

Studies on the Opto-Electronic Constants of Alkali-Halide Crystals

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Abstract

In this presentation, the correlation between refractive index n of alkali-halide crystals and both energy band gap E_g and Pauling's electronegativity difference Δx have been studied. The following relations are proposed for estimating the refractive index n :

$$n^2 + C = A/E_g^{1/2}$$

and

$$n^2 + C = E/(\Delta x)^{0.425},$$

where A , C and E are numerical constants. In addition, an interrelation between the energy band gap E_g and electronegativity difference Δx has been also proposed. The proposed relation is

$$E_g = 4.45(\Delta x)^{0.85}.$$

The estimated values of the refractive index are utilized to evaluate the electronic polarizability of alkali-halides by applying the Lorentz-Lorenz formula. The computed values of refractive index, energy gap and electronic polarizability are compared with those in literature.

Key Words: Refractive index, energy gap, electronegativity, electronic polarizability, alkali-halides.

1. Introduction

The optical refractive index is considered to be a fundamental property of a material. It is closely related to the electronic polarizability of ions, which plays an important role in determining the electrical properties of materials. Among the various parameters controlling the refractive index, energy band gap may be the most important parameter. Thus, it is of great interest to develop a correlation between refractive index and energy gap in solid materials.

The first attempt to obtain an interrelation between the refractive index and energy gap in semiconductors was made by Moss [1]. A review article on this subject can be found in reference [2]. The Moss formula is

$$E_g \cdot n^4 = 173, \tag{1}$$

where n is the refractive index and E_g is the energy gap (in units of eV). Kumar et al. [3] have proposed a modified relation that can be applied to alkali halides:

$$E_g \cdot n^4 = 52. \quad (2)$$

Recently, Reddy et al. [4, 5] proposed the following formula for alkali halides:

$$E_g = -9.12n + 22.2. \quad (3)$$

More recently, Reddy et al. [6, 7] have assumed another correlation between refractive index n and energy gap E_g as

$$E_g \cdot e^n = 36.3. \quad (4)$$

Duffy [8] assumed a linear relation between energy gap and the difference in the optical electronegativity values of the anion and cation (Δx^*) in alkali halides, with the relation

$$E_g = 3.72\Delta x^*. \quad (5)$$

The validity of the various proposed relations have been examined for all alkali halides, and pronounced deviations between standard and computed values of refractive index were observed.

In the present paper we propose simple equations relating refractive index with both energy gap and Pauling's electronegativity difference in alkali halides. The electronic polarizability of alkali halides was also calculated based on our proposed formulae for refractive index.

2. Theory

The systematic variations in the optoelectronic properties of alkali halides within the same group (by varying the anion from F^- to I^-) and among all groups (by varying the cation from Li^+ to Cs^+) may be clearly observed from the linear dependence of both the electronegativity difference Δx and energy gap E_g on the lattice parameter a , as illustrated in Figure 1. The values of a , Δx and E_g are shown in Table 1.

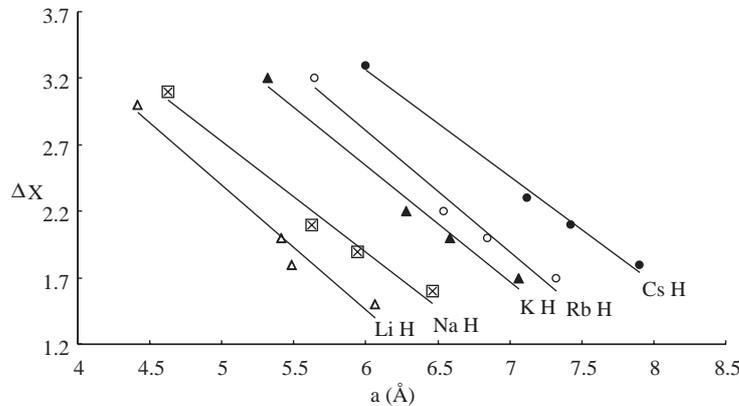


Figure 1a. Dependence of electronegativity difference Δx on the lattice parameter a (Å).

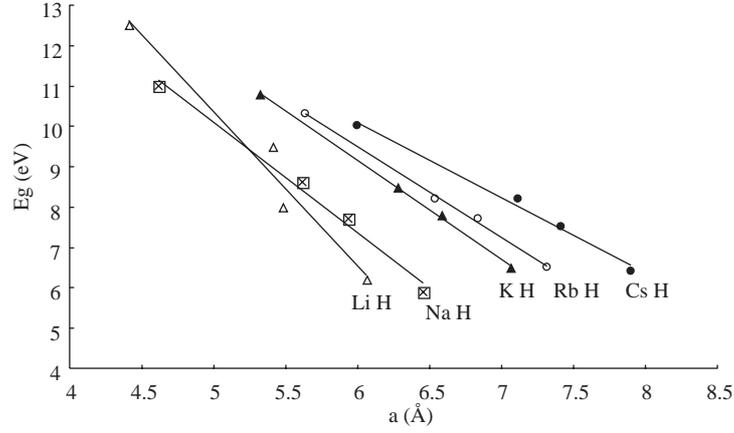


Figure 1b. Dependence of energy gap E_g (eV) on the lattice parameter a (Å).

Table 1. Lattice parameter, a (Å), electronegativity difference between anion and cation Δx and energy gap E_g (eV) of alkali halides.

Alkali halide groups (AH)	Lattice parameter, a (Å) Ref. [9]	Electronegativity Difference, Δx Ref. [10]	Energy Gap, E_g (eV)	
			Known Ref. [11]	Calculated via Eq. (12)
LiF	4.41	3.00	12.50	11.32
LiCl	5.41	2.00	8.02	9.50
LiBr	5.48	1.80	8.00	7.33
LiI	6.06	1.50	6.20	6.20
NaF	4.62	3.10	11.64	11.00
NaCl	5.62	2.10	8.36	8.60
NaBr	5.94	1.90	7.68	7.70
NaI	6.46	1.60	6.63	5.90
KF	5.32	3.20	11.96	10.80
KCl	6.28	2.20	8.69	8.50
KBr	6.58	2.00	8.02	7.80
KI	7.06	1.70	6.98	6.50
RbF	5.64	3.20	11.96	10.30
RbCl	6.54	2.20	8.69	8.20
RbBr	6.84	2.00	8.02	7.70
RbI	7.32	1.70	6.98	6.50
CsF	6.00	3.30	12.27	10.00
CsCl	7.12	2.30	9.03	8.20
CsBr	7.42	2.10	8.36	7.50
CsI	7.90	1.80	6.40	7.33

In Equations (1)–(4), the numerical constants were assumed to be unique for all alkali halides, and these relations differ only in the values of the numerical constants. Based on Reddy's formula, Eq. (4), we propose a general relation between n and E_g as

$$E_g \cdot e^n = \beta, \quad (6)$$

where β is a numerical constant which is not unique for all alkali halides. Now, according to Patterson and Subbaswamy [12], the energy gap E_g is related to the molar refractivity r_m of the alkali halide by the relation

$$E_g = 16.46(1 - r_m/V_m)^2 + 0.445, \quad (7)$$

where V_m is the molar volume. Equation (7) could be rewritten in a more general form as

$$E_g = k(1 - r_m/V_m)^2 + k', \quad (8)$$

where k and k' are numerical constants. The refractive index n is related to the ratio r_m/V_m by [8]

$$(n^2 + 2)(1 - r_m/V_m) = 3, \quad (9)$$

and by combining Equations (8) and (9) we get

$$n^2 + C = A/(E_g - B)^{1/2}, \quad (10)$$

where A , B and C are numerical constants. The numerical values of the constants of Eq. (10) were computed with the techniques found in Numerical Recipes [13] for fitting non-linear data. The computed values are found to be consistent among the various alkali halide groups. From these computations we found $E_g \gg B$, and for $E_g \gg B$ Eq. (10) becomes

$$n^2 + C = A/E_g^{1/2}. \quad (11)$$

In Figure 2a we show how E_g varies with the Pauling's electronegativity difference Δx , and that the relationship is not linear. However, the graph of $\log E_g$ versus $\log \Delta x$ may be considered linear, as indicated in Figure 2b. Accordingly, we may suggest the following relation for E_g :

$$E_g = 4.45(\Delta x)^{0.85}. \quad (12)$$

Values of E_g estimated from Eq. (12) are given in Table 1. The average percentage deviation between the computed and the known values is found to be 8.7%. Replacing E_g in Eq. (10) with that in Eq. (12), we get

$$n^2 + C = E/[(\Delta x)^{0.85} - D]^{1/2}, \quad (13)$$

where D and E are numerical constants to be computed. Equation (13) can be approximated to

$$n^2 + C = E/(\Delta x)^{0.425}. \quad (14)$$

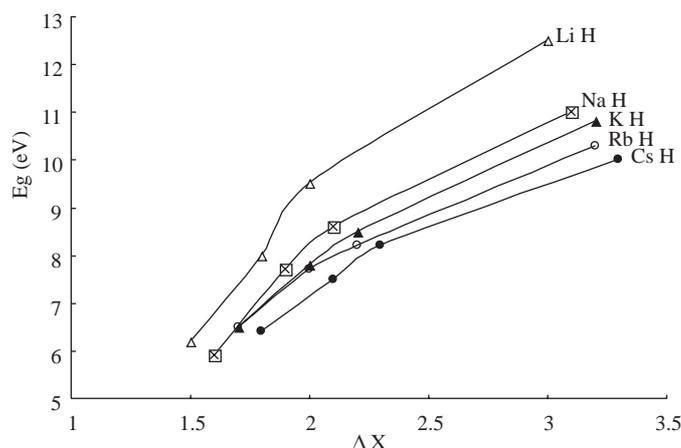


Figure 2a. Energy gap E_g (eV) versus electronegativity difference Δx .

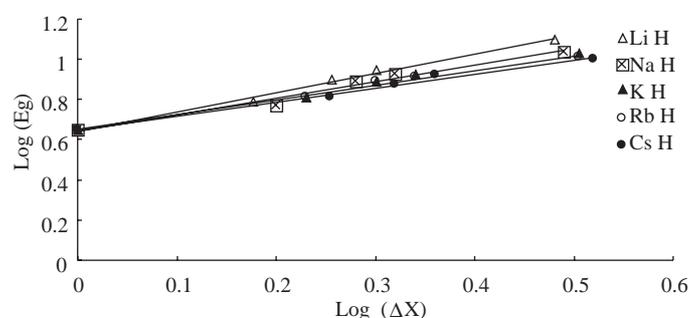


Figure 2b. Log E_g versus Log Δx .

We propose using Equations (11) and (14) to relate the refractive index n to, respectively, the energy gap E_g and Pauling's electronegativity difference Δx .

A ratio of constants A and E , A/E , which can indicate goodness of results, can be derived from a ratio of Eq. (11) and Eq. (14) and substitution from Eq. (12), and can be found to have the simple value of

$$A/E = (4.45)^{1/2}, \quad (15)$$

i.e. the square-root of the numerical constant in (12).

3. Results and Discussion

Numerical constants A , C and E together with the cation radius R^+ for different alkali halide groups are shown in Table 2. The values of these constants are not unique for all alkali halides, in contrast with the unique values predicted by other authors. We suggest that the constant C is dependent upon the cation radius R^+ in the case of alkali halides with the same crystal structure (NaCl type), as shown in Figure 3. Thus, on describing the behavior of alkali halides one may take into account the gradual increase in cation radius when going from Li^+ to Cs^+ . The ratio A/E in Table 2 seems to be nearly constant for all alkali halide groups and has an average value of 2.04. This value is in good agreement with the value of Eq. (15), i.e. $(4.45)^{1/2} = 2.11$.

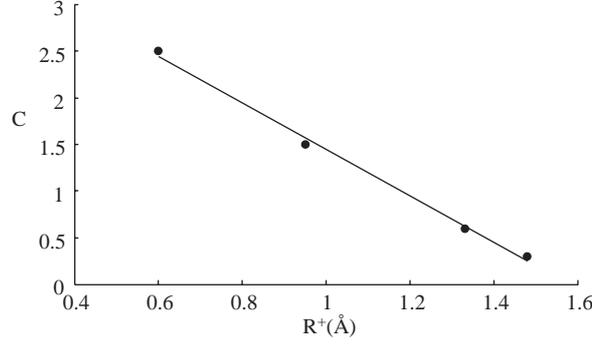


Figure 3. Dependence of constant C on the cation radius R^+ (\AA).

Table 2. The computed numerical constants A , C and E and the values of cation radius R^+ (\AA).

A H groups (H = F, Cl, Br, I)	A	C	E	A / E	R^+ (\AA) Ref. [14]
Li H	15.80	2.50	7.24	2.18	0.60
Na H	11.20	1.50	5.45	2.06	0.95
K H	8.30	0.60	4.08	2.03	1.33
Rb H	7.30	0.30	3.67	1.99	1.48
Cs H	9.90	0.90	5.11	1.94	1.69

The present values of the optical refractive index computed from Eqs. (11) and (14) were compared with those of Kumar, Eq. (2) and Reddy, Eq. (4). The results are presented with the known literature values of the refractive index in Table 3. The present values were found to be in a reasonable agreement with the experimentally known refractive index values. The average deviation in the present values is found to be less than 1.5%. The computed high frequency dielectric constant ε_∞ is also in good agreement with the literature values given by Aschcroft and Mermin [18], Reddy et al. [19] and Fernandez and Sarkar [20].

The values of the electronic polarizability α_e of alkali halides were estimated by applying the Lorentz-Lorenz relation [21], and is given by

$$\alpha_e = (M/d) \frac{n^2 - 1}{n^2 + 2} \cdot 3.95 \times 10^{-25}, \quad (16)$$

where M is the molecular weight and d is the density. Substituting n^2 from Eq. (11), we get for the polarizability

$$\alpha_e = (M/d) \frac{A - (C + 1)E_g^{1/2}}{A - (C - 2)E_g^{1/2}} \cdot 3.95 \times 10^{-25}. \quad (17)$$

Equation (17) relates the electronic polarizability directly to the energy gap of the alkali halides. We present in Table 4 the calculated and known values of the electronic polarizability. For comparison, values from literature are also included in the same table. The agreement between calculated and known values is found to be satisfactory.

Table 3. Values of the present calculated refractive index n and optical dielectric constant ϵ_∞ compared with those in literature.

A H	Refractive index, n					High frequency dielectric constant, ϵ_∞		
	presented Eq. (11)	presented Eq. (14)	Kumar Eq. (2)	Reddy Eq. (4)	known Ref. [15–17]	presented Eq. (11)	presented Eq. (14)	Known Ref. [18]
Li F	1.4032	1.4279	1.4428	1.0663	1.3915	1.97	2.04	1.96
Li Cl	1.6206	1.7001	1.5100	1.3407	1.6620	2.63	2.89	2.78
Li Br	1.7567	1.7719	1.5727	1.5126	1.7840	3.09	3.14	3.17
Li I	1.9610	1.9353	1.7230	1.7675	1.9520	3.85	3.75	3.80
Na F	1.3700	1.3673	1.4918	1.1941	1.3360	1.88	1.87	1.74
Na Cl	1.5229	1.5736	1.5681	1.4402	1.5400	2.32	2.48	2.34
Na Br	1.5925	1.6275	1.6120	1.5508	1.6412	2.54	2.65	2.59
Na I	1.7638	1.7214	1.7304	1.8170	1.7745	3.11	2.96	2.93
K F	1.3877	1.3743	1.4779	1.2125	1.3610	1.93	1.89	1.85
K Cl	1.4990	1.5226	1.5727	1.4519	1.4900	2.25	2.32	2.19
K Br	1.5401	1.5617	1.6069	1.5379	1.5590	2.37	2.44	2.34
K I	1.6296	1.6300	1.7087	1.7202	1.6770	2.66	2.66	2.62
Rb F	1.4052	1.3923	1.4953	1.2599	1.3980	1.97	1.94	1.96
Rb Cl	1.4998	1.5248	1.5869	1.4879	1.4930	2.25	2.33	2.19
Rb Br	1.5267	1.5600	1.6120	1.5508	1.5530	2.33	2.43	2.34
Rb I	1.6010	1.6214	1.7087	1.7202	1.6474	2.56	2.63	2.59
Cs F	1.4935	1.4753	1.5100	1.2894	1.4830	2.23	2.18	2.16
Cs Cl	1.6000	1.6391	1.5967	1.4879	1.6100	2.56	2.69	2.62
Cs Br	1.6477	1.6817	1.6509	1.5771	1.6700	2.71	2.83	2.42
Cs I	1.7359	1.7551	1.6950	1.7357	1.7876	3.01	3.08	2.62
Average	1.50	1.50	5.20	7.70		3.70	4.50	
Devia- tion (%)								

In summary of the present study, it may be concluded that Equations (11) and (14) are simple and useful relations for estimating the refractive index of alkali halides when one knows the energy gap and Pauling's electronegativity difference, respectively. In addition, one could employ Equation (12) to evaluate the energy band gap from the electronegativities.

Table 4. Values of the present calculated electronic polarizability α_e compared with values in literature and the necessary data of molecular weight M and density d of alkali halides.

A H	Mol. Weight M	Density d , Kg/m ³ Ref. [17]	Electronic polarizability α_e ($\times 10^{-30}$ m ³)			
			Known Ref. [14]	presented Eq. (16)	Kumar Ref. [3]	Reddy Ref. [6]
Li F	25.9374	2635	0.887	0.949	1.033	1.140
Li Cl	42.392	2068	2.976	2.846	2.428	2.551
Li Br	86.843	3464	4.120	4.062	3.269	3.508
Li I	133.8434	3494	6.145	7.366	6.011	6.950
Na F	41.9882	2558	1.148	1.467	1.885	1.810
Na Cl	58.4428	2165	3.237	3.257	3.498	3.473
Na Br	102.8938	3203	4.381	4.301	4.422	4.477
Na I	149.8942	3667	6.406	6.669	6.464	6.969
K F	58.1004	2480	1.991	2.182	2.626	2.283
K Cl	74.555	1984	4.080	4.358	4.901	4.692
K Br	119.006	2750	5.224	5.364	5.917	5.744
K I	166.0064	3130	7.249	7.450	8.133	8.470
Rb F	104.4684	3557	2.537	2.845	3.394	2.955
Rb Cl	120.923	2800	4.626	5.015	5.747	5.398
Rb Br	165.374	3350	5.770	5.992	6.796	6.513
Rb I	212.3744	3550	7.795	8.095	9.244	9.573
Cs F	151.9034	4115	3.601	4.241	4.373	3.847
Cs Cl	168.358	3988	5.690	5.698	5.694	5.439
Cs Br	212.809	4440	6.834	6.886	6.458	6.458
Cs I	259.8094	4510	8.859	9.138	8.768	8.971
Average Deviation, %				6.80	16.70	14.70

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