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STUDY ON ELASTIC, THERMODYNAMIC, AND OPTICAL PROPERTIES OF $Y_2TI_2O_7$ PYROCHLORE DETERMINED BY A SEMI-EMPIRICAL METHOD AT 300 K

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AUTHORS' CONTRIBUTIONS

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ABSTRACT

First-ever a straightforward semi-empirical method is employed to compute elastic parameters (elastic wave velocities, elastic moduli, Debye temperature), thermodynamic parameters (molar heat capacities at constant volume and pressure, Debye temperature, electronic contribution to molar heat capacity, lattice potential energy), and optical parameters (refractive index, optical energy bandgap, dielectric, electronic and ionic polarizabilities) for pyrochlore-type yttrium-titanate ($Y_2Ti_2O_7$) at 300 K. The results of our calculations are compared with the existing experimentally and theoretically determined data. The quite satisfactory agreement between the two validates the approach adopted. The value of molar heat capacity at constant volume computed based on the Einstein theory for pyrochlore is accordant with theoretically predicted value from the law of Dulong and Petit while the Debye theory fails to estimate the consistent value at 300 K. It appeared that electronic molar heat capacity contributes ~ 0.5 % to the total molar heat capacity and the electronic and lattice molar heat capacities are comparable at 14.5 K. The applicability of the oxide additivity rule is examined and found successful in predicting the dielectric, electronic, ionic polarizabilities and lattice potential energy of the complex oxide composition. The semi-empirical method used in the present investigation is found quite simple as compared to previous cumbersome evaluation methods.

Keywords: Pyrochlore; elastic parameters; thermodynamic parameters; optical parameters; oxide additivity rule.

1. INTRODUCTION

In the pyrochlore family, yttrium titanate ($Y_2Ti_2O_7$), is referred to as one of the salient members as it exhibits superior physical properties. $Y_2Ti_2O_7$ and its isostructural materials possess other important characteristics such as optical nonlinearity, high radiation tolerance, good mechanical strength (due to

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the short interatomic distances of Y-O (2.488 Å) and Ti-O (1.959 Å) bonds), chemical stability, low thermal conductivity, ionic conductivity, high optical bandgap, high up-conversion luminescence intensity in the visible wavelength [1,2]. Thus, these materials found a wide range of applications in various fields such as electrolytes in solid-oxide fuel cells, photocatalysts, high permittivity dielectrics, host material for optical emission, thermal barrier coating material for safe disposal of actinide containing nuclear waste, a potential inert matrix for transmutation, as a buffer layer on superconductor substrates, etc. [1-3]. $Y_2Ti_2O_7$ has a high melting temperature (T_M ~ 1873 K (experimentally determined value) [2], T_M = 2160 K ± 300 K (theoretically calculated value) [4]), high refractive index ($2.0 < \eta < 2.2$) [5], and ability to accept transition metal dopants in its structure including lanthanides and actinides make them a suitable candidate for ceramic pigments [2].

He et al. [6] have systematically investigated mechanical properties of $Y_2Ti_2O_7$ polycrystalline ceramic by employing different experimental methods, while Luan et al. [7] have performed elastic properties study on single-crystalline $Y_2Ti_2O_7$. On the other hand, theoretically predicted G_0 value using a generalized gradient approximation (GGA-92) is found to be 57 GPa only [4]. Scott et al. [8] have reported $B_0 = 204 \pm 3$ GPa determined from high-pressure synchrotron X-ray diffraction study, this value is quite consistent with the reported value of $B_0 = 205 \pm 4$ GPa by Panero et al. [9]. The B_0 value for a single crystal of $Y_2Ti_2O_7$ is found to be 243.3 ± 5.2 GPa [1]. The predicted values of B_0 by employing density functional theory based on different approximations are found in the range of 181 GPa – 209 GPa [10]. Besides, Turki et al. [4] have estimated E_0 = 156 GPa based on theoretical calculations. The E_0 value for a single crystal of $Y_2Ti_2O_7$ is found to be 321.1 ± 6.9 GPa [1]. Interestingly, the estimated E_0 value for $Y_2Ti_2O_7$ monofilaments was 345 GPa [6] but experimentally such a high value could not be proved. Johnson et al. [2] have reported Debye characteristic temperature (θ_0) of 970 K and molar heat capacity at constant pressure (C_p) ~ 210 J/mol.K at T = 300 K. Terki et al. [4] have reported theoretically estimated value θ_0 = 784.1 K and C_v ~ 210 J/mol.K at 300 K. The linear thermal expansion coefficient (α_a) at 300 K is reported to be $4.8 \times 10^{-6}\ K^{-1}$ [3] and $10.6 \times 10^{-6}\ K^{-1}$ by Farmer et al. [11] while Terki et al. [4] have reported an average $\alpha_a = 9.1 \times 10^{-6}\ K^{-1}$ and volume expansion coefficient (α_v) = $27.3 \times 10^{-6}\ K^{-1}$ calculated from 300 K to 1273 K data. The elastic parameters computed based on a first-principles calculation by the two different groups demonstrate huge differences. According to Pruneda and Artacho [12], the E_0 = 447 GPa, G_0 = 190 GPa and B_0 = 229 GPa. On the other hand, the estimated Hill's average modal values based on Voigt and Reuss approximation to random polycrystalline aggregates for $Y_2Ti_2O_7$ by Jiang et al. [10] are E_0 = 221.3 GPa, G_0 = 85.2 GPa and B_0 = 183.5 GPa and σ_0 = 0.30. Very recently, more realistic values of various elastic parameters have been reported in [13] based on density functional theory using local-density approximation (LDA) and GGA. Shimamura et al. [14] have carried out a systematic experimental investigation on a set of Zr-pyrochlores ($M_2Zr_2O_7$, where M = Sm, Y, La, Dy, Gd, and Nd) and found a general range of E_0 ~ 225 GPa to 275 GPa, G_0 ~ 90 GPa to 110 GPa and σ_0 ~ 0.27 to 0.30. Most recently Karthick et al. [15] have synthesized nanocrystalline $Y_2Ti_2O_7$, $Y_2\ Zr_2O_7$, $Y_2Hf_2O_7$ pyrochlores through mechanically activated annealing and reverse co-precipitation (RCP) techniques. The structural, microstructural, vibrational, and mechanical properties have been investigated systematically. Finally, regarding the optical parameters, $Y_2Ti_2O_7$ is known to have a high refractive index ($2.0 < \eta < 2.2$) [5]. Nanocrystals of $Y_2Ti_2O_7$ synthesized by sol-gel method have η = 2.34 at λ = 563 nm [16] while for thin films of $Y_{2-x}Er_xTi_2O_7$ (x = 0.0 – 2.0) series, η is found to vary between 2.20 to 2.09 [17]. On the other hand, optical energy bandgap (E_g) values are found to be 3.7 eV for nanocrystalline $Y_2Ti_2O_7$, 4.11 to 4.07 eV for Er^{3+} - substituted $Y_2Ti_2O_7$ system [17], and E_g = 3.44 eV for single crystalline$Y_2Ti_2O_7$ [1].

Availability of countable research reports on theoretical and experimental studies on optical, elastic, and thermodynamic properties of $Y_2Ti_2O_7$ and observed large discrepancies in elastic moduli values determined from such cumbersome evaluation methods [1-18] suggest the need to re-evaluate the values. This leads to the present study. In this communication, instead of adopting complex theoretical and experimental approaches, a very simple semi-empirical method based on a very primary structural parameter, X-ray density, has been employed to determine highly important optical, elastic, and thermodynamic parameters from the applications point of view for pyrochlore compound, $Y_2Ti_2O_7$ at 300 K in a systematic manner. To the best of our knowledge, this is a novel and first ever attempt in the field.

2. EXPERIMENTAL DETAILS

A stoichiometric amount of yttria (Y_2O_3) and titania (TiO_2) was used to synthesize the microcrystalline pyrochlore compound, yttrium titanate ($Y_2Ti_2O_7$), by a standard double sintering ceramic technique. The analytical reagent grade (purity > 99.5 %) powders were thoroughly mixed in agate pestle and mortar for four hours using acetone as a milling medium. The homogeneous powder was pelletized for improving solid-state reaction. The pelletized sample was pre-sintered at 900 °C for 12 hours in a programmable furnace and slowly cooled to room temperature at a rate of 2 °C per minute. In the final sintering process regrinded and repelletized sample of $Y_2Ti_2O_7$ was kept at 1300 °C for 12 hours and then cooled to room temperature by keeping the same rate of cooling. The sample was characterized for phase formation and structural parameters determination by X-ray powder diffractometry using CuKα radiation (λ = 1.5418 Å). Dielectric permittivity against frequency (20 Hz – 1 MHz) measurement was performed on HP4284A precision LCR meter at T = 300 K.

3. RESULTS AND DISCUSSION

The name pyrochlore comes from the mineral, $NaCaNb_2O_6F$ pyrochlore. The stoichiometry or general chemical formula of the pyrochlore system is $A_2B_2O_7$, which is ternary metallic oxide where the cations A and B have charges of +3 and +4 respectively. It is a well-established fact that polycrystalline yttrium titanate ($Y_2Ti_2O_7$) adopts a pyrochlore structure that has a high symmetry (space group Fd3m, O_h^7, no. 227).

Fig. 1 depicts a powder X-ray diffraction pattern recorded for $Y_2Ti_2O_7$. The refinement, indexing, and lattice parameter determination have been carried out by Rietveld refinement software, Fulprof 2k (version 6.20-Jan 2018-ILL JRC) program. Observed Bragg reflections in this diffractogram are found to be consistent with the pyrochlore structure (JCPDS – 4222-0413). That confirms the monophasic nature of the synthesized composition. The diffraction lines were found to be sharp, indicative of the polycrystalline nature of the sample. The lattice constant value (a = 10.046 ± 0.002 Å) thus resolute is in agreement with the values reported earlier [3,4,10,13,15] and that in turn used for further calculations.

The X-ray density (ρ_x) of the sample was determined by adopting the relation given by Smith and Wijn [19]:

$$\rho_{x} = (Z.\ M_w)/(N_{A.}\ a^3) \tag{1}$$

where M_w is the molecular weight of the composition (385.612 g/mol), N_A the Avogadro´s number, and a is the lattice constant (Table 1). As there is 8 formula unit in the unit cell, Z=8 is taken into account. The bulk density (ρ) and corresponding value of pore fraction (f) ($f = 1 - \rho/\rho_x$) are summarized in Table 1.The corresponding value of molar volume (V_m) is computed using the relation [20]:

$$(V_m\,(\text{cm}^3/\text{mol})) = M_w/\rho_x \tag{2}$$

These structural parameters are further used to facilitate calculations, analysis, and discussion on thermodynamic and optical parameters.

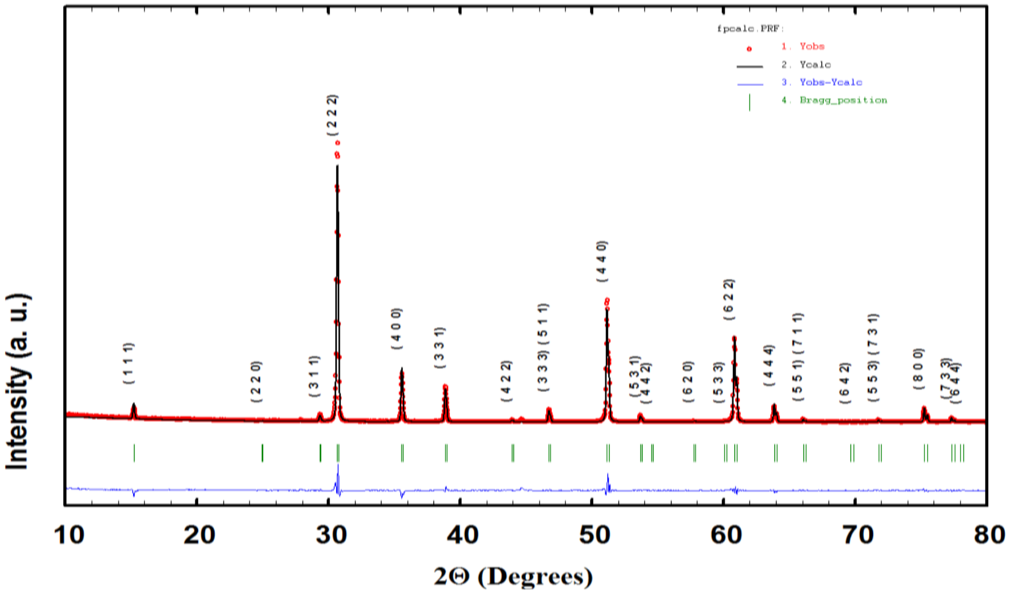

Fig. 1. Rietveld fitted room temperature (T = 300 K) X-ray powder diffraction pattern recorded for $Y_2Ti_2O_7$ pyrochlore

Table 1. Structural, elastic, thermodynamic, and optical parameters for $Y_2Ti_2O_7$ pyrochlore at 300 K

No.	Parameter	Value
1	Chemical formula	$Y_2Ti_2O_7$ (yttrium titanate)
2	Molecular weight (M_w)	385.612 g/mol
3	Total number of atoms in the molecule (p)	11
4	Mean atomic weight (m)	35.06 g/mol
5	Lattice constant (a)	10.046 Å
6	Number of formula unit in the unit cell (Z)	8
7	X-ray density (ρ_x)	5.053 g/cm^3
	Bulk density (ρ)	4. 303g/cm^3
	Pore fraction (f)	0.148
8	Molar volume (V_m)	76.31 cm^3/mol
9	a(m)	(-8.703) km/s
10	Longitudinal wave velocity (V_{l0})	8022.4 m/s
11	Shear wave velocity (V_{s0})	4631.7 m/s
12	Mean sound velocity (V_{m0})	5142.1 m/s
13	Longitudinal modulus (L_0)	325.2 GPa
14	Rigidity modulus (G_0)	108.4 GPa
15	Bulk modulus (B_0)	180.7 GPa
16	Poisson's ratio (σ_0)	0.250
	Poisson's ratio (σ_{0f})	0.274
17	Young 's modulus (E_0)	271.0 GPa
18	Lame's Constant (λ_{L0})	108.4 GPa
19	Vickers hardness (H_{v0})	18.02 GPa
20	Debye temperature (θ_0)	678.1 K
21	Lattice potential energy (U_{LP})	(-316.9) eV (Eq. (5))
22	Lattice potential energy (U_{LS})	(-382.1) eV (Eq. (6))
23	Lattice potential energy (U_{LS})	(-412.7) eV (Eq. (7))
24	Lattice potential energy (U_{LS})	(-377.34) eV (Eq. (8))
25	Molar heat capacity (C_v)	274.36 J/mol.K (Eq.(9))
26	Molar heat capacity (C_v)	182.26 J/mol.K (Eq.(10))
27	Debye temperature (θ_D)	245.7 K (Eq. (12))
28	Molar heat capacity (C_v)	38839.63 J/mol.K (Eq.(13)
29	Molar heat capacity (C_v)	267.77 J/mol.K (Eq.(14))
30	Molar heat capacity (C_p)	182.73 J/mol.K
31	Fermi energy (E_F)	4.317 x 10^{-19} J
32	Molar heat capacity C_v (electronic)	1.0 J/mol.K (Eq. (21))
33	Molar heat capacity C_v (total)	183.26 J/mol.K
34	Molar heat capacity C_v (electronic)	0.393 J/mol.K (Eq.(23))
35	$<\eta>$	2.046
36	E_g	2.49 eV and 3.28 eV
37	α_e	15.60 Å^3
38	α_D	29.58 Å^3
39	α_i	13.98 Å^3
40	α_e^T	18.06 Å^3
41	α_D^T	30.28 Å^3
42	α_i^T	12.22 Å^3

3.1 Elastic Properties

In the instance of a wide range of silicates and oxides including chromites, aluminates, spinels, ferrites, and garnets having the same mean atomic weight (m), the velocity of longitudinal waves (V_{l0}) is directly proportional to the ρ_x [21]. In the present investigation for $Y_2Ti_2O_7$ composition, $m = M_w/p = 35.06$ g/mol, (where p is the total number of atoms in the molecule i.e., 11). Following the work, the V_{l0} (km/s) in terms of ρ_x (g/cm^3) and a(m) (km/s), the function of m is given by [21]:

$$V_{l0} = a(m) + 3.31.\ \rho_x \tag{3}$$

In the process of approximating the value of a(m) for a given value of m we have contemplated the values of m and corresponding values of a(m), (for m = 21, a(m) = (-2.55) km/s, for m = 25, a(m) = (-5.7) km/s, and for m = 30, a(m) = (-8.6) km/s) [21]. For the multicationic oxide composition, $Y_2Ti_2O_7$, with m = 35.06 g/mol, the function a(m) is estimated to be (-8.703) km/s. The calculated values of V_{l0} and ρ_x are in turn used to deduce other elastic parameters, shear or transverse wave velocity (V_{s0}), mean sound velocity (V_{m0}), longitudinal modulus (L_0), rigidity modulus (G_0), bulk modulus (B_0), Young´s modulus (E_0), Poisson's ratio (σ_0), Lame´s constant (λ_{L0}), Vickers micro-hardness (H_{v0}) and characteristic Debye temperature (θ_0) in a void-free state using following standard formulae [22,23]:

$$V_{s0} \approx V_{l0}/\sqrt{3}$$

$$V_{m0} = [(3\,(V_{l0}^3 .\, V_{s0}^3))/\,(2\,V_{l0}^3 + V_{s0}^3)]^{1/3}$$
$$L_0 = \rho_x\, V_{l0}^2$$
$$G_0 = \rho_x\, V_{s0}^2$$
$$B_0 = L_0 - (4/3)\,G_0$$
$$\sigma_0 = (3B_0 - 2\,G_0)/(\,6B_0 + 2\,G_0)$$
$$E_0 = 2\,(1 + \sigma_0)\,G_0$$
$$\lambda_{L0} = L_0 - 2\,G_0$$
$$H_{v0} = [(1 - 2\,\sigma_0)\,E_0]/\,6\,(1 + \sigma_0)$$

and,

$$\theta_0 = (h/k_B)\,[(3.\,N_A\,.\,p.\,\rho_x\,(g/cm^3)/\,4\,\pi\,M_w\,(g/mol)\,]^{1/3}\,V_{m0}\,(cm/s) \quad (4)$$

where h is Planck´s constant, k_B is Boltzmann´s constant.

The calculated values of the elastic parameters are summarized in Table 1. The values of V_{l0} V_{s0}, and V_{m0} (Table 1) are in excellent agreement to those values, V_{l0} = 8415 and 8066 m/s, V_{s0} = 4668 and 4500 m/s, and V_{m0} = 5200 and 5011 m/s computed based on LDA and GGA [13], respectively. The semi-empirically determined values of L_0, G_0, B_0, and E_0 (Table 1) for Y_2Ti_2O $_7$ are in reasonable agreement with those computed based on density functional theory, L_0 = 374 and 313 GPa, G_0 = 113 and 99 GPa, B_0 = 216 and 186 GPa, and E_0 = 288 and 252 GPa, using LDA and GGA, respectively [13]. In the literature regarding the pyrochlore compound, $Y_2Ti_2O_7$, the experimental values of rigidity modulus (G_0) are reported to be 101 GPa (resonance method), 103 GPa (ultrasonic method), 104 GPa (cube resonance method) [6]. The bulk modulus (B_0) values determined experimentally are found to vary from 170 GPa (resonance method), 190 GPa (ultrasonic method) to 192 GPa (cube resonance method [6] and 171 GPa for a single crystalline $Y_2Ti_2O_7$ (resonant ultrasound spectroscopy) [7]. The experimentally determined Young's modulus (E_0) values are reported to be 253 GPa (resonance method), 262 GPa (ultrasonic method), and 265 GPa (cube resonance method) [6], and 263 GPa (resonant ultrasound spectroscopy) [7]. The value of σ_o for a stable, isotropic, and linear elastic material is greater than (-1) and less than 0.5 because of the requirement for Young´s modulus, shear modulus, and bulk modulus to have positive values. The σ_o is found to be ~ 0.25 (Table 1), in conformity with the theory of isotropic elasticity and the values, σ_o = 0.278 (LDA) and 0.274 (GGA), predicted by the first principle study [13]. The values of σ_o have also corresponded with the experimentally determined values, σ_o = 0.25 (resonance method) and σ_o = 0.27 (ultrasonic and cube resonance methods) [6]. The presently found value of σ_o is too small as compared to the calculated value of Poisson´s coefficient (0.365) [4]. On the other hand, data analysis turnout the following equation for the dependence of σ_0 as a function of pore fraction (f) given by σ_{0f} = 0.324(1-1.043f) [22]. The calculated value σ_{0f} is found to be 0.274, consistent with the value calculated from elastic moduli (Table 1). Young´s modulus, among all the elastic moduli, is of particular attentiveness since it is the key factor for the most frequently employed core shapes viz. rings and rods [24]. The parameter, λ_{Lo}, has no physical interpretation, but it assists in sampling the stiffness matrix in Hooke´s law. The two parameters, λ_{Lo} and $G_{o,}$ together constitute a parameterization of the elastic moduli for homogeneous isotropic media and are related to the other elastic moduli. The Vickers hardness (H_{v0}) determined from the nanoindentation test method for $Y_2Ti_2O_7$ composition is found to be 12.1 ± 0.1 GPa [6] and 11.4 GPa [1]. For monocrystalline $Y_2Ti_2O_7$, H_{v0} are found to be 10.77 GPa and 16.4 ± 0.4 GPa [1] while H_{v0} = 18 GPa has been reported for $Y_2Ti_2O_7$ prepared by reverse co-precipitation route [15]. The hardness at low load (15 gf) for single crystal $Y_2Ti_2O_7$ monofilaments is reported to be 24.06 GPa [6]. The presently found value of H_{v0} = 18.02 GPa (Table 1) is laying in the range of reported values. To understand solid-state problems that involve lattice-vibrations, such as electrical resistivity, scattering of the thermal neutron, and thermal conductivity, θ_0 is a salient parameter. The temperature at which maximum vibrations occur is known as $\theta_{0.}$ The θ_0 value (678.1 K) (Table 1) is consistent with the values, 691 K (LDA) and 653 K (GGA) [13].

The values of B_0 and G_0 are further used to calculate Pough´s ratio (B_0/G_0) and Frantesvich´s ratio (G_o/B_o). Accordingly, if B_0/G_0 is less than 1.75 and G_0/B_0 is greater than 0.571, the material becomes brittle while if B_0/G_0 is greater than 1.75 and G_0/B_0 is less than 0.571, the material becomes ductile. On the other hand, if Poisson´s ratio is higher than 0.33, the material possesses ductile nature while it is brittle with $\sigma_0 < 0.33$ [25]. In the present case, B_0/G_0 is found to be ≈ 1.67, G_0/B_0 is found to be ≈ 0.6, and $\sigma_0 = 0.25$ for .$Y_2Ti_2O_7$. The B_0/G_0 values, 1.92 (LDA) and 1.88 (GGA), [13] match well with the present value. The calculated values of ratios lead to conclude that the sample exhibit brittle nature under ambient conditions. In general, the difference between present semi-empirically determined values, and theoretically estimated values [13], and empirically experimentally found values [6,7,14] of elastic parameters is less than 5%. That validates the applicability of the present approach.

The elastic moduli and their pressure derivatives are suggestive of the short-range contributions to the lattice energy. Consequently, the parameters influencing the magnitude of elastic moduli are also concomitantly accountable for controlling the lattice energy (strength of bonding). In ionic solids, the strength of bonds present can be estimated from the lattice energy determination. The lattice energy of such ionic compounds can be calculated from the most conventional Kudriavtsev´s approach [26]. With certain assumptions, well discussed in [24,27,28], this can be further simplified and used to calculate lattice energy for microcrystalline materials (U_{LP}). The resultant equation is given by :

$$U_{LP}\,(eV) = (-\,3.108 \text{ x } 10^{-5})\,(M_w\,(kg/mol) \text{ x } V_{m0}^2\,(m^2/s^2)) \qquad (5)$$

The calculated value of U_{LP} for $Y_2Ti_2O_7$ composition is found to be (-316.9 eV) and is given in Table 1.

The lattice energy determination for single crystals by Kapustinskii´s equation [29] is referred to as one of the most successful approaches to calculate lattice energies for a wide range of monocrystalline materials (U_{LS}).

Accordingly,

$$U_{LS}\,(kJ/mol) = [(-1202.5 \text{ x } q \text{ x } |\,Z^+|\,|Z^-|)/\,(r^+ + r^-)] \text{ x } [\,1 - (0.345)/(r^+ + r^-)] \qquad (6)$$

Here, Z^+ is the weighted mean of cationic charge, Z^- is the mean ionic charge of the anion (i.e., oxygen), r^+ is the weighted mean ionic radius of metallic cations involved (0.75 Å) (Y^{3+}(0.89 Å) and Ti^{4+} (0.61 Å), coordination no.6) and r^- is the ionic radius of oxygen (1.32 Å). The U_{LS} in the present case is found to be (-37275.6 kJ/mol) (- 382.1 eV).

The lattice potential energy of complex ionic solids has also been determined employing the limiting relation between U_{LS}, M_w, and ρ_x suggested by Glasser and Jenkins [30]:

$$U_{LS}\,(kJ/mol) = (\rho_x \text{ x } N_A \text{ x } 2I^4 \text{ x } A^3 / 10^{21} \text{ x } M_w)^{1/3} \qquad (7)$$

where A is the standard electrostatic conversion term equals 121.39 kJ/mol/nm, I (= 39) is the ionic strength-related term. The factor 10^{21} converts cubic nanometer to cubic meter. In Table 1 the calculated value of U_{LS} is found to be (-40266.96 kJ/mol) and presented in eV (-412.7 eV) for the comparison purpose.

To compute the lattice energy of $Y_2Ti_2O_7$ oxide composition we have to diversify the relevancy of the oxide additivity rule employed to approximate the dielectric and electronic polarizability for complex oxide compositions [31], by taking into consideration the lattice energy of constituent oxides [32], Y_2O_3 and TiO_2 ($U_{LS}(Y_2O_3)$ = -12705 kJ/mol, and $U_{LS}(TiO_2)$) = -12054 kJ/mol). Accordingly,

$$U_{LS}\,(Y_2Ti_2O_7) = [(1)\,U_{LS}\,(Y_2O_3) + (2)\,U_{LS}\,(TiO_2)] \qquad (8)$$

When lattice energies of complex compounds are not obtainable oxide lattice energies are found applicable. The lattice energy value thus calculated is found to be (-36813 kJ/mol) = (-377.34 eV). The value is in good agreement with those calculated based on the other models and validates the present approach. No lattice potential energy values for polycrystalline and single-crystalline pyrochlore compositions in general and $Y_2Ti_2O_7$, in particular, are available in the literature for comparison purposes. This methodology was successfully employed earlier for lattice energy determination for many spinel ferrites, garnets, and superconducting oxide systems [33] and maybe extended to other complex oxide systems also.

It is found that the lattice energy value (U_{LP}) for a polycrystalline sample of $Y_2Ti_2O_7$ composition is much lower than their single crystalline counterpart (U_{LS}) computed based on three different approaches. The observed difference between the two (U_{LP}, U_{LS}, and $U_{LS} > U_{LP}$) can be explained as follows. Microcrystalline materials possess several small crystals or grains. The neighboring grains with distinct crystallographic orientations are separated by a grain boundary, which is a certain atomic distance wide region. It is possible to have varying degrees of crystallographic misalignment among adjoining grains. The atoms along a grain boundary are less regularly bounded as bond angles are large and that results in grain boundary energy. The degree of disorientation decides the magnitude of grain boundary energy, being larger for high angle boundaries [34]. The long-range range interactions are obstructed by these grain boundaries. This is the most probable cause, the lattice energy value for microcrystalline materials is smaller than its monocrystalline counterpart (Table 1).

3.2 Thermodynamic Properties

Following the law of Dulong and Petit [20], we can work out the theoretically expected value of isochoric molar heat capacity (C_v) using the equation [20]:

$$C_v \text{ (J/mol.K)} = 3pR \tag{9}$$

where p is the number of atoms in the chemical formula, $A_2B_2O_7$ ($Y_2Ti_2O_7$), (i.e., 11), R is the universal gas constant (8.314 J/mol.K). Consequently, the calculated value of C_v is found to be 274.36 J/mol K, which is the limiting value of heat capacity at $T \sim \theta_0$. In the present investigation θ_0 is much greater than 300 K (Table 1), thus, C_v at T = 300 K turns up anomalously low.

The C_v values in the temperature range of T = 0 - 900 K (well above θ_0) were computed based on the Einstein theory of heat capacity of solids [20] using equation (10) and graphically displayed for a $Y_2Ti_2O_7$ in Fig. 2.

$$C_v = 3pR\left(\frac{\theta_0}{T}\right)^2 \frac{\exp(\theta_0/T)}{[\exp(\theta_0/T)-1]^2} \tag{10}$$

It is found that for a $Y_2Ti_2O_7$, C_v = 182.26 J/mol.K at T = 300 K. At T = 30 K ($\leq 0.1\ \theta_0$), C_v is found to be 2.139 x 10^{-5} J/mol.K. The C_v values at 300 K are consistent with the limiting value as derived from Dulong and Petit law and reported by Terki et al. [4].

According to the Debye theory of the heat capacity of solids, the Debye temperature (θ_D) is related to the maximum phonon frequency (f_D) by [20]:

$$\theta_D = (h/k_B)\ f_D \tag{11}$$

Recalling the definition of θ_D as the temperature corresponding to f_D, and thus the minimum phonon wavelength (λ_{min}), one can re-write the above equation as [35]:

$$\theta_D = (h/k_B)\ (V_{m0}/\lambda_{min}) \tag{12}$$

Here, V_{m0} is the mean sound velocity (Table 1). The unit cell puts constrain on the λ_{min} of the vibration. Thus, λ_{min} is equal to the length of the unit cell, (λ_{min} = 10.046 x 10^{-10} m (Table 1)). Thus, θ_D can be calculated as:

$$\theta_D = (4.8 \times 10^{-11} \text{ (s.K)})\ (5142.1 \text{ (m/s)}) / (10.046 \times 10^{-10} \text{ (m)})$$

The θ_D is found to be 245.7 K

Besides, the Debye theory anticipates that at temperatures less than $\approx 0.1\theta_D$, C_v should vary as T^3 according to [20]:

$$C_v = [1939.7\ p]\ (T/\theta_D)^3 \text{ J/mol.K} \tag{13}$$

The computed value of C_v at T = 30 K is found to be 38.84 J/mol.K. The observed difference in C_v values at a low temperature determined from the Debye and Einstein predictions is because in the Debye model (and in reality also) there is a continuum of low energy vibrational modes that can be excited at low temperature. On the contrary, as expected at T = 300 K, the value is found to be 38839.63 J/mol.K. This value is much higher than those calculated from the Einstein theory and limiting value of 274.36 J/mol.K computed from the Dulong and Petit law. It is worth mentioning that the experimentally (empirically) determined C_v values and signature of C_v (T) in the temperature range T = 0 – 900 K including the maximally possible value of C_v discussed in [2,4] are in good agreement with those computed based on the Einstein theory (Fig. 2) and limiting value of C_v theoretically predicted from the Dulong and Petit law as discussed above. This indirectly validates our semi-empirical approach of θ_0 determination. The θ_0 value 678.1 K is quite consistent with the reported values, 691 K and 653 K, computed using the density functional theory [13]. Eventually, an effort has been made to compute C_v by using the Debye function (f_D) as follows [35]:

$$C_v = 3\ p\ R\ f_D \tag{14}$$

Introducing the Debye function (f_D): $f_D = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^4}{(e^x-1)^2}\,dx$, where, $x = \frac{\mathrm{h}\omega}{2\pi \mathrm{k_B T}}$ and $x_D = \frac{h\omega_D}{2\pi k_B T} = \frac{T}{\theta_D}$ and ω_D is the Debye frequency. The values f_D have been determined by considering T/θ_D ratio = 1.221 at T = 300 K , while T/θ_D ratio is found to be 0.122 at T = 30 K. The corresponding values of f_D are found to be 0.976 J/mol.K at T = 300 K while f_D = 0.14087 J/mol.K at T = 30 K. It is found that, C_v = 267.77 J/mol.K at T = 300 K and C_v = 38.65 J/mol.K at T = 30 K. The C_v value at low temperature T = 30 K is consistent but at T = 300 K the value differ much from those determined from the Debye T^3 law. The θ_D value, 245.7 K, is near to T = 300 K thus the calculated C_v value at T = 300 K is likely to approach the limiting value of C_v (= 274.36 J/mol.K) as expected at $T \sim \theta_D$.

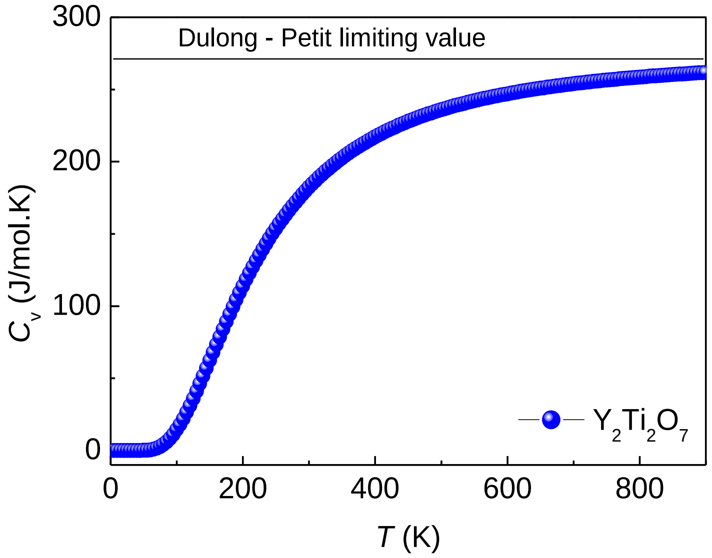

Fig. 2. Thermal variation of molar heat capacity curve generated based on the Einstein theory (Eq. (10)) with θ_0 = 678.1 K and T = 0 - 900 K. The horizontal l ine represents the limiting value from the Dulong and Petit law (Eq. (9)) for $Y_2Ti_2O_7$

The Debye T^3 law fails and the Einstein theory was found successful in the determination of consistent C_v values at T = 300 K is the subject of interest. This can be explained considering the following facts: (i) The Einstein theory considers the thermal component of the internal energy of a solid to be held by atoms vibrating independently in identical simple harmonic potentials. In contrast, the Debye theory considers the thermal component of the internal energy to be held by displacement (sound) waves. (ii) In the Debye theory, the quantum states of the solid are considered to be wave-like states that are occupied by phonons while in the Einstein theory, the quantum states of the solid are the quantum states of each simple harmonic potential. However, for phonons, there are two key differences in the Debye analysis. First, there is only one quantum state for each value of **k.** Second, for phonons, the energy is directly proportional to |**k**| since the energy of a phonon is E = ħω = ħV|**k**|. This expression has assumed that the speed of sound (V) that relates the frequency to the wavelength is independent of wavelength. This is not quite correct for wavelengths of the order of lattice spacing or so, but this is neglected in the Debye theory [20]. Further, this also suggests that the Einstein theory is suitable to estimate the molar heat capacity of materials with high values of Debye temperature ($\theta >> 300$ K).

The Kieffer model can successfully approximate the isobaric molar heat capacity (C_p), C_v, and vibrational entropy for a wide range of oxides and silicates [36]. Accordingly, C_v can be computed by modeling a simplified phonon density of state of a crystal [37] while C_p is determined using the relation:

$$C_p = C_v + (\alpha_a^2 \,.\, B_o .\, V_m .\, T) \quad (15)$$

where α_a is the coefficient thermal expansion, very recently it is reported to be 10.6 x 10^{-6} K^{-1} at T = 300 K for $Y_2Ti_2O_7$ [9], is used to calculate C_p at 300K.

$$C_p = (182.26) + (10.6 \times 10^{-6})^2\ (180.7 \times 10^9)\ (76.31 \times 10^{-6})\ (300)$$

$$C_p = 182.73 \text{ J/mol.K}$$

The well-established approximation, $C_p - C_v = 0.0011T$ [38], holds reasonably well for the composition under study.

It is possible to estimate the electronic contribution, C_v (electronic), to the total molar heat capacity, C_v (total), by using the following relation [20]:

$$C_v\ (\text{electronic}) = (\pi^2\, k_B^2\, g(E_F)\, T)/3 \quad (16)$$

where k_B is Boltzmann's constant (= 1.38 × 10^{-23} J/K), T = 300 K and the density of states function, $g(E_F)$, is given by :

$$g(E_F) = [V_m\,(2\, m_e^3\, E_F)^{½}] \,/\, \pi^2\, ħ^3 \quad (17)$$

Here, m_e is the mass of the electron (9.1 x 10^{-31} kg), and E_F is the Fermi energy. The E_F is given by:

$$E_F = ħ^2\, k_F^2 \,/\, 2\, m_e \quad (18)$$

where the Fermi wave vector, k_F, is given by:

$$k_F = (3\, n\, \pi^2)^{1/3} \quad (19)$$

here, n = N/V is the electron density. The n can be estimated in different ways but the easiest way is to divide the ρ_x by the mass of the cubic pyrochlore composition. By taking into account, the average valence of the composition, $Y_2Ti_2O_7$, n can be estimated as:

$$n = (2.545)\ (5.053 \text{ x } 10^{3}) / (385.612)\ (1.66 \text{ x } 10^{-27})$$

$$n = 2.009 \text{ x } 10^{28} \text{ electrons/m}^{3}$$

Thus, $k_F = [3\ (1.19 \text{ x } 10^{28})\ (3.14)^{2}]^{1/3}$

$$k_F = 0.841 \text{ x } 10^{10}\ \text{m}^{-1}$$

By substituting the value of k_F in equation (18), the value of E_F can be found:

$$E_F = [(1.054 \text{ x } 10^{-34})^{2}\ (0.841 \text{ x } 10^{10})^{2}] / ((2)\ (9.1 \text{ x } 10^{-31}))$$

$$E_F = 4.317 \text{ x } 10^{-19} \text{ J} = 2.7 \text{ eV} \qquad (20)$$

Substituting the values of V_m and E_F into the $g(E_F)$ yields:

$$g(E_F) = [76.31 \text{ x } 10^{-6}]\ [2\ (9.1 \text{ x } 10^{-31})^{3}\ (0.4317 \text{ x } 10^{-18})]^{1/2} / (3.14)^{2}\ (1.054 \text{ x } 10^{-34})^{3}$$

$$g\ (E_F) = 5.325 \text{ x} 10^{42} \text{ states/ J. mol}$$

which predicts an electronic heat capacity of :

$$C_V \text{ (electronic)} = [(3.14)^{2}\ (1.38 \times 10^{-23})^{2}\ (7.215 \times 10^{42})\ (300)] / 3 \qquad (21)$$

$$C_V \text{ (electronic)} = (1.0) \text{ J/mol.K}$$

This is to be compared with the contribution due to the lattice (i.e.,182.26 J/ mol.K). To put it another way, the electronic contribution to the total heat capacity is only around 0.55 %. This can be understood from the following facts. The electrons contributing to the conduction are very close to the Fermi energy. However, to contribute to bulk specific heat all the valence electrons would have to receive energy from the nominal thermal energy, k_BT. But, the Fermi energy is much greater than k_BT and the large majority of the electrons cannot receive such energy. Since there are no available energy levels within k_BT of their energy, the small fraction of electrons that are within the k_BT of the Fermi level does contribute a small specific heat and hence the electron specific heat is significant only at very low temperatures.

Thus, the total molar heat capacity at T = 300 K is given by:

$$C_v \text{(total)} = C_v \text{(lattice)} + C_v \text{(electronic)} \qquad (22)$$

$$= (182.26 + 1.0) \text{ J/mol.K}$$

$$C_v \text{(total)} = (183.26) \text{ J/mol.K}$$

For a quenched sample, C_v (total) is found to be 316.43 J/mol.K.

Alternatively, it is possible to calculate C_v (electronic) for a sample at T = 300 K using the Debye expression:

$$C_v \text{(electronic)} = (\pi)^{2}\ (R\ k_B\ T) / (2.\ E_F) \qquad (23)$$

$$= 1.696 \times 10^{-19} / E_F$$

$$= 0.393 \text{ J/mol.K}$$

Eventually, an attempt has been made to approximate the temperature at which C_v (electronic) and C_v (lattice) are commensurate by equating respective Debye equation [31]:

$$C_v \text{(electronic)} = ([(\pi)^{2} R\ k_B\ T] / 2.\ E_F) = ([12\ (\pi)^{4}\ R\ (T/\theta_0)^{3}] / 5) = C_v \text{(lattice)} \qquad (24)$$

Therefore, $(T^3/T) = [(\pi)^2\ R\ k_B\ (\ \theta_0)^3\ 5]/[24\ E_F\ R\ (3.14)^4]$

and $T^2 = 5\ k_B\ (\theta_0)^3 / 24\ (\pi)^2\ E_F,$

that results in [39],

$$T = [5\ k_B\ (\theta_0)^{3} / 24\ (\ \pi)^{2}\ E_F]^{1/2} \qquad (25)$$

It is found that C_v (lattice) and C_v (electronic) are comparable at T = 14.5 K.

3.3 Optical Properties

The factors that affect the refractive index (η) of the material are the wavelength of light (λ) used, density and polarizability of the substance, and crystalline form (micro-crystalline, nanocrystalline, amorphous, thin-film, etc.) [31,40]. Ellipsometry is a widely used experimental technique that simultaneously determines η and optical absorption coefficient for bulk materials and optically thick films. The η can also be measured by the dual-arm Z-scan method, dark-field Z-scan imaging technique, and prism refractometry [37]. Anderson and Schreiber corroborate the functionality of the η and density relationship. The outcomes confirmed that the laws of Gladstone-Dale and Drade are well-grounded with adequate correctness for oxide minerals with $m \sim 21$ g/mol [40]. Consequently, the mean value of η in terms of ρ_x is given by the following empirical relation [41]:

$$<\eta> = 1 + 0.207\ \rho_x \tag{26}$$

The <η> value computed for mineral spinel, magnesium aluminates ($MgAl_2O_4$), having $\rho_x = 3.57$ g/cm^3 and $m = 20.30$ g/mol [42], is found to be 1.739. This value is in excellent agreement with the reported one, η = 1.72 [33]. Besides, for a monocrystalline yttrium iron garnet ($Y_3Fe_5O_{12}$) with moderate values of ρ_x and m ($\rho_x = 5.17$ and $m = 36.48$ g/mol), < η > is found to be 2.07. This value is sufficiently close to the value η = 2.168 ± 0.003 at λ = 3 μm with a variation of 5 % between 1 μm to 6μm [43]. The well known ferroelectric material, $BaTiO_3$ possess very high value of $\rho_x = 6.006$ g/cm^3 [44] and $m = 46.64$ g/mol has shown η = 2.41 at λ = 632.8 nm and for the thin films with different crystalline forms, η = 2.0 (amorphous), η = 2.07 (microcrystalline), η = 2.51 (crystalline) at λ = 5000 Å [45]. The computed value of <η> is found to be 2.243. The successful application of the above equation (26) for a large class of oxide ceramics prompted and allow us to extend this approach for η and other related optical parameters determination for $Y_2Ti_2O_7$ pyrochlore. The <η> value is found to be 2.046, agrees well with the suggested range of η (2 < η < 2.2) for $Y_2Ti_2O_7$ composition [5].

The optical energy bandgap (E_g) has been calculated from the corresponding η value using the relations [46]:

$$E_g = (4.16 - \eta)/0.85$$

and

$$E_g = (4.084 - \eta)/0.62 \tag{27}$$

The E_g values are tuned out to be 2.49 eV and 3.28 eV, respectively. These values are following the theoretically computed E_g values (2.85 eV (LDA) and 2.81 eV (GGA)) reported in [13] and experimentally determined values for nanocrystalline $Y_2Ti_2O_7$ (3.7 eV) [17] and single-crystalline $Y_2Ti_2O_7$ (3.44 eV) [1] materials.

The following Lorentz-Lorenz equation [47] correlates the η, V_m and aggregate molar refraction for an isotropic material (R_m):

$$R_m\ (m^3/mol) = [(\eta^2 - 1)/ (\eta^2 + 2)]\ V_m \tag{28}$$

R_m is related to the material´s structure and is directly proportional to the molar electronic polarizability (α_e) of the material, through the following relation [40]:

$$\alpha_e = (3/4\ \pi\ N_A)\ R_m = R_m/2.52 \tag{29}$$

The value of α_e is found to be 15.6 Å^3. The Clausius-Mossotti relation expresses the real part of complex dielectric permittivity (ε′) in terms of the dielectric polarizability (α_D) given by [40]:

$$\alpha_D = 23.89 \times 10^{-2}\ [(a^3\ (Å^3)/Z)\ (\ (\varepsilon' - 1) / (\varepsilon' + 2))] \tag{30}$$

The value of ε′ (= 131) registered at T = 300 K and frequency of ~ 1 MHz (Fig. 3) is taken into consideration. Though, this relation is stringently applicable to the compounds in which ion or molecules has cubic symmetry nevertheless is roughly well-founded for many non-cubic crystals. The factor (3/4 π = 23.89 x 10^{-2}) hinges on the presumption of point dipole ions and cubic symmetry. A composition $Y_2Ti_2O_7$ under investigation belongs to cubic structure thus this formula is quite applicable. The value of α_D is found to be 27.85 Å^3. The α_D includes both α_e and ionic polarizability (α_i) ($\alpha_D = \alpha_e + \alpha_i$). The α_D, α_e, and α_i values are summarized in Table 1.

In keeping with the oxide additivity rule, the molecular polarizability of a complex substance can be divided into the molecular polarizabilities of simpler substances. This rule is found appropriate for α_D and α_e determination. Previously, it has been found that, this rule estimates polarizabilities values with an accuracy of 5 – 10%. Nevertheless, investigations on yttrium and other rare earth aluminates, spinels, chrysobery, phosphate , etc manifest that these compounds belong o a group of well-behaved oxides whose α_D values follow the additivity rule to 0.5 – 1.5% [40]. According to the oxide additivity rule, as suggested by Shannon and Rossman [40], it is possible to approximate the dielectric polarizability (α_D^T) and electronic polarizability (α_e^T) of any complex oxide system say $Y_2Ti_2O_7$ by taking into account α_D^T and α_e^T of the ingredient oxides, Y_2O_3 and TiO_2 (α_e^T (Y_2O_3) = 8.20 Å^3, α_e^T (TiO_2) = 4.93 Å^3, α_D^T (Y_2O_3) = 13.81 Å^3, and α_D^T (TiO_2) = 8.48 Å^3) [48]. Then

$$\alpha_e^T\ (Y_2Ti_2O_7) = \alpha_e^T\ (Y_2O_3) + 2 \times \alpha_e^T\ (TiO_2)$$

and

$$\alpha_D^T\ (Y_2Ti_2O_7) = \alpha_D^T\ (Y_2O_3) + 2 \times \alpha_D^T\ (TiO_2) \tag{31}$$

This methodology was found useful when α_e^T and α_D^T of the complex compounds are not accessible. The computed values of α_D^T, α_e^T, and α_i^T are comprised in Table 1 for juxtaposing. The percentage deviation between the observed and computed values is found to be negative. These negative deviations from additivity are presumed to have the outcome of cubic

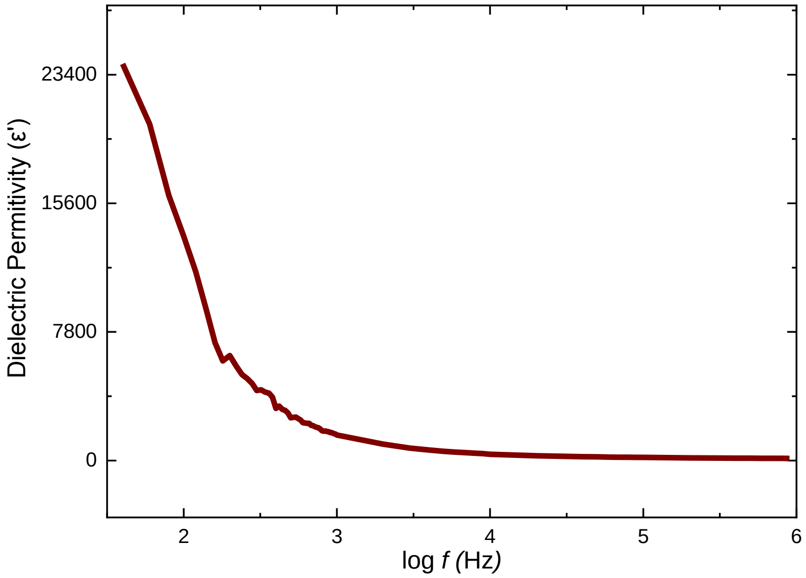

Fig. 3. Dielectric permittivity (ε') versus applied signal frequency (*f*) plot registered at *T* = 300 K for $Y_2Ti_2O_7$

pyrochlore structural constraints [49]. Importantly, observed deviations are relatively small when compared with other oxide systems [36,49]. This suggests that $Y_2Ti_2O_7$ belongs to normal dielectric materials. Further work is in progress.

4. CONCLUSIONS

It is inferred that the X-ray density-based semi-empirical method is simple and successful for various elastic, thermodynamic, and optical parameters determination for a yttrium-titanate ($Y_2Ti_2O_7$). The value of molar heat capacity at constant volume computed based on the Einstein theory for pyrochlore is accordant with theoretically predicted value from the law of Dulong and Petit while the Debye theory fails to approximate the consistent value at 300 K. The key physical differences between the two theories are found accountable. It is found that electronic molar heat capacity contributes ~ 0.5 % to the total molar heat capacity and the electronic and lattice molar heat capacities are comparable at 14.5 K. The oxide additivity rule was found successful in predicting the dielectric, electronic, ionic polarizabilities, and lattice potential energy of the complex oxide composition.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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