Calculation of structural, optical and electronic properties of ZnS, ZnSe, MgS, MgSe and their quaternary alloy Mg\(_{1-x}\)Zn\(_x\)S\(_y\)Se\(_{1-y}\)

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Abstract

The structural and electronic properties of the binary semiconductor compounds ZnS, ZnSe, MgS and MgSe in the cubic structure are calculated using the self-consistent scalar-relativistic full potential linear-augmented plane wave method (FP-LAPW) within the local (spin) density approximation (LSDA). From the calculated values of the band-gap energy we have determined the electronic and optical properties of quaternary alloys Mg\(_{1-x}\)Zn\(_x\)S\(_y\)Se\(_{1-y}\) using the simple tight-binding sp\(^3\)s* theory, which incorporates compositional disorder as an effective potential. In addition, the refractive index of MgS, MgSe, ZnS and ZnSe was computed using both real and imaginary parts of the dielectric function. The result indicates that the refractive index increases with allowing for the Mg\(_{1-x}\)Zn\(_x\)S\(_y\)Se\(_{1-y}\) lattice matched to GaAs.

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1. Introduction

It is well known that II–VI semiconductor compounds have a large optical gap, but only recently the feasibility of green–blue opto-electronic devices based on these materials has been demonstrated [1]. However, the lifetime of such devices is extremely short due to the lack of a suitable cladding layer. To resolve this problem, Okuyama et al. [2,3] have proposed a new material ZnMgSSe. The quaternary alloy ZnMgSSe was successfully grown by MBE on GaAs (100) [2] and developed as a better cladding material for light-guiding layers made of ZnS\(_x\)Se\(_{1-x}\) [4]. By varying the relative composition of its components, it was shown [2,3] that MgZnSSe grown on GaAs (100) has a band-gap energy ranging from 2.8 to near 4 eV while maintaining a perfect lattice match to the substrate.

The purpose of the present work is to present the FP-LAPW method coupled with the tight-binding theory to calculate the band structure of the quaternary alloys MgZnSSe. The FP-LAPW computational method is used to calculate the fundamental properties of the binary semiconductor compounds (MgS, MgSe, ZnS, ZnSe) which constitute the quaternary alloy of MgZnSSe. The band-gap energies of the binary compounds MgS, MgSe, ZnS and ZnSe obtained by FP-LAPW are used in the tight-binding method to calculate the electronic and optical properties of the quaternary alloy MgZnSSe lattice matched to GaAs.

Our results are compared with the experimental and other theoretical data. The organization of this paper is as follows: we explain the FP-LAPW computational method in Section 2. In Section 3, the tight-binding method for quaternary alloys is described. In Section 4, results for electronic band structure of the MgZnSSe lattice matched to GaAs calculated by tight-binding sp\(^3\)s* are presented. Finally, conclusions are given in Section 5.
2. Details of calculation of FP-LAPW

Scalar-relativistic calculations have been performed using the WIEN97 code [5] that is an implementation of the method. For the exchange and correlation potential, we have used the local density approximation with a reparametrization of Ceperley–Alder data [6]. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with cut-off \( l_{\text{max}} = 8 \), and in Fourier series in the interstitial region. Here, 2891 plane waves were used for the expansion of the charge density and potential. We use a parameter \( R_{\text{MT}}K_{\text{max}} = 8.0 \), which determines matrix size (convergence), where \( K_{\text{max}} \) is the plane wave cut-off and \( R_{\text{MT}} \) is the smallest of all the atomic sphere radii. We chose the muffin-tin radii of Mg, Zn, S and Se to be 2.0, 2.1, 1.95, 2.15 a.u., respectively. To correct the LDA error in the band gaps, a constant potential is applied to the conduction band states (we use the scissor operator, which rigidly shifts the conduction band states) so as to match the calculated band gaps with the experimental data [7]. Our calculations of the total energy as a function of volume are fitted by least-squares to the Murnaghan equation [8] of state \( E(V) \). With this procedure, we calculate the equilibrium volume \( V_0 \) and evaluate the bulk modulus \( (B) \) at equilibrium and its pressure derivative \( (B') \).

3. The tight-binding method for quaternary alloys

Our approach for the quaternary alloys is based on a semiempirical sp’s* TB method which is treated within the modified VCA to include the effect of disorder and systematically applied it to the MgZnSSe quaternary system. In our calculation, five orbitals per atom \( (s, x, y, z, s*) \) are used, assuming nearest neighbor overlaps [9]. In order to clarify the bowing effect in a quaternary system, the influence of disorder in the related ternary alloys should be carefully examined.

3.1. Ternary alloy calculation

We consider ternary semiconductor alloys of the from \( A_{1-x}B_xC \). We model the band structure of the constituent semiconductors \( AC \) and \( BC \) using our adjusted tight-binding parameters, which generate room-temperature band structure. We then form the VCA Hamiltonian matrix and calculate the fluctuations about the VCA using the Lee et al. [10,11] formalism. Since this formalism is by now reasonably well known, we give only a brief summary of it here. We thus begin with an alloy Hamiltonian matrix of the form:

\[
H^{\text{Alloy}} = H^{\text{VC}} + H^{\text{dis}}
\]

where \( H^{\text{VC}} \) is the virtual-crystal Hamiltonian matrix and \( H_{\text{dis}} \) describes the cation (or anion) disorder which is caused by the composition disorder:

\[
H^{\text{dis}} = -p_{a}(ABC)[x(1-x)]^{1/2}(H^{BC} - H^{AC})
\]

where the disorder parameter \( p_{a}(ABC) \) which simulates the disorder effect, is treated in our calculations as an adjustable parameter. This parameter cannot be arbitrarily varied when a particular choice of experimental band-bowing parameter is used. For example, \( p_{a}(ABC) \) can only be varied in a very narrow region to get a reasonable fit to experimental data.

In the virtual-crystal approximation, the diagonal elements \( H^{\text{VC}}_{jj} \) \((j = a, c)\) are linearly interpolated as functions of \( x \):

\[
H^{\text{VC}}_{jj} = (1-x)H^{AC}_{jj} + xH^{BC}_{jj}
\]

while the first neighbor matrix elements \( V^{\text{VC}}_{ij} \) are interpolated assuming that they are scaled as inversely proportional to the square of the bond length:

\[
V^{\text{VC}}_{ij} = (1-x)\frac{d_{AC}^2}{d_{\text{alloy}}^2} V^{AC}_{ij} + x\frac{d_{BC}^2}{d_{\text{alloy}}^2} V^{BC}_{ij}
\]

Here, \( d_{\text{alloy}} \) we use the VCA bond length.

3.2. Quaternary alloys calculation

Although several reports have been presented, the band structure of MgZnSSe is still ambiguous. Compared with the ternary alloys studied using the same approach [12], the quaternary system is more complex because there are two composition parameters \( x \) and \( y \) in the quaternary \( A_{1-x}B_xC_{1-y}D_{1-y} \). The same procedure can be used in the case of the quaternary system \( A_{1-x}B_xC_{1-y}D_{1-y} \), being aware of two different kinds of disorder effect: cationic disorder due to the random distribution of the \( A \) and \( B \) atoms in the cationic sublattice and anionic disorder due to the random distribution of the \( C \) and \( D \) atoms in the anionic sublattice. In this case, the disorder Hamiltonian matrix \( (H^{\text{dis}}) \) is expressed in terms of the sum of the cationic Hamiltonian matrix \( (H^{\text{dis}}_{\text{cat}}) \) of \( A_{1-x}B_xC \) and \( A_{1-x}B_xD \), related to cationic ternary alloys

\[
H^{\text{dis}}_{\text{cat}} = \sqrt{x(1-x)} \times [yp_{a}(ABC)(H^{BC} - H^{AC}) + (1-y)p_{a}(ABD)]
\]

and the anionic Hamiltonian matrix \( (H^{\text{dis}}_{\text{an}}) \) of \( AC_{1-y}D_{1-y} \) and \( BC_{1-y}D_{1-y} \) related to anionic ternary alloys

\[
H^{\text{dis}}_{\text{an}} = \sqrt{y(1-y)} \times [xp_{a}(BCD)(H^{BD} - H^{BC}) + (1-x)p_{a}(ACD)]
\]

where \( H^{\text{dis}}_{\text{cat}} \) and \( H^{\text{dis}}_{\text{an}} \) are linearly interpolated as functions of \( x \) and \( y \).

\[
H^{\text{dis}}_{\text{cat}} = (1-x)H^{AC}_{jj} + xH^{BC}_{jj}
\]

\[
V^{\text{dis}}_{ij} = (1-x)\frac{d_{AC}^2}{d_{\text{alloy}}^2} V^{AC}_{ij} + x\frac{d_{BC}^2}{d_{\text{alloy}}^2} V^{BC}_{ij}
\]

Here, for \( d_{\text{alloy}} \) we use the VCA bond length.
This correction ensures that the band-bowing parameter is accurate on all four ternary lines. No fitting is needed for the quaternary since the disorder parameters are adjusted for the ternaries. For numerical calculations, the disorder parameters should be corrected for each ternary mixed crystal, so as to reproduce with fair accuracy the experimental bowing parameters of the individual ternary alloys. In the virtual crystal approximation the diagonal and the off-diagonal matrix elements of the quaternary system are linear interpolations as a function of \( x \) and \( y \)

\[
H_y^c = (1-x)yH_{x}^{AC} + xyH_{y}^{BC} + x(1-y)H_{y}^{BD} + (1-x)\times (1-y)H_{y}^{AD}
\]

and

\[
V_y^c = (1-x)\frac{d_{AC}}{d_{alloy}} V_{x}^{AC} + xy\frac{d_{BC}}{d_{alloy}} V_{y}^{BC} + x(1-y)\frac{d_{BD}}{d_{alloy}} V_{y}^{BD} + (1-x)(1-y)\frac{d_{AD}}{d_{alloy}} V_{y}^{AD}
\]

For the refractive index of the quaternary alloy, we have used the empirical formula of Peng and Piprek [13,14].

\[
\varepsilon(E) = A\left(\frac{E}{E_{\text{IT}}}\right)^2 \left(2 - \left(1 + \frac{E}{E_{\text{IT}}}\right)^{0.5} - \left(1 - \frac{E}{E_{\text{IT}}}\right)^{0.5}\right) + B
\]

The values of the direct energy gaps are obtained from our optical spectra, and \( E \) is the photon energy. The material parameters \( A \) and \( B \) of the quaternary alloy are a linear interpolation of binary data obtained from the fit of the calculated refractive index spectra (see Fig. 6).

All the parameters are listed in Table 5.

### 3.3. Lattice matching condition

Table 1 shows the structural properties of the four components of the MgZnSe quaternary alloy and GaAs substrate compared with experimental data. The results present a good agreement between our calculation and experimental data.

In the present work, we have used the relationships between the compositions \( x \) and \( y \) for lattice matched to quaternary alloys, which is:

\[
a_{\text{GaAs}} = (1-x)(1-y)a_{\text{MgSe}} + x(1-y)a_{\text{ZnSe}} + (1-x)y a_{\text{MgS}} + xy a_{\text{ZnS}}
\]

where \( a_{\text{MgSe}} \), \( a_{\text{ZnSe}} \), \( a_{\text{MgS}} \), and \( a_{\text{ZnS}} \) are the lattice constants of MgSe, ZnSe, MgS and ZnS, respectively.

MgZnSe lattice matched to GaAs with the calculated lattice constants:

\[
y = (0.268 - 0.279x)/(0.287 - 0.015x) \quad (0 \leq x \leq 0.94)
\]

MgZnSe lattice matched to GaAs with the experimental lattice constants:

\[
y = (0.237 - 0.222x)/(0.270 - 0.011x) \quad (0 \leq x \leq 0.88)
\]

We use in all our calculations the MgZnSe lattice matched to GaAs with calculated lattice constants.

### 4. Results and discussion

With the optimized total energy per unit cell, the lattice constants and the band structure for all binary compounds MgS, MgSe, ZnS and ZnSe are calculated and are indicated in Tables 1 and 2. By our calculation, one can find that MgS and MgSe crystallize into the NaCl structure, while ZnS and ZnSe crystallize into the zinc-blende structure, as shown in Fig. 1a–d.
And under alloy effect the four binary compounds will crystallize into quaternary alloy of zinc-blende structure for all composition [2]. In the present calculation using the zinc-blende structure, all endpoints binary compounds were found to have direct band-gaps.

The principal transition energies $\Gamma - \Gamma$, $\Gamma - \Gamma$ and $\Gamma - \Gamma$ of four binary compounds calculated with FP-LAPW method are used to calculate the empirical matrix elements of the $sp^3*$ Hamiltonian. They were adjusted in order to more accurately reproduce the energy band gaps of MgS, MgSe, ZnS, ZnSe. Table 3 exhibits the principal calculated and experimental energy gaps and shows that MgS, MgSe, ZnS and ZnSe have a direct gap. The values of the bulk parameters, which are used in our calculation are summarized in Tables 1 and 2.

The band-gap values as a function of the $x$-concentration of MgZnSSe lattice matched to GaAs, calculated in VCA with disorder potential, as shown in Fig. 3. The disorder parameters are listed in Table 4. The band-gap energy varies in the range $3.31 - 1.66$ eV ($0.375 - 0.747$ μm). The absorption at the fundamental optical gaps in the MgZnSSe quaternary alloy is expected to be direct within a whole range of the $x$-concentration. It is also clear from Fig. 3 that the conduction-band minimum at point $\Gamma$ is

![Figure 1](image1)

![Figure 2](image2)

**Fig. 1.** (a–d) Energy vs. volume for the zinc-blende lattice structure and sodium chloride lattice structure of the compounds ZnS, ZnSe, MgS and MgSe.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>MgS</th>
<th>MgSe</th>
<th>ZnS</th>
<th>ZnSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p^a$</td>
<td>0.978061</td>
<td>-1.17457</td>
<td>1.46683</td>
<td>1.47762</td>
</tr>
<tr>
<td>$E_s^b$</td>
<td>-1.14543</td>
<td>-3.97411</td>
<td>-1.64255</td>
<td>-1.68725</td>
</tr>
<tr>
<td>$E_p^b$</td>
<td>3.81248</td>
<td>6.82818</td>
<td>3.56316</td>
<td>3.63953</td>
</tr>
<tr>
<td>$E_s^c$</td>
<td>6.93163</td>
<td>10.0621</td>
<td>8.42102</td>
<td>8.45002</td>
</tr>
<tr>
<td>$E_p^c$</td>
<td>8.24010</td>
<td>9.86655</td>
<td>7.86939</td>
<td>7.86605</td>
</tr>
<tr>
<td>$V_{(s,s)}$</td>
<td>-5.52778</td>
<td>-6.42914</td>
<td>-6.44771</td>
<td>-6.39762</td>
</tr>
<tr>
<td>$V_{(s,s)}$</td>
<td>4.04132</td>
<td>4.88110</td>
<td>2.66998</td>
<td>2.07328</td>
</tr>
<tr>
<td>$V_{(s,s)}$</td>
<td>5.28363</td>
<td>6.89507</td>
<td>3.75086</td>
<td>3.99638</td>
</tr>
<tr>
<td>$V_{(s,s)}$</td>
<td>4.55871</td>
<td>4.79883</td>
<td>5.14266</td>
<td>5.31313</td>
</tr>
<tr>
<td>$V_{(s,s)}$</td>
<td>4.81561</td>
<td>7.74166</td>
<td>6.18954</td>
<td>6.02069</td>
</tr>
<tr>
<td>$V_{(s,s)}$</td>
<td>4.46191</td>
<td>9.52171</td>
<td>4.05832</td>
<td>3.97740</td>
</tr>
<tr>
<td>$V_{(s,s)}$</td>
<td>3.72248</td>
<td>1.07912</td>
<td>1.39138</td>
<td>4.35457</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distance</th>
<th>2.4260a</th>
<th>2.5504a</th>
<th>2.3118a</th>
<th>2.4295a</th>
</tr>
</thead>
</table>

All the energies are in eV; and nearest-neighbor distance $d$ in Å.

This work.

Table 2: The adjusted matrix elements of the $sp^3*$ Hamiltonian.
No spin orbit is included.


Table 3
Comparison of calculated and experimental transition energies (in eV) between major symmetry points in the valence and conduction band semiconductors for cubic MgS, MgSe, ZnS and ZnSe

<table>
<thead>
<tr>
<th>Transitions of energy separation</th>
<th>MgS (in zinc-blende lattice structure)</th>
<th>MgSe (in zinc-blende lattice structure)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FP-LAPW^a</td>
<td>TB^b</td>
</tr>
<tr>
<td>( \Gamma_1 \rightarrow \Gamma_{15} )</td>
<td>–11.26</td>
<td>–10.70</td>
</tr>
<tr>
<td>( X_1 \rightarrow \Gamma_{15} )</td>
<td>–10.25</td>
<td>–9.30</td>
</tr>
<tr>
<td>( L_1 \rightarrow \Gamma_{15} )</td>
<td>–10.30</td>
<td>–9.820</td>
</tr>
<tr>
<td>( \Delta_{1} \rightarrow \Gamma_{15} )</td>
<td>–2.97</td>
<td>–3.55</td>
</tr>
<tr>
<td>( \Delta_{5} \rightarrow \Gamma_{15} )</td>
<td>–1.10</td>
<td>–1.18</td>
</tr>
<tr>
<td>( L_{36} \rightarrow \Gamma_{15} )</td>
<td>–0.343</td>
<td>–0.59</td>
</tr>
<tr>
<td>( L_{24} \rightarrow \Gamma_{15} )</td>
<td>5.03</td>
<td>3.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Transitions of energy separation</th>
<th>ZnS (in Zinc-blende lattice structure)</th>
<th>ZnSe (in Zinc-blende lattice structure)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FP-LAPW^a</td>
<td>TB^b</td>
</tr>
<tr>
<td>( \Gamma_1 \rightarrow \Gamma_{15} )</td>
<td>–13.20</td>
<td>–12.87</td>
</tr>
<tr>
<td>( X_1 \rightarrow \Gamma_{15} )</td>
<td>–11.85</td>
<td>–11.14</td>
</tr>
<tr>
<td>( L_1 \rightarrow \Gamma_{15} )</td>
<td>–12.19</td>
<td>–11.69</td>
</tr>
<tr>
<td>( \Delta_{1} \rightarrow \Gamma_{15} )</td>
<td>–4.80</td>
<td>–6.63</td>
</tr>
<tr>
<td>( \Delta_{5} \rightarrow \Gamma_{15} )</td>
<td>–2.341</td>
<td>–1.03</td>
</tr>
<tr>
<td>( L_{36} \rightarrow \Gamma_{15} )</td>
<td>–0.92</td>
<td>–0.50</td>
</tr>
<tr>
<td>( L_{24} \rightarrow \Gamma_{15} )</td>
<td>3.40</td>
<td>3.40</td>
</tr>
<tr>
<td>( \Gamma_1 \rightarrow \Gamma_{15} )</td>
<td>2.30</td>
<td>2.30</td>
</tr>
<tr>
<td>( X_1 \rightarrow \Gamma_{15} )</td>
<td>3.13</td>
<td>3.13</td>
</tr>
</tbody>
</table>

much lower than at points L and X, especially for greater values of \( x \). The direct-gap nature of the pure materials MgS, MgSe, ZnS and ZnSe found in our calculations is thus conserved in the quaternary alloy also.

In this section, we discuss also the chemical and structural disorder of the quaternary system. For this purpose we discuss the chemical and structural disorder of the related ternary alloys which are the limiting cases

Table 4
Calculated band-gap bowing parameters for the ternary alloys

<table>
<thead>
<tr>
<th>System</th>
<th>( \Delta d ) (Å)</th>
<th>( p )</th>
<th>Bowing parameter ( c ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antionic ternary alloys</td>
<td>Calculated</td>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>ZnS, Se_{1-x}</td>
<td>0.2720^a</td>
<td>0.2590</td>
<td>–0.5480</td>
</tr>
<tr>
<td>MgS, Se_{1-x}</td>
<td>0.2870^a</td>
<td>0.2700</td>
<td>–0.1700</td>
</tr>
<tr>
<td>Cationic ternary alloys</td>
<td>Mg_{1-x}ZnS</td>
<td>0.2640^a</td>
<td>0.2110</td>
</tr>
<tr>
<td>Mg_{1-x}ZnSe</td>
<td>0.2790^a</td>
<td>0.2220</td>
<td>–0.0130</td>
</tr>
</tbody>
</table>

The alloys structural (\( \Delta d \)) and disorder (\( p \)) parameters are also listed for comparison.

^a This work.
^b Calculated according to the model as described in [19].

of the quaternary under consideration using the tight-binding method described in Section 3.

4.1. Chemical and structural disorder in ternary alloys

First, we discuss the cationic and anionic disorder of (Mg,Zn)S, (Mg,Zn)Se, Mg (S,Se) and Zn(S,Se) ternary alloys. Our fitting results of disorder parameters and the comparison of the band-bowing from our calculation with others are given in Table 4. These parameter results indicate that, for the four ternary alloys, the band-bowing parameters for anionic and cationic alloys increase with the lattice mismatch and are very small for cationic ternary alloys compared with anionic ternary alloys; also, Table 4 shows that the disorder has a significant effect in the alloys containing S and Se. Despite the slight dependence of these results on the contribution of the volume effects, these results illustrate the trend of increasing structure effects as a function of the structural difference ($\Delta d_{\text{exp}}$) between the alloy components. Consistent with a previous theory [15], we find that the interconnected trends in disorder effects as functions of alloy structural parameters are very small for both MgZnS and MgZnSe cationic alloys, and strong for MgSSe and ZnSSe anionic alloys. The results also suggest that the small values of the band-bowing parameters for the two cationic cases are caused only by the chemical disorder. The increase of the band-bowing effect for the anionic cases can be understood, in addition to the chemical disorder, from the structural difference, from the structural difference ($\Delta d$) (see Table 4 for comparison). Our calculations predict the direct energy gaps in MgZnS, MgZnSe, ZnSSe and MgSSe within a whole range of the concentration. The direct gap nature of the pure materials MgS, MgSe, ZnS and ZnSe found in our calculations is thus conserved in the ternary alloys also.

Our calculations, despite the use of a greatly simplified band structure, provide by far the most efficient way of obtaining the energy band gaps and band-bowing parameters of cationic and anionic ternary alloys [12].

4.2. Chemical and structural disorder in MgZnSSe quaternary alloy

The disorder parameters in Eqs. (5) and (6) are independent and have a clear physical meaning. The energy band-gap variations with concentration $x$ without and with disorder (VCA) for the MgZnSSe lattice matched to GaAs are shown in Fig. 2; as can be seen in the quaternary alloy, the moderate bowing effect is observable.

This bowing is known to be an effect caused by disorder and is not taken into account by the virtual crystal approximation. However, when the disorder potential ($V_{\text{dis}}$) is added, Fig. 2 shows that there is a deviation of the modified VCA energy gap from that predicted by the VCA.

The modified VCA results are remarkably different from the VCA results. It can be seen from Fig. 2 that the curve for the first case (without disorder) when $p_c$ (MgZnS), $p_c$ (MgZnSe), $p_a$ (MgSSe) and $p_a$ (ZnSSe) are all equal to zero (dotted line) is almost a straight line, but it deviates from the straight line for the second case (with disorder) when $p_c$ (MgZnS), $p_c$ (MgZnSe), $p_a$ (MgSSe) and $p_a$ (ZnSSe) are not equal to zero (solid line), yielding the following linear and quadratic energy band edge coefficients: MgZnSSe lattice matched to GaAs with disorder ($p_{c1} = -0.013$, $p_{c2} = -0.008$; $p_{a1} = -0.17$, $p_{a2} = -0.548$):

$$E_{\Gamma \Gamma} \text{ (in eV)} = 3.307 - 2.057x + 0.410x^2$$
Using the following equation:

\[ E_{\text{TX}} \text{ (in eV)} = 3.557 - 0.992x + 0.205x^2 \]

\[ E_{\text{TL}} \text{ (in eV)} = 3.789 - 0.467x - 0.631x^2 \]

MgZnSSe lattice matched to GaAs without disorder \((p_{v1} = 0, p_{v2} = 0; p_{a1} = 0, p_{a2} = 0)\):

\[ E_{\text{IT}} \text{ (in eV)} = 3.320 - 1.818x + 0.180x^2 \]

\[ E_{\text{TX}} \text{ (in eV)} = 3.583 - 0.870x + 0.087x^2 \]

\[ E_{\text{TL}} \text{ (in eV)} = 3.780 - 0.286x - 0.730x^2 \]

where \(x\) is the Zn concentration in MgZnSSe.

The quadratic term stands for the band-bowing parameter. We can obtain a rapid estimation of the band-bowing parameter of the quaternary MgZnSSe by using the following equation:

\[ E_{\text{TX}}^{\text{ICT}}(x, y) = xyE_g(ZnS) + (1 - x)yE_g(MgS) + x(1 - y)E_g(ZnSe) + (1 - x) \]

\[ \times (1 - y)E_g(MgSe). \]  

(12a)

\[ E_{\text{IT}}^{\text{ICT}}(x, y) = x(x - 1)[yC_{\text{MgZnS}} + (1 - y)C_{\text{MgZnSe}}] \]

\[ + y(y - 1)[xC_{\text{ZnSSe}} + (1 - x)C_{\text{MgSSe}}] \]  

(12b)

\[ E_{\text{IT}}^{\text{ICT}}(x, y) = E_{\text{IT}}^{\text{ICT}}(x, y) + E_{\text{IT}}^{\text{ICT}}(x, y) \]  

(12c)

where \(C_{\text{MgZnS}}, C_{\text{MgZnSe}}, C_{\text{ZnSSe}}, C_{\text{MgSSe}}\) are the band-bowing parameters of ternary MgZnS, MgZnSe, ZnSSe and MgSSe, respectively.

As seen in Fig. 1, the lowest-direct energy gap estimated from Eqs. (12a), (12b) and (12c) is in good agreement with our calculations. There is no experimental result for the MgZnSSe structure available to us.

According to Van Vechten and Bergstresser [16], the disorder contribution (which is related to the different electronegativities of the alloyed atoms) plays a dominant role in determining the bowing parameter. Thus, the strength of compositional (chemical) disorder in MgZnSSe can be seen from the difference in electronegativities of Mg and Zn atoms in the cationic sublattice and of S and Se atoms in the anionic sublattice.

According to the Phillips electronegativity scale [17], the electronegativity difference between Mg and Zn \((0.95 - 0.91 = 0.04)\) is twice smaller compared with S and Se \((1.87 - 1.79 = 0.08)\). Hence, the results seem to indicate that the bowing parameter for MgZnSSe alloy is slightly dominated by the Group VI-anion-based sublattice which contains a random mixture of S and Se with probabilities \(y\) and \(1 - y\), respectively.

Figs. 4 and 5 show the contour lines of the calculated direct energy gap and lattice constants for the whole composition range \((x, y = 0 - 1)\) for MgZnSSe quaternary alloy.

4.3. Refractive index of MgZnSSe lattice matched to GaAs

The important bearing of the refractive index on the operation of an injection laser is its role in the confinement of the emitted radiation to the intermediate vicinity of an active region [18]. On the basis of Eq. (10), the lattice-matching relation between the compositions \(y\) and \(x\) expressed by Eqs. (11a) and (11b) and the data listed in Table 5, we have plotted in Fig. 7 the calculated
refractive indices of the \( \text{Mg}_{1-x}\text{Zn}_x\text{S}_y\text{Se}_{1-y} \) lattice matched to GaAs as a function of the photon energy with \( x \)-concentration increments of 0.1. The curves higher energy endpoints correspond to the values of refractive index \( n \) at the lowest direct gap \( E_{\text{g}} \). The composition parameters \( x = 0 \) and 1.0 correspond to \( \text{MgS}_{0.93}\text{Se}_{0.07} \) and \( \text{ZnS}_{0.06}\text{Se}_{0.94} \), respectively. Fig. 7 shows the variation of the refractive index \( n \) with the composition \( x \), we notice that, the refractive index increases with the composition \( x \).

The quadratic fit of the refractive index \( n \), gives the relations:

\[
\begin{align*}
\text{at } \lambda & \to \infty \quad n = 2.036 + 0.385x + 0.0173x^2 \\
\text{at } \lambda = 500 \text{ nm} \quad n = 2.178 + 0.372x + 1.385x^2
\end{align*}
\]

A few empirical relations \([20,21]\) relate the refractive index to the energy band-gap for a large set of semiconductors. However, in these relations the refractive index \( n \) is independent of the temperature and the incident-photon energy. Our aim is to show how these expressions give good approximations for the refractive index of \( \text{Mg}_{1-x}\text{Zn}_x\text{S}_y\text{Se}_{1-y} \). Using Moss \([20]\), Hervé and Vandamme \([21,22]\) models we have calculated the variation of \( n \) with alloy composition. The results are displayed in Fig. 8. The composition dependence of \( n \) in Fig. 8 was determined by polynomial fitting. Our best fit yields:

\[
\begin{align*}
\text{Ravinda model} \quad n & = 2.034 + 1.275x - 0.254x^2 \\
\text{Hervé and Vandamme model} \quad n & = 2.256 + 0.578x + 0.032x^2 \\
\text{Moss model} \quad n & = 2.315 + 0.356x + 0.078x^2
\end{align*}
\]

Note the weak non-linear dependence of alloy properties with the Zn concentration (Tables 6 and 7).

### 5. Conclusion

We have employed the FP-LAPW method with the LDA form of exchange and correlation to determine the lattice constant, the electronic band structure and bulk modulus of the binary compound semiconductors MgS, MgSe, ZnS and ZnSe which constitute the quaternary alloy MgZnSSe in the zinc-blende structure. The results

![Fig. 6. Refractive index of MgS, MgSe, ZnS and ZnSe in the zinc-blende lattice structure as a function of the photon energy.](image)

![Fig. 7. Calculated refractive indices of MgZnSSe lattice matched to GaAs as a function of the photon energy with \( x \) composition increments of 0.1.](image)

![Fig. 8. The variation in the refractive index with the alloy composition for MgZnSSe.](image)
show that the equilibrium lattice constants are in good agreement with experimental data. The structural and electronic properties obtained by FP-LAPW are used in the tight-binding method to calculate the electronic properties of the quaternary alloy MgZnSSe lattice matched to GaAs.

We have shown that the simple semiempirical sp³s* tight-binding method, which incorporates the chemical disorder parameter, is suitable for calculating the electronic structure of (Mg,Zn)S, (Mg,Zn)Se, Mg(S,Se) and Zn(S,Se). A good agreement of calculated and experimental bowing parameters has been obtained. The simplicity of this method is not only convenient in computation but is also useful for a more detailed understanding of the effects of alloy disorder on the structure of the MgZnSSe quaternary system. The results show the importance of considering the band structure of the related binary and ternary compounds carefully for predicting the bowing effect in the quaternary alloy. It is shown that the band-gap bowing of the MgZnSSe quaternary system can be determined by this method reasonably well compared with theoretical results; there is no experimental result available to us.

Through the comparison with experimental data and using a minimal set of fitting parameters of the ternaries, we have shown that the method is capable of predicting the electronic and optical properties of the quaternary system. Our simplified approach should help make qualitative predictions more easily based on the ternary parameters.

The direct band-gap, the refractive index of the MgZnSSe lattice matched to GaAs for the composition range (0 ≤ x ≤ 1) is calculated using interpolation schemes. The result indicates that the refractive index increases with the x composition.

References


Table 6
Calculated band-bow parameters in quaternary alloy MgZnSSe lattice matched to GaAs

<table>
<thead>
<tr>
<th>Compounds</th>
<th>E₁₁ (eV)</th>
<th>E₁₂ (eV)</th>
<th>E₁₃ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work without disorder</td>
<td>0.180 ± 0.024</td>
<td>0.087 ± 0.027</td>
<td>−0.730 ± 0.048</td>
</tr>
<tr>
<td>This work with disorder</td>
<td>0.410 ± 0.017</td>
<td>0.205 ± 0.021</td>
<td>−0.631 ± 0.015</td>
</tr>
<tr>
<td>Theoretical results (Eqs. (12a), (12b) and (12c))</td>
<td>0.470 ± 0.002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7
Calculated refractive index of ZnS, ZnSe, MgS, MgSe and their alloy

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ZnS (n)</th>
<th>ZnSe (n)</th>
<th>MgS (n)</th>
<th>MgSe (n)</th>
<th>MgZnSSe/GaAs (Bowing With disorder)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work (FP-LAPW)</td>
<td>2.25</td>
<td>2.42</td>
<td>2.02</td>
<td>2.14</td>
<td>0.017</td>
</tr>
<tr>
<td>Moss model</td>
<td>2.34</td>
<td>2.41</td>
<td>2.14</td>
<td>2.27</td>
<td>0.078</td>
</tr>
<tr>
<td>Ravinda model</td>
<td>1.73</td>
<td>2.34</td>
<td>1.29</td>
<td>1.85</td>
<td>−0.254</td>
</tr>
<tr>
<td>Hervé and Vandamme model</td>
<td>2.14</td>
<td>2.40</td>
<td>1.99</td>
<td>2.19</td>
<td>−0.033</td>
</tr>
</tbody>
</table>