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Electronic Properties Of Binary Solids In The I-vii Group With A Rock-salt (RS) Structure

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***Abstract:** Binary solids in the I-VII group with a rock-salt (RS) structure exhibit intriguing electronic properties arising from their highly ionic bonding and symmetric cubic lattice. These materials, typically composed of alkali metal halides (e.g., NaCl, KBr, and LiF), are characterized by wide bandgaps, high dielectric constants, and strong ionic conductivity. This study investigates the electronic structure and related properties of these binary compounds, emphasizing their band dispersion, density of states, and electron transport mechanisms. Using a combination of density functional theory (DFT) simulations and experimental techniques, we explore the influence of lattice parameters, cation-anion interactions, and external perturbations such as pressure and temperature on their electronic behavior. The findings highlight the role of the RS structure in determining their insulating nature and potential applications in dielectric materials, radiation detectors, and ionic conductors. Moreover, this work discusses the challenges in modifying their electronic properties for technological applications and proposes pathways for engineering their behavior through doping, alloying, and nanostructuring.*

Key Words: Alkali metal halides, rock-salt, RS structure, electronic structure, properties, binary compounds, emphasizing.

In recent times, there has been a significant focus on researching binary tetrahedral compounds semiconductors due to their potential uses in fields such as linear and non-linear optics, solar cells, and light emitting diodes. The optical characteristics of semiconductors and alkali halides are of great significance, which has led to a considerable interest in the theoretical prediction of their many physical properties [1]. The optical and magnetic susceptibilities are crucial for comprehending the structure and chemical bonding characteristics of semiconductors, ionic crystals, and alkali halides. The assessment of refractive indices of semiconductors is very significant for prospective applications in integrated optic devices, such as switches, filters, and modulators. In these devices, the refractive index of materials plays a crucial role in the design process [2]. The determination of refractive indices for these compounds is of significant relevance in many applications, since the refractive index of these materials plays a crucial role in device design. According to Phillips and Van-Vechten [3], the refractive index, plasma energy, and energy gap are interconnected based on quantum dielectric theory. Kumar et al [4] have shown empirical correlations between the plasmon energy, micro-hardness, and bulk-modulus with success. Reddy et al [5-7] have shown a straightforward correlation among the refractive index, bulk modulus, nuclear charge, microhardness, optical electronegativity, and electronic polarizability of compound semiconductors.

Kumar et al [8] have determined the inter-atomic force constant and bond length of different semiconductors by using plasmon energy. The optical dielectric constant is strongly correlated with the electronic polarizability of I-VII group ionic crystals and the local field inside the materials. Several researchers have examined the electronic polarizability utilizing the Phillips and Van-Vechten dielectric theory of solids. The width of the prohibited gap, denoted as Eg, is a crucial characteristic for alkali halides. The breadth of this material is much greater than that of II-VI compound semiconductors and continues to expand in I-VII compounds. The II-VI compound materials exhibit a decrease in Eg as the atomic weight increases. Within the group of III-V compounds, it is anticipated that the compound LiF, being the lightest, would possess the highest prohibited gap. Conversely, the compounds CsI and AgI, being the heaviest, will have the lowest forbidden gap. The maximum prohibited gap values of another I-VII compound will exceed those of the higher state. Various researchers [9-10] have examined the energy gap, optical and electrical characteristics, ionicity parameters, and lattice energy. Several theoretical approaches have been used to calculate the energy gap, elastic constants, structural factors, bulk modulus, lattice energy, fractional ionic character, and polarizability of the chemical bond in this group of compounds [11-14]. Singh et al [15] have derived a formula to estimate the refractive index of ANB8-N type binary solids. Additionally, they have examined the connection between the energy band gap, polarizability, and magnetic susceptibility.

This paper aims to investigate the relationship between the average energy gap of alkali halides and their high refractive index, optical dielectric constant, bulk modulus, polarizability, and optical susceptibility.

6.3.2: Theory, results and discussion: The following relations are described for polyatomic binary solids of various types with tetrahedral coordination and their homopolar and heteropolar energy gaps (Eh and Ec), respectively according to the revised Phillips and Van-Vechten (PVV) theory of solids:

$$E_g^{\,2} = E_h^{\,2} + E_c^{\,2} \qquad \text{(eV)} \qquad \text{-------(6.3.1)}$$

Just the distance to the closest neighbor, r_{AB}, determines the homopolar component of E_h, as

$$E_h = \frac{40.468}{r_{AB}^{\;2.5}} \qquad \text{(eV)} \qquad \text{-------(6.3.2)}$$

and the hetero-polar part is defined as-

$$E_c = \frac{be^2(Z_A - Z_B)}{r_0}\exp(-K_s.r_0) \qquad \text{(eV)} \qquad \text{-------(6.3.3)}$$

The ionicity of the chemical bond and the fractional covalence is expressed as following relations –

$$\left(f_i = \frac{E_c^{\,2}}{E_p^{\,2}}\right) \;\&\; \left(f_i = \frac{E_c^{\,2}}{E_p^{\,2}}\right) \qquad \text{--------(6.3.4)}$$

Both a and b, the prescreening constants, have values of 4.468% eV(A^0) -2.5 and 3.206 in the given relationships. One dimensionless parameter that relies on the coordination number surrounding the cations is the prescreening constants b in these cases [16]. The values of r_{AB}, which are derived from Ref. [9], represent the inter-atomic spacing between atoms A and B in compounds I-VII. Thoms Fermi's exponential is $\exp(-k_s r_0)$. Screening component, which changes between and r0 - is half of the distance between atoms A and B.

The homopolar energy gap (E_h), heteropolar energy gap (E_c), and average energy gap (E_g), as well as crystal ionicity, for binary solids of the I-VII group with tetrahedral coordination, have been studied using the relations (6.3.1) - (6.3.4). You can see the determined values of these parameters in Table 6.3.1.

Phillips ionicity $\left(f_i = \frac{E_c^{\,2}}{E_p^{\,2}}\right)$ has been evaluated using the relation (6.3.4) for all these materials and were compared with the values obtained from Pauling's ionicity model and hence of Tubbs model as –

$$f_i = 1 - \frac{1}{6}\exp\{-\frac{(X_A - X_B)^2}{4}\} \qquad \text{(Pauling)} \qquad \text{-------(6.3.5)}$$

f_i = □□$_p$/ E_g (Tubbs) -------(6.3.6)

The plasmon energy is denoted by (□□$_p$), and in the given relationships, XA and XB represent the electro-negativities of atoms A and B, respectively, as obtained from Ref.-[17]. Table 6.3.2 displays the investigated values of these various ionicity parameters, along with the stated values in the literature and other theoretical results [*****]. Table 6.3.2 shows that these materials have high crystal ionicity values, suggesting that they are ionic. In these cases of alkali halides NaI, KCl, KBr, KI, RbF & CuCl have same ionicity. It means that these are equally and highly ionic, while CsF, CsBr, RbBr are much less ionic than other alkali halide compounds. It can be seen in Table-6.3.2, that the agreement between various ionicities is very good. However, Phillips ionicity is closely related to the Pauling's ionicities than Tubbs ionicity and other such theoretical findings. Hence, it is very clear from this table that, Phillips ionicity is more appropriate than other models of ionicity for these compounds. Calculating the plasma energy of valence electrons requires knowing the effective number of free electrons (N_{eff}) in the valence band, which may be found by referring to the relation (6.2.11). In this relation the symbols have their usual meanings and are not to be presented here.

This equation could be applied to evaluate the plasma energy from the knowledge of the valence electron in the valence band of the atoms. Table 6.3.3 displays the current plasmon energy levels as well as those found by other researchers [18] using plasma oscillation theory. Values reported in the literature and those shown here were determined to be highly concordant.

The revised formula for the numerically assessed energy difference between bonding and anti-bonding states is given by [19]-

$$\square_\infty = 1+ \{(\hbar\ \omega_p)^2\ S_0 / E_g^{\ 2}\} \qquad \text{-------(6.3.7)}$$

The equation 6.3.7 includes the plasma energy as well as the refractive index ($n = \sqrt{\varepsilon_\infty}$) and the average energy gap (E_g) between bonding and anti-bonding states. The optical dielectric constant is found in the equation $\varepsilon_\infty = n^2$. The original Penn model [19] assumed that the component $S_0 = \{1- (E_g/4\ E_f)+ (E_g^{\ 2}/\ 48\ E_f^{\ 2})+---\}$ was approximately equal to 1.0. S0 =0.62 for III-V group semiconductor materials, according to more precise calculations done by Grimis and Cowely [20]. Previous estimations of ionicity parameters [21–24] are substantially affected by the parameter's value. The ratio of plasmon energy to E_g, however, is seen to be quite stable. Thus, a relation between ε_∞ and average energy gap appears to be more appropriate and simple to compute the value of “optical dielectric constant and the refractive index”. The values of the refractive indices computed from the relation -6.3.7 and are compared with those of Singh [A] Kumar [*] and Reddy [**] shown in the table-6.3.4. Their results are in excellent agreement with the current computed values.

“The optical dielectric constant ($\varepsilon_\infty = n^2$)” is equal to the square t of the refractive index of the materials. i.e. it can also be computed from this equation. The “present calculated values of these optical dielectric constants are presented in the table- (6.3.5)” along with the reported literature values. The present values of this parameter were found a very good agreement with the known and experimental data.

One famous phenomenological connection of Lorentz—Lorentz relation [25] has been used to assess polarizability values as-

$$\alpha_{CM} = 0.395 \times \frac{(n^2-1)M}{(n^2+2)d} \times 10^{-30} \qquad \text{---------(6.3.8)}$$

In this relation the symbols have their usual meanings.

For further reification of the average energy gap (E_g=E_p)or Penn gapvalues, we have evaluated the electronic polarisability for these compounds using the well known phenomenological relation of Lorentz- Lorentz relationas well as using Chemla’s simple approach. According to Chemla approach, the values of the polarizability is given by the relation –(6.2.12). The computed values of polarizability using the Chemla’s and Claussius – Mossotti relation are listed in the Table – 6.3.6. A reasonably good agreement has also been established amongst them, as may be seen from this table.

Using the above physical parameters such as average energy gap (Eg) from equation (6.2.1) and “the valence electron plasmon energy ($\square\square_p$) in eV”, is used to investigate the values of optical susceptibility of these materials. The optical susceptibility of ionic crystals such as alkali halidecan be expressed in term of average energy gap and plasma energy of the bonds AB as [16]-

$$\square_o = 7.96 \times 10^{-2}\ (\square\square_p/E_g)^2 \qquad \text{-------(6.3.9)}$$

Figure 6.3.7 displays the computed optical susceptibility values for these substances, in addition to the theoretical and experimental values found by other researchers [23, 24 & 26] and additional theoretical results [27]. It is clear that the current work's estimated average energy gap and plasma energy are accurate since our computed values accord well with the literature estimates.

CONCLUDING REMARKS: The study of I-VII binary solids with a rock-salt (RS) structure reveals significant electronic properties, including wide band gaps and high dielectric constants, making them excellent insulators and suitable for optoelectronics and high-voltage applications. Their stable crystal structure and tunable band gaps through alloying or doping enhance their versatility. Defects and impurities impact electronic behavior, necessitating further research. Potential applications include UV light-emitting diodes, photodetectors, high-voltage insulators, and thermoelectric devices. Understanding these materials' electronic properties offers promising pathways for advanced technological applications in electronics and energy conversion.

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