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RESEARCH ARTICLE

PHONON STUDY OF ZIRCONIUM OXIDE (ZrO_2) BY USING (VTBFS) MODEL

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ABSTRACT

Density functional theory (DFT) is currently the method of choice for first principles studies of crystalline materials, which depict fundamental issues of structure and properties of various phases of zirconia. But Lattice dynamics is one of the method by help of it the complete structure properties can be analyzed .So due to availability of experimental data author has motivated for the theoretical lattice dynamical study for ZrO_2.In present communication is focused on theoretical study of structure analysis of ZrO2, with particular emphasis on vibrational phonon properties by use of van der Waals three-body force shell model (VTBFSM). Present model includes van der Waals interactions (VWI) and three-body interactions (TBI) in the frame work of both ion polarizable rigid shell model (RSM).The available Density functional theory (DFT) was used to optimize the crystal structure of ZrO2thereafter studied about the thermodynamic properties, dispersion relation and density of state (DOS) at the temperature of 300K and 1100Kcalculated by use of present theoretical model (VTBFSM) and Phonon-VASP software. The model predictions are found to be in reasonable for complete harmonic dynamical behavior of the crystals and well agreement with their experimental reported results (Togo *et al*., 2008; Tojo *et al*., 1999; Luo *et al*., 2009).

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INTRODUCTION

The pioneer work of Kellerman (1940) the lattice dynamics of the alkali halides has been devoted a considerable attention theoretically as well as experimentally. Lowdin's (1947) and Lundqvist's (1952) theory of ionic solids leads to a many – body force of which the three-body component is the first important term. This term explains the Couchy discrepancy in alkali halides in an approximate way. Science it considers the crystal lattice as static and thus completely ignores the displacements of the electron clouds relative to the corresponding nuclei. In the vibrating lattice the shells move relative to their respective cores and thus give rise to electronic polarization. The electrons of each atom shift with respect to the nucleus in the presence of other atoms and consequently an atom becomes an electric dipole. The instantaneous dipole moment of a closed shell atom induces as the van der Waals interaction potential. Thus, the inclusion of (VWI) and (TBI) effects in (RSM) (Woods *et al*., 1960) will employ the Hietler London and the free-electron approximations. The effects of van der Waals interactions and three-body interactions in the framework of ion polarizable (RSM) with short-range interactions effective up to the second neighbour. Therefore, it may be inferred that the most realistic model for complete harmonic dynamical behavior of the crystals under consideration can be developed by introducing the effect of van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of (RSM). The present model is known as van der Waals three-body force shell model which is used in present study. Zirconia is a white crystalline oxide of zirconium. Its most naturally occurring form, with a monoclinic crystalline at room temperature and transitions to tetragonal and cubic at higher temperatures.Zirconium dioxide (ZrO_2) are ceramics among the oldest oxide-ceramic materials but were refined into a material with high-performance properties only fairly recently. Zirconia (ZrO_2), is an extremely important ceramic material of great technological potential due to its outstanding mechanical and electrical properties, high dielectric constant and wide band gap.Today, high-performance ceramics refer to materials whose range of characteristic ceramic properties such as resistance to corrosion and high temperatures has been complemented by non-applicable properties such as high stability and toughness which so far have only been known from metals. Due to their specific electrical, magnetic and thermal properties, modern ceramics have also found their way into other applications. Depending on the main application, high-performance ceramics can be divided into functional ceramics (electrical or magnetic functions) and the so-called structural or engineering

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ceramics (mechanical function) (Salmang-Scholze *et al*., 1983). In recent years, its energy gap (*Eg*≈6 eV) and dielectric properties suggested its potential to replace SiO_2 in advanced metal oxide semiconductor (MOS) devices in gate stack, dynamic access memory devices, and optical applications. (Houssa *et al*., 2000; Wang *et al*., 2001; Lin *et al*., 2003). ZrO_2 show unusual behavior in their electrical resistivity and heat capacity at constant pressure. There is also a large decrease with increasing temperature of the elastic constants. On variation in temperature ZrO_2 shows significant properties.At low thermal conductivity use is ceramic fiber insulation for crystal growth furnaces, fuel cell stack insulation and infrared heating systems.The crystal structures of zirconia are illustrated in Fig.1

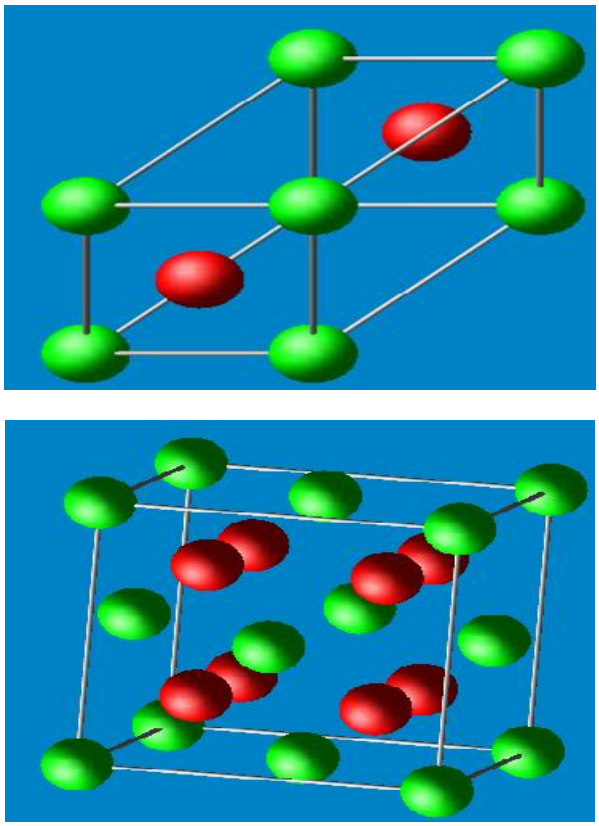

Fig 1. (a) Primitiveunit ShellStructure of ZrO_2 (b) Crystallographic unit shell

Density functional theory (DFT) which has depict for first principles studies of crystalline materials, fundamental issues of structure and properties of various phases of zirconia (Jaffe *et al*., 2005; Kuwabara *et al*., 2005). So due to availability of experimental data, the theoretical lattice dynamical study for ZrO_2 has reported in present communication. The lattice parameter from neutron diffraction at room temperature were found equal a=b=3.594 ^{0}A and c=5.182^{0}A and ($\alpha=\beta=\gamma=90^0$) (Bouvier *et al*., 2001). The structure is close to a distorted cubic structure and is often described in a pseudo-cubic set of axis.The incorporation of the effects of van der Waals & three-body interactions (Gupta and Upadhyaya, 1979; Gupta and Upadhyaya, 1980; Singh and Gupta, 1976; Mishra *et al*., 1981; Singh *et al*., 1980) has used in lattice dynamical study of ZrO_2. The present model is based on the framework of ion polarizable (RSM) by Dick and Over Hauser (1958) and Woods *et al*. (1960) by two different groups of workers, which has been applied for study of lattice property with short-range interactions effective up to the second neighbor. In view of the remarkable success achieved from rigid ion model (RIM) and rigid shell model (RSM) to describe the complete lattice dynamics of alkali halides it seems worthwhile to explore the adequacies of (RIM) and (RSM) in doing so far ZrO_2.

Theoreticalformalism of VTBFSM

The general formalism of VTBFSM can be derived from the crystal potential whose relevant expression per unit cell is given by

$$\Phi = \Phi^{C} + \Phi^{R} + \Phi^{TBI} + \Phi^{VWI} \qquad \ldots\ldots\ldots(1)$$

Where, First term Φ^C is Coulomb interaction potential. This interaction potential is long-range in nature. Thus, total Coulomb energy for the crystal is

$$\Phi^{C}(r) = \sum_{j}{}' \Phi^{C} \sim_{M} \frac{Z^2 e^2}{r_0}\left(r_{ij}\right)$$

whereα_m is the Modelung constant and r_0 is the equilibrium nearest neighbours distance. Second term Φ^R is short-range overlap repulsion potential.

$\Phi^{R}\left(r_{ij}\right) = ar_{ij}^{n}$ (Born Potential) and

$\Phi^{R}\left(r_{ij}\right) = b\exp.\left(-r_{ij}/\circ\right)$ (B-M) Potential)

Where, a (or b) and η(orρ) are the Born exponents called the strength and hardness parameters, respectively. Third term Φ^{TBI} is three-body interactions potential. As a natural consequence of the anti-symmetry requirement on the wave function (Verma and Singh, 1970), this alteration in the electronic charge density causes a charge depletion which depends on the inter nuclear separation and interacts with all other charges via Coulomb force law and gives rise to long-range TBI introduced by Lowdin (1947) and Lundqvist (1961). This interaction potential is expressed as

$$\Phi^{TBI} = \sim_{m} \frac{Z^2 e^2}{r_0}\left[\frac{2n}{Z} f(r)_0\right]$$

Where, the term $f(r)_0$ is a function dependent on the overlap integrals of the electron wave-functions. Φ^{TBI} is also long-range in nature hence it is added to the $\Phi^{C.}$ and last term Φ^{VWI} is van der Waals interaction potential and owes its origin to the correlations of the electron motions in different atoms closely the method used by Wood *et al*. (1960). By using the potential energy expression (1), the equations of motion of two cores and two shells can be given as.

$$\mu^2 MU = (R + Z_m C' Z_m)U + (T + Z_m C' Y_m)W \qquad \ldots\ldots\ldots..(2)$$

$$0 = (T^T + Y_m C' Z_m)U + (S + K + Y_m C' Y_m)W \qquad \ldots\ldots\ldots(3)$$

Here, *U* and *W* are vectors describing the ionic displacements and deformations respectively, *Zm*and *Ym*are the diagonal matrices of modified ionic charges and shell charges, respectively, *M* is the mass of the core, *T* and *R* are the repulsive Coulombian matrix respectively; *C'* and *Ym*are the

long-range interaction matrices which includes Coulombian and three-body interaction respectively; *S* and *K* are core-shell and shell-shell repulsive interaction matrices respectively T^T is the transpose of the matrix *T*. All these variables are as described in (Rignanese, 2005). The introduction of VWI and TBI in the framework of RSM with the elimination of *W* from eqs (2) and (3) leads to the secular determinant:

$$\left| D\left(\vec{q}\right) - \mu^2 MI \right| = 0 \qquad \text{……..(4)}$$

Here $\underline{D}$ (q) is the (6 x 6) dynamical matrix for Rigid Shell model expressed as :

$$\underline{D}(\vec{q}) = \left(\underline{R'} + \underline{Z}_m \underline{C'} \underline{Z}_m\right) - \left(\underline{T} + \underline{Z}_m \underline{C'} \underline{Y}_m\right) \times \left(\underline{S} + \underline{K} + \underline{Y}_m \underline{C'} \underline{Y}_m\right)^{-1} \left(\underline{T}^T + \underline{Y}_m \underline{C'} \underline{Z}_m\right) \qquad (5)$$

The numbers of adjustable parameters have been largely reduced by considering all the short-range interactions to act only through the shells. This assumptions leads to $\underline{R} = \underline{T} = \underline{SC'}$ is modified long-range interaction matrix have been given by (Kresse, 1995).

$$C' = C + \left(Z_m^{-2} Zr_0 f_0'\right) V \qquad \text{……(6)}$$

Where f_0' is the first –order space derivative and $Z_m$modified ionic polarizability. If we consider only the second neighbour dipole-dipole van der Waals interaction energy, then it is expressed as:

$$\Phi_{dd}^{VWI}(r) = -S_V \left| \frac{C_{++} + C_{--}}{6r^6} \right| = \Phi^V(r) \qquad (7)$$

……..

Where, S_v is lattice sum and the constants C_{++} and C_{--} are the van der Waals coefficients corresponding to the positive-positive and negative-negative ion pairs, respectively.

Vibrational Properties of ZrO_2

The term for is function dependent on overlap integrals of electron wave functions. Similarly, expressions for two distinct optical vibration frequencies (ω_L and ω_T) are obtained as:

$$\left(\omega_L^2\right)_{q=0} = R' + \frac{(Z'e)^2}{Vf_L} \frac{4\pi}{3V} \left(Z_m^2 + 6\gamma'^2\right) \qquad \text{…..(8)}$$

$$\left(\omega_T^2\right)_{q=0} = R_0' - \frac{(Z'e)^2}{Vf_T} \frac{4\pi}{3\varepsilon f} Z_m^2 \qquad (9)$$

…….

$$R_0' = R_0 - e^2 \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right); \; Z' = Z_m + d_1 - d_2,$$

$$R_0 = \frac{Z^2 e^2}{V} (A_{12} + 2B_{12})$$

$$f_L = 1 + \left(\frac{\alpha_1 + \alpha_2}{V} \right) \frac{4\pi}{3V} \left(Z_m^2 + 6\gamma'^2\right)$$

$$f_T = 1 - \left(\frac{\alpha_1 + \alpha_2}{V} \right) \cdot \frac{4\pi}{3V} \left(Z_m^2\right)$$

where α_1, α_2 electrical polarizabilites and Y_1, Y_2 are shell charge parameters of positive and negative ions.

Thermodynamically properties of ZrO_2

Zirconia has polymorphic crystallographic structures a phase transition is said to occur when the changes in structure details of the phase are caused by the variation of free energy. At room temperature, the structure of zirconia is monoclinic, and this structure will not change until 1170 °C. The heat capacity, free energy, entropy and internal energy are compared with that computed from the phonon spectra. This comparison is usually done by plotting theheat capacity, free energy, entropy and internal energy with T. Lattice dynamics is also one of the important aspects in such studies, because it has been suggested that soft phonon mode mechanism is the major cause of zirconia phasetransformations (Manicone *et al*., 2007). At high temperatures, quantum consideration carry significance changes shown in experimentally but at low temperature ofshows significant propertiesand the validity of the present model. The heatcapacity, free energy, entropy and internal energy at temperature T is calculating the exact variation of temperatures.Thermodynamic property of zirconia (ZrO_2) ns were calculated and also carried out using thePackage VASP (Lowdin, 1947; Lundqvist, 1961; Rignanese, 2005) coupled with PHONON (Tojo *et al*., 1999). Density of state, temperature dependence of free energy, specific heat capacity at constant volume were calculated and compared with experimental or others' simulation results (Luo *et al*., 2009; Pistorious and Clark, 1968). Specific heat capacity atconstant volume (Cv) was calculated using the following equation (Manicone *et al*., 2007).

$$U = \int_0^{\nu_m} \frac{h\nu^3 VF}{e^{h\nu/kT} - 1} d\nu \qquad \text{…(10)}$$

$$\text{and } C_\nu = \frac{3R}{6000} \sum_\nu g(\nu) E(\nu) d\nu \qquad \text{….(11)}$$

where *E(v)* is the Einstein function, R is the gas constant and *g(v)dv* are the number of frequencies lying in the interval *(v-dv/2)* to *(v+dv/2)*. According to thermodynamics, the equilibrium of a solid at a temperature Tis determined by the minimum value of the free energy.

$$F = E - TS \qquad \text{…….(12)}$$

The change in entropy (ΔS) of a system was originally defined for a thermodynamically reversible process as

$$\Delta S = \int \frac{\delta Q_{Rev}}{T} \qquad \text{…….(13)}$$

Density of States

To determine the phonon density of states for each polarization is given by using Monte Carlo sampling method.

$$g(\mu) = dN / d\mu = N \int_{BZ} \sum_{j} ¢[\mu - \mu_j(q)]dq = (VK^2 / 2®^2)dK / d\mu \quad (14)$$

$N = (L/2\pi)^3 (4\pi K^3/3)$, K is wave vector and $L^3=V$. where N as a normalization constant such that $\int g(\mu)d\mu = 1$ and g $(\mu)d\mu$ is the ratio of the number of eigen states in the frequency interval $(\mu, \mu + d\mu)$ to the total number of eigen states $\mu_j(q)$ is phonon frequency of the j^{th} normal mode of the phonon wave vector q.

Computation

All calculation carried out using (DFT) based Phonon- VASP code and (VTBFS) model. The effect of pressure on the crystal structure, electronic structure and vibrational properties represented in our calculation. The Internal energy, entropy, free energy and heat capacity curve at temperature from at 300K and 1100K has shown in Fig .2-5.Before staring calculation we have to optimize geometry of the crystal firstly then conducted PHONON -VASP software calculations. Using the first principles calculations, the properties of ZrO2 has been investigated. The calculated thermodynamical curve has shownthe validity withaavailable experimental data.The internal energy value 7(kcal/mol) has obtained at 300K but at higher temperature the energy value is changed attended and 84.5(kcal/mol) at 1100K.

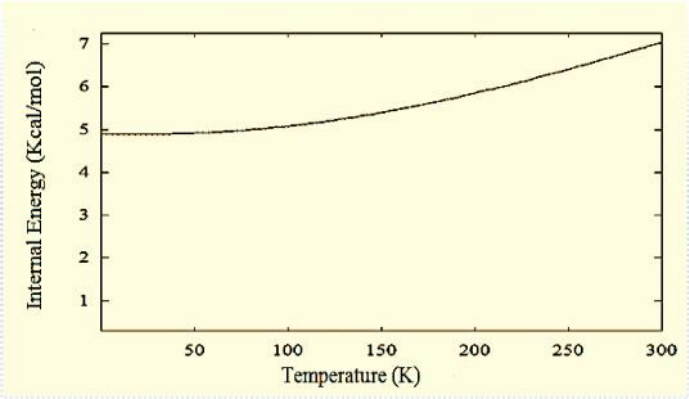

Fig.2(a) Internal Energy of ZrO_2 at 300K

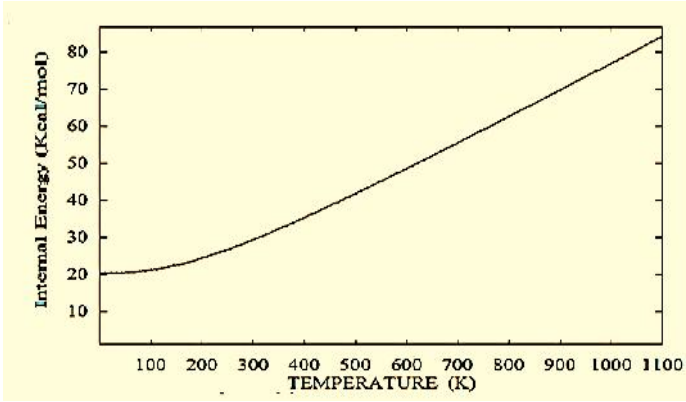

Fig.2(b) Internal Energy of ZrO_2 at 1100K

The curvefor free energy has shown in Fig 3.(a) value of free energydecreasing continuously till attaining the value of 300K. In Fig 3.(b) we have obtained the value of free energy of ZrO_2 at the temperature of 1100K which is falling sharplyup to the value of -60 (kcal/mol).

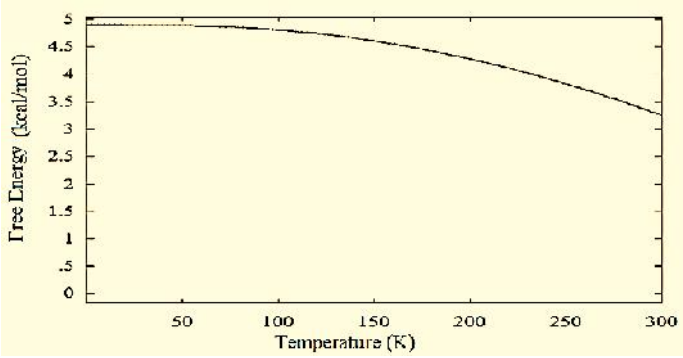

Fig.3 (a) Free Energy of ZrO_2at 300K

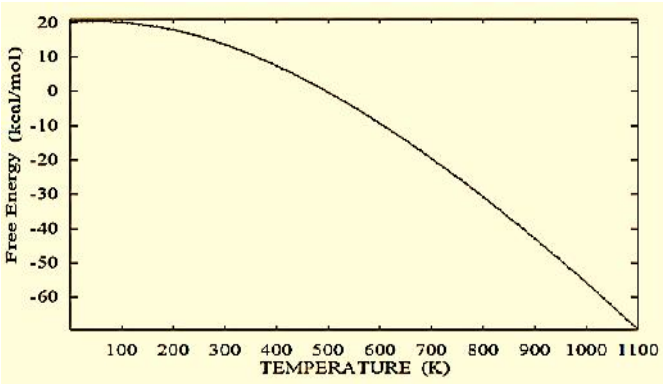

Fig.3(b) Free Energy of ZrO_2 at1100 K

The entropy versus temperature curvefor ZrO_2 has shown in Fig 4.(a) and (b) the curve spread over a wide range of temperature. In Fig.4(a) entropy value continuously decrease up to 60K and then sharply for zero value which shows orderliness. While in fig.4 (b) entropy value sharply fall look linearly from 700K to 300 K and after this value then some abrupt changes noted till zero value so in case of higher temperature entropy is more ordered then at 300K.

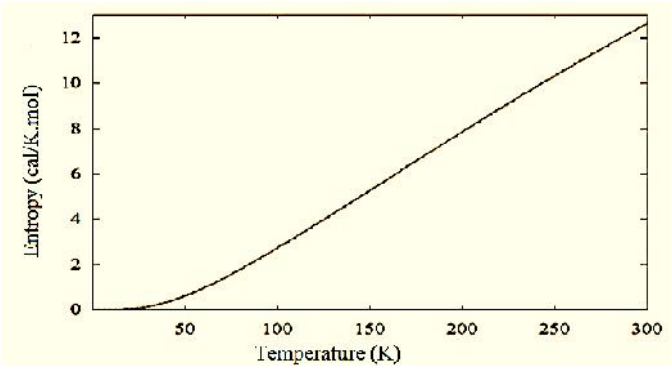

Fig.4(a)Entropy of ZrO_2 for 300K

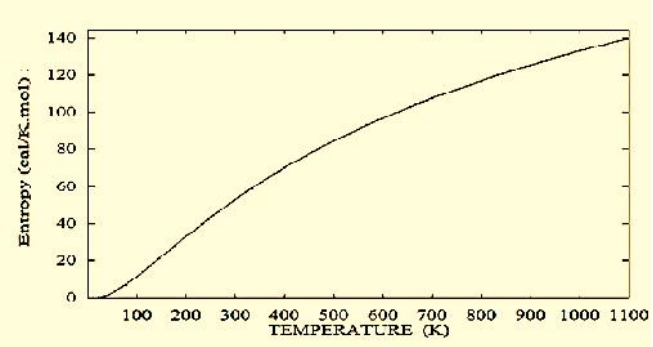

Fig.4 (b) Entropy of ZrO_2 for 1100K

Table 1. Phonon dispersion relations along the symmetry directions

Index	SymP	q1	q2	q3	Kx	Ky	Kz
1	Γ	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	X	0.5000	0.0000	0.5000	0.0000	0.1979	0.0000
3	W	0.5000	0.2500	0.7500	0.0990	0.1979	0.0000
4	L	0.5000	0.5000	0.5000	0.0990	0.0990	0.0990
5	Γ	1.0000	1.0000	1.0000	0.1979	0.1979	0.1979

Table 2. Effective charges of Transverse and Longitudinal modes

Mode	Frequency in (THz)	Real Frequency			Imaginary Frequency		
		Zx	Zy	Zz	Zx	Zy	Zz
TO	0.000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000
TO	7.634	1.1656	0.1559	0.0897	0.0000	0.0000	0.0000
TO	7.634	0.0899	0.0043	-1.1759	0.0000	0.0000	0.0000
TO	7.634	0.1557	-1.1690	0.0076	0.0000	0.0000	0.0000
TO	7.634	1.1656	0.1559	0.0897	0.0000	0.0000	0.0000
TO	17.370	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TO	17.370	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000
TO	17.370	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000
TO	7.634	0.0899	0.0043	-1.1759	0.0000	0.0000	0.0000
LO	0.000	0.0000	0.0000	-0.0000	0.0000	0.0000	-0.0000
LO	19.751	0.2216	0.2216	-0.2216	-0.0000	-0.0000	0.0000
TO	7.634	1.1656	0.1559	0.0897	0.0000	0.0000	0.0000
TO	7.634	0.0899	0.0043	-1.1759	0.0000	0.0000	0.0000
TO	17.370	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000

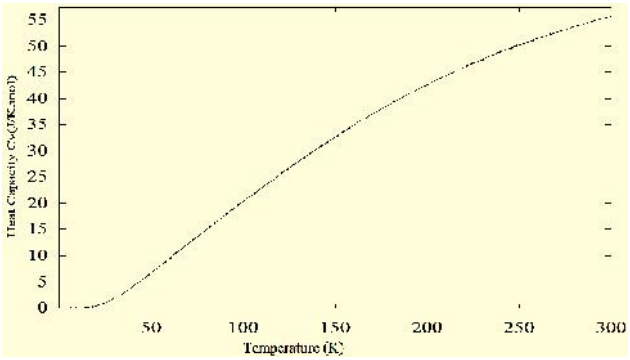

Fig.5(a) Heat Capacity of ZrO_2 at 300K

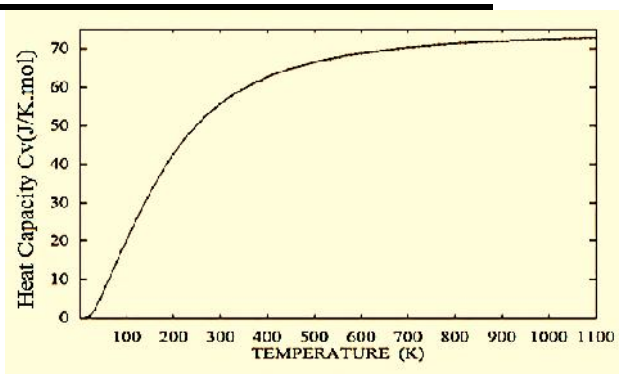

Fig.5(b) Heat Capacity of ZrO_2 at 1100K

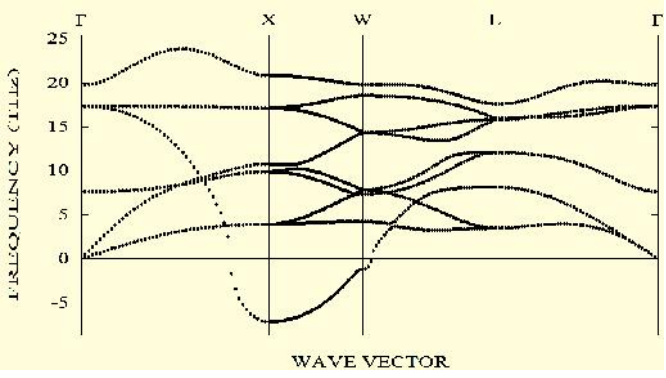

Fig.6. Phonon dispersion curve of ZrO_2

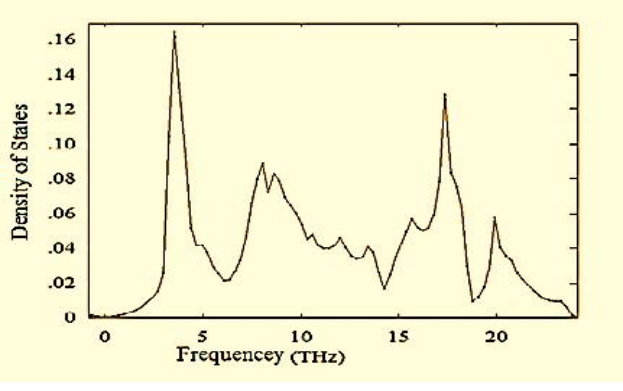

Fig.7. Density of states curve of ZrO_2

In the Fig 5.(a) and 5.(b) the temperature verses heat capacity graph has shown. The specific heat curve decreases exponentially with the lowering of temperature. At 0 K the internal energy minimum value and the heat capacity is zero. As the temperature of ZrO_2 raised the involvement of different type of mechanism of heat absorption become apparent. The energy of the ZrO2 is used as a reference to properly the theoretical study of density of states DOS. This theoretical finding is in qualitative agreement with the experimental observations. The illustrated thermodynamic properties obtained and confirmed the ceramic characteristics of ZrO_2. The phonon dispersion relation curve has shown in Fig.6 and theoretical data along symmetry direction is reported in Table-1. The effective charge along transverse and longitudinal mode with real and imaginary frequency along three coordinates has reported in Table-2.

An accurate description of phonon frequencies is a stringent test for a theoretical model. The lower section of Γ-X direction indicates higher longitudinal energy while most of the branches in the X-L direction converge as non-degenerate, thus leading to the expected nine branches for a typical cubic structure has shown in dispersion relation curve in Fig.6. The DOS curve with frequency value is reported in Fig .7. At lower frequency at 5 THz the peak attended the maximum value, there are many states available for occupation and on increasing the frequency value a local density of states (LDOS) available, frequency of 18.5 THz more occupied states are available andless occupied states are above the 20THz frequency range.

RESULTS

The present modal is based on this concept thatin solid phase the lattice vibrations are quantized and can be described by quasi-particles, phonons. It is assumed that the phonons represent a normal mode vibration thus all parts of the lattice vibrate withthesamefrequency. This has been applied for study of lattice property with short-range interactions effective up to the second neighbor.In the present study despite the lower symmetry of ZrO_2 and the uncertainty as to the exact nature of the distortion of the lower–temperature structure. A tremendous change in the nature of slope has been observed in 300 K and 1100K temperature. Our theoretical study at lower temperature side shows a better agreement but at the higher temperature side slight disagreement may be ascribed to the non-inclusion of the harmonic interactions in used present model, which it may be inferred that the incorporation of van der Waals interactions is essential. The Complete phonon dynamical properties of ZrO_2 theoreticallyreported hasbeen agreed with experimental reported data.

Conclusion

To sum up, we can say that the contributions of (VWI) and (TBI) are essential for the description of the complete lattice dynamical study of ZrO_2. By used of present model (VSTBFSM) we have successfully calculated the value of internal energy, free energy, heatcapacity, entropy value, phonon dispersion relation anddensity of states of ZrO_2. Therefore, it is concluded that the most realistic model for study of complete harmonic dynamical behaviour of the Zirconia can be completely reported by introducing the effect of van der Waals interactions (VWI) and expression for the contribution of (TBI) to the dynamical matrix, which has been rigorously derived and evaluated successfully in present study. The (TBI) has adequately described the lattice dynamics, dielectric, photo-elastic, relative stability, polymorphic phase-transition, an harmonic –elastic and thermal properties.So the present model has provided a new tool for future researcher for complete theoretical analysis of crystals in the availability of the some required experimental data. The presentmodel (VTBFSM) has been successfully used by some researchers (Luo *et al*., 2009; Pistoriou and Clark, 1968; Ram and Kushwaha, 1985; Kushwaha and Kushwaha, 1980; Singh and Khare, 1982; Singh and Prabhakar, 1988; Srivastava *et al*., 2010; Srivastava and Upadhyaya, 2010; Tiwari *et al*., 2010; Srivastava and Upadhyaya, 2011; Srivastava, 2012; Srivastava, 2013) for the complete theoretical phonedynamics ofdifferent alkali halide crystals and also for semiconducting materials which had proven importance and validity of the present model.

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