EMPIRICAL RELATION FOR ELECTRONIC AND OPTICAL PROPERTIES OF BINARY TETRAHEDRAL SEMICONDUCTORS

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The concept of ionicity developed by Phillips and Van Vechten originated from the dielectric analysis of the semiconductors and insulators have been used to evaluate various bond parameters of binary tetrahedral ($A^{II}B^{VI}$ and $A^{III}B^{V}$) semiconductors. An overview of the understanding of correlation between atomic number and the opto-electronic properties of zinc blende crystal structured solids is presented here. In this paper, an advance hypothesis of average atomic number of the elements in a compound has been used to evaluate intrinsic electronic and optical parameters such as ionic gap (E_c), average energy gap (E_g), crystal ionicity (f_i) and dielectric constant (ε) of binary tetrahedral semiconductors.
KEYWORDS: Ionicity; atomic number; zinc blende; energy gap

The largest part of modern technology on the earth is based on solid state materials. Ample research dedicated to the physics and chemistry of solids during the past four decades has produced sizeable breakthroughs in comprehending the properties of solids as a whole. So, it is captivating to go through the behaviour and various properties of other solids. The modern microelectronic industry uses the semiconductors of particular omnitriangulated nature in zinc blende crystallographic structure. This nature gives rise to unique physical properties in materials. A great amount of theoretical and experimental work has been completed in recent past on mechanical, structural and optical properties of zinc blende ($A^{III}B^{V}$ and $A^{II}B^{VI}$) semiconductors [1-7]. It is due to their exciting semiconducting properties and various practical applications in the area of non-linear optical laser devices, photovoltaic detectors, light emitting diodes, solar cells, and integrated optical devices such as switches, filters and modulators. The hypothesis of crystal ionicity of chemical bonding has been demonstrated its potential in the characterization of molecular and solid state properties. This proposed various ionicity scales to associate with a broad spectrum of physical and chemical properties such as cohesive energy, elastic constants, heat of formation, crystal structure, bulk modulus etc [8]. Levine [8], Phillips and Van Vechten [9-11], and many more researchers [12-16] have evolved several theories and evaluated ionicity in the case of basic compounds.

Because of the trouble related to the experimental procedure and its price, also complicacies in getting correct values of physical properties, researchers moved to evaluating the physical properties of solids by means of theoretical methods. But owning to the elaborated process, as well difficult computational methods require a sequence of approximation; these methods have always been complex and developed for only limited semiconductors [17]. Consequently, we realized it would be of immense interest to present an another possible interpretation of the ionic gap (E_c), average energy gap (E_g), crystal ionicity (f_i) and dielectric constant (ε) in binary tetrahedral ($A^{II}B^{VI}$ and $A^{III}B^{V}$) semiconductors.

Numerous researchers have attempted to evaluate electronic and optical parameters of binary tetrahedral semiconductors with the help of ionic charge and valance electrons. But considering the different screening factors present in compound crystallography, we have used a new concept of average atomic number of interacting elements in a compound and found excellent results comparable to previous workers for the ionic gap (E_c), average energy gap (E_g), crystal ionicity (f_i) and dielectric constant (ε) in binary tetrahedral ($A^{II}B^{VI}$ and $A^{III}B^{V}$) semiconductors. In our suggested relations only few variables such as atomic number and ionic charge on cation and anion are needed as input data, to calculate many electronic and optical properties of these compounds and the method emerge relevant to other materials, too.

THEORY, RESULTS AND DISCUSSION

As stated in modified theory of dielectric of solids [9-11, 18-20] for tetrahedral coordinated compounds, average energy gap (E_g), connected bonding and anti binding (sp^3) hybridized orbital can be separated into two shares due to symmetric and anti symmetric portions of the potential inside a unit cell. These shares are ionic or heteropolar (E_c) and covalent or homopolar (E_h), which can be expressed in the following relation:

$$E_g^2 = E_c^2 + E_h^2 \tag{1}$$

The ionic or heteroplar share E_c is inversely related to the bond length d as:

$$E_c = K_1 d^{-1} e^{-K_s r_o} \tag{2}$$

where K_1 is an arbitrary constant and depends on the difference between valence states of an atom and is given by $K_1 = bc^2\Delta z$, where prescreening factor b depends on the coordination number [21] around the cation i.e. $b = 0.089 \, N_c^2$, here

N_c is average coordination number and c-electronic charge, $\Delta z = 4$ for IIB chalcogenides. The values of $N_c = 4$, b=1.424 and hence $K_1 = 262.784$ are for zinc blende type structure. Thomas-Fermi screening parameter K_s has been ascertained taking into account eight electrons per molecule (two for Zn, Cd & Hg and six for O, S, Se & Te) and $r_o = d/2$.

The covalent or homopolar share E_h is related to the bond length d as:

$$E_h = A d^{-K_2} \tag{3}$$

where A and K_2 are constants, which remain unaffected in different crystal structures with values A = 40.468 eV/Å$^{2.5}$ and $K_1 = 2.5$. These values are A= 39.74 and $K_1 = 2.48$ as reported by PVV [10]. Therefore, the values of E_c and E_h depend on number of bonds emerge from cations and bond length.

The crystal ionicity f_i of the chemical bond is expressed as the fraction of ionic character as follows.

$$f_i = E_c^2 / E_g^2 \tag{4}$$

V. Kumar [22-24] has expressed those electronic properties of zinc blende ($A^{II} B^{VI}$ and $A^{III}B^V$) crystals in terms of Plasmon energy $\hbar\omega_p$ as follows:

$$E_h \text{ (eV)} = 0.04584 (\hbar\omega_p)^\nu, \tag{5}$$

$$E_c \text{ (eV)} = 10.722 (\hbar\omega_p)^{2/3} \times \exp [-6.2554(\hbar\omega_p)^{-1/3}] \tag{6}$$

Here $\hbar\omega_p$ is in eV, ν is a constant. E_c and E_h are the ionic and homopolar gaps, respectively.

Jayaraman et al. [25], Srideshmukh et al. [26], and Krishnan et al. [27] established that significantly reduced ionic charges must be used to obtain better agreement with experimental values of these parameters. Verma et al. [28] have been applied this concept for obtaining better agreement with theoretical data for ionic gap (E_c), average energy gap (E_g), crystal ionicity (f_i) and dielectric constant (ϵ) of binary tetrahedral ($A^{II}B^{VI}$ and $A^{III}B^V$) semiconductor, which can be expressed in terms of product of ionic charges as follows:

For binary tetrahedral (zinc blende) semiconductors:

$$E_c = 90 \, d^2 / (Z_1 Z_2)^{0.7} \text{ eV}, \tag{7}$$

$$E_g = 90 \, d^{2.12} / (Z_1 Z_2)^{0.5} \, eV \tag{8}$$

Here, Z_1 and Z_2 are the ionic charges and d is the bond length in Å. On solving equations (2) and (7, 8), crystal ionicity f_i can be expressed as follows:

$$f_i = 0.87891 \, d^{0.24} / (Z_1 Z_2)^{0.4} \tag{9}$$

Levine and Penn [8, 29] have given the relation for dielectric constant ϵ as follows:

$$\epsilon = 1 + (\hbar\omega_p)^2 / (E_g)^2 \tag{10}$$

Considering the above empirical relations and using the concept of product of ionic charges given by Verma at el. [28] and our hypothesis of average atomic number of elements in the binary tetrahedral semiconductor, we have proposed following empirical relations for electronic and optical parameters such as ionic gap (E_c), average energy gap (E_g), crystal ionicity (f_i) and dielectric constant (ϵ) and further evaluated their values. The evaluated values are in excellent agreement with the values reported by Levine [8], V. Kumar [22-24]. Our endeavour of determining ionic gap E_c, average energy gap E_g, crystal ionicity f_i, and dielectric constant ϵ has not been required experimental values of the dielectric constant although the previous models needed this value in their computations except Verma et al. [28]. These values are presented in the table 1 and 2.

$$E_c = 65 / (Z_1 Z_2)^{0.8} \left(\frac{a_{Z1} + a_{Z2}}{2}\right)^{0.6}, \tag{11}$$

$$E_g = 91 / (Z_1 Z_2)^{0.6} \left(\frac{a_{Z1} + a_{Z2}}{2}\right)^{0.5}, \tag{12}$$

$$f_i = 1.6 \left(\frac{a_{z1} + a_{z2}}{2}\right)^{0.25} / (Z_1 Z_2)^{0.25}, \tag{13}$$

We have found dielectric constant (ϵ) same as given in relation (10). Here, Z_1, Z_2 are ionic charges and a_{Z1}, a_{Z2} are atomic numbers of the elements in the compound.

Table 1. This table presents the values of ionic gap E_c and average energy gap E_g of binary tetrahedral semiconductors.

Solids	a_{z1}	a_{z2}	E_c [8]	E_c[24,30]	E_c [28]	E_c[This work]	E_g [8]	E_g[24,30]	E_g [28]	E_g[This work]
AlP	13	15	3.76	3.31	3.47	4.00	6.04		5.18	6.50
AlAs	13	33	3.82	3.36	3.27	3.29	5.81		4.87	5.07
AlSb	13	51	3.08	2.71	2.73	2.90	4.68		4.02	4.30
GaP	31	15	3.3	2.9	3.47	3.29	5.76		5.18	5.07

Solids	a_{z1}	a_{z2}	E_c [8]	E_c[24,30]	E_c [28]	E_c[This work]	E_g [8]	E_g[24,30]	E_g [28]	E_g[This work]
GaAS	31	33	2.92	2.51	3.22	2.90	5.21		4.79	4.30
GaSb	31	51	2.13	1.87	2.75	2.63	4.14		4.05	3.80
InP	49	15	3.35	2.95	3.0	2.90	5.16		4.44	4.30
InAs	49	33	2.74	2.41	2.84	2.63	4.58		4.19	3.80
InSb	49	51	2.15	1.89	2.45	2.43	3.76		3.58	3.44
ZnS	30	16	6.16	6.05	6.23	6.31	7.82	7.73	7.92	8.25
ZnSe	30	34	5.51	5.57	5.64	5.55	6.98	7.09	7.12	7.00
ZnTe	30	52	4.38	4.54	4.89	5.03	5.66	5.75	6.13	6.18
CdS	48	16	5.78	5.1	5.29	5.55	7.01	6.47	6.65	7.00
CdSe	48	34	5.31		4.97	5.03	6.42		6.23	6.18
CdTe	48	52	4.43	4.19	4.32	4.66	5.40	5.29	5.37	5.60
HgS	80	16		5.08	5.33	4.73		6.45	6.71	5.71
HgSe	80	34		4.14	4.93	4.43		5.22	6.18	5.24
HgTe	80	52			3.97	4.18			4.92	4.87

Table 2. This table presents the values of dielectric constant ϵ and crystal ionicity f_i of the binary tetrahedral semiconductors.

Solids	a_{z1}	a_{z2}	$\hbar\omega_p$ [32]	ϵ [5]	ϵ [31]	ϵ [28]	ϵ[This work]	f_i [8]	f_i [24]	f_i [28]	f_i [This work]
GaP	31	15	16.8	9.495	9.11	11.52	11.95	0.328	0.325[d]	0.449	0.379
GaAS	31	33	16	12.302	10.88	12.16	14.82	0.315	0.303[d]	0.453	0.394
GaSb	31	51	14.9		14.44	14.53	16.35	0.265	0.264[d]	0.461	0.404
InP	49	15	13.9	9.706	9.61	10.8	11.43	0.421	0.419[d]	0.457	0.394
InAs	49	33	13.7	13.55	12.03	11.69	13.98	0.359	0.357[d]	0.46	0.404
InSb	49	51	13.2		15.68	14.6	15.69	0.329	0.327[d]	0.468	0.413
ZnS	30	16	16.68[b]	5.7[c]	5.2[a]	5.44	5.08	0.621	0.613	0.619	0.593
ZnSe	30	34	15.78[b]	5.9[c]	6[a]	5.91	6.08	0.623	0.617	0.627	0.615
ZnTe	30	52	13.8[b]	6.7[c]	7.28	6.07	5.98	0.599	0.626	0.637	0.632
CdS	48	16	14.87[b]		5.3[a]	6	5.51	0.679	0.621	0.631	0.615
CdTe	48	52	13.09[b]		7.21	6.94	6.46	0.675	0.629	0.647	0.646
HgS	80	16	14.85[b]			5.9	7.75		0.622	0.631	0.643
HgSe	80	34	12.98[b]			5.41	7.12		0.629	0.637	0.655

[a]Ref. [8], [b]Ref. [24], [c]Ref. [33], [d]Ref. [30]

SUMMARY AND CONCLUSIONS

The suggested empirical relations have been applied to calculate ionic gap E_c, average energy gap E_g, crystal ionicity f_i, and dielectric constant ϵ of binary tetrahedral ($A^{II}B^{VI}$ and $A^{III}B^{V}$) semiconductors. This shows average atomic number of the elements in the compounds is a crucial parameter for evaluating electronic and optical properties. The ionic gap (E_c) and average energy gap (E_g) of these compounds have been found inversely proportional to the average atomic number and product of ionic charges of the compounds. The crystal ionicity (f_i) is directly related to average atomic number and inversely to product of ionic charges, while dielectric constant (ϵ) is directly related to both the parameters. This is interesting to note that the suggested relations are straightforward, extensively relevant and values obtained are in good agreement with published values as compared to earlier workers. The hypothesis proposed herein will be supportive to the researchers for exploring new analogous materials with aimed ionic gap (E_c), average energy gap (E_g), crystal ionicity (f_i) and dielectric constant (ϵ). Arguably this hypothesis may easily be broadened to ternary tetrahedral semiconductors, for which work is in progression out comes will be revealed in expected paper.

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**ЕМПІРИЧНЕ СПІВВІДНОШЕННЯ ЕЛЕКТРОННИХ ТА ОПТИЧНИХ ВЛАСТИВОСТЕЙ
БІНАРНИХ ТЕТРАЕДРИЧНИХ НАПІВПРОВІДНИКІВ**

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Концепція іонності, розроблена Філліпсом та Ван Вехтеном, виникла в результаті діелектричного аналізу напівпровідників, а ізолятори використовувались для оцінки різних параметрів зв'язку двійкових чотиригранних напівпровідників (AIIBVI та AIIIBV). Тут представлений огляд розуміння кореляції між атомним номером та оптоелектронними властивостями твердих кристалів із змішаною кристалічною структурою цинку. У цій роботі попередня гіпотеза середнього атомного числа елементів у сполуці була використана для оцінки власних електронних та оптичних параметрів, таких як іонна щілина (E_c), середня заборонена зона (E_g), іонність кристалів (f_i) та діелектрична проникність (ε) подвійних тетраедричних напівпровідників.
КЛЮЧОВІ СЛОВА: іонність; атомний номер; цинкова обманка; заборонена зона