Lattice dynamical study and ultrasonic properties of thorium carbide (ThC)

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Abstract

In this paper thermophysical andultrasonic propertiesofthorium carbide (ThC)inthe effects of three-body interaction (TBI) and by use of VTBFS model is reported.we are theoretically reporting elastic constants, pressure derivatives, dispersion relation curve, specific heat curve, combined density of states (CD's) and equation of state and some ultrasonic propertiesof the thorium carbide (ThC). The achieved results are good with earlier reportedresults,whichgive very important information of this compound for further research.

Keywords: Thermophysical &ultrasonic properties, elastic constants, elastic moduli, Debye Temperature and phonon interaction.

1 Introduction:

Thorium-based materials are currently being investigated in relation with their potential utilization in Generation-IV reactors [1] due to many additional physical advantages, likely higher melting points, corrosion resistivity, lower thermal expansion coefficients and larger thermal conductivity.The identity of thorium carbide (ThC)can be understood correctlyby energy gap& dielectric constants and large -ve ion polarizability.Due to extraordinary properties in optical vibration frequencies, it is highly demanding field for experimental and theoretical researchers [2-14]. Every atom which is situated on the cube centre of opposite in nature is bordering by 8 opposite charges nearby and 12 same charged nextnearby. It'sarising from the interpretation of the reasonable models for solids, can be developed on (TBI) effect in RIM & RSMframework.The study of propagation of ultrasonic waves in pure liquids and in its mixtures are well established for determining the properties and the structure of matter through intermolecular interactions. Its prime importance in deciding the structure and properties of crystal, phase transitions, etc. In the last decades we have been observed fascinating progress in the field of ultrasonics. Many experimental investigations of semiconductors, metals, magnetic crystals, quantum liquids, glasses, superconductors, insulators phase transition and particular data have been discussed by ultrasonics. In the study and accurately determination is measured of highly sensitive molecular interactions by use of ultrasonic velocity and their useful acoustical parameters. Velocity of ultrasonic with density, viscosity, and dielectric methods[15,16].

In recent years Richard et al. [17] have generated a pseudopotential and investigated the crystal structure of thorium. For this material Bouchet et al. [18] have presented results of high-pressure lattice dynamics and thermodynamic properties using Density Functional Theory (DFT) and the pseudo-potential method. Also, for thorium, Hu et al. [19] have reported on a first-principles study of the phase transition and thermodynamic properties. Likewise, Jaroszewicz et al. [20] have derived an inter-atomic pair potential for thorium by using Chen-Möbius inversion of cohesive energy. With this interatomic potential they have calculated [21], elastic and thermal properties. For thorium dioxide,Lu et al. [22] have investigated

the thermodynamic properties and structural stabilities similarly, Wang et al. [23] have obtained mechanical properties, electronic structure, and phonon dispersion of ground state thorium dioxide as well as the structure behaviour at high-pressures. Based on DFT Lu et al. [24] investigatedelectronic structure; mechanical and thermodynamic properties derived from lattice dynamics data of thorium nitride. Modak and Verma [25] have studied the electronic properties, phonon dispersion relations, elastic constants, structural phase transitions of ThN by means of pseudopotential DFT methods. With the full-potential all-electron linearized augmented plane wave plus local orbital method Atta-Fyn and Ray [26] obtained the structural, electronic, and magnetic properties of ThN. In the case of ThC, structural, mechanical, electronic, and thermodynamic properties were investigated by Aydin et al. [27] by means of plane-wave pseudopotential calculations. LimandScuseria [28] have studied structural parameters and electronic properties of ThC using gaussian-type-orbitals and densityfunctional theory with several types of functionals.

2 Material and Method

The Thorium chalcogenides seem to be purely ionic in nature because the constituent ions follow the additivity rule of ionic radii. Due to interaction between ions TRIM and TRSM models have been used in different approaches. PDCs ofthorium carbide (ThC)is drawn by using TRIM and TRSM, for further studies of specific heats, CDS peaks, phonon Raman spectra, anharmonic properties, and study of phase transition ofi have used TRS model only. The present study will be helpful in making qualitative understanding of all these mention properties. The crystal potential per unit cell expressed as

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

Φ^{C}use as 1ong-range coulomb interaction potentia1

On consideration of single ion only i.e polarizable and deformable consideration by Singh et.al [29-30] presented and modified the secular determinant equation

$$\left|\underline{D}(\vec{q})-\omega^{2}\underline{M}\underline{I}\right|=0 \quad (2)$$

Here $\underline{D}$ (q) is the (6 x 6) dynamical matrix for Rigid Shell model. The dipole-dipole van der Waal's interaction (VWI) energy up to second neighbour is expressed as:

$$\Phi_{dd}^{VWI}(r)=-S_{V}\left|\frac{C_{++}+C_{--}}{6r^{6}}\right|=\Phi^{V}(r) \quad (3)$$

using secular equation (2) for elastic constants equation can give as:

$$C_{11}=\frac{e^{2}}{4r_{0}^{4}}\left[0.7010Z_{m}{}^{2}+A_{12}/6+B_{12}/3+5.4283\xi'^{2}\right] \quad (4)$$

$$C_{12}=\frac{e^{2}}{4r_{0}^{4}}\left[-0.6898Z_{m}{}^{2}+A_{12}/6-2B_{12}/3+5.4283\xi'^{2}\right] \quad (5)$$

$$C_{44}=\frac{e^{2}}{4r_{0}^{4}}\left[-0.3505Z_{m}{}^{2}+A_{12}/6+B_{12}/3\right] \quad (6)$$

2.1 Vibrational Properties of (ThC)

The term fo 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:

$$(\mu\omega_L^2)_{q=0} = R_0' + \frac{(Z'e)^2}{Vf_L}\frac{8\pi}{3}\left(1 + 12Z_m^{-2}Z_{r0}f_0'\right) \quad (7)$$

$$(\mu\omega_T^2)_{q=0} = R_0' - \frac{(Z'e)^2}{Vf_T}\frac{4\pi}{3} \quad (8)$$

2.2 Thermodynamically properties

Density of state, temperature dependence of free energy, specific heat capacity at constant volume were calculated. The Cv is calculated by using the following equation [31].

$$U = \int_0^{\upsilon_m} \frac{h\upsilon^3}{e^{h\upsilon/kT} - 1} d\upsilon \quad (9)$$

and $$C_\upsilon = 3NK_B \frac{\sum_\upsilon \{E(x)\}G(\upsilon)d\upsilon}{\sum_\upsilon G(\upsilon)d\upsilon} \quad (10)$$

Where $E(x)$ is the Einstein function difiend as $E(x) = x^2 \frac{e^{(x)}}{\{e^{(x)} - 1\}^2}$ and $\sum_\upsilon G(\upsilon)d\upsilon$ =Total number of frequencies considered lying in frequency interval.

2.3. Density of states

To determine the phonon (DOS) for each polarization is given by VTBFS model.The phonon density is given as $g(\omega) = \frac{dN}{d\omega} = N\int_{BZ}\sum_j \delta[\omega - \omega_j(q)]dq = \left(\frac{VK^2}{2\pi^2}\right).\left(\frac{dK}{d\omega}\right)$ (11)

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 $\int g(\omega)d\omega = 1$ and $g(\omega)d\omega$ is the ratio of the number of eigenstates in the frequency interval.

2.2. Ultrasonic and Debye Velocities

Ultrasonic velocity plays a vital role in the characterization of materials. The propagation of ultrasonic waves through anisotropic solids depends on the strains along the <100>, <110>, <111> directions. When ultrasonic waves propagate through a medium, their velocity has three modes of propagation, one longitudinal acoustical (V_L) and two shear acoustical (V_{S1}, V_{S2}). The expressions for V_L, V_{S1} and V_{S2} are presented elsewhere.[32,33] Along the <100> crystallographic direction:

$$V_L = \sqrt{C_{11}/d}$$

$$V_{s1} = V_{s2} = \sqrt{C_{44}/d} \quad (12)$$

Along the <110> crystallographic direction:

$$V_L = \sqrt{(C_{11} + C_{12} + C_{44})/2d}$$

$$V_{s1} = \sqrt{C_{44}/d}$$

$$V_{s2} = \sqrt{(C_{11} - C_{12})/d} \quad (13)$$

Along the <111> crystallographic direction:

$$V_L = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3d} \quad (14)$$

$$V_{S1} = V_{S2} = \sqrt{(C_{11} - C_{12} + C_{44})/3d}$$

where d is the density of chosen material. The Debye average velocity V_D can be determined using Debye theory.[33]V_D is average of V_L, V_{S1} and V_{S2} and expressed as:

Along the <100> and <111> direction

$$V_D = \left[\frac{1}{3}\left\{\frac{1}{V_L^3} + \frac{2}{V_s^3}\right\}\right]^{\frac{-1}{3}} \quad (15)$$

Along the <110> direction

$$V_D = \left[\frac{1}{3}\left\{\frac{1}{V_L^3} + \frac{1}{V_{s1}^3} + \frac{1}{V_{s2}^3}\right\}\right]^{\frac{-1}{3}} \quad (16)$$

3. Computation: In this paper We calculate the Debye temperature from the elastic constants using Eq. (4-6). Another procedure to calculate Θ_D is by fitting CV, in the low temperature range the CV's Debye approximate ion Eq. (9-10). This yields Θ_D = 298 K. These two values are in good agreement, the differ in theoretical result by less than 13.7%. The experimental results for Θ_D were obtained on basis of C_P measurements. The PDOS is plotted in Fig. 1.

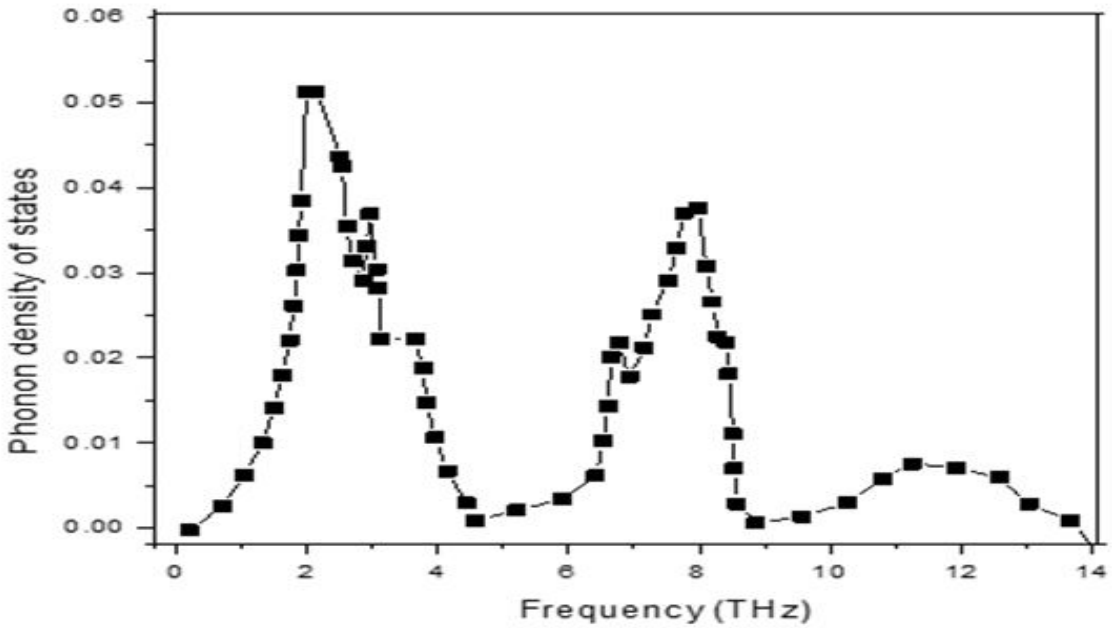

Figure-1 Phonon density of States curve

The integration over the Brillouin zone has been performed with the tetrahedron method [34]. There is only a little overlap between the projected PDOS for thorium and carbon. We observe that the PDOS is

almost split into two: the range of 0–5 THz. This behaviour is related to the much higher weight of thorium with respect to carbon. Molar heat capacities of ThC. CV derived from phonon frequencies as a function of temperature. In Fig. 2 we present the molar heat capacity C_V .In this range it is noted a very good agreement with the experimental result. At high temperature'sdifference between C_V and $C_P$the convergence of C_V to the Dulong–Petit's limit.

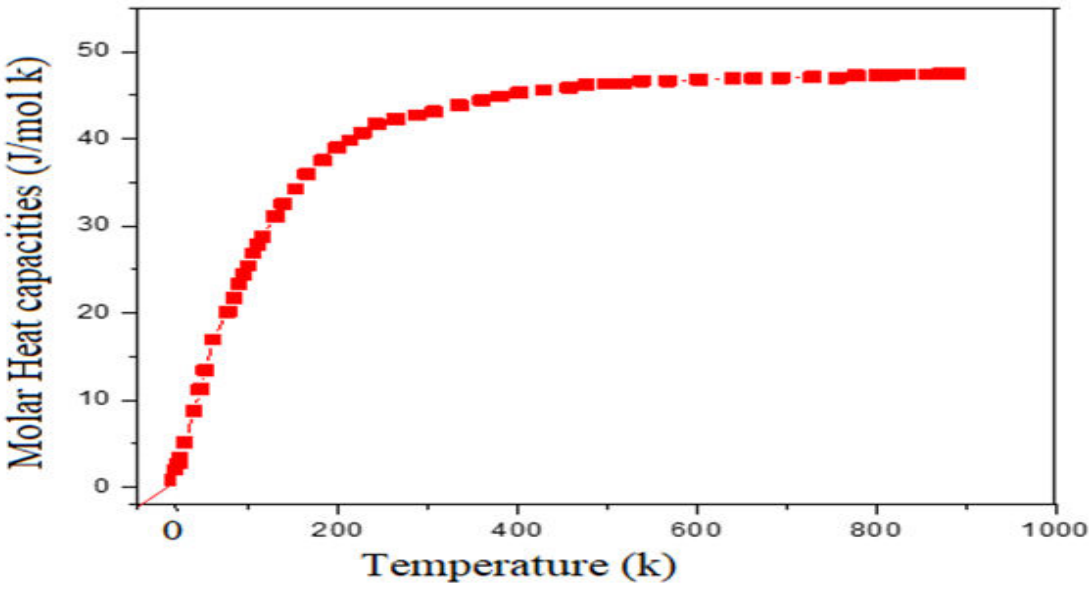

Figure-2 Molar Heat capacities curve

In Figure-3 the phonon dispersion curves calculated along several symmetry directions at zero pressure and zero kelvin conditions. We observe six phonon modes (3 acoustic and 3 optics branches) in the dispersion relations, this is in accordance with a primitive cell with two atoms in the transverse and longitudinal branches of the phonon dispersion curves. The elastic constant s, derived from the acoustic branches of the phonon spectrum, and related magnitudes.

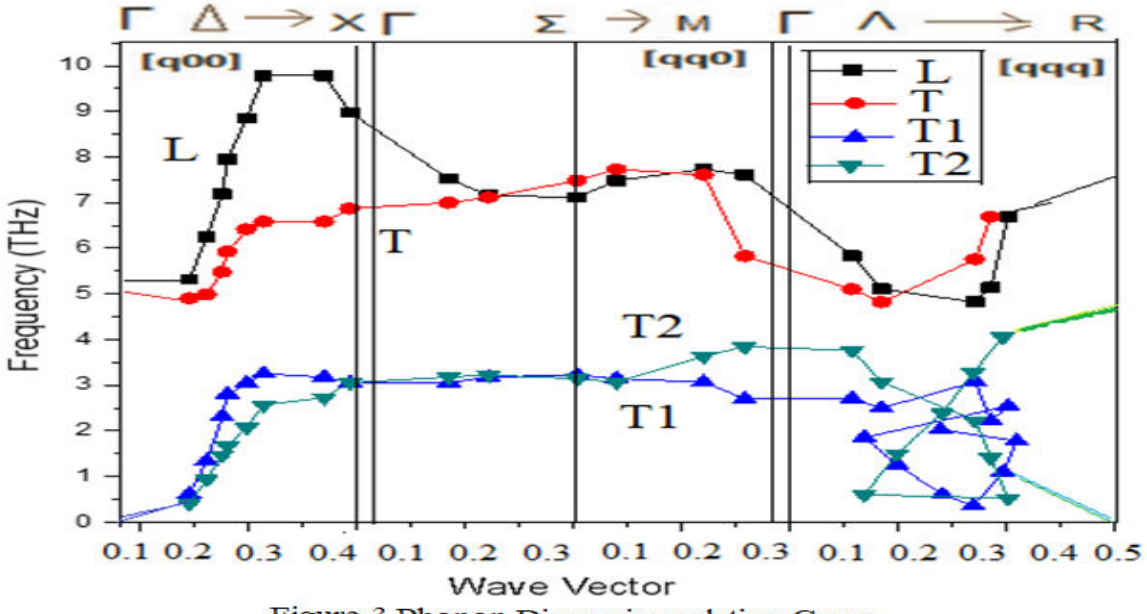

Figure-3 Phonon Dispersion relation Curve

Table 1 - Input data for ThC in terms of $C_{11,}$ C_{12} ,$C_{44,}$Gand E in (GPa) ,d (gm/cm^3),v_l ,v_s(cm/s)

Input Data	C_{11}	C_{12}	C_{44}	d	G	E	Longitudinal Wave velocity v_l	Shear wave velocitiesv_s
ThC (Shein et.al)	252.2[35]	96.3[35]	60.2[35]	10.61[35]	66.7[35]	174.1[35]	----------	----------
ThC (Aydin et.al)	276.4[34]	87.2[34]	99.1[34]	10.61[34]	87.8[34]	222.2[34]	----------	----------
Present Study	243.5	86.65	73.63	10.61	72.32	171.37	5.1357	3.028

Table-2Calculated Elastic moduli of the ThC

Input Data	Bulk Modulus (B)	Tetragonal Modulus (C_s)		Young's Modulus (Y)	Poisson's Ratio (ν)	Anisotropic Ratio (A)	Micro Hardness (Parameter) (H)
		Along <100>	Along <110>				
Using Parameter of (Sheinet.al)[35]	148.2666	60.2	77.95	414.0386	0.30439	0.77228	20.696
Using Parameter of (Aydin et.al) [34]	150.2666	99.1	94.6	498.7707	0.25547	1.0475	32.381
Present Study	138.9333	73.63	78.42	428.0591	0.27821	0.9388	24.7580

Table- 3Calculated Orientation dependent ultrasonic velocities V_L, V_{S1} ,V_{S2} and V_D (in $10^3 ms^{-1}$) of ThC at room temperature

Material Orientation	V_L (Longitudinal Acoustical)		V_{S1} (Ist Shear acoustic)		V_{S2} (2nd Shear acoustic)		V_D (Debye Temperature)	
	Using value (Sheinet.al)	Using value (Aydin et.al)	Using value (Sheinet.al) et.al)	Using value (Aydin et.al)	Using value (Sheinet.al) et.al)	Using value (Aydin et.al)	Using value (Sheinet.al) et.al)	Using value (Aydin et.al)
<100>	4.8754	5.1039	2.3819	3.0561	2.3819	3.0561	2.67562	3.38141
<110>	4.3886	4.6695	2.3820	3.05624	4.2540	4.0879	3.11962	3.69449
<111>	4.6410	5.1591	2.6056	3.0085	2.6056	3.0085	2.89952	3.88497

3. Result & Discussion

In this report we have calculated about theUltrasonic and thermophysical properties of ThC use of [VTBFS] model. The effect of pressure on the crystal structure and electronic-vibrational properties are reported in calculation. The input data and present calculated value are reported of ThC is reported in Table-1Elastic moduli for the ThC is reported in table -2 and**o**rientation dependent ultrasonic velocities, Debye velocity in Table-3 taking the values of input constants from and calculated the parameter[11,12].The phonon density of states (PDOS) is predominantly a function of the local atomic structure, and sensitive to the atomic-level stresses and microstructure. The ultrasonic and thermophysical properties with lattice dynamical calculations of ThCbased on different available parameters. Orientation dependent ultrasonic velocities in table-3 reported theoretically by using the experimental data [13-17].The phonon density of states curve is shown in Figure-1. Ultrasonic velocity plays a vital role in the characterization of ThC. The propagation of ultrasonic waves depends on the strains along the <100>, <110>, <111> directions. The Molecular heat capacitiescurve VsMolar heat capacities has shown in Figure-2withthe available theoretical and experimental result which has shown parallel to the present calculated results.The phonon dispersion relation curve is reported in Figure-3.

4. Conclusion

In the present study despite the lower symmetry ofThC the uncertainty as to the exact nature of the distortion of the lower–temperature structure. Our study at the lower temperature side shows a good agreement and at higher temperature side slight disagreement occurred, whichit may be deduced the incorporation of van der Waals interactions is essential. The Complete thermophysical property ofThCare theoretically reported, which have agreed with reported data. [15-22]. The present authors and other researchers have been already used the present model and successfully reportedthermophysical properties of alkali halides and semiconductor materials [23-32].To sum up the contributions of VWI are essential for the description of the lattice dynamics and thermodynamical study of ThC compound.

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