Dielectric Properties of Complex Structured Solids

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ABSTRACT

An overview of the understanding of correlation between valence electron plasmon energy and the optical properties such as optical dielectric constant ($\varepsilon_\infty$) of ternary $A^I\text{B}^\text{III}\text{C}^\text{VI}_2$ and $A^\text{II}\text{B}^\text{IV}\text{C}^\text{V}_2$ semiconductors is presented here. We have presented an expression relating the optical dielectric constant of ternary ($A^I\text{B}^\text{III}\text{C}^\text{VI}_2$ and $A^\text{II}\text{B}^\text{IV}\text{C}^\text{V}_2$) chalcopyrites with the plasmon energy ($\hbar\omega_p$). The dielectric constant of these solids exhibit a linear relationship when plotted on a log–log scale against the plasmon energy $\hbar\omega_p$ (in eV) and the data points are lies on the straight line. We have applied the proposed relation on these semiconductors and found a better agreement with the values evaluated by earlier researchers.

Keywords: A. Semiconductors D. Optical properties.

1. INTRODUCTION

The complex structured compound semiconductors of the type $A^I\text{B}^\text{III}\text{C}^\text{VI}_2$ and $A^\text{II}\text{B}^\text{IV}\text{C}^\text{V}_2$ have attracted considerable attention because of their interesting semiconducting, electrical, structural, mechanical and optical properties. Compared to the binary analogues these compounds have higher energy gaps and lower melting points because of which they are considered to be important in crystal growth studies device applications. The ternary compounds are direct gap semiconductors with tetragonal chalcopyrite crystal structure. These families of material are relevant in many fields including non-linear optics, optoelectronic and photo-voltaic devices. The chalcopyrite structure, this is shown in fig.-1, is common to the compounds of chemical formula $A^I\text{B}^\text{III}\text{C}^\text{VI}_2$ and $A^\text{II}\text{B}^\text{IV}\text{C}^\text{V}_2$. Structurally these compounds are derived from that of the binary sphalerite structure (III-V and II-VI) with a slight distortion.
Therefore, like binary compounds they have a high non-linear susceptibility. However, because of the presence of two types of bonds in chalcopyrites they become anisotropic. This anisotropy gives rise to high birefringence. High non-linear susceptibility coupled with high birefringence in these compounds makes them very useful for efficient second harmonic generation and phase matching. Apart from it, the other important technological applications of these materials are in light emitting diodes, infrared detectors, infrared oscillations, lasers etc.\textsuperscript{1-9}.

![Figure 1: Crystal structure of (a) chalcopyrite lattice and (b) defect chalcopyrite crystals](image)

Due to the difficulties associated with experimental processes and their cost, as well as difficulties in obtaining accurate values of physical properties, researchers moved to calculating the physical properties of solids through theoretical methods. But due to the lengthy process and the complicated computational methods involving a series of approximations, such a method has always been complicated\textsuperscript{10}. A considerable amount of empirical work has been done during the last few years\textsuperscript{11-14}, on solid-state properties of materials. Condensed matter theorists can predict crystal structures, lattice constants, phase diagrams and related properties very accurately. Recently, many workers\textsuperscript{11-17} have been some significant break through in the prediction of solid-state properties of solids. These improvements depend heavily on new developments in empirical techniques, and to a greater extent on the insights gained through close collaborations between theorists and experimentalists doing research on solid-state properties of materials. Empirical concepts such as valence electron, empirical radii, electronegativity, ionicity and plasmon energy are then useful\textsuperscript{11-14}. These concepts are directly associated with the character of the chemical bond and thus provide means for explaining and classifying many basic properties of molecules and solids. Recently, Yadav and co-authors\textsuperscript{18, 19}
have developed empirical relations for electronic, optical and mechanical properties of zinc blende and rock-salt structured binary solids using the plasmon oscillations theory of solids. In many cases, empirical relations do not give highly accurate results for each specific material, but they still can be very useful. In particular, the simplicity of empirical relations allows a broader class of researchers to calculate useful properties, and often trends become more evident. It is now well established that the plasmon energy of a metal changes, when it undergoes a chemical combination and forms a compound. This is due to fact that the plasmon energy depends on the number of valence electrons in semiconductors, which changes when a metal forms a compound. Therefore, we thought it would be of interest to give an alternative explanation for the optical dielectric constant for $A^{II}B^{III}C^{VI}_2$ and $A^{II}B^{IV}C^{V}_2$ semiconductors.

The purpose of this work is to obtain optical properties of complex structured ($A^{II}B^{III}C^{VI}_2$ and $A^{II}B^{IV}C^{V}_2$) semiconductors using the plasma oscillations theory of solids. The present investigations are organized as follows: the theoretical concept is given in Section 2 and we present the discussion and simulation results for optical properties of complex structured semiconductors in this Section also. Finally, the conclusion is given in the last Section 3.

2. THEORY, RESULTS AND DISCUSSION

The dielectric constant of a material is one of the key parameters for device design in nearly all fields of modern electronics. Furthermore, it is of fundamental importance for the behavior of charge carriers, dopants, defects and impurities in insulators and semiconductors. The dielectric constants are determined by the polarizability of the atoms and are expected to increase with the atomic number. This is based on the fact that the high-frequency dielectric constant of a solid may be expressed in terms of the polarizability of its constituent atoms $\alpha_i$ –

$$\varepsilon_{\infty} = 1 + \left[ \left( N_i \alpha_i / \varepsilon_0 \right) / \left( 1 - \sum N_i \alpha_i / \varepsilon_0 \right) \right]$$

(1)

where $N_i$ is the number of the atoms of species $i$ per unit volume, $\varepsilon_0$ is the free space permittivity and $\gamma$ is the Lorentz factor. Nag studied the high-frequency and static dielectric constants of cubic semiconductors and proposed a modification in equation (1). The dielectric constant may be expressed in terms of the average atomic number of constituent atoms ($Z_{av}$) by the following relation:

$$\varepsilon = (a - bZ_{av})^{-1}$$

(2)

where $a$ and $b$ are constants, which depends on the group of compounds.

Xue et al., proposed a modification in equation (2) and have shown that the high-frequency dielectric constant may also be expressed in terms of the atomic number of the cation ($Z_A$) by the following relation:

$$\varepsilon_{\infty} = (a'' - b''Z_A)$$

(3)

Here $a''$ and $b''$ are constants. Srivastava has been calculated the optical dielectric constant of the X-Y bond using the well known relation.

\[ \varepsilon_{\infty} = 1 + \left( \frac{\hbar \omega_{p,XY}}{E_{p,XY}} \right)^2 \]  

(4)

In this eq. the dielectric constant of the material depends upon the plasmon energy \((\hbar \omega_{p,XY})\), which depends on the density of the conduction electrons and the effective number of the core electrons via valence electrons, which changes, when metal forms a compound. Srivastava theory\(^7,25,26\), Kumar et al.,\(^27\) found that substantially reduced plasmon energy must be used to get better agreement with the experimental and theoretical values. The plasmon energy of the materials depends on the number of valence electrons. Using this idea\(^10,18,19\) we have recently presented the optical, electronic and mechanical properties such as energy gap \((E_g)\), heteropolar gap \((E_c)\), ionicity \((f_i)\), cohesive energy \((E_{coh})\), bulk modulus \((B)\), electronic polarizability \((\alpha_e)\) and optical susceptibility \((\chi)\) of zinc blende and rock-salt structured binary solids in term of plasmon energy \(\hbar \omega_p\) (in eV) are given as follows;

\[ E_g = M (\hbar \omega_p)^{1.413} \]  

(5)

\[ \alpha_e = N(\hbar \omega_p)^{-2.82} \]  

(6)

Where \(M\) and \(N\) are constants and depend upon the various types of bonds in crystal structures.

Any change in the crystallographic environment of an atom is related to core electrons via the valence electrons. The change in wave function that occurs for the outer electrons usually means a displacement of electric charge in the valence shell so that the interaction between valence, shell and core electrons is changed. This leads to a change in binding energy of the inner electron and to a shift in the position of the absorption edge. The dielectric constant of various types of bonds (A-C and B-C) for \(\text{A}^\text{I}B^\text{II}C^\text{VI}_2\) and \(\text{A}^\text{II}B^\text{IV}C^\text{V}_2\) ternary chalcopyrite semiconductors exhibits a linear relationship, when plotted against the plasmon energy \((\hbar \omega_p)\), the data points are lies on the straight line and are presented in Figs. 2-5. From Figs., it is quite obvious that the dielectric constant trends in these compounds decreases with increases in their plasmon energy. Similarly, based on above expressions and discussion, we are of the view that the dielectric constant of various type of bonds (A-C and B-C) for \(\text{A}^\text{I}B^\text{II}C^\text{VI}_2\) and \(\text{A}^\text{II}B^\text{IV}C^\text{V}_2\) ternary chalcopyrite semiconductors can be evaluated using their plasmon energies by the following relation;

\[ \varepsilon_{\infty, XY} = D(\hbar \omega_{p,XY})^{1.333} \]  

(7)

Where \(D\) is the constant and has values 414.67 and 302.89 for A-C and B-C bonds, respectively, in \(\text{A}^\text{I}B^\text{II}C^\text{VI}_2\) and 255.56 and 537.55 for these bonds in \(\text{A}^\text{II}B^\text{IV}C^\text{V}_2\) ternary chalcopyrite semiconductors respectively. In this relation, Plasmon energy of the chemical bonds A-C abnd B-C in \(\text{A}^\text{I}B^\text{II}C^\text{VI}_2\) and \(\text{A}^\text{II}B^\text{IV}C^\text{V}_2\) ternary chalcopyrite semiconductors has been taken from refs.\(^7,27\). A detailed discussion of optical properties of these materials has been given elsewhere\(^1,6,7,9,23,24\) and will not be presented here. Using Eq. (7), the dielectric constant \((\varepsilon_{\infty})\) for these materials has been calculated. The results are presented in Table-1 & 2. The calculated values of these parameters are in fair agreement with the values reported by Verma\(^9\), Levine\(^23\) and Kumar\(^27\).
Fig. 2: Plot of dielectric constant versus plasmon energy of A-C bond in $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{C}^{\text{VI}}_2$ chalcopyrites

Fig. 3: Plot of dielectric constant versus plasmon energy of B-C bonds in $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{C}^{\text{VI}}_2$ chalcopyrites

Fig. 4: Plot of dielectric constant versus plasmon energy of A-C bond in $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}^{\text{V}}_2$ chalcopyrites
Fig. 5: Plot of dielectric constant versus plasmon energy of B–C bond in A^{IIIB}IV_{C_{V}}^{2} chalcopyrites

Table 1: In this table we present the dielectric constant of A^{IIIB}IV_{C_{V}}^{2} class ternary chalcopyrites

<table>
<thead>
<tr>
<th>Comp.</th>
<th>h(\omega_{\text{p,AC}}) (in eV)</th>
<th>A-C Bond</th>
<th>h(\omega_{\text{p,BC}}) (in eV)</th>
<th>B-C Bond</th>
<th>Dielectric constant (ε_{Total})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlS_{2}</td>
<td>25.110</td>
<td>5.645</td>
<td>5.622</td>
<td>18.295</td>
<td>6.289</td>
</tr>
<tr>
<td>CuAlTe_{2}</td>
<td>20.859</td>
<td>7.229</td>
<td>7.247</td>
<td>15.518</td>
<td>7.832</td>
</tr>
<tr>
<td>CuGaTe_{2}</td>
<td>20.703</td>
<td>7.301</td>
<td>7.303</td>
<td>15.195</td>
<td>8.055</td>
</tr>
<tr>
<td>AgAlSe_{2}</td>
<td>20.090</td>
<td>7.600</td>
<td>7.585</td>
<td>17.510</td>
<td>6.667</td>
</tr>
<tr>
<td>AgAlTe_{2}</td>
<td>18.681</td>
<td>8.374</td>
<td>8.345</td>
<td>15.408</td>
<td>7.907</td>
</tr>
<tr>
<td>AgGaS_{2}</td>
<td>21.201</td>
<td>7.074</td>
<td>7.081</td>
<td>18.598</td>
<td>6.053</td>
</tr>
<tr>
<td>AgGaTe_{2}</td>
<td>18.905</td>
<td>8.241</td>
<td>8.225</td>
<td>15.149</td>
<td>8.087</td>
</tr>
<tr>
<td>AgInS_{2}</td>
<td>21.979</td>
<td>6.742</td>
<td>6.754</td>
<td>16.313</td>
<td>7.327</td>
</tr>
<tr>
<td>AgInSe_{2}</td>
<td>20.513</td>
<td>7.392</td>
<td>7.415</td>
<td>15.291</td>
<td>7.987</td>
</tr>
<tr>
<td>AgInTe_{2}</td>
<td>18.751</td>
<td>8.332</td>
<td>8.345</td>
<td>13.860</td>
<td>9.105</td>
</tr>
</tbody>
</table>
Table-2: In this table we present the dielectric constant of $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}^{\text{V}}$ class ternary chalcopyrites

<table>
<thead>
<tr>
<th>Comp.</th>
<th>A-C Bond</th>
<th>B-C Bond</th>
<th>Dielectric constant ($\varepsilon_{\text{Total}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_{\text{60p,AC}}$</td>
<td>$\varepsilon_{\text{7(1)}}$</td>
<td>$\varepsilon_{\text{T(1)}}$</td>
</tr>
</tbody>
</table>

3. CONCLUSION

From the above results and discussions obtained by using the proposed approach, it is quite obvious that the parameters such as dielectric constant ($\varepsilon_{\infty}$) and electronic susceptibility ($\chi_e$) of the chemical bonds in complex structured $\text{A}^{\text{II}}\text{B}^{\text{III}}\text{C}^{\text{VI}}$ and $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}^{\text{V}}$ and $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}^{\text{V}}$ ternary chalcopyrite semiconductors reflecting the optical properties and can be expressed in terms of plasmon energies of these materials, which is definitely a surprising phenomenon and need further investigation of the reason. The calculated values of these parameters are presented in Table-1 & 2. From Figs. 2-5, we observe that the dielectric constant for the chemical bonds A-C and B-C in $\text{A}^{\text{II}}\text{B}^{\text{III}}\text{C}^{\text{VI}}$ and $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}^{\text{V}}$ ternary chalcopyrite semiconductors are inversly related to the plasmon energy. We note that the investigated values of these parameters by our proposed empirical relations are in close agreement with available theoretical values reported by previous researchers. The various evaluated parameters show a systemic trend and are consistent with the available theoretical values reported so far, which proves the validity of the proposed approach. It is also note worthy that the proposed empirical relation is simpler and widely applicable since we have been reasonably successful in calculating these parameters using the plasmon energy of the materials. It is natural to say that this model can easily be extended to rock-salt and zinc-blende structured crystals for which the work is in progress and will be appearing in forthcoming papers. Hence it is possible to predict the order of electronic properties of ternary chalcopyrite compounds from their plasmon energies.

REFERENCES