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Relationship of density and other related parameters with refractive index in $A^N B^{8-N}$Binary Compounds

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Abstract

The inter dependence between refractive index and density and other related parameters of binary compounds has been studied. It is found that the available experimental on refractive index and density d may be expressed by the relations $(n-1)/d = CM^{-u}$ and $(n^2-1)/(n^2+2)=KM^{-v}$, where C and K are constants, the exponents u and v are approximately equal to 0.4,and M is the averaged atomic mass of a substance. The interrelation ship is discussed in terms of the classical theory of dielectrics and the Phillips –Vechten description of the dielectric constant. Also a simple method on optical electronegativity has been proposed for calculating the energy gap, refractive index, electronic polarizabilty of different $A^N B^{8-N}$ type binary crystals .The electronic structure was calculated by first principle, density functional theory based on potential linear agumental planes wave method. Then the dielectric constants are computed .The simple method of evaluating ionic sizes from the observed optical susceptibilities based the Phillips –Vanvechten theory is considered. A set of radii for which both the additivity rule of interionic distances and the condition of constancy of the compensation coefficient treated to the deficiency of the free –electron model have been taken in to consideration .The only input needed are the lattice constants and the refractive data. The approach is applied to the alkali halides and alkaline chalcogenides containing low lying conduction band d levels. A relationship between density, energy gap and ionic sizes is established with refractive index data for the crystals.

Key Words : Refractive index ,density, Energy gap, electronic polarizabilty, Binary Crystals, optical susceptibility .

Introduction

The refractive index of a semiconducting material is of considerable interest for both fundamental and applied consideration. Knowledge of the refractive index of compound semiconductors is essential for designing lasers in optoelectronic devices and in solar cell applications. The interrelation between the high frequency refractive index 'n' and energy gap with other related parameters for these materials has been a matter of great interest. Crystals are often treated as composed of hard atomic spheres. It is known that strictly speaking, those spheres are neither hard nor exactly spherical. Therefore the radius of an atom in a crystal i.e. crystal radius does not have an accurate meaning and can have various definitions[1-4]However, despite its simplicity the idea of crystal radii is widely used by chemists, physicist and crystallographers. In investigations the concepts of additive radii providing the observed nearest neighbor distances with in a given family of salts is very useful. It is known that the density d of several minerals having oxygen as anion and a constant averaged atomic mass M is linearly related to their averaged refractive index ‘n’. This relation means that density decides the value of refractive index independently of composition,Phase and symmetry. In literature several dependences have been proposed to describe the relationship between refractive index and density. The important ones are the Gladstone-Dale, Lorentz, Drude and Allen Laws. The applicability of these laws to the interpretation of data on the dependence of refractive index on density was considered by Anderson and Schreiber[2], Maj[6] showed that from the dispersion formula for refractive index,it is possible to derive relations which may be considered as Gladstone-Dale and Drude laws. The purpose of present study is to study to investigate the interdependence between the refractive index and density of inorganic solid substances. The average value of refractive index of non cubic systems was calculated using various relations with energy gap and electronic dielectric constant. In the case when the number of available data on density is more than one, the average density is taken in to consideration. The average atomic mass is calculated by dividing the molecular weight of the substance by number of atoms in the chemical formula[1-4].

Method of Analysis:- The relationship between density and refractive index has been studies by the plots of (n-1),(n^2-1) and (n^2 -1)/ (n^2 +2) against d/M [3]. The dependence of (n-1)/d,(n^2 -1)/d and n^2 -1)/ (n^2 +2) /d on M, however, are monotonous. It may be noted the data may be described by the relations[3]

$$(n-1)/d = CM^{-U} \qquad (1)$$

&

$$[(n^2 -1)/ (n^2 +2)]d = KM^{-v} \qquad (2)$$

Where C and K are constants and the exponents u and v have a value of about 0.4.The values of C and K are listed in Table -1. It can be shown that the smoothing of the dependences expressed by (1) and (2) is intimately connected with the relationship between n and d. However, the values of specific refractivity CM^{-u} and specific refraction (KM^{-v}=R) also depend on the average atomic mass. The relationship observed between d and n may be explained by two approaches. The first approach is based on the classical theory of dielectrics given by Mott and Gurney [ ]. According to the classical theory, when both the Lorentz and overlap fields are present, the specific refraction may be given by the expression

$$R = [n^2 -1)/ (n^2 +2)] = (4\pi\alpha\ d/3M)[1- 3'\Upsilon\ (n^2-1)4\pi(n^2+2)] \qquad (3)$$

Where α is the polarizabilty of the microscopic unit, M is its mass and Y is the overlap field induced by the presence of large formable ions, its value may be assumed between 0 and 4π/3.As Y increases R decreases. In the absence of overlap field i.e. when $Y = 0$, equation (3) reduces to the Lorentz –Lorentz law and when $Y = 4\pi/3$ this equation transform to the Drude Law.

Table -1 Values of C ,K and ΄ϒ .[3].

Type of Crystal	C	K	Bonding Type	Value of ΄ϒ
Alkali Fluoride	0.520	0.320	Covalent	
Alkali Chloride	1.024	0.581	Terahedral	21.5
Alkali Bromide	0.991	0.547	Octahedral	15.0
Alkali Iodide	1.187	0.634	Six fold ionic coordination	
Upper limit	1.30	0.750	Alkali Metals	6.0
Lower Limit	0.45	0.250	Halides	3.75
Average For majority	0.65	0.375		

The relationship between d and n may also be given by Using Penn [10] model of dielectric constant at long wavelength. The approach is based on the Phillips –Van Vechten[11] dielectric theory. The refractive index can be related th the average energy gap as .

$$n^2 - 1 = [(\hbar \omega_p / E_g)^2] S_0 \quad (4)$$

(4)

In the original Penn model, the factor S_0 is taken nearly equal to unity. However, more accurate calculations performed Grimes and Cowley [12] by taking $S_0 = 0.62$.This value of S_0 modifies the earlier estimates of ionicity parameters. Where ϵ_∞ is the electronic constant, E_g is the average energy gap between bonding and antibonding states and ω_p is the plasma frequency which is given by

$$\omega^2_p = (4\pi Ne^2/m) \quad (5)$$

Where 'e' and 'm' are the electronic charge and mass respectively. 'N' is the number of valance electrons per unit volume (N= 8/V). for the compounds the expression for the valance plasma energy can also be given as

$$\hbar \omega_p = 28.8 \sqrt{(Nd/m)}, \quad (6)$$

Here d and m are density and molecular weight respectively. The Energy gap E_g can be split in to an ionic (Heteropolar) part C and Covalent (Homopolar) part E_h such that

$$E^2_g = E^2_h + C^2 \quad (7)$$

The homopolar part E_h has been taken in dependence universally on interatomic separation 'R' as follows

$$E_h = RA^{-k} \quad (8)$$

Where A and k are the constant i.e. remain unchanged in different crystals. Values of E_g can be calculated with the help of equation (1-3) using experimental data on electronic dielectric constant ϵ_∞ and unit cell volume. The parameters A and k are then evaluated by applying (5) and (6) to purely covalent crystals like diamond and silicon, which have the heteropolar energy C=0 and therefore $E_g = E_h$. For diamond $\epsilon_\infty=5.7$ and R= 1.54A^0 where as for silicon $\epsilon_\infty=12.0$ and R=2.34 A^0. It is found that A=54.0 eV or $54\text{x}10^{-19}$J$(A^0)^{2.52}$and k=2.52. Using the values we have calculated E_h from equation (6) by taking appropriate values of R for other solids. We have also used an alternative form for the homopolar energy E_h represented by an exponential law given as

$E_h = A'(-k'R)$ (9)

Following the same procedure as described above we have obtained $A'=139 \times 10^{-19}$J and $k'=1.32(A^0)$.Values of E_h obtained from above relation are given in Table 2.The hetropolar part of E_g is related to the ionic binding and represents the dielectrically screened potential difference between the fields produced by the ion cores of the two atoms participating in a given bond centre. Following Levine[5] C^2 for an individual bond for a compound may be given by,

$C^2 = 4b^2e^4 [(Z_A - Z_B(n/m)]^2/R\{ \exp (-k_sR_0)\}$ (10)

Where Z_A and Z_B are the valance states of the atoms A and B respectively. k_s is Thomas Fermi screening parameter, R_0 is R/2 is the nearest neighbor distances and b is the adjustable parameter that depends on coordination number around the cation i.e. $b=0.089N^2_C$, where N_C is average coordination number, for NaCl type crystal structure N_C =6 and b=3.204.

Also the value of hetropolar part of energy gap C is also provided as

$C=C_0R^{-s}$ (11) (10)

Here C_0 and s are constants for a given cation or for a cation group values of C_0 and s are given in table -2

Table-2

Values of parameters the hetropolar energy C by the power law Equ.10 [21]

Cation	C_0	n
Li	250	2.90
Na	382	3.02
K,Rb,Cs	225	2.33
Cu	154	3.14
Ag	586	3.95
Be	813	6.79
Mg	215	3.26
Ca,Sr,Ba	156	2.61
Zn,Cd	55	2.21
Al,Ga,In	294	5.01

Using the equations (6-8) and putting the values in equation (5), theoretically the values of average energy gap for the compounds can be evaluated. The chemical bond length R may be correlated with d and average mass by the relation[3]

$R = F(d/M)^{-1/3}$ (12) (11)

Where F is proportionality constant. From above equations we obtain

$(n^2 -1)/(n^2+2)= 1/1+C_C (d/M)^{0.4} + CE_h (d/M)^{0.65}$

(13)

Where C_c and C_E are the averaged coefficients .For a particular crystal structure, the density of valance electrons, the valiancy of the atom under consideration and ionicity of the bond. For $C_C = CE_h = 3.2$, the dependence given by equation (13) is plotted[3].A large scatter in the experimental points with respect to the theoretical curve is due to the fact that we have considered the average behavior of atoms and that the values of n correspond to wavelength 589 nm. Since in this approach bond length plays a decisive role, it is particularly necessary to consider the relationship of this parameter with the atomic mass. A modification of the well known Moss formula relating to the refractive index to the energy gap as applicable to alkali halides is presented Its importance in the evaluation of electronic polarizabilities is also found which latter on used to derive a relationship between the density and refractive index. Using the Lorentz –Lorentz equation the energy gap of the binary solids can be related to the electronic polarizabilty. The electronic polarizabilty of the binary solids plays an important role in determining their electrical properties. The role electronic polarizabilty is similar to that of energy gap in quantum theory of solids.The electronic polarizabilty (α) of a material is also related to the refractive index as follows,

$$\alpha = [(n^2 - 1)/(n^2 + 2)]/(3M/4\pi Nd) \qquad (14)$$

Where n is the refractive index of the substance, d is its density at temperature T, M is its molecular weight and N is the Avogadro number. Above equation for refractive index is based on the classical theory of the dielectric constant due to Claussius and Mossotti [24,25].The following expression has been obtained between energy (E_g) and electronic polarizability (α) for I-VII, II-VI and III-V Binary Compounds[7]

$$\alpha = [12.41 - 3\sqrt{(E_g - 0.365)}/12.41](M/d) x \quad 0.395 x 10^{-24} \ Cm^3 \qquad (15)$$

Ravinder et.al.[9] proposed a linear relationship relating the variation of the optical refractive index n with energy gap E_g as,

$$n = 4.08 - 0.62E_g \qquad (16)$$

A linear relationship also established between n and energy gap E_g given by Sajjad Ahmad et.al.[7]

$$n = A - \ln E_g \qquad (17)$$

Where A= 3.6 eV is a numerical constant. The value of E_g has been evaluated by using equation (7) using the subsequent equations (8-11).Evaluation of refractive index can be done by using either the equations (15) and (16). The density of the Binary solids can be related with polarizabilty using equation (14). Further density d and refractive index n can be interrelated.

Result and Discussion

The refractive index (n)is the most important optical property of materials. Its square (n^2) is equal to electronic dielectric constant (ϵ_∞), which is related to electronic polarizabilty. The average ionic gap is also a very useful parameter in understanding the trends over the periodic table for a class of semiconductors, provided that the value of the dielectric constant is available. The high frequency dielectric constant is explicitly dependent on the valance electron plasma energy, an average energy gap or Penn gap and the Fermi energy. The electronic dielectric constant, the energy gap between the bonding and antibonding states and the interionic nearest neighbor separation for a given crystal are related to each other. We have estimated the values of refractive index, energy gap, density related to electronic polarizabilty are listed in table -3.It can be observed from the table that there is a linear relationship between the density and refractive index. It is also observed from the table that the energy gap values for the group semiconductors with common cation decreases while refractive index and electronic polarizability increases. It is found that the behavior of different materials with in a group of compounds is almost similar but significantly different from the compounds of other groups. Even in I-VII compounds the behavior of Cu halides and Ag halides is different from those alkali halides, Similarly in II-VI group of compounds the behavior of Zn chalcogenides and Cd chalcogenides is also different from that of alkali earth chalcogenides. This is mainly because of different nature of chemical bond of these compounds.

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Table -3

Estimated values of Energy gap (E_g), refractive index. Electronic Polarizabilty, density of I-VII Binary Compounds

Crystals	(Interatomic separation) R (A^0)	Energy gap Eg (eV)	Molecular Weight	Electronic polarizabilty α ($x10^{-24}$ cm^3)	Refractive index (n)	Density (g/cm3)
LiF	2.01	9.49	25.94	0.89	1.39	2.64
LiCl	2.57	7.02	42.39	2.98	1.66	2.07
LiBr	2.75	5.91	86.84	4.12	1.78	2.46
Lil	3.09	4.38	133.84	6.15	1.95	3.49
NaF	2.31	9.99	41.99	1.15	1.34	2.56
NaC1	2.81	8.13	58.44	3.24	1.54	2.17
NaBr	2.98	7.21	102.89	4.38	1.64	3.20
Nal	3.23	6.00	149.89	6.41	1.77	3.67
KF	2.64	9.77	58.10	1.99	1.36	2.48
KCI	3.14	8.59	74.55	4.08	1.49	1.98
KBr	3.31	7.96	119.00	5.22	1.56	2.75
Kl	3.56	6.88	166.00	7.25	1.68	3.13
RbF	2.77	9.43	104.47	2.54	1.40	3.56
RbC1	3.27	8.56	120.92	4.63	1.49	2.80
RbBr	3.44	8.02	165.37	5.77	1.55	3.35
Rbl	2.69	7.15	2123.37	7.80	1.65	3.55
CsF	3.03	8.65	151.90	3.60	1.48	4.12
CsC1	3.57	7.50	168.36	5.69	1.61	3.99

CsBr	3.70	6.95	212.81	6.83	1.67	4.44
CSI	3.95	5.88	259.81	8.86	1.79	4.51

Table -4

Estimated values of Energy gap (E_g), refractive index. Electronic Polarizabilty, density of II-VI Binary Compounds

Crystals	(Interatomic separation) R (A^0)	Energy gap Eg (eV)	Molecular Weight	Electronic polarizabilty α ($x10^{-24}$ cm^3)	Refractive index (n)	Density (g/cm3)
ZnO	1.95	3.20	81.37	2.86	1.98	5.61
ZnS	2.36	3.70	97.43	5.91	2.42	3.98
ZnSe	2.45	2.58	144.33	6.53	2.50	5.42
ZnTe	2.63	2.10	192.97	8.14	2.88	6.34
CdS	2.52	2.40	144.46	7.57	2.42	4.82
CdSe	2.62	1.70	191.36	9.13	2.45	5.51
MgS	2.60	3.90	56.38	4.53	2.20	2.84
MgTe	2.75	2.60	151.91	6.00	2.51	4.54
CaO	2.40	6.15	56.08	2.90	1.81	3.32
CaS	2.84	5.40	72.14	6.13	2.11	2.50
CaSe	2.96	5.00	119.04	7.62	2.15	3.57
SrO	2.57	5.80	103.62	3.72	1.84	4.70
SrS	2.94	4.80	119.68	6.80	2.11	3.70
SrSe	3.42	4.60	166.58	8.47	2.15	4.38
SrTe	3.24	4.00	215.22	10.84	2.29	4.83
BaS	3.18	4.00	169.4	8.61	2.12	4.25
BaSe	3.31	3.35	216.30	9.88	2.84	5.02
BaO	2.76	5.20	153.34	5.22	1.84	5.72
MgSe	2.73	2.98	103.27	6.00	2.25	4.21

Table -5

Estimated values of Energy gap (E_g), refractive index. Electronic Polarizabilty, density of III-V Binary Compounds

Crystals	(Interatomic separation) R (A^0)	Energy gap Eg (eV)	Molecular Weight	Electronic polarizabilty α ($x10^{-24}$ cm^3)	Refractive index (n)	Density (g/cm3)
AlN	1.86	3.80	40.99	2.79	2.20	3.26
AlP	2.35	3.00	57.96	5.47	2.72	2.85
AlAs	2.43	2.40	101.90	7.49	2.88	3.81
AlSb	2.66	1.50	148.73	10.19	3.19	4.22
GaN	1.94	3.40	83.73	3.06	2.21	6.10
GaP	2.36	2.24	100.69	6.95	2.96	4.13
GaAs	2.43	1.40	144.64	8.20	3.27	5.32
Gasb	2.65	0.07	191.47	11.07	3.86	5.62

InIN	2.13	2.40	128.83	4.29	2.27	6.88
InP	2.54	1.25	145.79	9.01	3.16	4.79
InAs	2.62	0.33	189.74	10.49	3.53	5.66
InSb	2.80	0.18	236.57	13.39	3.93	5.78

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