



Analysis of Ionicity using Plasmon Energy and Electro Negativity Difference of Binary Tetrahedral Semiconductors and Ionic Compounds

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Abstract

The homopolar energy gap (E_h) and the total energy gap (E_g) of binary tetrahedral(II-VI and III-V) semiconductors and ionic(I-VII) compounds have been estimated from plasmon energy and electronegativity difference between bonding atoms of compounds. Accordingly two relations have been proposed. Constants appearing in the proposed relation for E_h have been shown to be characteristics of crystal structures of the crystals. Similarly, the constants appearing in the relation for E_g have been found to be the characteristics of the cations of the compounds in their respective families. Using the estimated values of E_h and E_g , ionicity (of these crystals) has been calculated employing Phillips-Van Vechten -Levine (PVL) formalism. The calculated values of ionicity are in excellent agreement with those reported by different researchers.

Keywords: Plasmon energy, ionicity, binary tetrahedral semiconductors, ionic compounds.

Introduction

There has been several attempts made at understanding the homopolar (covalent) and heteropolar (ionic) energy gap and total energy gap of semiconductors (elemental and compounds)¹⁻⁹. Various theories have been developed to calculate these gaps and ionicity of binary tetrahedral semiconductors, which have drawn considerable interest of researchers¹⁰⁻¹³ in recent years, to understand various properties of these compounds. This is because of their interesting semiconducting properties and various applications in the field of electronics, photovoltaic detectors, light emitting diodes and solar cells. In this paper, the covalent contribution to energy gap has been calculated using Plasmon energy and the total energy gap has been correlated with the electronegativity difference between the bonding atoms of compounds.

Methodology

According to Phillips and Van-Vechten¹⁻³ in tetrahedrally coordinated semiconducting crystals and octahedrally coordinated ionic crystals, energy gap E_g between bonding and antibonding (SP^3) hybridized orbitals may be decomposed into contributions due to symmetric and antisymmetric parts of the potentials within the unit cell. These contributions are (i) heteropolar or ionic contributions represented by C (ii) homopolar or covalent contributions represented by E_h , which satisfy the following relation

$$E_g^2 = E_h^2 + C^2 \quad (1)$$

In the spectroscopic definition of ionicity, E_h and C are regarded as Cartesian coordinates and are transformed to more symmetrical polar coordinates. Then E_g is the polar radius and Φ is the ionicity phase angle given by

$$\tan \Phi = C/E_h \quad (2)$$

The ionicity of a chemical bond in terms of fractional ionic character is defined as

$$f_i = \sin^2 \Phi = C^2/E_g^2 \quad (3)$$

and the covalency or the fractional covalent character is given by

$$f_c = \cos^2 \Phi = E_h^2/E_g^2 \quad (4)$$

$$\text{Thus } f_i = 1 - f_c = 1 - E_h^2/E_g^2 \quad (5)$$

The average homopolar energy gap, E_h is a function of the nearest neighbour distance, d given by¹⁻³

$$\text{Equation } E_h = \frac{39.74}{d^{2.48}} \quad (6)$$

$$\text{And } C = 14.4 \text{ b exp}(-k_s r_o) [(Z_A/R_A) - (Z_B/R_B)] \quad (7)$$

where $\text{exp}(-k_s r_o)$ is the Thomas-Fermi screening factor

$$\text{with } k_s = (4K_F/\Pi a_B)^{1/2} \quad (8)$$

$$\text{and } r_o = 1/2.d \quad (9)$$

here a_B is the Bohr radius, k_F is the Fermi wave vector, Z_A and Z_B is the number of valence electrons on the A and B atoms of binary compound AB and r_A and r_B is the covalent radius of A and B atom. The physical interpretation of Equation (7) is that the antisymmetric energy gap C is given by the difference between the coulomb potentials of atoms A and B forming the compound AB. But the main problem in the relation is that 'b' is not uniquely defined, which may lead to some error in the results. In order to avoid this uncertainty, an alternative approach has been suggested involving Plasmon energy and electronegativity in which the need of calculating C is bypassed.

As per Equation (6), the homopolar band gap is related to bond length, magnitude of which depends upon the nature of bonding

which, in turn, depends upon the valence electrons of the bonding atoms of molecules. Since Plasmon energy also is a function of valence electron number it was thought worthwhile to find a correlation between homopolar energy gap and Plasmon energy. The values of homopolar energy gap and Plasmon energy of elemental semiconductors in (table -1,^{1,2}) are used to find such a correlation.

In this attempt a graph was plotted for $\log E_h$ versus $\log \hbar\Omega_p$ which is a straight line (figure-1)

From the linear graph of $\log E_h$ versus $\log \hbar\Omega_p$ the following relation is proposed: $E_h = A (\hbar\Omega_p)^B$ eV (10)

where $A=0.0448$ and $B= 1.6609$ for tetrahedrally elemental semiconductors and the Plasmon energy as $\hbar\Omega_p = \hbar\sqrt{4\pi N e^2 / m}$ (11) where N is the effective number of free electrons taking part in plasma oscillation e is the charge and m is the mass of the electron. In a similar attempt, $\log E_g$ was plotted against $\log \Delta x$, where Δx is the difference in electronegativity of bonding atoms of the compounds given in figure-2.

From the graph, the following relation is proposed for the total energy gap E_g : $E_g = M (\Delta x)^N$ (12)

where M and N are constants for compounds of given cation family. Values of M and N for binary tetrahedral (II-VI and III-V) semiconductors and ionic (I-VII) compounds are given in table 2.

Table-1
Homopolar energy of elemental semiconductors.

Elements	$\hbar\Omega_p$	E_h (Calculated)	E_h (Phillips) ^{1,2}	E_h (Christensen) ¹⁶
C	31.2	13.5	13.5	13.31
Si	16.5	4.71	4.77	6.82
Ge	15.6	4.29	4.31	6.38
Sn	12.7	3.05	3.01	5.18

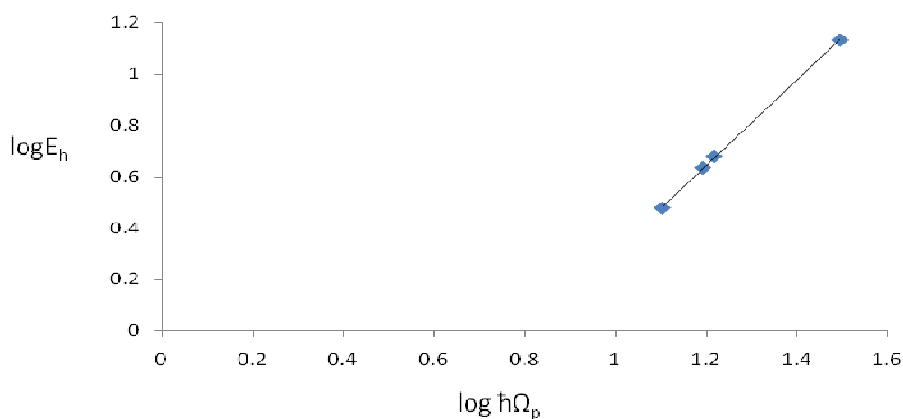


Figure-1
Plot of $\log E_h$ versus $\log \hbar\Omega_p$ for elemental semiconductors

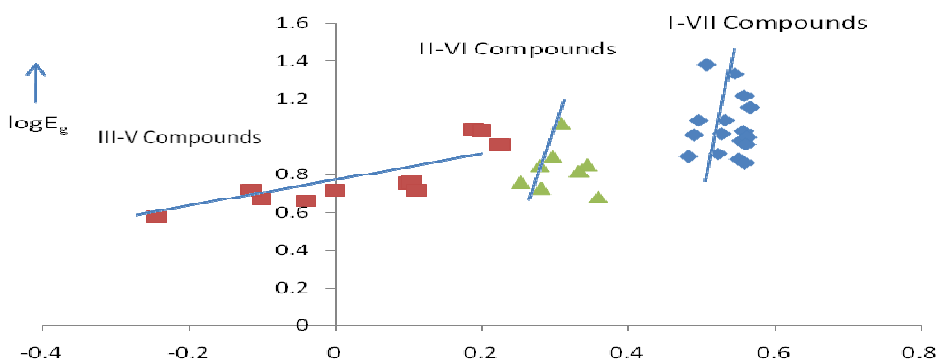


Figure-2
Plot of $\log E_g$ versus; $\log \Delta x$ for all the compounds

Table-2
 Values of parameters extracted from fitted equation(12).

Cation	M	N	Cation	M	N
Li	4E-09	19.138	Zn	0.3156	4.8957
Na	3E-09	17.955	Cd	1.6046	1.8588
K	3E-22	40.409	Al	5.4736	1.1627
Rb	6E-23	41.2	Ga	6.2855	0.6945
			In	5.1975	0.7266

Table-3
 Ionicity of II-VI binary tetrahedral semiconductors

Compounds	$h\Omega_p$ (eV)	f_i Calculated	f_i Phillips	f_i Levine	f_i Christensen
ZnO	21.48	0.490	0.616	0.653	
ZnS	16.71	0.719	0.623	0.621	0.764
ZnSe	15.78	0.660	0.630	0.623	0.740
ZnTe	14.76	0.608	0.609	0.599	0.560
CdS	14.88	0.752	0.685	0.649	0.794
CdSe	14.01	0.714	0.699	0.684	0.841
CdTe	13.09	0.642	0.717	0.675	0.739

Table-4
 Ionicity of III-V binary tetrahedral semiconductors.

Compounds	$h\Omega_p$ (eV)	f_i Calculated	f_i Phillips	f_i Levine	f_i Christensen
AlN	22.97	0.176	0.449	0.445	
AlP	16.65	0.581	0.307	0.303	0.421
AlAs	15.75	0.391	0.274	0.273	0.367
AlSb	13.72	0.304	0.250	0.440	0.163
GaN	21.98	0.207	0.500	0.500	
GaP	16.50	0.631	0.327	0.330	0.361
GaAs	15.35	0.413	0.310	0.313	0.310
GaSb	13.38	0.244	0.261	0.264	0.108
InN	18.82	0.351	0.578	0.569	
InP	14.76	0.650	0.421	0.432	0.534
InAs	14.07	0.508	0.357	0.347	0.553
InSb	12.73	0.202	0.321	0.315	0.303

Table-5
 Ionicity of I-VII ionic Compounds.

Compounds	$h\Omega_p$ (eV)	f_i Calculated	f_i Phillips	f_i Levine	f_i Christensen
LiF	25.96	0.877	0.915	0.914	0.9136
LiCl	17.99	0.905	0.903	0.903	0.9043
LiBr	16.27	0.881	0.899	-	-
LiI	13.25	0.884	0.899	0.896	0.8944
NaF	20.11	0.942	0.946	-	-
NaCl	15.68	0.924	0.890	0.890	0.8889
NaBr	14.37	0.916	0.946	0.946	0.9462
NaI	12.79	0.915	0.935	0.936	0.9261
KF	16.83	0.921	0.934	0.933	0.9319
KCl	13.29	0.956	0.927	0.929	0.9292
KBr	12.38	0.941	0.955	0.954	0.9585
KI	11.17	0.927	0.953	0.951	0.9508
RbF	15.03	0.958	0.952	0.953	0.9522
RbCl	12.40	0.955	0.950	0.948	0.9479
RbBr	11.59	0.952	0.955	0.955	0.9583
RbI	10.53	0.955	0.957	0.954	0.9538

Results and Discussion

The homopolar energy gap, E_h and total energy gap, E_g for binary (II-VI, III-V) semiconductors and ionic (I-VII) compounds were calculated using equation (10) and (12). From these values of E_h and E_g , the ionicities of corresponding compounds have been estimated using equation (5) and also are given in table 3 to 5.

It is worth noting that for binary (II-VI and III-V) tetrahedral semiconductors of zinc blende structure the same set of A and B as those of elemental semiconductors were used in calculating E_h . The values of A and B are 0.0299 and 1.69522 respectively for I-VII ionic compounds. The close resemblance between estimated values and those reported earlier¹⁻³ shows the reliability of the proposed relation and it indicates that A and B are the characteristics of a crystal structure. This is an important observation.

In the estimation of E_g from electronegativity difference using equation (12) is noted that M and N are characteristics of a cation family. In other words, they remain constants for the compounds of a metal (cation) with varying anions. From close observation it is found that E_h decreases with decreasing value of $\hbar\Omega_p$, lowering in $\hbar\Omega_p$ indicates lower bond strength, which in turn, gives lower value of covalent character and hence decrease in E_h . It has been reported that solids having more covalent character in bonding of constitutional atoms of the molecules are harder¹⁸. This is in consonance with the observation noted above. Similarly in a given cationic family E_g decreases with decreasing Δx , thereby indicates that ionicity decreases with E_g . An important observation in the plot of C, the heteropolar energy gap (calculated using equation-1) versus E_h the homopolar energy gap that apart from the critical ionicity is found at $F_{is}=0.60$ (figure-3).

The line corresponding to $F_i=0.783$ separates the four-fold coordinated compounds (II-VI and III-V compound semiconductors) from the six fold coordinated ionic compounds,

while line through the subcritical ionicity $F_{is}=0.60$ separates II-VI semiconductors from III-V compounds.

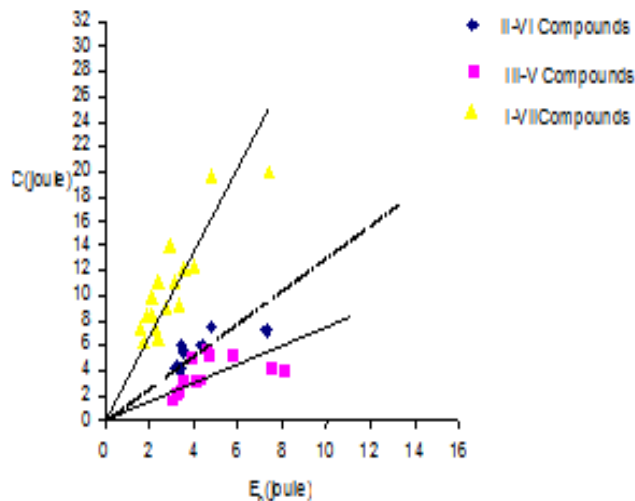


Figure-3
Plot of E_h versus C for binary semiconductors and ionic compounds

Conclusion

The homopolar energy gap has been correlated with plasmon energy and the total energy gap has been correlated with electronegativity difference between bonding atoms of the compounds. The physical meanings of constants appearing in the proposed relation have been given. They have been shown to be characteristics of crystal structure and the cationic family of compounds. In this investigation a subcritical ionicity $F_{is}=0.60$ have been proposed in addition to the well known critical ionicity¹. $F_i=0.705$. Closer agreement of estimated values of ionicity reveals that the reliability of the proposed model. Plasmon energy and electronegativity difference of binary tetrahedral semiconductors, ionic compounds and elemental semiconductors are given in table 6 to table 9.

Table-6
Plasmon energy and electronegativity of II-VI binary tetrahedral semiconductors.

Compounds	Mol.Wt	Density	Bond length ^{14,15}	$\hbar\Omega_p$ (eV)	Δx ¹⁹
ZnO	81.37	5.66		21.48	2.038
ZnS	97.43	4.1	2.34	16.71	1.985
ZnSe	144.34	5.42	2.45	15.78	1.905
ZnTe	192.99	6.34	2.64	14.76	1.790
CdS	144.46	4.82	2.53	14.88	2.211
CdSe	191.36	5.66	2.63	14.01	2.156
CdTe	240.00	5.86	2.81	13.09	1.912

Table-7
Plasmon energy and electronegativity of I-VII Ionic compounds

Compounds	Mol. Wt	Density	Bond length Ref.[14,15,19]	$\hbar\Omega_p$ (eV)	Δx Ref.[19]
LiF	25.93	2.635	2.87	25.96	3.223
LiCl	42.39	2.068	2.57	17.99	3.141
LiI	133.84	3.494	3.032	13.25	3.041
NaCl	58.44	2.165	2.81	15.68	3.419
NaBr	102.89	3.203	2.97	14.37	3.381
NaI	149.89	3.667	3.23	12.79	3.343
KF	58.10	2.480	2.66	16.83	3.631
KCl	74.55	1.984	3.14	13.29	3.621
KBr	119.00	2.750	3.29	12.38	3.597
KI	166.00	3.130	3.53	11.17	3.572
RbF	104.46	3.557	2.82	15.03	3.694
RbCl	120.92	2.800	3.27	12.40	3.662
RbBr	165.37	3.350	3.42	11.59	3.649
RbI	212.34	3.550	3.66	10.53	3.637

Table-8
Plasmon energy and electronegativity of III-V Ionic compounds

Compounds	Mol. Wt	Density	Bond length Ref.[14,15,19]	$\hbar\Omega_p$ (eV)	Δx Ref.[19]
AlN	40.99	3.26	1.892	22.97	1.548
AlP	57.95	2.42	2.360	16.65	1.260
AlAs	101.90	3.81	2.433	15.75	1.000
AlSb	148.73	4.218	2.656	13.72	0.792
GaN	83.73	6.10	1.94	21.98	1.591
GaP	100.69	4.13	2.360	16.50	1.273
GaAs	144.64	5.316	2.450	15.35	0.769
GaSb	191.47	5.618	2.649	13.38	0.495
InN	128.83	6.88	2.154	18.82	1.682
InP	145.79	4.787	2.154	14.76	1.294
InAs	189.74	5.66	2.614	14.07	0.913
InSb	236.57	5.775	2.805	12.73	0.569

Table-9
Plasmon energy of elemental semiconductors

Elements	At.Wt.	Density	Bond length Ref.[14,15]	$\hbar\Omega_p$ (eV)
C	12.01	3.52	1.54	31.2
Si	28.086	2.329	2.35	16.5
Ge	72.59	5.3234	2.45	15.6
Sn	118.69	7.030	2.84	12.7

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