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.83 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.29 eV.

3.3.8 $ZnS_{0.75}Se_{0.25}$ Band Structure Calculation

Figure 3.22 shows the Brillouin zone for $ZnS_{0.75}Se_{0.25}$ supercell. The atomic position are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 A^0, c =

10.8186 A^0, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25 and $R_{AC} = R_{BC}$ = 6.6136 A^0.

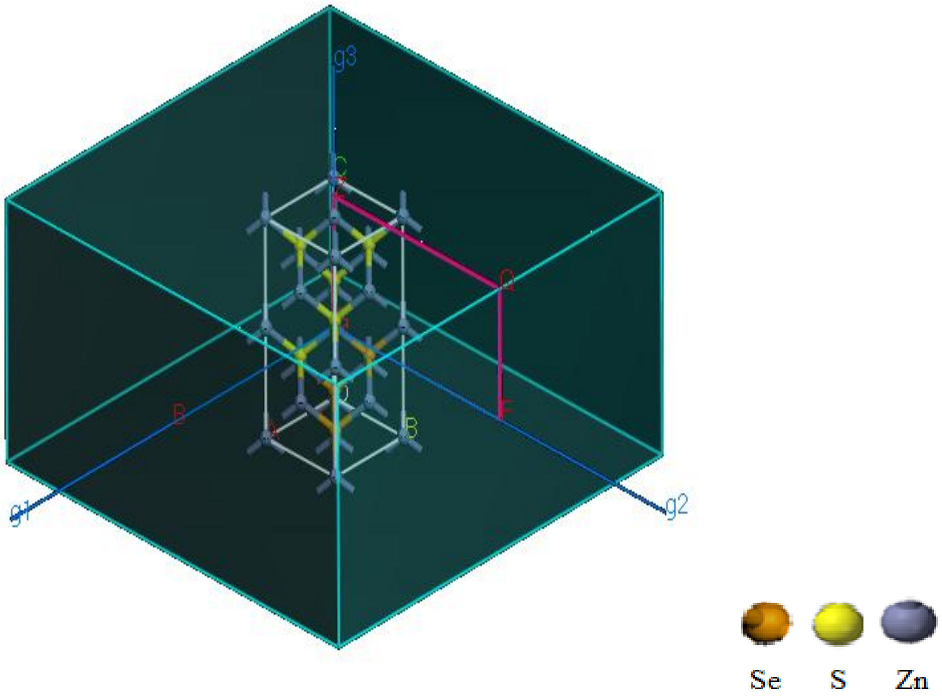

Figure 3.22: Brillouin zone for $ZnS_{0.75}Se_{0.25}$ crystal structure.

Figure 3.23 and Figure 3.24 shows the band structure and the density of states for $ZnS_{0.75}Se_{0.25}$ respectively. The band structure of $ZnS_{0.75}Se_{0.25}$ has energetically separated low lying bands, positioned around -13 eV, and is derived from *Se* 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -6.5eV.

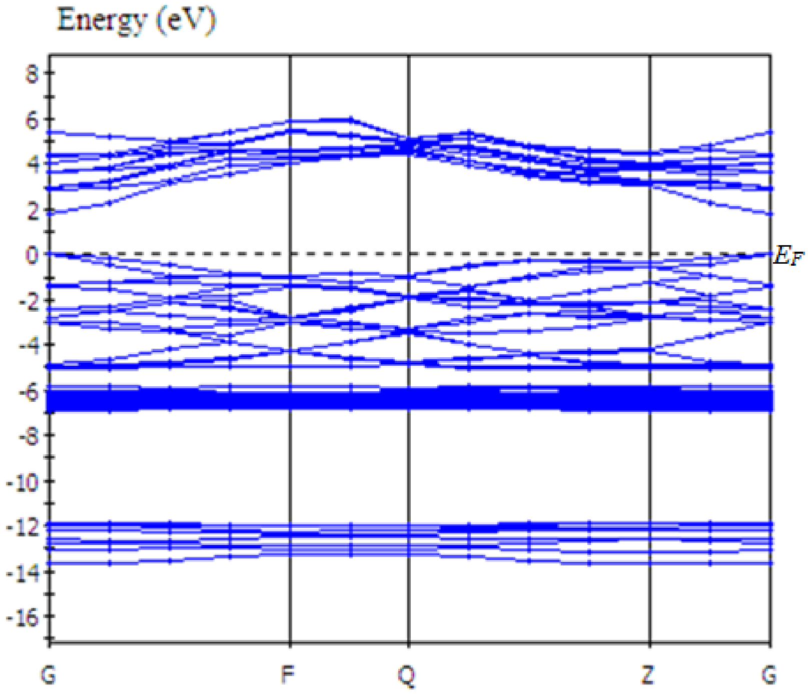

Figure 3.23: The calculated energy band structure for $ZnS_{0.75}Se_{0.25}$.

At the symmetry G point, the energy gap is 1.82 eV and upon applying the 1.7 correction factor *Eg* is 3.1 eV. This is close to the experimental results given by Homann *et al*. [2006] which is 3.17 eV and near to the experimental results which is 3.34 eV as reported by Ebina *et al*. [1974], and little different from theoretical results given by Swarnkar *et al*. [2009] which is 3.47 eV and by using LCAO [Homann et al., 2006] which is 3.47 eV. *Eg* is 3.02 eV upon applying the 1.66 correction factor and this is near to the experimental results 3.17 eV as reported by Homann *et al*. [2006] and different from the other results reported in the literature.

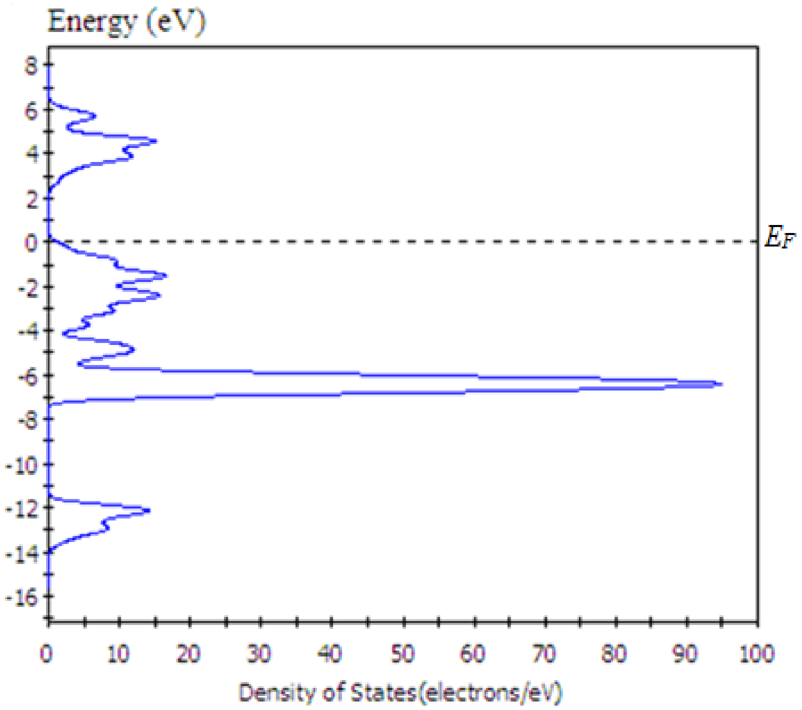

Figure 3.24: Total density of states for $ZnS_{0.75}Se_{0.25}$.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.82 eV at the symmetry G point. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e. 1.7) which gives 3.28 eV.

3.3.9 $ZnS_{0.875}Se_{0.125}$ Band Structure Calculation

Figure 3.25 shows the Brillouin zone for $ZnS_{0.875}Se_{0.125}$ supercell. The atomic position are a_1 = (2.7, -2.7,0), a_2 = (2.7, 2.7, 0), a_3 = (0,0,5.4) where a = 5.4 $\overset{0}{A}$, c = 10.8186 $\overset{0}{A}$, and η =1, and the atomic positions are τ_A = (0,0,0), τ_B = (2.7,0,2.7), τ_{C1} = (1.35,1.35,1.35), τ_{C2} = (4.05,1.35,4.05), u= 0.25 and $R_{AC} = R_{BC}$ = 6.6136 $\overset{0}{A}$.

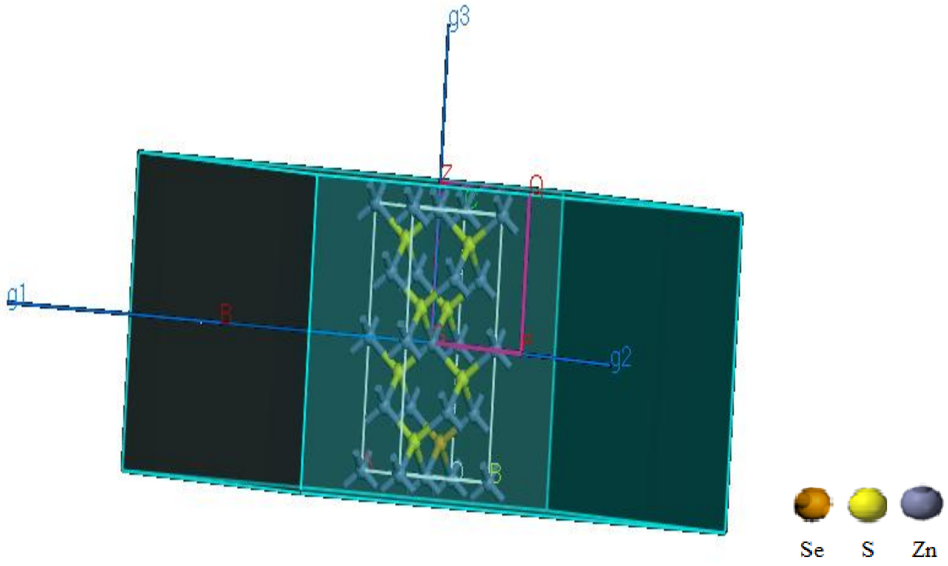

Figure 3.25: Brillouin zone for $ZnS_{0.875}Se_{0.125}$ crystal structure.

Figure 3.26 and Figure 3.27 show the band structure and the density of states for $ZnS_{0.875}Se_{0.125}$ respectively. The band structure of $ZnS_{0.875}Se_{0.125}$ has energetically separated low lying bands, positioned around -13 eV, and is derived from *Se* 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the *Zn* 3d states located around -6.2eV.

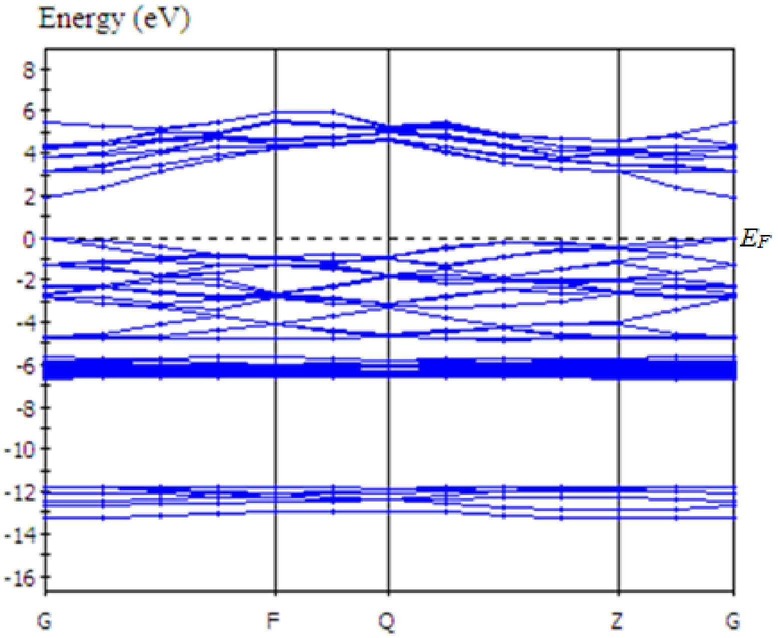

Figure 3.26: The calculated energy band structure for $ZnS_{0.875}Se_{0.125}$.

At the symmetry G point, the energy gap is 1.9 eV and upon applying the 1.7 correction factor *Eg* is 3.32 eV. This is no experimental and theoretical results reported. Eg is 3.15 eV upon applying the 1.66 correction factor.

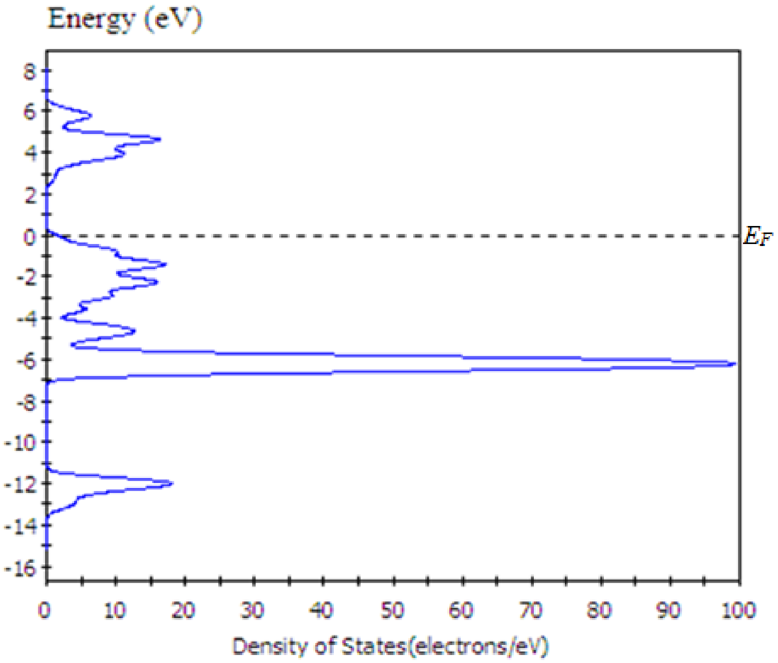

Figure 3.27: Total density of states for $ZnS_{0.875}Se_{0.125}$.

Near the Fermi level (E_F) in the valence-band region, there is a manifold of several bands, nominally derived from the *Se* 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.9 eV at the symmetry G point. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.42 eV.

Figure 3.28 describes the relation between the energy gap *Eg* and the concentration x ($0<x<1$) from the results of CASTEP applying the 1.66 and 1.7 correction factors, and omitting the values of the energy gap for *ZnS* and *ZnSe*. The difference between the values of energy gap of ZnS, ZnSe and the values given in the literatures are because of applying the LDA.

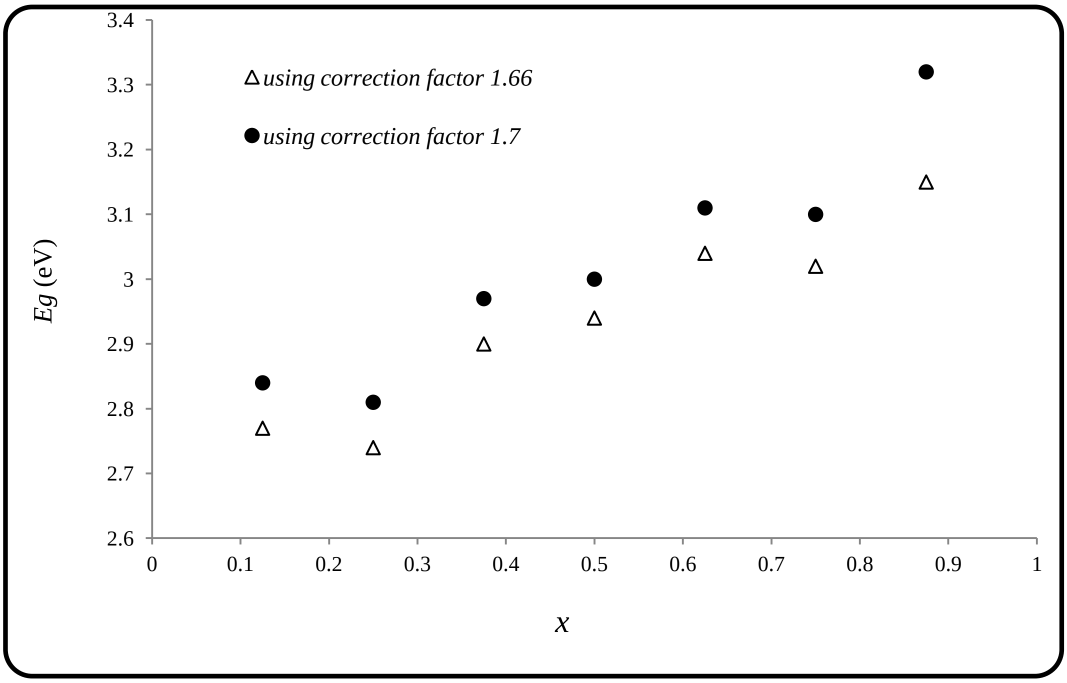

Figure 3.28: ***Eg*** **as a function of** ***x*** **from CASTEP computation upon applying the 1.7 and 1.66 multiplicative correction factors.**

3.4 SUMMARY

The first-principle calculations were applied using the CASTEP computer code based on density functional theory. Computations have been performed via local-density approximation (LDA). Calculations of the band structure and density of states for ZnS_xSe_{1-x} alloy based on parameters given in Eqn. (3.1) to Eqn. (3.4) at the Brillouin zone shows that *ZnS* and *ZnSe* have unit cell vectors $a_1 = (2.7, -2.7,0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0,0,5.4)$ with lattice constant $a = 5.4\ \overset{0}{\mathrm{A}}$ and atomic positions $\tau_A = (0,0,0)$, $\tau_B = (2.7,0,2.7)$, $\tau_{C1} = (1.35,1.35,1.35)$, $\tau_{C2} = (4.05,1.35,4.05)$, with the two fundamental bonds lengths $R_{AC} = R_{BC} = 6.6136\ \overset{0}{\mathrm{A}}$. The calculations of the band structure for ZnS_xSe_{1-x} when $(0< x <1)$ at the Brillouin zone gives unit cell vectors $a_1 = (2.7, -2.7,0)$,

$a_2 = (2.7, 2.7, 0)$, $a_3 = (0,0,5.4)$ where $a = 5.4\ \overset{0}{A}$, $c = 10.8186\ \overset{0}{A}$, atomic positions $\tau_A = (0,0,0)$, $\tau_B = (2.7,0,2.7)$, $\tau_{C1} = (1.35,1.35,1.35)$, $\tau_{C2} = (4.05,1.35,4.05)$, and two fundamental bonds lengths $R_{AC} = R_{BC} = 6.6136\ \overset{0}{A}$.

The values of energy gap for ZnS_xSe_{1-x} $(0 \leq x \leq 1)$ were calculated by using a multiplicative correction factor 1.7 to adjust the theoretical band gap to experimental result.