International Journal of Engineering Research-Online
A Peer Reviewed International Journal
Articles available online http://www.ijoer.in; editorijoer@gmail.com

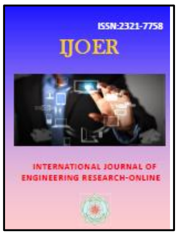
Vol.6., Issue.4, 2018
July-Aug

RESEARCH ARTICLE

ISSN: 2321-7758

ESTIMATING IONISATION POTENTIALS OF FEW TERINARY SEMICONDUCTORS FROM OPTICAL ELECTRONAEGATIVITY AND ENERGY GAP

D V RAGHURAM[1*], Y GOWRI SANKAR[2], N SRINIVASA RAO[3]
[1,2]Department of Physics, Hindu College, Guntur, AP, India.
[3]Department of Physics, SARM Degree College, Allagadda, Kurnool (Dt), AP, India
[*]Corresponding Author, raghuramvenkat@gmail.com.



ABSTRACT

Optical electronegativities are electronegativities of the atoms which are drawn from optical electron spectra. The author found a linear dependence between ionization potential, energy gap and optical electronegativity difference. The ionization potential of few ternary semiconductors is estimated by knowing the optical electronegativity difference. The ionization potentials of tetrahedral semiconductors is hard to determine. The author using the empirical formula estimated the ionization potentials of few tetrahedral semiconductors and found to be in good agreement with the literature values. The average percentage deviation of optical electronegativity difference by this present method is minimum. A related work on optical electronegativity and refractive index of materials is published in Elsevier[21].

Key words: Ionisation potential, optical electronegativity, optical basicity, bond energy, bond polarizability.

Introduction:

The principal physical properties of a semiconductor may be derived as functions of the nature of principal atoms present, the bond lengths separating them and the physico-chemical parameters of the respective atoms present in the material and also their special arrangement[1]. It has long been recognized that many of the physical properties of simple and compound semiconductors are governed by the position in a periodic chart of the component atoms; there the search for key parameter, which characterize both the individual and bonded atoms may be a very useful way to define and predict some typical properties of a given semiconductor. A detailed knowledge of the ionization potentials and electron affinities are used as important parameters in which semi-empirical theories from which molecular quantities are calculated.

Garbato et al[1,2] deduced an empirical relation between average nuclear effective charge and ionization potential of the compound. Atomic properties like interatomic distance, principal quantum number, effective nuclear charge are used for the estimation of ionization potentials of the compounds. The first ionization potential of the atom, nuclear effective charge, Rydberg constant and principal quantum number are well connected with the relation given by Moore[3].

Only few attempts have been made in this direction to estimate ionization potentials of the semiconductor compounds with the inclusion of atomic parameters[1,2,4]. As such the author made an attempt to correlate ionization potential with semiconducting parameters like energy gap and optical electronegativity. Recently Duffy[5,6] has established many correlations between optical electronegativity, energy gap, electronic polarizability and optical basicity for various compounds. The concept of the optical electronegativity has been well magnified by Jorgensen[7] in literature. In order to differentiate between Pauling electronegativity and Jorgensen electronegativity the word optical electronegativity has coined. Originally optical electronegativities are electronegativities of the atoms which are drawn from the optical electron transfer spectra. Optical electronegativity was developed for isolated complexes unaffected by cooperative effects, the relationship suggests that a localized approach to the transference of electrons from the valence band to conduction band is not inappropriate despite the usual approach in terms of delocalized band theory. It has been recognized that many of the atomic and molecular parameters have been linked to the properties of semiconductors.

The knowledge of ionization potentials is important to astro physical, many physical and chemical problems. The ionization potentials and dissociation energies are of great importance in the interpretation of molecular spectra and structure in the studies of interaction between molecules and molecules and atoms[8,9]. The ionization potential of an atom or molecule is defined as the energy required to remove an electron from the highest occupied atomic or molecular orbital of the species in its ground electronic state.

Different experimental methods[10] are available in the literature for the determination of ionization potentials of the atoms and molecules. The following are some useful experimental and theoretical methods for the determination of ionization potentials.

(A).There two main processes which lead to the removal of electron or electrons from atoms or molecules to produce the corresponding ions. Impinge of electrons with sufficient energy can ionize atoms or molecules by the following process.

(i) $AB + e = AB^+ = 2e$ ------------ (1)

(ii) Ionization is caused by interaction of quanta of sufficiently high energy to enable the process to occur as

$AB + h\nu = AB^+ + e$ ------------- (2)

(B). Ionization potential from Koopman's theorem:

Koopman[11] in his theorem drawn a conclusion that there is a link between the position of bands in photo electron spectra and the energies of molecular orbitals. The orbital energy in the Hartree- Fock limit is the negative of the Ionization potential for the removal of an electron from the orbital. The theorem applies strictly only to molecules in which all orbitals are either filled with two electrons or empty but this covers the majority of the stable molecules. It also rests on the assumption that on ionization that remaining electron do not adjust their positions to the new potential in an anion. In other words, the molecular orbitals for the positive ion are the same as those for the neutral molecule. The last assumption is clearly not exact but the errors inherent in it are not usually sufficiently large to invalidate the association between molecular orbital energies and ionization potentials expressed through Koopman's theorem.

A corollary of Koopman's theorem is that distribution of the positive chare in the ion may be determined from the wave function of the molecular orbital from which the electrons have been removed. If ρ(r) is the total electron density function for the ground state of the neutral molecule, then the electron density in the ion obtained by removing an electron, $\psi_k = [\rho(r) - \psi_k^2 (r)]$

If this total electron density is broken down to contributions on individual atoms and then combined with the distribution of positive nuclear charges, one can obtain the distribution of the net positive charge on the individual atoms.

(C). Ionization potentials through cyclic process:

An ionized molecule AB^+ in its lowest electronic state may be expected normally to dissociate to an ionized atom A^+ and a neutral atom B, both in their lowest states. If the dissociation energies of the neutral molecule, D (AB) and of the ionization potential of the atom A, then the ionization potential I (AB) of the molecules are clearly related by the expression[8]

$I(AB) = D(AB) + I(A) - D(AB^+)$ -------------- (3)

The atomic ionization-potential I(A), D (AB) and D (AB^+) are known accurately from spectroscopic data and other experimental metods[8,12,13]. In few cases the molecule ionization potentials can be determined from the limit of Rydberg series in a band spectra, or from the maximum wave length of photo-ionization. In other cases values are available from the measurement of ionization thresholds by electron beams, this method tends to give vertical ionization potentials known values of I (A), D(AB)and D (AB^+) are substituted in equation (3), then the ionization potential of a molecule ie., I (AB) can be evaluated.

(D). Ionization potential through Garbato et al., process:

Garbato et al[1,2]., proposed a relation between nuclear effective change and ionization potential of a compound AB as given below

$$Z^*_{AB} = n\frac{(I_{AB})^{\frac{1}{2}}}{R} \quad \text{-------------- (4)}$$

Where 'n' is the arithmetic mean of 'n_A' and 'n_B'. Here 'n_A' and 'n_B' are the principal quantum numbers of the outermost electrons of the constituent atoms. 'I_{AB}' and 'R' are the ionization potential and Rydberg constant, respectively. Futher Garbato et al, suggested an empirical relation to estimate the nuclear effective charge by means of the arithmetic mean of the atomic nuclear effective charges and it is as follows.

$$Z^*_{AB} = aZ + b$$

Where 'a', 'b' are constants and values are different for different groups of semiconductors[1,2.]

(E). Present method:

Keeping in view the limitations of the above methods the author has proposed a simple and straight empirical relations for the evaluation of ionization potentials of II-VI, III-V and ternary compounds by utilizing the energy gap (E_g) and optical electronegativities (ΔX^*) values alone. the suggested empirical relations are as follows.

$$I = 0.343\, E_g + 5.057 \quad \text{------------ (5)}$$

For III- V group semiconductors

$$I = 1.330\, E_g + 5.03 \quad \text{------------ (6)}$$

$$I = 1.209\, E_g + 4.26 \quad \text{----------- (7)}$$

For II- VI group semiconductors

$$I = 3.228\, \Delta X^* + 4.813 \quad \text{----------- (8)}$$

$$I = 0.339\, E_g + 6.188 \quad \text{----------- (9)}$$

For Ternary compounds

$$I = 1.207\, \Delta X^* + 6.171 \quad \text{---------- (10)}$$

Where 'I', 'E_g' and 'ΔX^*' are ionization potential, energy gap and optical electronegativity difference of the constituent atoms respectively. The numerical constants in the above equations are the result of a fit of the experimental data.

Table (1), Ionization Potential (I) of A^{III}-B^{V} semiconductors

S.No.	Semiconductor	Energy gap (Eg)	Difference of electronegativity ΔX*	Ionization potential I (ev)				
				Experimental. Ref.(19)	PVV.Ref.(4)	Garbato et al.Ref.(1, 2)	Present study.Eqn. (5)	Present study.Eqn. (6)
1.	AlP	3.00	0.80	---	6.03	6.14	6.086	6.09
2.	GaP	2.24	0.60	---	6.11	5.76	5.825	5.83
3.	InP	1.27	0.30	5.72	5.74	5..38	5.483	5.43
4.	AlAs	2.16	0.60	----	5.63	5.94	5.798	5.83
5.	GaAs	1.35	0.40	5.59	5.70	5.64	5.520	5.56
6.	InAs	0.36	0.10	5.44	5.27	5.32	5.180	5.16
7.	AlSb	1.60	0.40	5.47	5.39	5.51	5.606	5.56
8.	GaSb	0.71	0.20	5.03	4.90	5.29	5.301	5.30
9.	InSb	0.18	0.10	5.07	4.61	5.05	5.119	5.16
Average deviation				-----	3.09	2.56	3.16	3.25

Table (2) Ionization Potential (I) of A^{II}-B^{VI} semiconductors

S.No.	Semiconductor	Energy gap (E_g)	Difference of electronegativity ΔX^*	Ionization potential I (ev)				
				Experimental. Ref.(19)	PVV.Ref.(4)	Garbato et al.Ref.(1, 2)	Present study.Eqn. (5)	Present study.Eqn. (6)
1.	ZnS	3.54	1.05	8.73	8.09	8.65	8.543	8.320
2.	ZnSe	2.58	0.80	7.55	7.43	7.55	7.383	7.486

3.	ZnTe	2.26	0.70	5.89	6.31	6.67	6.995	7.152
4.	CdS	1.70	0.45	7.35	7.54	7.52	7.165	7.152
5.	CdSe	1.70	0.45	6.88	7.08	6.73	6.319	6.317
6.	CdTe	1.44	0.35	6.01	6.02	6.05	6.000	5.984
Average deviation				-----	3.62	3.22	5.65	6.37

Table (3). Ionization Potential(I) of Ternary compounds

S.No.	Semiconductor	Energy gap (E_g)	Difference of electronagativity ΔX^*	Ionization Potential, I (ev)		
				Experimental. Ref.(19)	Present study.Eqn.(5)	Present study.Eqn.(6)
1.	$ZnSiP_2$	2.3	0.564	7.07	6.967	6.852
2.	$CdSiP_2$	2.2	0.658	6.88	6.933	6.965
3.	$ZnGeP_2$	1.8	0.535	6.87	6.798	6.817
4.	$CdGeP_2$	1.7	0.462	6.71	6.764	6.728
5.	$ZnSnP_2$	1.46	0.446	6.59	6.683	6.709
6.	$CdSnP_2$	1.16	0.314	6.46	6.581	6.550
7.	$ZnSiAs_2$	1.64	0.457	6.75	6.744	6.722
8.	$CdSiAs_2$	--	0.417	6.58	---	6.574
9.	$ZnGeAs_2$	0.85	0.309	6.58	6.476	6.544
10.	$CdGeAs_2$	0.53	0.153	6.47	6.368	6.356
11.	$ZnSnAs_2$	0.65	0.196	6.37	6.408	6.407
12	$CdSnAs_2$	0.26	0.070	6.25	6.276	6.255
Average deviation				-----	1.05	1.00

Results and discussion:

The crystal structure nature can also be understood with the help of the ionicity. Electronegativity difference of the compound elements will give an idea of degree of ionicity and estimate the bond energy. Finally, the concept of the bond is also associated with the bond energy. After careful examination of the crystal structure it is known that the Wurtzite structure of favorable for crystals with large charge differences of electronegativity between two kinds of atoms. In other works, the general tendency is such that the Wurtzite structure is more proven than the Zinc-blende structure in having a higher degree of ionicity[15] . Manca made an attempt to correlate bond energies and band gaps for variety of binary semiconductors and insulators. The studies of Manca[14] reveals that the width of the forbidden band in semiconductors of diamond, Zinc-blende type structures in Wurtzite- type crystals increases with the increasing of bond energy.

It has proved by Garbo et al.,[1,2] the some simple models with the atomic and molecular parameters should be good enough to account for the main properties of III-V, II-VI and tetrahedral semiconductors with the use of few numerical constants[1,2]. In fact several quantities, including dielectric constants, cohesive energies and ionization potentials have been calculated. In similar lines a linear dependence between ionization potential, energy gap and optical electronegativity difference[5,6] of element in a compound is found, ionization potential and optical electronegativity will give the insight view of bonding. The magnitude of ΔX^* indicates the nature of on bonding and the compounds studied are covalent in nature. The numerical constants involved in the above relations [eqns. (5), (6), (7), (8), (9) and (10)] are very small, probably because of very close ionicity values in these compounds. The estimated ionization potentials for II-VI, III-V and ternary compounds are in excellent agreement with experimental values. The average percentage deviations are calculated and presented in tables (1), (2) and (3). The necessary energy gap values and optical electronegativities are taken from Lide[13], Moss[17,] Joshi[18] and Duffy[5,6]. It was somewhat difficult to estimate ΔX^* values for tetrahedral semiconductors. In order to avoid the difficulty, Reddy and Nazeer[20] suggested procedure has been employed in estimating the optical electronegativity difference (ΔX^*). Once ΔX^* values are known the ionization potentials of tetrahedral semiconductors can be estimated by using eqn. (10). The minimum average percentage deviation indicates the soundness (importance) of the present study.

This work is a part of M.Phil., titled, 'Bonding Characteristics of Materials' submitted by the author at S K University during 1997.

Acknowledgements

I thank Prof. R R Reddy, S K University, Anantapur for helping in pursuing this research work.

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