HSPI Inc. The Open Access Publisher

IJPRA ISSN 2766-2748 INTERNATIONAL JOURNAL OF PHYSICS RESEARCH AND APPLICATIONS

Research Article

Electronic and Thermo-Dynamical Properties of Rare Earth RE_2X_3 (X=O, S) Compounds: A Chemical Bond Theory

Pooja Yadav[1], DS Yadav[2]* and DV Singh[1]

[1]Department of Physics, Agra College, Agra-282002, UP, India

[2]Department of Physics, Ch. Charan Singh PG College, Heonra (Saifai), Etawah-206001, UP, India

Abstract

The electrical, mechanical, and thermodynamic properties of cubic structured rare earth sesqui-chalcogenides RE_2X_3 (RE = La-Lu, X = O, S) are examined in this work using the chemical bond theory of solids. For these materials, the values of the homopolar gaps (E_h), ionic gaps (E_c), and average energy gaps (E_p) have been assessed. It has been discovered that the calculated values of the homopolar gap (E_h) and average energy gap (E_p) are in great agreement with the values derived from the Penn and Phillips models. The electrical, mechanical, and thermodynamic properties of these materials (RE_2O_3), such as their bulk modulus and heat of formation, have been estimated using the bond ionicity values. The computed values accord very well with the theoretical results that have been published thus far.

PACS No.: 71.20.Eh, 71.15.Mb, 61.50.Ks, 71.15.Mb

More Information

***Address for correspondence:** DS Yadav, Department of Physics, Ch. Charan Singh PG College, Heonra (Saifai), Etawah-206001, UP, India, Email: dhirendra.867@rediffmail.com

Submitted: April 11, 2024
Approved: April 23, 2024
Published: April 24, 2024

How to cite this article: Yadav P, Yadav DS, Singh DV. Electronic and Thermo-Dynamical Properties of Rare Earth RE_2X_3 (X=O, S) Compounds: A Chemical Bond Theory. Int J Phys Res Appl. 2024; 7: 048-052.

DOI: 10.29328/journal.ijpra.1001083

https://orcid.org/0000-0001-8315-9743

Keywords: RE_2O_3 and RE_2S_3; Electronic properties; Mechanical properties; Thermodynamic properties

Introduction

Because of its numerous technological applications in the fields of electroluminescence, cathode-luminescence source, crystals for chemical organic reactions, high-K gate dielectrics, optical components of high power lasers, oxygen ion conducting electrolyte in solid oxide fuel cells, and materials with strongly hydrophobic surfaces, RE_2O_3 with C-type bixbyite crystal structure has received a lot of attention recently [1-7]. Each rare earth atom contributes three electrons to the extremely electronegative O ions in rare earth sesqui-oxides, with the remaining 4f electrons remaining firmly localized at the rare earth site. Larger oxygen coordination numbers are found in the lighter lanthanides because the f-electrons are less firmly connected to the parent atom's nucleolus. Because of the interaction between valence electrons and localized 4f electrons, these materials exhibit several abnormal physical features. Because localized magnetic moments readily hybridize with valence and conduction electrons, valence fluctuation states also exist in these compounds despite their insulating nature and lack of carriers. Because of the Coulomb correlation effect, the 4f band splits into two sub-bands that are separated by 6–12 eV, which results in RE_2S_3 insulators. The crystal structures of these materials are known to fall into three different polymorphic [8] forms: (1) A-type, hexagonal, and, most of the time, space group P3m1 (2)- B-type, monoclinic; typically belongs to space group C2Im (3)- Cubic C-type, typically belonging to space group Ia3. Goldschmidt et al. conducted the first thorough investigation of the rare earth sesquioxides in 1925 [9], and his initial phase classifications (A, B, and C-type) are still in use today. Using the tight-binding linear muffin-tin orbital (TB-LMTO) method and the self-interaction corrected local spin density (SIC-LSD) methodology, Petit, et al. [10] conducted a first-principles investigation on rare earth oxides, namely RE_2O_3 (RE = Ce to Ho). Many attempts have been made in the past few years [11-17] to comprehend the electrical, optical, mechanical, and thermodynamic properties of rare earth oxides (RE_2O_3) using a variety of techniques. Authors [18,19] have effectively used the modified dielectric theory of solids to study the electrical, optical, and mechanical properties of binary semiconductors in the II-VI and III-V groups. Using the modified dielectric theory of solids, we have computed the electrical, thermodynamic, and mechanical properties of RE_2O_3 & RE_2S_3 (RE= La-Lu, except for the radioactive element Pm) with C-type bixbyite and Th_3P_4 type structure in this study [20,21]. To the best of my knowledge, however, the modified PVV theory of solids has not yet been used to study the electrical, thermodynamic, and mechanical properties of RE_2O_3 & RE_2S_3 (RE = La-Lu, except the radioactive element Pm). For these materials, the values of homopolar gaps (E_h), ionic gaps (E_c), and average energy gaps (E_p) are examined using this concept to obtain greater agreement. We can ascertain these criteria to find these materials' Phillips ionicity. Utilizing the deduced ionicity value, the bulk-modulus and formation heat are examined. The heat of formation and bulk-modulus values thus obtained are in excellent agreement with those reported in the literature thus so far [12,15-17].

Computational method

To decompose the average energy gap (E_p) between bonding and anti-bonding (sp^3) hybridized orbitals into contributions from symmetric and anti-symmetric parts by the potential within the unit cell, the average energy gap (E_p) can be split into heteropolar or ionic part (E_c) and homopolar or covalent part (E_h) using the modified dielectric theory of solids [20,21]. These contributions take the following form: E_c stands for heteropolar or ionic contribution, and E_h for homopolar or covalent contribution.

$$E_p^2 = E_h^2 + E_c^2 \qquad (1)$$

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

$$E_h = Ad_{AB}^{-K_1} \qquad (2)$$

Where A = 40.468 eV(A°)2.5 and the exponent K_1 = 2.5 are the constants, i.e., remain unchanged in different crystals. A = 39.74 and K_1 = 2.48 were similar values found by Phillips and Van-Vechten [22]. The following relation can be used to determine the ionic contribution:

$$E_c = K_2 d_0^{-1} \cdot e^{-k_s . d_0} \qquad (3)$$

Where b is an adjustable parameter that depends on coordination number 22 around the cation, i.e., b = 0.089 Nc^2, and $K_2 = be^2(Z_A\text{-}Z_B)$ is a numerical constant. Z_A and Z_B are the valence states of atoms A and B, respectively. Nc is the average coordination number, Ks is the Thomas Fermi Screening Parameter (TFSP), d_0 = (d/2) (d is the nearest adjacent distance), and b is 4.6137 for C-type RE_2O_3 and 2.532 for Th_3P_4 type RE_2S_3. According to the physical interpretation of equation (3), E_c is the difference between the Screened Coulomb Potentials of atoms A and B with core charges Z_A and Z_B. The covalent radii, d_0, are where these potentials should be assessed. The Thomas-Fermi screening factor e-K_s.d_0 reduces the charge of the ion cores by screening out the remaining electrons, which influences the chemical trend of a compound. Only a small portion of the electrons are in the bond. This screening factor is connected to the effective number of free electrons in the valence band along with the bond length. As a result, the number and length of bonds emerging from the cations determine the values of E_c and E_h. Ten electrons per molecule were taken into consideration for determining the value of K_s, which is defined as follows:

$$k_s = 2a_B^{-0.5}(3N/\pi V)^{0.167} \qquad (4)$$

Where a_B is Bohr radius.

The E_h, E_c, and E_p values for these materials have been determined by using the aforementioned relations (1)–(4). Phillips models [23] and Penn [24] can also yield the values of E_h* and. E_p*. The following form represents E_h* following the Phillips model:

$$E_h^* = \frac{\hbar\omega_p S_0}{\sqrt{\varepsilon_0 - 1}} \qquad (5)$$

And E_p* using the Penn model, defined as

$$E_p^* = \frac{\hbar\omega_p S_0}{\sqrt{\varepsilon_\infty - 1}} \qquad (6)$$

Where the valence electron plasmon energy is represented by ħωp, and the static and optical dielectric constants, ε_0 and ε_∞, are taken from separate sources [14,25]. The defined variable S0, which is changeable, is [24]; 0.78 for RE_2O_3 and 0.80 for Re_2S_3. The defined

$$S_0 = 1 - \left(\frac{E_g}{4E_f}\right) + \frac{1}{3}\left(\frac{E_g}{4E_f}\right)^2 \qquad (7)$$

The valence electron plasmon energy is given by the relation[23] –

$$\hbar\omega_P = 28.8\sqrt{\frac{N_{eff}\, d}{M}} \qquad (8)$$

where N_{eff} – effective no. of the valence electrons, *d*-density, and *M*-molecular weight of the material.

Phillips ionicity $(f_1 = E_c^2 / E_g^2)$ has been assessed for each of these materials to have an additional check on the E_c and E_h values. The results are compared with those derived from the Tubbs ionicity model [26] and Pauling ionicity model [27], which are defined as:

$$f_i = E_P / \hbar\omega_P \cdot S_0 \qquad (9)$$

$$f_i = 1 - \frac{1}{6}\exp\left(-\Delta X^2 / 4\right) \qquad (10)$$

Where ΔX represents the difference in electro-negativity between the O and S atoms and RE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Table 1 makes it abundantly evident that there is a fair amount of consistency between the different ionicities.

Bulk-modulus

In terms of cell volume, the bulk modulus using the Neumann technique [28] has been determined using the computed values of crystal ionicity as

$$B = B_0 V^{-n} \qquad (11)$$

is the constant depends upon the covalence and b_0 = 4.143 × 10^4 & b_1 = 1.034 for cubic structured RE_2O_3, which

Table 1: In this table, we have presented the values of Plasmon energy ($\hbar\omega_p$ in eV), Homoppolar energy gaps (E_h), Ionic Gap (E_c), Average energy gap (E_g), and Penn gap (in eV), and bond iconicity magnitudes (Phillips, Tubbs, and Pauling Model) of C-type RE_2X_3 (X = O, S) compounds.

RE_2X_3	$\hbar\omega_p$	Energy gaps (in eV)					Bond ionicity		
		E_h	E_c	E_p	E_h*	E_p*	Phillips Model	Tubbs Model	Pauling Model
La_2O_3	16.46	4.442	6.434	7.819	4.435	7.861	0.67	0.61	0.70
Ce_2O_3	16.89	4.535	6.478	7.908	4.579	7.999	0.67	0.60	0.69
Pr_2O_3	16.89	4.631	6.685	8.133	4.608	7.908	0.67	0.60	0.72
Nd_2O_3	16.97	4.631	6.617	8.076	4.658	8.076	0.67	0.61	0.68
Sm_2O_3	17.42	4.781.	6.818	8.327	4.844	8.231	0.67	0.60	0.68
Eu_2O_3	17.58	4.989	7.215	8.772	4.919	8.084	0.67	0.58	0.70
Gd_2O_3	17.72	5.044	7.288	8.863	4.992	8.172	0.67	0.59	0.68
Tb_2O_3	17.68	5.329	7.822	9.465	5.014	8.158	0.68	0.59	0.68
Dy_2O_3	18.14	5.329	7.762	9.415	5.178	8.376	0.67	0.59	0.68
Ho_2O_3	18.25	5.329	7.702	9.366	5.246	8.444	0.67	0.59	0.68
Er_2O_3	18.38	5.389	7.774	9.459	5.321	8.528	0.67	0.59	0.68
Tm_2O_3	18.55	4.989	6.865	8.486	5.406	8.642	0.65	0.59	0.68
Yb_2O_3	18.69	4.989	6.816	8.447	5.487	8.757	0.65	0.60	0.66
Lu_2O_3	18.79	5.574	6.779	8.776	5.557	8.878	0.60	0.60	0.68
La_2S_3	16.11	3.347	4.865	5.905	3.244	6.039	0.68	0.38	0.53
Ce_2S_3	16.55	3.474	4.844	5.964	3.072	5.688	0.66	0.35	0.53
Pr_2S_3	16.66	3.507	5.138	6.221	3.611	5.714	0.68	0.34	0.53
Nd_2S_3	16.87	3.507	5.072	6.166	3.429	6.666	0.67	0.41	0.53
Sm_2S_3	17.10	3.574	5.160	6.277	3.275	6.956	0.67	0.41	0.52
Gd_2S_3	17.26	3.574	5.097	6.225	3.510	5.525	0.67	0.32	0.52
Tb_2S_3	17.47	3.608	5.128	6.269	3.552	5.706	0.67	0.33	0.52
Dy_2S_3	17.58	3.713	5.317	6.484	3.461	5.709	0.67	0.32	0.52
Ho_2S_3	17.63	3.642	5.196	6.346	3.725	6.652	0.67	0.38	0.52
Er_2S_3	17.71	3.713	5.294	6.466	3.741	5.734	0.68	0.32	0.52
Tm_2S_3	17.77	3.713	5.513	6.646	3.754	6.724	0.67	0.38	0.52
Yb_2S_3	17.77	3.747	5.362	6.541	3.754	5.805	0.67	0.33	0.52
Lu_2S_3	17.86	3.785	5.423	6.613	4.077	5.831	0.67	0.33	0.52

Table 2: In this table, we present the estimated values of bulk-modulus (B, in GPa) and heat of formation (ΔH_f, in KJ/mole) of C-type RE_2O_3 compounds.

RE_2O_3	Bulk modulus using			Reported	D_{AB}	The heat of formation using			Reported*
	Phillips ionicity	Tubbs ionicity	Pauling ionicity			Phillips ionicity	Tubbs ionicity	Pauling ionicity	
La_2O_3	155.0	138.8	160.5	123.5[a]	0.512	427.78	386.03	442.99	428.57 ± 0.19
Ce_2O_3	163.2	145.0	168.1	129.9[a]	0.512	434.10	388.80	447.12	435.00 ± 6.00
Pr_2O_3	164.8	145.4	176.2	134.3[a]	0.500	438.22	389.83	467.79	436.80 ± 1.60
Nd_2O_3	167.5	151.4	169.8	139.2[a]	0.490	426.72	388.40	432.97	432.15 ± 0.24
Sm_2O_3	175.1	155.7	177.7	146.7[a]	0.475	429.13	384.71	436.00	433.89 ± 0.48
Eu_2O_3	171.2	150.6	183.6	145.0[b]	0.446	427.54	367.16	443.13	-
Gd_2O_3	182.0	158.8	184.5	154.9[a]	0.416	427.54	386.02	444.91	433.94 ± 0.85
Tb_2O_3	188.2	163.1	189.5	-	0.433	453.46	392.40	452.25	436.80 ± 2.00
Dy_2O_3	190.8	166.5	193.4	191.0[c]	0.423	440.86	383.34	441.81	445.84 ± 0.93
Ho_2O_3	194.2	169.7	197.2	200.0[c]	0.432	447.96	391.49	451.21	449.50 ± 1.15
Er_2O_3	200.0	173.1	201.1	167.5[a]	0.430	452.73	395.45	455.77	453.59 ± 0.45
Tm_2O_3	201.0	174.0	202.1	171.2[a]	0.464	430.29	388.57	447.84	451.40 ± 1.40
Yb_2O_3	207.0	180.5	199.6	181.0[c]	0.464	428.09	395.15	434.67	433.68 ± 0.53
Lu_2O_3	211.5	185.4	211.6	214.0[c],	0.455	439.91	405.13	459.14	452.80 ± 3.30

[a]Ref. [15], [b]Ref. [12], [c]Ref. [17], [*]Ref. [16].

depends upon the structure of rare earth sesquioxides and the exponent has values 1.147. In cubic structured RE_2O_3, In, b_0 = 4.143 × 10^4 & b_1 = 1.034 rely on the structure of rare earth sesquioxides, and the exponent has a value of 1.147, the constant is dependent on the covalence FC.

Heat of formation

It is possible to write the heat of formation [29,30] of rare earth sesquioxide using the bond ionicity values that were obtained above-

$$\Delta H_f = \Delta H_0 \left(\frac{d_{Ge}}{d_{XY}} \right)^S D(XY) f_{i,XY} \qquad (12)$$

Where d_{ue} and d_{XY} are the bond lengths of germanium and the RE_2O_3, respectively, ΔH_0 = 1190, S = 3.0, and the factor D(XY) is defined as

$$D(XY) = 1 - b \left(\frac{E_2(XY)}{\bar{E}(XY)} \right)^2$$

Where $\bar{E}(XY)$ is the average of $E_0(XY)$ and $E_1(XY)$ and $E_2(XY)$

are higher critical energies of the compound *(XY)*, $E_0(XY)$ is the lowest direct energy gap, and b = 0.0467. The values of $E_0(XY)$, $E_1(XY)$, and $E_2(XY)$ can be either taken from the experimental reflectivity data or calculated theoretically using relations given by Neumann[30].

Results and discussion

The values of E_h, E_c, E_g, E_p, and fi that have been examined for RE_2O_3 compounds based on the current investigation are listed in Table 1. The values of fi for various materials have been researched and determined using the Phillips ionicity model, utilizing Equation (1-4). The results are compared with the values derived from the Tubbs and Pauling ionicity model and are displayed in Table 1. There is good agreement between the bond ionicity values of various materials. We have calculated the bulk modulus (B, in GPa) and heat of formation (-ΔHf, in KJ/mole) of RE_2O_3 using different ionicities, and the results are displayed in Table 2. Table 2 makes it quite evident that the computed values of B and H from the several ionicities we used show a decent degree of agreement with the other existing theoretical conclusions. Therefore, we believe that the values generated from Phillips ionicity are more appropriate than the values derived from Tubb's and Pauling's ionicity models.

Conclusion

For cubic-structured rare earth sesqui-oxides and sulfides, the values of E_h, E_c, and E_p have been examined using the modified dielectric theory of solids. It has been demonstrated that the examined values agree with the values found in the Penn and Phillips models. The computed data above have been further examined by deriving Phillips ionicity from them. We can calculate these C-type RE_2O_3 compounds' bulk modulus (B) and heat of formation (-ΔHf) using the estimated values of Phillips ionicity. While there is a significant difference between our predicted bulk modulus values and the published experimental data, the heat of formation values of these materials are in good agreement accord with previously published literature values. Thus, we conclude that the chemical bond theory of solids can be used for both cubic and Th_3P_4 type RE_2X_3 compounds in light of the aforementioned data.

Credit authorship contribution statement

Pooja Yadav: Writing an original draft, Review of Literature, Dhirandra Singh Yadav: Methodology, Conceptualization, Formal analysis, Data curation, Supervision, Review & editing: Data presentation, D V Singh: Ideas, Final writing.

References

1. Kitai AK. Oxide phosphor and dielectric thin films for electroluminescent devices. Thin Solid Films. 2003; 445:367.
2. Barrera EW, Pujol MC, Diza F, Choi SB. Emission properties of hydrothermal Yb3 +, Er3 + and Yb3 +, Tm3 + -codoped Lu2O3 nanorods: upconversion, cathodoluminescence and assessment of waveguide behavior. Nanotechnology. 2011; 22:075205.
3. Andreeva D, Ivanov I, Ilieva L. Gold catalysts supported on ceria doped by rare earth metals for water gas shift reaction: Influence of the preparation method. Appl. Catal. A. 2009; 357:159.
4. Pan TM, Hung WS. Physical and electrical characteristics of a high-k Yb2O3 gate dielectric. Appl. Surf. Sci. 2009; 255:4979.
5. Zelmon DE, Nothridge JM, Haynes ND. Appl. Opt. 2013; 52:3825.
6. Orlovskaya N, Lukich S, Subhash G. Mechanical properties of 10 mol% Sc2O3–1 mol% CeO2–89 mol% ZrO2 ceramics. J. Power Sources. 2010; 195:2774.
7. Azimi G, Dhiman R, Kwon H M. Hydrophobicity of rare-earth oxide ceramics. Varanasi KK. Nat. Mater. 2013; 12:315.
8. Zinkevich M 2007 Prog. in Material Science 52 7597
9. Goldschmidt V M, Ulrich E and Barth T. A Theoretical Study of Binary and Ternary Hydride-Bonded Complexes N(Beh2)...X with N = 1 or 2 and X = K+ or Ca+2. Skrifter Norske Videnskaps-Akadoslo, I: Mat. Naturev, Kl.5. 2011.
10. Petit L, Svane A, Szotek Z, Temmerman WM. First-principles study of rare-earth oxides. Phys. Rev. B. 2005; 72:205118.
11. Abrashev M V, Todorov N D, Geshev J. Raman spectra of R2O3 (R—rare earth) sesquioxides with C-type bixbyite crystal structure: A comparative study. J. Appl. Phys. 2014; 116:103508.
12. Sheng J, Gang B L, Jing L. The Phase Transition of Eu2O3 under High Pressures. Chin. Phys. Lett. 2009; 26:076101.
13. Hirosaki N, Ogata S, Kocer C. Ab initio calculation of the crystal structure of the lanthanide Ln2O3 sesquioxides. J. Alloys Compounds. 2003; 351:31-34.
14. Xue D, Betzler K, Hesse H. Dielectric constants of binary rare-earth compounds. J. Phys.: Condens. Matter. 2000; 12:3113.
15. Rahm M, Skorodumova NV. Phase stability of the rare-earth sesquioxides under pressure. Phys. Rev. B. 2009; 80:104105.
16. Remay H. Introduction. Home Inorganic Reactions in Water Chapter. Inorganic Chemistry. 1956; 2:247.
17. (a) Jiang S, Liu J, Li X. Structural transformations in cubic Dy2O3 at high pressures. Solid Stat. Comm. 2013; 169:37-41.
    (b) Jiang S, Liu J, Li X. Phase transformation of Ho2O3 at high pressure. J. Appl. Phys. 2011; 110:013526.
    (c) Jiang S, Liu J, Lin C. Pressure-induced phase transition in cubic Lu_2O_3. J. Appl. Phys. 2010; 108:083541.
18. Yadav DS. Electronic properties of aluminum, gallium and indium pnictides. Phys. Scr. 2010; 82:65705.
19. Yadav DS, Verma AS. Electronic, optical, and mechanical properties of AII-BVI semiconductors. International Journal of Modern Physics B, 2012, vol. 26, 1250020.
20. Singh OP, Gupta VP. Electronic properties of europium chalcogenides (EuO, EuS, EuSe, EuTe). Phys. Stat. Sol. (b). 1985; K153:129.
21. Singh DV, Gupta VP. Bulk Moduli of Sm, Eu, and Yb Monochalcogenides. Phys. Stat. Sol. 1992; (b) K71:171.
22. Van-Vechten JA. Quantum Dielectric Theory of Electronegativity in Covalent Systems. I. Electronic Dielectric Constant. Phys. Rev. 1969; 182:891.
23. Phillips JC. Bonds and Bands in Semiconductors (New York: Academic). 1973.
24. Penn DR. Wave-Number-Dependent Dielectric Function of Semi conductors. Phys. Rev. 1962; 128:2093.
25. Zhue VP, Shelykh AI. Sov. Phys. Semiconductor. 1989; 23:245.
26. Tubbs MR. A Spectroscopic Interpretation of Crystalline Ionicity. Phys. Stat. Solidi. 1970; 41:61.

27. Pauling L. The Chemical Bonds (Ithaca, NY: Cornell University Press). 1960.

28. Neumann H. Bulk modulus — volume relationship in alkali halides with rocksalt structure. Cryst. Res. Tech. 1988; 23:531.

29. Phllips JC, Van-Vechten JA. Phys. Rev. 1970; B 2:2147.

30. Neumann H. Cryst. Res. Tech. 1983; 18:167.