STRAIN DERIVATIVES OF ELECTRONIC DIELECTRIC CONSTANTS OF SAME CATION MIXED BINARY SOLIDS IN I-VII FAMILY

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Abstract : The behavior of mixed binary crystals in particular family is similar by mixing of different proportions. A general formulation has been developed using ion dependent dielectric theory. The pure crystals have fixed values of optical and dielectric parameters which do not in general match exactly with the values required in opto-electronic compounds for specific use. Thus, it is proposed to develop the mixtures of binary compounds which may have their properties matching exactly with the values required in opto-electronic compounds.

The mixtures under consideration have same cation in same family and same anion in covalent family. The computed volume derivatives of optical dielectric constants for different mixtures has been reported along with compounds with experimental values of some coworkers. It is found that the computed values by present formulation are much closer to experimental values with different proportions. The Results may be use for various industrial and technological applications

Index Terms: Ion dependent, Strain derivative, optical dielectric constant, mixed binaries.

Introduction :

In the present work we intend to put forward a theory to study the effect of hydrostatic pressure on the electronic dielectric properties of a large number of ionic solid families in the simple A^NB^{8-N} type binary solids. When pressure is applied on any solid,, it's volume and density both vary which introduce changes in their optical refractivity. The studies on the strain derivatives of optical dielectric properties and average energy gaps of solids are directly related to their photo elastic behaviour[(1)] proposed for the first time a cation dependent formulation for alkali halides ionic crystals which was extended and generalized by [(2,3)] for all cation dependent ionic and anion dependent for covalent crystals. This generalized ion dependent dielectric theory has been successfully used for a large number of related applications [(4,5,6,7,8,9,10)]. In the present paper, we are going to use this theory to develop an ion dependent formulation for the strain derivatives of electronic dielectric constants and successively derive the strain polarisabilities of mixed binary crystals where λ, called the strain polarisability parameter. This λ factor for predicting the photoelastic should be a very useful behaviour of dielectric theory.

Theory:

In order to predict the volume derivatives of the I-VII family ,we shall use a well-established ion dependent electronic theory applicable in general to all concerned families (3,4,5). It is well established that the dielectric behavior of the families with high ionicity is cation dependent.

The generalised ion dependent quantum theory of electronic dielectric behaviour for simple binary [(4)] and complex families [(5)] gives a simple relation between high frequency dielectric constant (ϵ_∞) and interatomic separation (R). This relationship can be written as: -

$$\epsilon_\infty = 1 + A R^S \qquad \ldots\ldots. \quad (1)$$

where *s* is a constant in a particular family and A is an ion characteristic. It is a cation property in ionic solids and anion property in covalent ones.

It is well known that the volume (V) of a unit cell is proportional to R^3. Thus, we can write

$$V = C R^3 \qquad \ldots\ldots. \quad (2)$$

where C is a constant. Differentiating equation (2) with respect to R, we get

$$dV/dR = 3(CR^2) = 3V/R \qquad ./\ldots.. (3)$$

On the application of hydrostatic pressure, the inter atomic separation (R) changes, thereby varying V. Thus, differentiating equation (1) with respect to V, we get

$$(d\epsilon\infty/dV) = ASR^{s-1}(dR)/(dV) + R^s dA/dV \quad \cdots\cdots(4)$$

Using equation (3) and (1) in (4)

$$\left(\frac{d\epsilon\infty}{dV}\right) = (\epsilon\infty - 1)\left[\frac{S}{3} + \frac{V}{A}\frac{dA}{dV}\right] \quad \ldots\ldots (5)$$

It is to be noted that the terms in this equation are dimensionless. In fact, S is a family characteristic and its values are different in different families. thus, A in equation (1) will have complicated and varied dimensions in different families. In order to extend a generalized formulation for all families, it is very inconvenient to use the direct derivative of A viz. (dV/dA). Thus, equation (5) is arranged in such a manner so as to include a dimensionless volume derivate of A i.e. $(V/A)\ (dA/dV)$ rather than a direct derivative (dA/dV). This also enables us to get a dimensionless volume derivative of ϵ_∞ viz.$(d\epsilon_\infty/dV)$.

The base equation of the present formulation equation (1) was derived by neglecting the effect of core-d electrons. A was said to be a definite characteristic of same cation solid in ionic families and same anion compounds in covalent groups. However, presence of core-d affects the number of free electrons per atom which subsequently changes the plasma frequency by small amount [(1)]. On this account the ion characteristics will vary a little from one ionic to another with same cation due to variation in the plasma frequency of the crystal [(3)] and this variation may not be negligible. Thus, the variation of ion characteristic A with volume for same ion solids may not really vanish but we expect the derivative $(V/A)\ (dA/dV)$ to remain constant in the same ion solids. This is due to the fact that the variation of volume would produce a pronounced deformability of cation than anion in ionic solids and of anion than cation in covalent ones as the optical behaviour of ionic solids are purely cation dependent while that of covalent solids are purely anion dependent. The experimental values of ϵ_∞ and s for all mixed binary solids in all different proportions[(11)] have estimated the values of $(V/A)\ (dA/dV)$ for all different cation in ionic I-VII binary crystals have done the same things for all different anion in covalent III-V binary crystals.

All mixtures in our present consideration have same cation in ionic familyand anion in covalent family. Thus, all numbers of a mixtures group of same cations in ionic family or same anion in covalent family will have same value of $(V/A)\ (dA/dV)$ is all mixing proportion. Thus, our input data is complete and the strain derivative of ϵ_∞ i.e. $(V/A)\ (dA/dV)$ can be calculated directly from equation (3)

Results : In I-VII insulator family the experimental data for (LiI) is not available and thus the mixtures containing LiI could not be taken up for comparison. However, rest of the mixtures are showing fairly good agreement with the estimated experimental values.

The predicted values of the volume derivatives of high frequency dielectric constant may have a vast range of application. Since the optical refractive index (n) is directly related to the ϵ_∞ as, $n^2 = \epsilon_\infty$. We can get any desired amount of variation in the refractive index by applying strain derivatives in the field of photo electricity and photo conductivity. The other fields of interest are of semiconductor electronics and high-power laser technology as well as the solar technology [12,13..]

Calculated and experimental values for solids in the I- VII family Mixing proportion 10% - 90% (S=3.00)

Cation	Mixtures	ϵ_∞	R	(V/A) (dA/dV)	V ($d\epsilon_\infty$/dV) Calculated values	V ($d\epsilon_\infty$/dV) Experimental values(a)
Li	LiF−LiCl	2.62	2.525	−1.406	−0.657	−0.552
	Li F−LiBr	3.07	2.693	−1.406	−0.840	−0.624
	LiF−LiI	3.61	2.929	−1.406	−1.059	
	LiCl−LiF	1.98	2.081	−1.406	−0.397	−0.381
	LiCl−LiBr	3.15	2.734	−1.406	−0.872	−0.645
	LiCl−LiI	3.69	2.963	−1.406	−1.092	
	LiBr−LiF	2.03	2.109	−1.406	−0.418	−0.389
	LiBr−LiCl	2.75	2.589	−1.406	−0.710	−0.581
	LiBr−LiI	3.74	2.977	−1.406	−1.112	
	LiI−LiF	2.09	2.156	−1.406	−0.442	
	LiI−LiCl	2.81	2.619	−1.406	−0.734	
	LiI−LiBr	3.26	2.778	−1.406	−0.917	
Na	NaF−NaCl	2.24	2.778	−1.690	−0.855	−0.810
	NaF−NaBr	2.51	2.926	−1.690	−1.041	−0.938
	NaF−NaI	2.96	3.169	−1.690	−1.352	−1.120
	NaCl−NaF	1.76	2.372	−1.690	−0.524	−0.525
	NaCl−NaBr	2.57	2.965	−1.690	−1.083	−0.972
	NaCl−NaI	3.02	3.203	−1.690	−1.393	−1.237
	NaBr−NaF	1.79	2.396	−1.690	−0.545	−0.539
	NaBr−NaCl	2.33	2.837	−1.690	−0.917	−0.860
	NaBr−NaI	3.05	3.216	−1.690	−1.414	−1.250
	NaI−NaF	1.84	2.439	−1.690	−0.579	−0.568
	NaI−NaCl	2.38	2.868	−1.690	−0.952	−0.889
	NaI−NaBr	2.65	3.009	−1.690	−1.138	−1.015
K	KF−KCl	2.16	3.109	-1.640	-1.030	-0.888
	KF−KBr	2.34	3.248	-1.640	-0.857	-1.040
	KF−KI	2.61	3.462	-1.640	-1.030	-1.350
	KCl−KF	1.84	2.726	-1.640	-0.537	-0.551
	KCl−KBr	2.38	3.286	-1.640	-0.883	-1.082
	KCl−KI	2.65	3.496	-1.640	-1.056	-1.392
	KBr−KF	1.86	2.747	-1.640	-0.550	-0.567
	KBr−KCl	2.22	3.166	-1.640	-0.780	-0.946
	KBr−KI	2.67	3.508	-1.640	-1.068	-1.408
	KI−KF	1.89	2.782	-1.640	-0.569	-0.602
	KI−KCl	2.25	3.192	-1.640	-0.800	-0.981
	KI−KBr	2.43	3.324	-1.640	-0.915	-1.133
Rb	RbF−RbCl	2.17	3.249	−1.620	−0.752	−0.984
	RbF−RbBr	2.35	3.425	−1.620	−0.837	−1.050
	RbF−RbI	2.62	3.593	−1.620	−1.004	−1.345
	RbCl−RbF	1.93	2.875	−1.620	−0.576	−0.612
	RbCl−RbBr	2.38	3.462	−1.620	−0.855	−1.197
	RbCl−RbI	2.65	3.627	−1.620	−1.023	−1.392
	RbBr−RbF	1.95	2.902	−1.620	−0.589	−0.630
	RbBr−RbCl	2.22	3.318	−1.620	−0.756	−1.049
	RbBr−RbI	2.67	3.643	−1.620	−1.035	−1.410
	RbI−RbF	1.98	2.928	−1.620	−0.607	−0.652
	RbI−RbCl	2.25	3.331	−1.620	−0.775	−1.071
	RbI−RbBr	2.43	3.499	−1.620	−0.887	−1.237

Calculated and experimental values for solids in the I- VII family Mixing proportion 30% - 70% (S=3.00)

Cation	Mixtures	ϵ_∞	R	(V/A) (dA/dV)	V ($d\epsilon_\infty$/dV) Calculated values	V ($d\epsilon_\infty$/dV) Experimental values(a)
Li	LiF−LiCl	2.46	2.429	-1.406	-0.592	-0.509
	Li F−LiBr	2.81	2.571	-1.406	-0.734	-0.565
	LiF−LiI	3.23	2.774	-1.406	-0.905	
	LiCl−LiF	2.14	2.209	-1.406	-0.462	-0.424
	LiCl−LiBr	3.05	2.698	-1.406	-0.832	-0.629
	LiCl−LiI	3.47	2.885	-1.406	-1.002	
	LiBr−LiF	2.29	2.285	-1.406	-0.523	-0.448
	LiBr−LiCl	2.85	2.627	-1.406	-0.757	-0.597
	LiBr−LiI	3.62	2.929	-1.406	-1.063	
	LiI−LiF	2.47	2.398	-1.406	-0.596	
	LiI−LiCl	3.03	2.714	-1.406	-0.824	
	LiI−LiBr	3.38	2.829	-1.406	-0.966	
Na	NaF−NaCl	2.12	2.687	-1.690	-0.772	-0.738
	NaF−NaBr	2.33	2.812	-1.690	-0.917	-0.836
	NaF−NaI	2.68	3.019	-1.690	-1.159	-1.042
	NaCl−NaF	1.88	2.486	-1.690	-0.607	-0.596
	NaCl−NaBr	2.51	2.934	-1.690	-1.041	-0.944
	NaCl−NaI	2.86	3.126	-1.690	-1.283	-1.150
	NaBr−NaF	1.97	2.549	-1.690	-0.669	-0.638
	NaBr−NaCl	2.39	2.869	-1.690	-0.959	-0.888
	NaBr−NaI	2.95	3.167	-1.690	-1.345	-1.192
	NaI−NaF	2.12	2.661	-1.690	-0.772	-0.726
	NaI−NaCl	2.54	2.959	-1.690	-1.062	-0.976
	NaI−NaBr	2.75	3.063	-1.690	-1.207	-1.074
K	KF−KCl	2.08	3.022	-1.640	-0.691	-0.804
	KF−KBr	2.22	3.137	-1.640	-0.780	-0.922
	KF−KI	2.43	3.319	-1.640	-0.915	-1.163
	KCl−KF	1.92	2.832	-1.640	-0.588	-0.635
	KCl−KBr	2.34	2.257	-1.640	-0.857	-1.048
	KCl−KI	2.55	3.424	-1.640	-0.992	-1.289
	KBr−KF	1.98	2.889	-1.640	-0.627	-0.685
	KBr−KCl	2.26	3.197	-1.640	-0.806	-0.980
	KBr−KI	2.61	3.464	-1.640	-1.030	-1.339
	KI−KF	2.07	2.983	-1.640	-0.684	-0.789
	KI−KCl	2.35	3.273	-1.640	-0.864	-1.084
	KI−KBr	2.49	3.372	-1.640	-0.953	-1.202
Rb	RbF−RbCl	2.11	3.164	−1.620	-0.688	-0.892
	RbF−RbBr	2.25	3.309	−1.620	-0.775	-1.020
	RbF−RbI	2.46	3.449	−1.620	-0.905	-1.172
	RbCl−RbF	1.99	2.977	−1.620	-0.613	-0.705
	RbCl−RbBr	2.34	3.426	−1.620	-0.830	-1.159
	RbCl−RbI	2.55	3.557	−1.620	-0.961	-1.311
	RbBr−RbF	2.07	3.049	−1.620	-0.651	-0.760
	RbBr−RbCl	2.26	3.349	−1.620	-0.781	-1.086
	RbBr−RbI	2.61	3.608	−1.620	-0.998	-1.366
	RbI−RbF	2.14	3.122	−1.620	-0.706	-0.826
	RbI−RbCl	2.35	3.409	−1.620	-0.837	-1.152
	RbI−RbBr	2.49	3.535	−1.620	-0.923	-1.280

Calculated and experimental values for solids in the I- VII family Mixing proportion 50% - 50% (S=3.00)

Cation	Mixtures	ϵ_∞	R	(V/A) (dA/ dV)	V ($d\epsilon_\infty$/dV) Calculated values	V ($d\epsilon_\infty$/dV) Experimental values(a)
Li	LiF−LiCl	2.30	2.324	-1.406	-0.527	-0.466
	Li F−LiBr	2.55	2.436	-1.406	-0.629	-0.506
	LiF−LiI	2.85	2.599	-1.406	-0.757	
	LiCl−LiBr	2.95	2.663	-1.406	-0.891	-0.612
	LiCl−LiI	3.25	2.802	-1.406	-0.913	
	LiBr−LiI	3.50	2.880	-1.406	-1.015	
Na	NaF−NaCl	2.00	2.590	-1.690	-0.690	-0.667
	NaF−NaBr	2.15	2.686	-1.690	-0.793	-0.737
	NaF−NaI	2.40	2.851	-1.690	-0.966	-0.884
	NaCl−NaBr	2.45	2.902	-1.690	-1.005	-0.916
	NaCl−NaI	2.70	3.045	-1.690	-1.173	-1.063
	NaBr−NaI	2.85	3.116	-1.690	-1.276	-1.133
K	KF−KCl	2.00	2.929	-1.640	-0.640	-0.720
	KF−KBr	2.10	3.018	-1.640	-0.704	-0.804
	KF−KI	2.25	3.159	-1.640	-0.800	-0.977
	KCl−KBr	2.30	3.227	-1.640	-0.820	-1.014
	KCl−KI	2.45	3.357	-1.640	-0.928	-1.187
	KBr−KI	2.55	3.149	-1.640	-0.992	-1.271
Rb	RbF−RbCl	2.05	3.073	-1.620	-0.651	-0.789
	RbF−RbBr	2.15	3.154	-1.620	-0.713	-0.891
	RbF−RbI	2.30	3.294	-1.620	-0.806	-0.999
	RbCl−RbBr	2.30	3.361	-1.620	-0.806	-1.119
	RbCl−RbI	2.45	3.484	-1.620	-0.889	-1.232
	RbBr−RbI	2.55	3.549	-1.620	-0.961	-1.234

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