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Electronic, Mechanical and Thermal Properties of Binary Rare-earth Semiconducting Materials

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ABSTRACT

Using the modified dielectric theory of solids, the electronic, mechanical and thermal properties of many rare-earth mono-nitrides (LaN, CeN, PrN, NdN, SmN, GdN, TbN, DyN, HoN, ErN, TmN, YbN & LuN) are presented here The values of energy gaps such as homopolar gaps (E_h), heteropolar gaps (E_c) and average energy gaps (E_p in eV) were evaluated for these binary rare earth semiconducting materials with face centered cubic (FCC) NaCl-type structure. The derived values of average energy gap (E_p) are found to be in excellent agreement with the values obtained from the Penn model. Electronic polarizability was investigated using Chemla's relation and the investigated values are shown to be in accordance with the results obtained from the Clausius–Mossotti relation. Phillips ionicity (f_i) was evaluated and the obtained values were compared with the values obtained from Tubbs and Pauling's ionicity model. The evaluated values of crystal ionicity were used to calculate the mechanical and thermal properties such as bulk-modulus (B in GPa) and heat of formation ($-\Delta H_f$ in Kcal/mol) of these compounds. An excellent agreement has been found between calculated and experimental data as compared to other such theoretical findings. The results for bulk modulus (B) differ from experimental values by the following amounts LaN-0.87%, TbN-2.79%; and the results for Heat of formation ($-\Delta H_f$) differ from experimental values by the following amounts: LaN-0.49%, CeN-0.03%, PrN-0.90%, NdN-1.39%, SmN-0.35%, GdN-1.12%, TbN-0.51%, DyN-0.56%, HoN-0.03%, ErN-0.33%, TmN-0.33%, YbN-0.34 & LuN-0.57%.

Keywords: Electronic properties, Mechanical and Thermal properties, REN's.

1. INTRODUCTION

In the recent past much attention has been given towards the study of electronic properties of binary rare earth semiconducting materials (LaN, CeN, PrN, NdN, SmN, GdN, TbN, DyN, HoN, ErN, TmN, YbN & LuN) with FCC NaCl-type structure because of their outstanding optical, electronic, magnetic properties such as dielectric constant, bulk modulus, cohesive energy, low thermal conductivity and magnetic moment. Therefore mono-nitrides of rare earth metals are extensively investigated both by theoretically and experimentally[1-5]. The rare earth nitrides adopt a FCC NaCl structure with space group Fm-3m (225) and in Nacl-type REN's with the exception of CeN (tetravalent) the cation is trivalent. In them, each RE atom is coordinated by 6-nitrogen atoms and, conversely, each atom of nitrogen is coordinated by 6-RE atoms. The large difference in electro-negativity between nitrogen (3.0) and RE (1.1-1.5) leads to a strong affinity and a predominantly ionic character of the REN bonds[6]. No experimental data for thermal expansion, thermal conductivity or elastic stiffness coefficient, including Young's modulus, have yet been obtained, with the exception of CeN. Kanchana *et al*.,[7] have studied the elastic properties of CeN and found the results are in close agreement with the experimental values. Mulokozi[8] has studied the heat of formation of rare earth compounds and proposed a relationship for heat of formation in terms of nearest-neighboring distance d_{RX}. Several researchers[3, 4, 9-11] have theoretically explored the elastic properties and hardness of LaN, PrN, TbN and HoN and Yang *et al*.,[12] have studied the entire rare earth nitride series and compared their results with literature. D Xue *et al*.,[13] have studied the dielectric properties of binary rare earth semiconductors from the dielectric theory of chemical bonds for solids.

Recently, authors[14,15] have investigated the electronic, optical and mechanical properties of $A^{III}B^{V}$ and $A^{II}B^{VI}$ semiconductors using the modified dielectric theory of solids[16-18]. In the present work we have applied the above theory to rare earth semiconducting materials. Using above theory the values of E_h, E_c and E_p have been computed. The computed values have been used to evaluate the electronic polarisability and ionicity for these materials. Making use of evaluated ionicity the bulk modulus and heat of formation of these compounds have been investigated.

2. COMPUTATIONAL METHOD

According to modified dielectric theory of solids[16-18], the average gap (E_p) can be decomposed into a heteropolar part (E_c) and a homopolar part (E_h) are given in the following form:

$$E_g^2 = E_h^2 + E_c^2 \tag{1}$$

crystal ionicity as - $$f_i = E_c^2 / E_g^2 \tag{2}$$

The homopolar part E_h depends on the nearest neighbor separation d_{AB} as follows:

$$E_h = A d_{AB}^{-K_1} \tag{3}$$

where A & K_1 are the constants, i.e., remains unchanged in different crystals and have values A = 40.468 eV$(A^{\circ})^{-2.5}$ and the exponent K_1 = 2.50. The heteropolar part of E_p is related to the ionic binding and represents the dielectrically screened potential difference between the fields produced by the ion-core of the two atoms participating in a given bond at the bond centre[19] and is given by the following form:

$$E_c = \frac{be^2(Z_A - Z_B)}{d_0} e^{(-K_S . d_0)} \tag{4}$$

where Z_A and Z_B are valence state of atoms A and B, respectively. K_S is the Thomas Fermi Screening parameter, d_0 is $d_{AB}/2$ (d_{AB} is the nearest-neighbour distance), and b is the adjustable parameter that depends on co-ordination number around the cation, i.e., b = 0.089 N_c^2, where N_c is average coordination number. For NaCl type crystal structure N_c = 6 and b = 3.204.

Using eqs. (1), (3) & (4), we have derived the values of E_h, E_c and E_p for rare earth nitrides. The calculated values have been presented in Table-1. The values of E_p can be obtained from Penn model[20] also. According to Penn model E_p follows from;

$$E_p = \frac{\hbar\omega_p}{\sqrt{\varepsilon_\infty - 1}} S_0 \tag{5}$$

Where $\hbar\omega_p$ is the valence electron plasmon energy and ε_∞- optical dielectric constant and are taken from the source[13] and the adjustable parameter S_0 is defined in the following form as-

$$S_0 = 1 - \left(\frac{E_g}{4E_f}\right) + \frac{1}{3}\left(\frac{E_g}{4E_f}\right)^2 \approx 0.75 \tag{6}$$

The valence electron plasmon energy is given by the relation[21]-

$$\hbar\omega_p = 28.8\sqrt{\frac{N_{eff}\, d}{M}} \tag{7}$$

Here N_{eff} – effective number of valence electrons, d- density and M- molecular weight of these compounds.

The Phillips ionicity has been evaluated for all these materials. The computed values have been compared with the values obtained from Tubb's[22] and Paulling ionicity model[23] also.

$$f_i = \frac{E_p}{\hbar\omega_p} \qquad (8) \quad \text{Tubb's}$$

$$f_i = 1 - \frac{1}{6}\exp\left\{-\frac{(X_A - X_B)}{4}\right\} \qquad (9) \quad \text{Pauling}$$

Where X_A & X_B are the electro-negativities the atoms A and B of REN's[24]. It can also be seen from Table-1, that there is not very good agreement between various ionicities. However the Phillips ionicity is close to Tubb's ionicity as compared to Pauling's ionicity.

2.1 Electronic Polarizability

In order to have a further check on the values of E_c and E_h, we have derived the values of electronic polarizability from these data. The electronic polarizability (α_{AB}) according to Chemla's approach[25] is given by the following equation:

$$\alpha_{AB} = \frac{(2a_0)^3 E_0^2 D_{AB}}{E_p^2} \tag{10}$$

Where a_0- Bohr radius, $E_0=me^4/2\hbar$ and $D_{AB} \approx 1.0$

The values of (α_{AB}) have been evaluated using eqn. (10) and the obtained values have been compared with the values obtained from the well-known phenomenological relation of Clausius and Mossotti,

$$\alpha_{AB} = 0.395\times10^{-24}\frac{(\varepsilon_\infty - 1)M}{(\varepsilon_\infty + 2)d} \tag{11}$$

From above relation (10) and (11), the calculated values of polarizability are present in Table -1. We found an excellent agreement between them.

2.2 Heat of formation

Heat of formation is an important thermal property of materials and several researchers[23,26] have discussed it in term of the electro-negativity difference of the atoms constituting the system. The above derived values of ionicities have been used to evaluate the heat of formation (ΔH_f), which is given by the following form as[27]:

$$\Delta H_f = \Delta H_0\left(\frac{d_{Ge}}{d_{AB}}\right)^s D(AB)\, f_{iAB} \tag{12}$$

Where d_{Ge} and d_{AB} are the nearest-neighbor distance of germanium and the binary compound AB, respectively, and D(AB) is given by the relation[28,29]

$$D(AB) = 1 - b\left[\frac{E_2(AB)}{\bar{E}(AB)}\right]^2 = 1 - b\left[\frac{2E_2(AB)}{E_0(AB)+E_1(AB)}\right]^2 \tag{13}$$

where E_0(AB) is the lowest direct energy gap, E_1(AB) and E_2(AB) are higher critical energies of the compound, E(AB) is the average values of energy E_0(AB) and E_1(AB) and b= 0.0467 [28].

2.3 Bulk modulus

Using the derived values of Phillips ionicity ($f_i=E_c^2/E_p^2$), the bulk modulus by Neumann simple approach[30]-

$$B = B_0 V^{-n} \tag{14}$$

Where exponent n has value 1.147 and the factor B_0, for NaCl-type structured rare earth nitrides, is given by-

$$B_0 = b_0(1 - b_1 f_i) \tag{15}$$

In above eqn.(15), b_0 and b_1 are the adjustable parameters have values 6.343×10^4 and 1.034 respectively and depends upon the structure of the semiconducting materials.

3. RESULTS AND DISCUSSION

Based on above modified dielectric theory of solids, the investigated values of the energy gaps and plasmon energy of these binary rare earth compounds are tabulated in the Table-1. The crystal ionicity (f_i) values for these semiconducting materials have been investigated using Phillips ionicity model (Eq.-2) and compared with the values obtained by the Tubb's ionicity model and hence of Paulling's. These results are shown in the same Table-1. The values of electronic polarizability are computed using relations (10) & (11) and are presented in Table-1 and there is a fairly good agreement here also. In Table-2; the computed values of bulk-modulus B (in GPa) and heat of formation (in Kcal/mole) using the Phillips ionicity (f_i) are compared with previously reported experimental data[8,31,32] and other such theoretical findings[2-4,11,12]. We find that the values of mechanical and thermal properties derived from their ionicity are much closed to the reported experimental data as compared to values of these parameters investigated by several researchers. We therefore think that the derived values of Phillips ionicity are more appropriate compared to other such theoretical findings.

Table-1: In this table we present the calculated values of plasmon energy ($\hbar\omega_p$ in eV), energy gaps, ionicity and electronic polarizability of rare earth mono-nitrides

REN	Z_A	Z_B	$\hbar\omega_p$	Energy gaps (in eV)				Ionicity (f_i)			Polarizal
				E_h	E_c	E_p	E_{penn}	Phillips	Tubb's	Pauling	Chemla
			Eq. (7)	Eq.(3)	Eq.(4)	Eq.(1)	Eq.(5)	Eq. (2)	Eq. (8)	Eq. (9)	Eq.(10)
LuN	1	5	16.83	3.98	3.25	5.15	5.12	0.39	0.30	0.57	6.86
CeN	1	5	18.66	4.57	3.39	5.69	5.70	0.36	0.30	0.56	5.52
PrN	1	5	17.21	4.26	3.32	5.41	5.28	0.38	0.30	0.56	6.44
NdN	1	5	18.06	4.29	3.35	5.45	5.57	0.38	0.30	0.57	5.79
SmN	1	5	18.59	4.51	3.38	5.64	5.75	0.36	0.31	0.56	5.36
GdN	1	5	18.93	4.62	3.39	5.73	5.95	0.35	0.31	0.56	5.07
TbN	1	5	19.23	4.78	3.43	5.88	6.08	0.34	0.31	0.53	4.87
DyN	1	5	19.39	4.85	3.43	5.93	6.16	0.34	0.31	0.52	4.74
HoN	1	5	19.57	4.93	3.44	6.01	6.25	0.33	0.31	0.53	4.60
ErN	1	5	19.71	5.01	3.45	6.08	6.32	0.32	0.32	0.52	450
TmN	1	5	19.97	5.09	3.47	6.16	6.44	0.32	0.32	0.53	4.33
YbN	1	5	20.09	5.15	3.47	6.21	6.51	0.31	0.32	0.52	4.24
LuN	1	5	20.22	5.21	3.47	6.26	6.59	0.31	0.32	0.52	4.12

*CM- Claussius-Mossotti

Table 2: In this table, we present the calculated values of bulk modulus (B in GPa) and heat of formation (-ΔH_f in Kcal/mole) of rare earth mono-nitrides

REN	Phillips (f_i)	B_0 Eq. (15)	Bulk modulus (B)			D_{AB} Eq. (13)	Heat of formation (-ΔH_f)	
			Calc. Eq.(14)	Refs. [2-4, 11,12]	Expt. [31,32]		Calc. Eq.(12)	Expt. [8]
LuN	0.39	3.78	121.64	130, 122		0.81	71.42	71.07
CeN	0.36	3.98	154.55	210, 121	153	0.78	74.83	74.81
PrN	0.38	3.85	138.45	140, 121, 129		0.80	75.79	75.11
NdN	0.38	3.85	138.72	140, 197		0.78	74.02	73.00
SmN	0.36	3.98	153.18	180, 127		0.78	74.26	74.00
GdN	0.35	4.04	162.37	150, 111		0.79	75.84	75.00
TbN	0.34	4.11	171.08	150, 155.53	176	0.79	76.04	76.43
DyN	0.34	4.11	174.35	160, 121		0.79	77.30	76.87
HoN	0.33	4.17	180.91	170, 138, 137.9		0.80	77.39	77.36
ErN	0.32	4.24	186.77	160		0.81	77.07	77.92
TmN	0.32	4.24	192.45	190, 138		0.80	78.14	78.40
YbN	0.31	4.30	198.11	190, 136		0.82	78.52	78.79
LuN	0.31	4.30	201.14	170, 183		0.82	79.56	79.11

4. CONCLUSIONS

Using the modified dielectric theory of solids, the values of average energy gap (E_p) have been shown to be in accordance with the values obtained from Penn model. In order to have a further check on the above calculated data, the electronic polarizability and crystal ionicities have been investigated from them. The derived polarizability has been found in very good agreement with the values obtained from the well-known Classius-Mossotti relation. The values of Phillips ionicity lead us to determine the bulk modulus and heat of formation for these semiconducting materials and the values have been shown to be an excellent agreement with the previously reported experimental data as compared to other such theoretical findings. Hence, in the light of above findings, we conclude that the modified dielectric theory of solid is applicable even to binary rare-earth mono-nitrides with (FCC) NaCl-type structure in LaN, CeN, PrN, NdN, SmN, GdN, TbN, DyN, HoN, ErN, TmN, YbN and LuN.

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