Calculation of lattice thermal expansion coefficient of RBO₄ (R=lanthanides, Sc, Y, B=P, As) compounds having monazite and zircon structure

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ABSTRACT:

Two simple functional empirical relations are proposed to estimate the lattice thermal expansion coefficient of RBO₄ (R=Lanthanides, Sc, Y, B=P, As) compounds having monazite and zircon structure. Based on least square fitting, the new empirical relations are proposed for the calculation of lattice thermal expansion coefficient. These empirical relations relating the lattice thermal expansion coefficient with the ratio of average principal quantum number and group electronegativity of the compound. It is also related with the plasmon energy of the compounds. Our calculated values are in excellent agreement with the values reported previous researchers. No experimental data is required in the calculation in this model.

Keywords: Rare earth orthophosphates, Rare earth orthoarsenates, lattice thermal expansion coefficient, Plasmon energy, electronegativity.

Introduction:

The linear thermal coefficients of expansion is one of the fundamental properties of material because it in closely related to the anharmonicity of the material. Knowledge of liner thermal expansion coefficient is also very useful in high temperature composite ceramics, luminescence, diode pumped solid state laser. The coefficient of thermal expansion is a material property that is indicative of the extent to which a material expands upon heating over small temperature ranges. The thermal expansion of uniform linear objects in proportional to temp. change different substance expand by different amount. Most solid materials expand upon heating and contract when cooled. The change in length with temperature for a solid material can be expressed as

$$\frac{l_f - l_0}{l_0} = \alpha(T_f - T_0) \quad (1)$$

$$\frac{\Delta l}{l_0} = \alpha \Delta T \quad (2)$$

$$\alpha = \frac{1}{\left(\dfrac{\Delta l}{\Delta T}\right) l_0} \quad (3)$$

where l_0 and l_f represent the original and final length with temperature changes from T_0 to T_f respectively. When a material in heated, molecular activity increase and energy stored in the bonds between atoms in changed. With increase in store energy the length of the molecular bond also increases consequently solid expand when heated and contract when cooled.

The coefficient of linear thermal expansion is inversely proportional to the bond strength of the material and to the melting point of material. Hence metal with high melting point (strong bonding) have low thermal expansion coefficients. As temperature is a measure of total kinetic energy of the atoms in the systems. In a solid, temperature is a measure of vibration energy of the atoms. In the crystal structure of a simple solid, we find that the atoms or ions are arranged in a regular three dimensional array. As temperature of the crystal in raised more thermal energy in objected

into the crystal, the ions vibrate with greatest and greater amplitude, and the mean distance of separation of the ion increase, eventually the amplitude becomes sufficiently large to overcome the restraining forces which hold the solids together and the solid melts. The coefficient of the thermal expansion in inversely proportional to the bond strength of the material and hence to the melting point of the material. In order to determine the thermal expansion coefficient, two physical quantities displacement and temperature must be measured on a sample that is undergoing a thermal cycle. Three of the main technique used for coefficient of thermal expansion measurement is dilatometry interferometer method by Tian et.al(2016), Lucas et.al(2000), Hikichi et.al (1988,1987), Mullica et.al (1984), Ewing et.al (1991), Clavier et.al (2011) and thermo chemical analysis by Errandonea et.al (2008), Acharya et.al (2017), Optical imaging can also be used at extreme temperature. X-ray diffraction can be used to study changes in the lattice parameter but may not correspond to bulk thermal expansion. Theoretically Yilmaz (2004) used finite element analysis software (FEA) to measure the coefficient of thermal expansion. The evaluation of liner thermal coefficient of expansion of RBO_4 compounds of monazite and zircon structure is of considerate importance in material science and geological science. For isotropic solids the coefficient of linear thermal expansion and the specific heat at constant volume C_v are related by the Gruneisen (1912) relation.

$$\alpha = \frac{\gamma C_v}{3BV} \qquad (4)$$

where B is the bulk modulus, C_v in the molecular specific heat capacity, V in the molar volume and γ in the gruneisen parameter. γ varying between 1.00 and 3.0 for most of the materials. Gruneisen constant can also be expressed in terms of atomic volume (V) and the change in the atomic vibration frequency (υ) by the following relation.

$$\gamma = \frac{d \ln \upsilon}{d \ln V} \qquad (5)$$

Hence from the study of thermal expansion of solids, information on the interatomic forces in crystal can also be inferred, because thermal expansion coefficient in related to the vibration in $\gamma's$ with the change in volume and in intimately with the vibration spectra which in turn in related with interatomic forces. Rare earth phosphate and arsenate belong the family of rare earth zircons, having high melting point (between 1900^0c-2000^0c) and show excellent thermal stability in both oxidizing and reducing atmosphere has studied by Mogilevsky (2003), Marshall et.al (1999), Patwe et.al (2009). Rare earth phosphate are synthesized by direct reaction between rare earth oxide and phosphoric acid. Rare earth phosphate have biological role and they have shown non toxicity and bio compatibility in different bio-medical application mainly bio imagine phosphor/luminescent labelity materials for bio-imagine. Thermal properties of RPO_4 and $RAsO_4$ compounds are dependent or its composition and its molecular and/or atomic arrangement. The bonding character and network between ions or atoms in a molecule or solid are eventually and directly determine its structure, the atomic or ionic arrangement and its properties. After the establishment of quantum theory of molecules, it became one of the important topic to explore and understand the bonding nature in molecules and solids. The chemical bond in RPO_4 and $RAsO4$ compounds are usually divided into two types namely covalent and ionic depending on their electronic structure. Although their no sharp boundary between the ionic bonding and covalent bonding from quantum chemical point of view, yet it is convenient and effective to consider each of these a separate entity in discussing and interpreting various properties of a molecular or crystal.

2. Review of earlier works

As a practical criterion of judging the bonding. Nature, commonly accepted definition of the partial ionic character of a single bond between atoms A and B was established by Pauling in (1932). He proposed that an amount of ionic character

of a bond AB in equal to $1 - \exp\left[-\frac{(X_A - X_B)^2}{4} \right] \qquad (6)$

where X_A and X_B are the respective Pauling electronegativities of atoms A and B.

Ionic character of being 50% corresponds to electro negativity difference 1.7 in the Pauling scale. Ionic or covalent character of a bond is a useful concept and thus has been extensively studied in terms of various levels of quantum chemical calculation about the electronic structure of various bonds. Reviews concerning bond covalence and its

application have been made by dielectric theory of solids by Philips and Van Vechten (PV theory) (1970, 1969) and the bond charge model proposed by Levine (1973). It is known that PVL (Philips, Van Vecten, Levine) theory can deal only with binary crystals. Zhang et.al (1999) has pointed out that the composition of a crystal can be described by chemical bond parameters and any complex crystal can be decomposed into different kinds of pseudo binary crystal. These binary crystals are related to each other and every binary crystal includes only one type bond but the properties of those pseudo binary crystal are different from those of real binary crystals, although chemical bond parameters can be calculated in a similar way. During the last decades, few article and reviews were devoted for the study of physical chemical properties of RBO_4 compounds having monazite and zircon structure. Therefore intense interest has been paid on the physical and chemical properties of these materials because of its potential applications. Van Uitert et al. (1977) have shown that the average thermal expansion coefficient of a large variety of cubic and close packed materials depend upon the confidence of preferred orbital extension and site symmetry as well as melting point (mp in ^{0}C). The expression is given below

$$\alpha_L M_p \approx 0.016 \quad \text{Close packed structure-} \tag{7}$$

$$\alpha_L M_p \approx 0.027 \quad \text{Rectilinear arrays} \tag{8}$$

$$\alpha_L M_p \approx 0.020 \quad \text{Rutile structure of 4f rare earth oxide} \tag{9}$$

$$\alpha_L M_p \approx 0.021 \quad \text{Tetrahedral structure} \tag{10}$$

They have shown in equation (7) that the product $\alpha_L M_p$ tend to be constant for a given structure. The product $\alpha_L M_p \approx 0.016$ is the characteristic of materials that have closed-packed structure, be they anion close pack, cation close pack or close pack metals. For rectilinear anion or anion + cation arrays tend to have product $\alpha_L M_p \approx 0.027$ .The decrease in rectilinearity of the array as well as nonmatching orbital extension can lead to a decrease in thermal expansion in case of rutile structure. For tetrahedral semiconductors (group IV, III-V and II-VI) the product of $\alpha_L M_p \approx 0.021$ which is between rectilinear array and rutile structure due to the consideration of ionicity and bond length. According to Neumann (1983, 1980) lattice thermal expansion varies inversely on the melting temperature T_m for binary tetrahedral semiconductors, lattice thermal expansion way be expressed as

$$\alpha_L = \frac{A}{T_m} - B(d - d_0)^3 \tag{11}$$

where A and Tm is constant, Tm is the melting temperature in kelvin and d is the nearest neighbor distance (in A^0). The value of A=0.021 for all tetrahedral coordinated compounds (in A^0) as estimated from a hard sphere model based on diamond structure. The value of d_o is equal to the nearest neighbor distance of diamond, that is $d_o=1.545 A^0$, The value of B are equal to 17.0, 3.3,10.0,16.1 and 4.2 ($10^{-6} K^{-1} A^0 3$) respectively for A^{IV} , $A^{II}B^{VI}$, $A^{III}B^V$, $A^{II}B^{IV}C_2^V$ and $A^I B^{III} C_2^{VI}$ semiconductors and d_o are respectively 1.549, 1.382,1.561,1.573 and 1.330 A^0. Kumar et al. (2001, 2002) has calculated the linear thermal expansion coefficient of tetrahedral coordinated $A^{II}B^{VI}$ and $A^{III}B^V$ semiconductors and chalcopyrite structure solids. He proposed the following expression for linear thermal expansion coefficient in terms of plasmon energy of II-VI and III-V compounds.

$$\alpha_L = \frac{0.021}{T_m} - B\left[15.30(\hbar\omega_p)^{-2/3} - d_0\right]^3 \tag{12}$$

where the bond length of $A^{II}B^{VI}$ semiconductors, $d = 15.30(\hbar\omega_p)^{-2/3}$ (d in A^0 and $\hbar\omega_p$ in eV). For a compounds, the plasmon energy in expressed as $\hbar\omega_p = 28.8\sqrt{\dfrac{Z\rho}{M}}$

where Z in the effective no. of valence electrons talking part in plasma oscillation, ρ is the specific gravity and M is the molecular weight, T_m is the melting temperature. The value of B are equal to 3.3 and 10.0 (($10^{-6} K^{-1} A^0 3$) and d_0 are

respectively 1.382 and 1.561 A⁰ respectively. For ternary chalcopyrite of $A^{II}B^{IV}C_2^{V}$ and $A^{I}B^{III}C_2^{V}$ semiconductors which is considered as similar to those of $A^{III}B^{V}$ and $A^{II}B^{IV}$ semiconductors. The value of d has taken the mean value of bond length, that is $d = \dfrac{d_{A-C} + d_{B-C}}{2}$ where d_{A-C} and d_{B-C} are the individual bond length of $A-C$ and $B-C$ bond in the compounds and the value of d is calculated by the expression $d = 15.30(\hbar\omega_p)^{-2/3}$. The value of B are 16.1 and 4.2 (10^{-6}K⁻¹A⁰3) respectively and do are 1.573 and 1.330 A⁰ respectively for $A^{II}B^{IV}C V_2$ and $A^{I}B^{III}C_2^{V}$ semiconductors respectively. Omar et al. (2007) Omar et al. (2007) developed a relation based on the valence electron of the lattice of solids for the calculation of lattice thermal expansion coefficient (α_L) of normal tetrahedral semiconductors. According to them lattice thermal expansion of these semiconductors may be expressed as

$$\alpha_L = (\frac{0.021}{T_m}) - \left[0.0256\{m(C-A)+n(C-B)\} - \{(B-A)+[B-(B-A)]\}\frac{1}{q} \right]^{-1/3.5} (d-1.545)]^3 \ (13)$$

where A, B and C are the number of valence electrons in the first, second and third atoms for a certain compound groups, q is the number of cations or anions in the compounds and m, n are the number of the first and second cation lattices respectively. Verma et al. (2009,2011) calculated lattice thermal expansion coefficient of zinc blende solids in terms of ionic charge. Ionic charge of materials is associated with the valence electrons. The change in crystallographic environment of an atom is related to core electrons via the valence electrons. For II-VI & III-V semiconductors the lattice thermal expansion coefficient may be expressed as

$$\text{Lattice thermal expansion } \alpha_L = \{\frac{K}{\sqrt{(T_m Z_1 Z_2)}}\} - \sqrt{d} \quad (14)$$

where T_m is the melting temperature, d is the nearest neighbor distance in A⁰, Z_1 and Z_2 are ionic charges of cation and anion respectively, and K is a constant. The value of constant K for zinc blende type crystal structure in 775. For chalcopyrite type crystals, lattice thermal expansion may be expressed as lattice thermal expansion

$$\alpha_L = \{\frac{A}{4\sqrt{(T_m Z_A Z_B Z_C)}}\} - d^{2.5} \quad (15)$$

where A in constant, T_m in the melting temperature, d is the nearest neighbor distance in A⁰ and Z_A, Z_B and Z_C are ionic charge of A, B and C respectively. The value of A in 235. A.A. Khan (1974) has established lattice thermal expansion coefficient relation with radius ratio ($\dfrac{r_+}{r_-}$) of with type crystal. The expansion in give bellow

$$\alpha = 113.4 - 290.9(\frac{r_+}{r_-}) + 379.8(\frac{r_+}{r_-})^2 - 166.6(\frac{r_+}{r_-})^3 \quad (16)$$

The effective size of an ion may different slightly for different members of isomorphous alkali halides. The difference Δx between the observed and calculated bond length may reflect the influence of r_+ and r_- calculated. In the NaCl structure there is only one type of bond between octahedral coordinated cations and anions and the difference Δx. The expression between linear coefficient of expansion and Δx may be expressed as

$$\alpha = 42.6 + 135.9\Delta x \quad (17)$$

The correlation coefficient between α and Δx is very high so equation in highly useful. According to megaw's work (1968, 1971) the thermal expansion of a crystal structure can be expressed empirically as the sum of bond length

expansion and titlting effect. Bond length expansion coefficient are function Pauling bond strength ($\frac{Z}{P}$) where Z is cation charge and P is cation coordination. The empirical relationship is as follows

$$\alpha \propto \frac{P^2}{Z^2} \qquad (18)$$

where structures are linked by their corners only, tilting is considered. These are cases where polyhedral are octahedral or tetrahedral, hard enough for change of shape and when linked three dimensionally. In such case tilt angle can change independently with temperature and oscillations of the angle characterize one lattice mode. If there is more than one 'soft parameter e.g. second independent tilt about another axis ,then both tilt change continuously and a stage is reached there is a discontinuous jump and will have lower energy. Feng et al. (2013) has calculated linear thermal coefficient of expansion using empirical method. The thermal expansion characterizes the anharmonicity of crystal structure at finite temperature. In theoretically thermal expansion coefficient can be calculated from the difference of two specific heats:

$$C_P(T) - C_V(T) = \alpha^2 V(T) T B_0(T) \qquad (19)$$

where C_P and C_V are isothermal and isobaric specific heats respectively. α refers to volumetric thermal expansion coefficient; $V(T)$ is the equilibrium, cell volume at temperature T. The bulk modulus $B_0(T)$ can be obtained from either elastic constants or the empirical fitting of equation of state. The temperature dependence of isobaric heat capacity C_P for each BPO$_4$ compound was measured by Popa and Konings (2006) .The expression for $C_P(T)$ for high T is given below

$$C_P / JK^{-1}mol^{-1} = 133.2371 + 12.7933.10^{-3}(\frac{T}{K}) - 3.0972.10^6(\frac{T}{K})^2 \qquad (21)$$

and expression for $C_V(T)$ is given below

$$CV(T) = 9nN_A K_B (\frac{T}{\Theta_D})^3 \int_0^{\Theta_D} \frac{x^4 e_x}{(e^x - 1)^2} dx \qquad (22)$$

where n is the total number of atoms per BPO$_4$ compound, N_A and K_B are Avogadro's number and Boltzmann constants respectively. Yusuku Tsuru et al. (2010) investigated the relationship between thermal expansion coefficient with cohesive energy of metal and ceramics using least square analysis. They found that linear thermal expansion coefficient α_L is inversely proportional to the cohesive energy E_C .The relation is as follows

$$\alpha_L E_{COH} = C \qquad (23)$$

where C is a constant and C values were determined from the experimental values of cohesive energies and the linear thermal expansion coefficient to be 48.14(0.720, 46.7390.68), 57.54(0.62) and 65.04(0.54)[10^{-6}eV/K] at 295,500,1000 and 1200K respectively. The cohesive energy is calculated by the ab-initio method. The calculated cohesive energy per atom is defined as

$$E_{coh} = (\sum E_{atom} - E_{total}) / N \qquad (24)$$

where E_{coh} is the cohesive energy, E_{total} is the total energy of the material calculated by the BFGS geometry optimization method. E$_{atom}$ is the total energy of a neutral atom and N is the number of atoms in the material. Kistaiah et al. (1989, 1981) determined lattice parameter as a function of temperature from the analysis of X-ray diffraction. From these results he evaluated thermal expansion AgGaS$_2$.The variation of all structural parameter with temperature was described by the polynomial of second order in temperature,

$Q = A + BT + CT^2$, the equations obtained are

$$a(nm) = 0.57488(\pm 0.00013) + 5.6172(\pm 0.0520) \times 10^{-7}T + 5.8582(\pm 0.0477) \times 10^{-9}T^2 \qquad (25)$$

$$c(nm) = 1.03219(\pm 0.00022) - 5.8416(\pm 0.0870) \times 10^{-6}T - 5.6654(\pm 0..799) \times 10^{-9}T^2 \qquad (26)$$

The thermal expansion coefficient α_Q of a given crystal parameter Q can be determined using the relation as

$$\alpha_Q(T) = \frac{1}{Q_0}\frac{dQ}{dT} \qquad (27)$$

where Q_0 is the value of parameter Q at room temperature. $\ln Q_T$ can be expressed in terms of parabolic curve

$$\ln Q_T = A + BT + CT^2 \qquad (28)$$ where T is the temperature in degree Celsius.

Differentiation of equation (4) gives the coefficient of expansion $\alpha_Q(T) = \frac{d}{dT}(\ln P_T) = B + 2CT$ (29),

So

$$\alpha_a(T) = 1.051 \times 10^{-6} + 2.016 \times 10^{-8}T \qquad (30)$$

$$\alpha_c(T) = 5.616 \times 10^{-6} + 1.116 \times 10^{-8}T \qquad (31)$$

Hazen et al. (1977) has proposed an empirical relation between bond expansion and bonding variables in oxygen based minerals are

$$\bar{\alpha} = 32.9(0.75 - \frac{Z}{P}) \times 10^{-6}C^{-1} \qquad (32)$$

where Z is the cation charge, P is the cation coordination number, $\bar{\alpha}$ is the mean coefficient of linear expansion from 23^0c to 1000^0c. Using this empirical relation it is possible to predict bond expansion for other cation polyhedra and thus provide a basis for estimating structural variation with temperature and pressure for many oxygen based minerals. Zhang et al. (2008) has found the thermal expansion property of inorganic crystal by studying the lattice energy and the structural parameter. They proposed a semi empirical method for evaluation of linear expansion coefficient from lattice energy for both simple and complex crystals. For A^NB^{8-N} type crystal, the relation between the linear expansion coefficient and the parameter γ is fitted as $\alpha = -3.1685 + 0.8376\gamma(10^{-6}K)$ (33)

where the parameter γ is inversely proportional to the lattice energy of monocharge and one chemical bond of a crystal as

$$\gamma = \frac{KZ_A N_{CA}}{U(AB)\Delta_A}(10^{-6}/K) \qquad (34)$$

where K is Boltzmann constants, Z_A, N_{CA} are the number of valence and coordination number of cation A in the chemical bond respectively. $U(AB)$ is the lattice energy of the crystal in KJ/mol. Δ_A is a correction factor which is given in Table 1.

Table1.The correction parameter of the position of cation in chemical periodic table

Row	1	2	3	4	5	6
Δ_A	1	1	1.23	1.45	1.56	1.74

(1)   Calculation of linear expansion coefficient for $A_m B_n$ type crystal is

$$\gamma_{mn} = \frac{KZ_A N_{CA}}{U(A_m B_n)\Delta_A}\,\beta_{mn}(10^{-6}/k) \qquad (4.35)$$

where $\beta_{mn} = \dfrac{m(m+n)}{2n}$ and lattice energy $U(A_m B_n) = U(AB)_i^I\,\beta_{nm}$

where $U(AB)^I$ is the lattice energy of $A^N B^{8-N}$ type of crystal and

$$U(A_m B_n)^I = \frac{2540(m+n)m(Z_A)^2}{2nd}(1-\frac{0.4}{d})f_i \qquad (4.36)$$

where Z_A is the valence of A ion, f_i is the fractional iconicity of the chemical bond.

(2)   Calculation of linear expansion coefficient for complex crystals

The complex crystal is decomposed into sum of different binary crystals like $A_{mi}^i B_{nj}^j$ and linear expansion coefficient of complex crystal is written as

$$\alpha_{mn}^\mu = -3.1685 + 0.8376\gamma_{mn}^\mu \qquad (4.37)$$

where parameter γ is

$$\gamma_{mn}^\mu = \frac{KZ_A^\mu N_{CA}^\mu}{U(mn)^\mu \Delta_A^\mu}\,\beta_{mn}^\mu$$

where all the symbols have been described in equation but it is only for binary component and lattice energy of complex crystal is

$$U = \sum_\mu U(mn)^\mu \qquad (4.38)$$

where $U(mn)^\mu = U(mn)_i^\mu + U(mn)_c^\mu$

RBO$_4$Crystals have definite structure which is related to bond energy. This bond energy is responsible for the formation of structure of solids. The bond energy comes from a perfect sharing of electrons of R-O and B-O bond which could be related to the electronegativity of all the atoms of the crystal. The R-O and B-O bonding is a consequence of electrostatic interaction between nuclei and electrons obeying Schrodinger equation. Ionic bonding is caused by the electrostatic attraction positively and negatively charged ions. The ions are produced by a transfer of electrons between two atoms with a large difference of electronegativity. In the RBO$_4$ compounds the bonding characteristics of group atom is considered and then electronegativity of anionic polyhedra is calculated. The ionic contribution of R-O and B-O bond is reflected in the non-directional behaviour and is estimated from electronegativety of R-G (BO$_4$) anionic polyhedra. The group electronegativity is calculated by

$$\chi_G = \frac{N_G}{\sum \dfrac{u}{x}} \qquad (39)$$

where N_G is the number of atoms in the group formula. u is the number of atoms in the species formula, x is the electronegativity of the atom. Group electronegativity have been derived by both experimental and computational method.

In RBO_4 compounds the directional character of R-O and B-O bond could be related to the average principal quantum number of all constituent atoms of compound. The directional character of the R-O and B-O bond formed by atoms delineates the covalent contribution. The principal quantum number n of the valence shall of an atom is a measure of the directional character of bonds formed by the atoms in the compound. As n increases the atomic orbital's involved in the bond formation and hence the bond themselves gradually lose their directional properties. Therefore we introduce a suitable average quantum number $\bar{n}$ to the bond formed between unlike atoms. In this case average principal quantum number ($\bar{n}$) is expressed as

$$\bar{n} = \frac{\sum c_i n_i}{\sum c_i} \qquad (40)$$

where n_i the principal quantum is number of the valence electrons of atom of kind i and c_i is the number per formula unit of atom of this kind. For example in $LuPO_4$ compounds, the principal quantum number for La,P,O is 6,3,2 respectively and the number of atom per formula unit is 4,therefore ,using equation(40) the average quantum number of LuPO4 compound is calculated as

$$\bar{n} = \frac{\sum c_i n_i}{\sum c_i} = \frac{4*6+4*3+4*2}{12} = 3.666 \text{ and the elecronegativity is also calculated by the formula } \chi_G = \frac{N_G}{\sum \dfrac{v}{x}}$$

(41)

where N_G is the number of atoms in the group formula, v is the number of atoms in the species formula x is the electronegativity of the atom constituting the compound. For example electronegativity of LuPO4 is calculated as below

$$x_{PO_4} = \frac{5}{\dfrac{1}{x_P}+\dfrac{4}{x_0}} = \frac{5}{\dfrac{1}{11\cdot 2}+\dfrac{4}{48\cdot 4}} = 29.0815$$

$$x_{LuPO_4} = \frac{6}{\dfrac{1}{x_{Lu}}+\dfrac{4}{x_{PO_4}}} = \frac{6}{\dfrac{1}{52.9}+\dfrac{1}{29.085}} = 112.5922$$

Table 1. Some important physical properties of rare-earth elements

Name	Symbol	At. No.	Electron Configuration (Core =Xe^{54})	Ionic* radii (Å)	Electro Negativity Ref.( )	Valence electron	Principal Quantum number
Lanthanum	La	57	$5d^1 6s^2$	1.160	1.13	3	5,6
Cerium	Ce	58	$4f^1 5d^1 6s^2$	1.143	1.89	4	4,5,6
Praseodymium	Pr	59	$4f^3 6s^2$	1.126	2.92	5	4,5,6

Neodymium	Nd	60	$4f^46s^2$	1.109	4.28	6	4,6
Promethium	Pm	61	$4f^56s^2$	1.093	6.00	6	4,6
Samarium	Sm	62	$4f^66s^2$	1.079	8.13	8	4,6
Europium	Eu	63	$4f^76s^2$	1.066	10.71	9	4,6
Gadolinium	Gd	64	$4f^75d^16s^2$	1.053	13.8	10	4,5,6
Terbium	Tb	65	$4f^96s^2$	1.040	17.4	11	3,4
Dysprosium	Dy	66	$4f^{10}6s^2$	1.027	21.6	12	4,5
Holmium	Ho	67	$4f^{11}6s^2$	1.015	26.4	13	4,6
Erbium	Er	68	$4f^{12}6s^2$	1.004	31.9	14	4,6
Thulium	Tm	69	$4f^{13}6s^2$	0.994	38.1	15	4,6
Ytterbium	Yb	70	$4f^{14}6s^2$	0.985	45.1	16	4,6
Lutetium	Lu	71	$4f^{14}5d^16s^2$	0.977	52.9	17	4,6
Scandium	Sc	21	$4d^15s^2$	0.870	1.18	3	4,5
Yttrium	Y	39	$3d^14s^2$	1.019	0.868	3	3,4
Phosphorus	P	15	$3s^23p^3$	1.95	11.2	5	3
Arsenic	As	33	$3d^{10}4s^24p^3$	1.85	11.1	5	4
Oxygen	O	8	$2s^22p^4$	1.52	48.4	6	2

Electro negativities of Lanthanides, Sc and Y, taken from Dulal C. Ghosh et.al Theoretical Chem. (2009) 124,295-301

We introduce another parameter as Plasmon energy of RBO_4 compounds of monazite and zircon structure for the calculation of lattice thermal expansion coefficient of the compounds. The Plasmon energy is evaluated by the formula given below

$$\hbar\omega_p = 28.8\sqrt{\frac{n\sigma}{w}} \qquad (42)$$

where n is the no. of valence electrons taking part in plasma oscillation, σ is the specific gravity and w is the molecular weight. As lattice anharmonicity affects the attractive force between valence electron and nucleus and also the distance between nucleus and valence electron i. e. principal quantum number, therefore, in order to estimate the lattice anharmonicity, principal quantum number as well as electronegativity has been considered in this research work. We determine average principal quantum number from principal quantum number using equation (40) and also group electronegativity from equation (41) from electronegativity of each atom of the RBO_4 compounds having monazite and zircon structure. We find the ratio of average principal quantum number and group electronegativity and correlated with lattice thermal expansion coefficient by linear regressional methods and the equation obtained in this method are as follows

$$\alpha(10-6/K) = m_1\left(\frac{\bar{n}}{\chi_G}\right) + m2 \qquad (43)\ RBO_4(\text{R=lanthanides; B=P, As}) \text{ compounds with} \quad \text{zircon structure}$$

$$\alpha(10-6/K) = m3\left(\frac{\bar{n}}{\chi_G}\right) + m4 \qquad (44)\ RBO_4(\text{R=lanthanides; B=P, As}) \text{ compounds with} \quad \text{zircon structure}$$

we plotted a graph between the ratio of average principal quantum number and group electronegativity given in fig.1 and fig.2. Using these equations, the lattice thermal expansion coefficient is estimated and the estimated values are given in

table 1 and 2. The percentage average deviation is calculated. We also empirically proposed another linear relation between linear thermal expansion coefficient with Plasmon energy of RBO_4 compound with zircon and monazite structure. The plasmon energy of RBO_4 compound with zircon and monazite structure is calculated by the equation (42) and A graph is plotted between Plasmon energy and linear thermal coefficient of expansion of RBO_4 compounds having monazite and zircon structure which is given in fig.3 and fig.4 A linear proposed relation between Plasmon energy and linear thermal expansion coefficient is expressed below:

$$\alpha(10-6/K) = m5(\hbar\omega_p) + m6$$ (45) RBO_4(R=lanthanides; B=P, As) compounds with   monazite structure

$$\alpha(10-6/K) = m7(\hbar\omega_p) + m8$$ (46) RBO_4(R=lanthanides; B=P, As) compounds with   monazite structure

where m1, m2, m3, m4, m5, m6, m7, m8 are constants and their numerical values are given in the table 1(a)

Table1 (a). Values of numerical constants.

Crystal	Structure	m1	m2	Structure	m 5	m6
RPO_4	Monazite	0.5928	7.481	Zircon	0.4197	-4.3735
$RAsO_4$	Monazite	0.3946	7.5125	Zircon	0.4819	-5.3317
		m3	m4		m7	m8
RPO_4	Monazite	1.8478	5.3735	Zircon	0.5928	7.481
$RAsO_4$	Monazite	1.6546	5.6831	Zircon	0.3946	7.5125

Table 2. Lattice thermal expansion coefficient (LTEC) of RBO_4 crystals within monazite structure

S.No	Crystal	Group Electronegativity $\chi_G = \dfrac{N_G}{\sum \dfrac{v}{x}}$ Eqn.(41)	Average Principal quantum no. $\bar{n}$ Eqn.(40)	$\dfrac{\bar{n}}{\chi_G}$	α (cal) Eq.(43)	α Ref.[53]
1	$LaPO_4$	3	6.80	0.561	7.78	7.81404
2	$CePO_4$	3.33	5.05	0.344	7.71	7.68513
3	$PrPO_4$	3.66	65.31	0.230	7.66	7.61752
4	$NdPO_4$	3.66	74.36	0.163	7.61	7.57809
5	$SmPO_4$	3.66	83.02	0.096	7.54	7.53801
6	$EuPO_4$	3.66	91.27	0.078	7.51	7.52734
7	$GdPO_4$	3.66	98.95	0.065	7.47	7.51970
8	$LaAsO_4$	3.66	106.08	0.561	7.72	7.73423
9	$CeAsO_4$	3.66	112.59	0.344	7.68	7.64842
10	$NdAsO_4$	3	6.803	0.163	7.56	7.57717

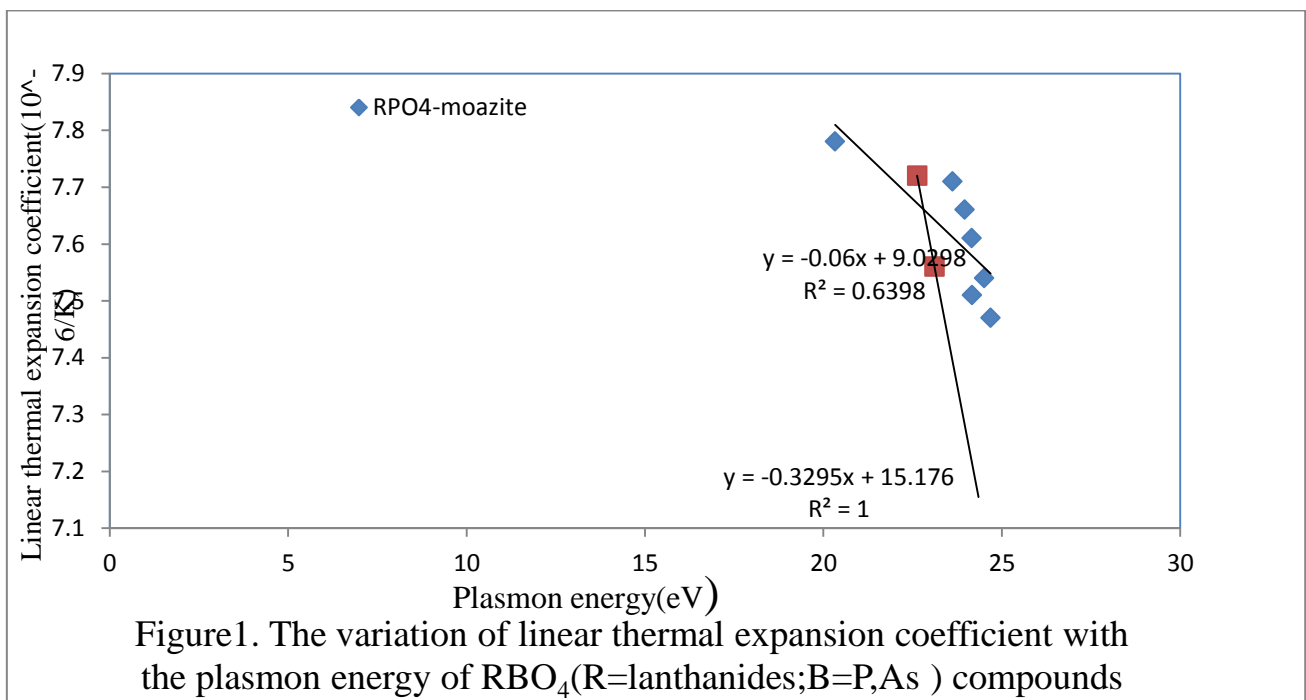Table 3. Lattice thermal expansion coefficient (LTEC) of RBO_4 crystals within zircon structure

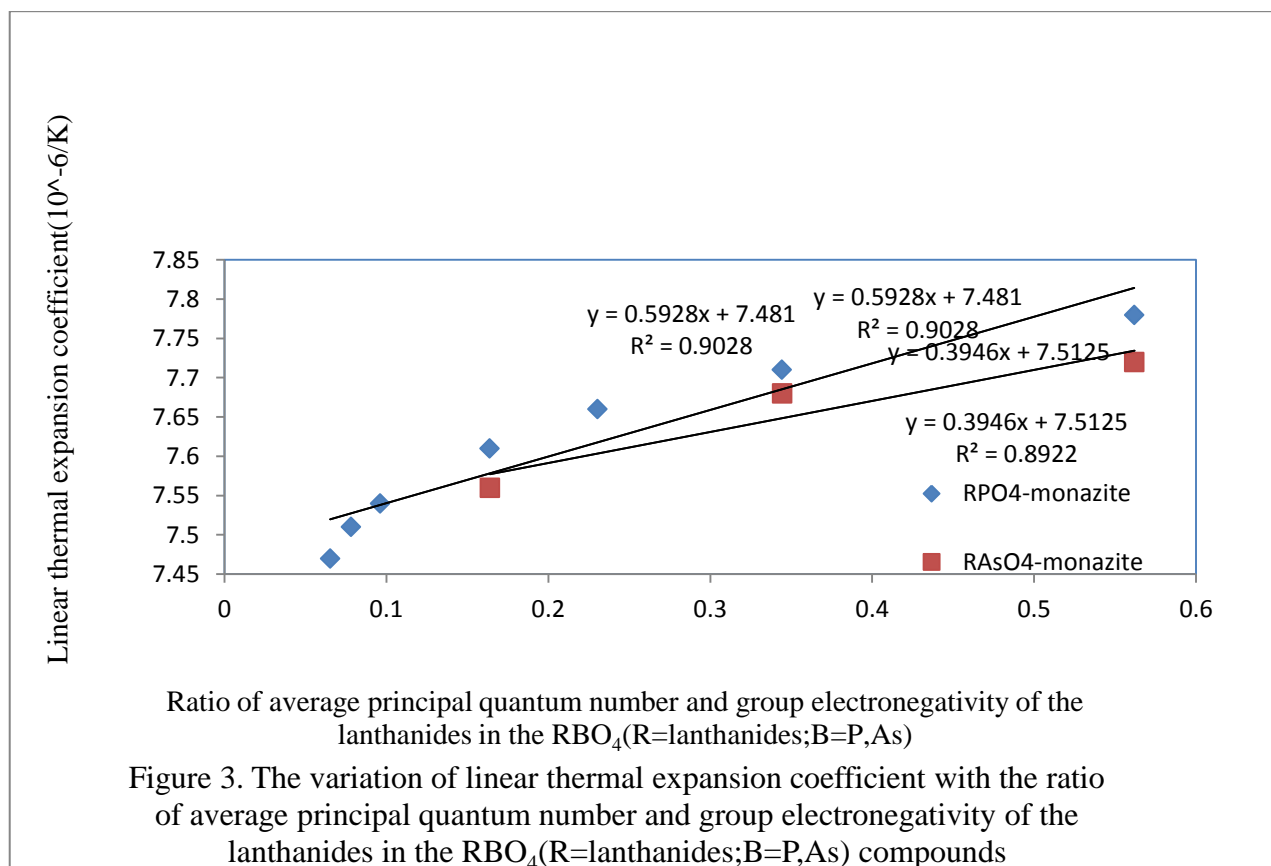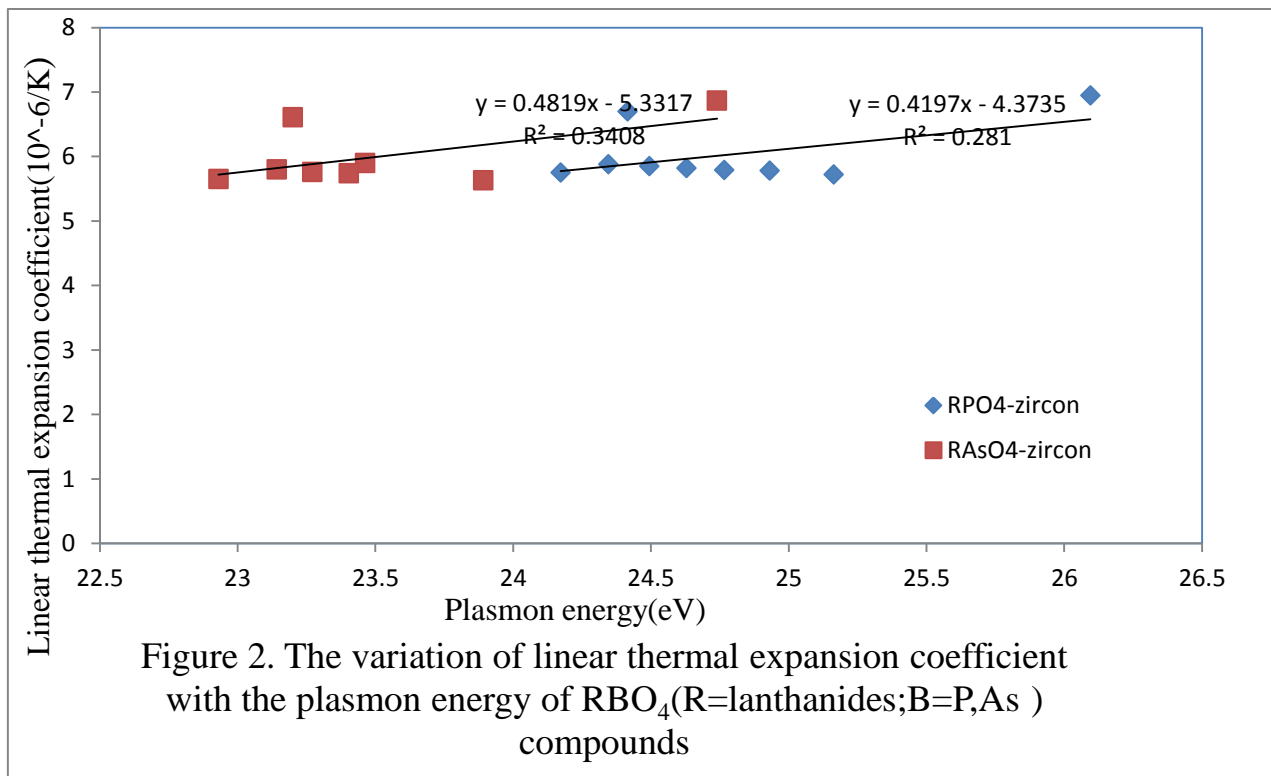| S.No	Crystal	Group Electronegativity $\chi_G = \dfrac{N_G}{\sum \frac{v}{x}}$ Eqn.(41)	Average Principal quantum no. $\bar{n}$ Eqn.(40)	$\dfrac{\bar{n}}{\chi_G}$	α (cal) Eq.(44)	α Ref.[53]
1	$ScPO_4$	3	6.80	0.441	6.95	6.555
2	YPO_4	3.33	5.05	0.659	6.7	6.958
3	$TbPO_4$	3.66	65.31	0.056	5.88	5.844
4	$DyPO_4$	3.66	74.36	0.049	5.85	5.832
5	$HoPO_4$	3.66	83.02	0.044	5.82	5.822
6	$ErPO_4$	3.66	91.27	0.04	5.79	5.815
7	$TmPO_4$	3.66	98.95	0.037	5.78	5.809
8	$YbPO_4$	3.66	106.08	0.035	5.75	5.804
9	$LuPO_4$	3.66	112.59	0.033	5.72	5.801
10	$ScAsO_4$	3	6.803	6.87	6.413	6.87
11	$YAsO_4$	3.666	5.056	6.61	6.883	6.61
12	$SmAsO_4$	4	38.12	5.9	5.857	5.9
13	$TbAsO_4$	4	65.2	5.8	5.785	5.8
14	$DyAsO_4$	4	74.22	5.76	5.772	5.76
15	$HoAsO_4$	4	83.03	5.74	5.763	5.74
16	$YbAsO_4$	4	105.1	5.65	5.746	5.65
17	$LuAsO_4$	4	112.3	5.63	5.742	5.63

Table 4. Lattice thermal expansion coefficient (LTEC) of RBO_4 crystals within monazite structure

S.No.	Crystal	Mol.Wt. (M)	Density (ρ)	Plasmon Energy(eV) $(\hbar\omega_p)$ Eq.(42)	α (cal) Eq. (45)	α Ref.[53]
1	$LaPO_4$	251.89	3.92	20.32	7.78	7.809
2	$CePO_4$	235.07	4.94	23.62	7.71	7.611
3	$Pr\,PO_4$	235.879	5.1	23.96	7.66	7.591
4	$NdPO_4$	239.213	5.26	24.16	7.61	7.579
5	$SmPO_4$	245.3	5.55	24.51	7.54	7.558
6	$EuPO_4$	246.93	5.43	24.16	7.51	7.579
7	$GdPO_4$	252.22	5.79	24.68	7.47	7.547
8	$LaAsO_4$	277.82	5.36	22.63	7.72	7.725
9	$CeAsO_4$	279.03	6.23	24.34		7.160
10	$NdAsO_4$	283.16	5.7	23.11	7.56	7.565

Table 5. Lattice thermal expansion coefficient (LTEC) of RBO_4 crystals within zircon structure

S.No.	Crystal	Mol.Wt. (M)	Density (ρ)	Plasmon Energy(eV) $(\hbar\omega_p)_{Eqn.(42)}$	α (cal) Eqn.(46)	α Ref.[53]
1	$ScPO_4$	139.93	3.59	26.1	6.95	7.220
2	YPO_4	183.88	4.13	24.42	6.7	6.413
3	$TbPO_4$	253.9	5.67	24.35	5.88	6.379
4	$DyPO_4$	257.47	5.82	24.49	5.85	6.450
5	$HoPO_4$	259.9	5.94	24.63	5.82	6.515
6	$ErPO_4$	262.23	6.06	24.77	5.79	6.581
7	$TmPO_4$	263.9	6.18	24.93	5.78	6.660
8	$YbPO_4$	268.01	5.9	24.17	5.75	6.295
9	$LuPO_4$	269.94	6.44	25.16	5.72	6.772
10	$ScAsO_4$	183.87	4.24	24.74	6.87	5.992
11	$YAsO_4$	227.82	4.62	23.2	6.61	5.347
12	$SmAsO_4$	289.28	6	23.46	5.9	5.458
13	$TbAsO_4$	297.84	6.01	23.14	5.8	5.323
14	$DyAsO_4$	301.42	6.15	23.27	5.76	5.377
15	$HoAsO_4$	303.85	6.27	23.4	5.74	5.432
16	$YbAsO_4$	311.96	6.18	22.93	5.65	5.234
17	$LuAsO_4$	313.88	6.75	23.89	5.63	5.637

Figure1. The variation of linear thermal expansion coefficient with the plasmon energy of RBO_4(R=lanthanides;B=P,As) compounds

Figure 2. The variation of linear thermal expansion coefficient with the plasmon energy of RBO_4(R=lanthanides;B=P,As) compounds

Ratio of average principal quantum number and group electronegativity of the lanthanides in the RBO_4(R=lanthanides;B=P,As)

Figure 3. The variation of linear thermal expansion coefficient with the ratio of average principal quantum number and group electronegativity of the lanthanides in the RBO_4(R=lanthanides;B=P,As) compounds

Figure 4. The variation of linear thermal expansion coefficient with the ratio of average principal quantum number and group electronegativity of the lanthanides in the RBO_4(R=lanthanides;B=P,As) compounds

Result and discussion

There is a very good linear relation between linear thermal expansion coefficient and ratio of average principal quantum number with the group electronegativity of RBO_4 compounds having monazite and zircon structure. It is revealed that thermal expansion has direct correlation with average principal quantum number as well as group electronegativity. The principal quantum number which is the distance between nucleus and outermost valence electron and electronegativity is the attractive power of an atom in forming the bond, which ultimately affects the amplitude of vibration and anharmonicity, ultimately affects the linear thermal coefficient of expansion. The coefficient of variation (CV) or relative standard deviation (RSD) is found out by the formula given below

$$RSD = \frac{s*100}{\bar{x}} \qquad (69)$$

where RSD is the relative standard deviation , s is the standard deviation and $\bar{x}$ is the mean of the data. In case of the lattice thermal coefficient of expansion is estimated by equation (43) and equation (44), the value of coefficient of variation is 5.08 and value of coefficient of variation of calculated values is 6.53 for RBO_4 compounds of zircon structure for reported values (53). For RBO_4 compounds of monazite structure the coefficient of variation of calculated value is 7.12 using equation (45) and equation (46) and for reported values is 8.32.

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