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First-Principles Calculations of the Structural, Mechanical and Thermodynamics Properties of Cubic Zirconia

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Abstract

The structural, mechanical and thermodynamics properties of cubic zirconium oxide ($cZrO_2$) were investigated in this study using *ab initio* or first-principles calculations. Density functional theory was used to optimize the crystal structure of $cZrO_2$ and thereafter, simulations were conducted to predict the lattice parameters and elastic constants. The Zr-O bond distance was calculated as 2.1763 Å with unit cell density of 6.4179 g/cm^3. The data obtained were used to determine Young's modulus, bulk modulus, Poisson's ratio and hardness of $cZrO_2$ as 545.12 GPa, 136.464 GPa, 0.1898 and 12.663(H_v) respectively. The result indicates that $cZrO_2$ is mechanically stable with thermodynamics properties of a refractory material having potential for structural and catalytic applications in various forms as a nanomaterial.

Keywords

Cubic Zirconium Oxide, First-Principles Calculation, CASTEP, Elastic Constants

1. Introduction

Recently, zirconium oxide in cubic polymorph has attracted interest due to its mechanical and thermal properties. These interests have resulted in the use of $cZrO_2$ to various applications such as catalysts, fuel cells, oxygen sensors and others [1]-[4]. Thus $cZrO_2$ has been synthesized at nanoscale in various forms. The sol-gel method

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was used to produce ZrO_2 nanoparticles with fairly uniform dimension ranging from 50 nm to 90 nm [5]. ZrO_2 nanosheets with thickness in the range of 3.2 - 4.2 nm were produced through bottom-up synthesis by impregnation of graphene oxide in cyclohexane containing Zr-based alkoxides [6]. Also, ZrO_2 nanotubes have been prepared via several methods such as direct anodization, template-assisted depositions and hydrothermal treatments [2]; the nanotubes obtained have different inner and outer diameters, thicknesses and lengths.

For efficient and cost-effective applications of $cZrO_2$, its structural and mechanical properties are required at molecular and atomic scale. But due to complexity and high cost of equipment, only limited experiments have been conducted to characterize required properties of $cZrO_2$ at nanoscale and/or atomic level [2] [4]. This led to computational modeling and simulation of various properties of $cZrO_2$ based on atomistic and continuum approaches [1] [2]. However, most of the simulations already conducted are limited to properties such as electronic structures, phonon dispersion, surface adsorption and diffusion [7]-[13] with limited emphasis on structural and mechanical properties.

Therefore, in this study the first-principles calculations are utilized to numerically predict the structural characteristics, mechanical properties and thermodynamic properties of $cZrO_2$. The values obtained are used to analyze the structural stability of $cZrO_2$ and compared available data for further simulation(s).

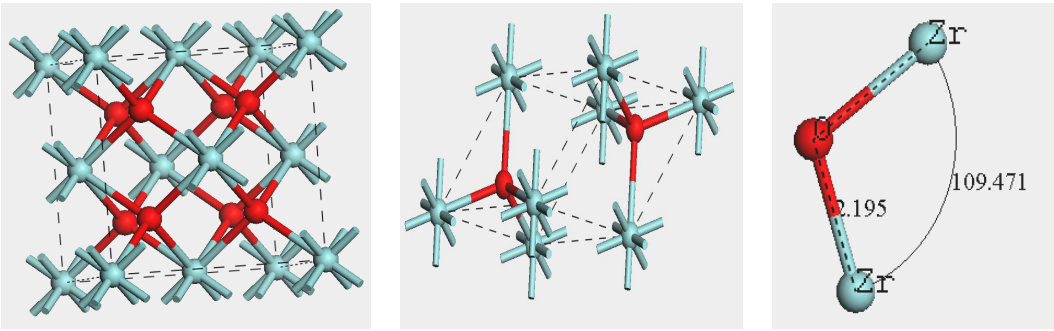
2. Computational Methods

The 3D structure of $cZrO_2$ was modeled from available data [2] using the *surface builder* tools of the *Material Studio* software [14]. The crystal structure of$cZrO_2$ was optimized geometrically in order to obtain initial lattice parameters and density based on density function theory (DFT) as implemented in Cambridge Sequential Total Energy Package (CASTEP) code [15]. In this calculation, the Generalized Gradient Approximation (GGA) having Burke-ErnZerhof Potential (PBE) for solids was used [13]. To obtain accurate structures, the calculations were conducted in the irreducible Brillouin zone with 8 × 8 × 8 k point mesh Monk horst-Pack scheme [16]. In order to obtain plane wave expansions, a kinetic energy cut-off value of 380 eV was used. Thereafter the Broyden- Fletcher-Goldfarb-Shannon (BFGS) optimization method was used with fixed basis quality to obtain the symmetric crystal structure of $cZrO_2$. During the optimization process, the total energy was designed to converge to 5×10^{-6} eV and the force per atom diminished to 0.002 eV/Å. The optimized structure of $cZrO_2$ was then simulated to obtain required mechanical and thermodynamics properties.

3. Results and Discussion

3.1. Crystal Structure

The bulk crystal structure of $cZrO_2$ belongs to the *Fm*-3m space [4] [9] and is modeled in various forms as seen in **Figure 1**. The geometric structure has influence on the properties of the material even at nanoscale [2]. After optimization, all the lattice parameters were recorded and compared with values obtained from other simulations and experiments as summarized in **Table 1**. It was observed that the deviation of the lattice parameters is less than 3% from the experimental values, which may be due to the approximation method used during optimization.



(a) (b) (c)

Figure 1. Crystal structure of $cZrO_2$ in various forms: (a) Unit Cell; (b) Primitive Cell; (c) Zr-O Bond (O_2 and Zr atoms are represented by red and light blue balls respectively).

Table 1. Lattice parameters of optimized $cZrO_2$.

Parameters	Simulations		
	Present Study	Other(s)	Experimental
a = b = c (Å)	3.55381	3.58031 [4]	3.6012 [17]
Bond Length (Zr-O), Å	2.1763	2.19537 [2]	2.205 [5]
Volume ($Å^3$)	31.8808	32.5850 [3]	32.723 [17]
Density (g/cm^3)	6.41791	6.081 [18]	6.151 [18]

3.2. Mechanical Properties

The mechanical properties of $cZrO_2$ are based on the elastic constants of the crystal which indicates response to external forces. There are six components of stress and a corresponding six components of strain for the general 3-D case. Thus, Hooke's law may be expressed as:

$$\sigma_i = C_{ij}\varepsilon_j \tag{1}$$

$$\varepsilon_i = S_{ij}\sigma_j \tag{2}$$

where C = stiffness or elastic constant, S = compliance, σ = stress and ε = strain. In matrix format, the stress-strain relation showing the 36 (6 × 6) independent components of stiffness can be represented as [3]:

$$\begin{pmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{pmatrix} = \begin{pmatrix}C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16}\\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26}\\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36}\\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46}\\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56}\\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}\end{pmatrix}\begin{pmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{pmatrix} \tag{3}$$

The number of independent elastic constants in $cZrO_2$is three (3), *i.e.* C_{11}, C_{12} and C_{44} which are computed as 596.33, 137.04 and 74.34 GPa respectively. Also the bulk modulus (B) was calculated as 290.134 GPa using the Voigt model, which is comparable to experimental value [17].

With reference to Born-Huang's lattice dynamic theory [19], the mechanical stability of a cubic system is based on the conditions expressed in Equations (4) and (5).

$$C_{11} > 0, C_{44} > 0, C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0 \tag{4}$$

$$C_{12} < B < C_{11} \tag{5}$$

Based on conditions outlined in Equations (4) and (5), the structure is mechanically stable due to lattice parameters and orientation of the crystal. The stability will make polycrystalline $cZrO_2$ less vulnerable to generating micro cracks [19].

For $cZrO_2$, computed Young's modulus (E) is 545.12 GPa, shear modulus (G) based on Voigh model is 136.464 GPa and the Lame modulus based on Reus model is 222.195 GPa. The G/B ratio indicates the ductility or brittleness of a material [19] and was found out to be 0.469, which indicates that $cZrO_2$ ionic and brittle. This is becausefor covalent and ionic materials, the typical relations between bulk modulus and shear modulus are as $G \approx 1.1B$ and $G \approx 0.6B$, respectively [20]. The Poisson's ratio (υ) of $cZrO_2$ vary from 0.14 to 0.189, which indicates less metallic and ionic character in the Zr-O bond.

In crystals, hardness quantifies the resistance to deformation and may be predicted using microscopic models [17]. The hardness (Hv) of $cZrO_2$ is determined using a semi-empirical equation defined as follows [21] [22]:

$$H_v = 0.92K^{1.137}G^{0.708}, K = G/B \tag{6}$$

The obtained hardness (Vickers number) for $cZrO_2$ is 12.663, which is consistent with the chemical bonding and elastic modulus as analyzed above and in similar other studies [19]-[22].

3.3. Thermodynamic Properties

The thermodynamic properties of a solid have direct relevance to its phonon characteristics as it indicates the quantum of elastic strain energy [19]. Hence, the phonon dispersion curve of a material elucidates the thermal properties based on the concept of lattice vibrations and interpretation of lattice dynamics [15]. Using the method of linear response with 0.05 1/Å q-vector grid spacing, the phonon dispersion curves (PDC) for $cZrO_2$ was generated as shown in **Figure 2**. The lower section of G-X direction indicates higher longitudinal energy while most of the branches in the X-K direction converge as non-degenerate, thus leading to the expected nine branches for a typical cubic structure [19].

With the aid of data from the phonon dispersion curves (PDC), quasi-harmonic approximation was used to evaluate some temperature dependent properties of $cZrO_2$ such as entropy, enthalpy, free energy and Debye temperature as illustrated in **Figure 3** and **Figure 4**. From **Figure 3**, the zero-point energy was computed to be 0.20385 eV and the heat capacity per unit cell had a maximum value of 16.8957 cal/K (0.07069 kJ/K) at 992.25 K. Debye temperature gives an approximation for the low temperature heat capacity of insulating crystalline solids. The maximum Debye temperature for $cZrO_2$ was found to be 946 K which is similar to 963 K for Y_2O_3 stabilized $cZrO_2$ determined experimentally using neutron powder diffraction [23]. All the computed thermodynamics properties of $cZrO_2$ indicates it has less thermal conductivity despite having high ionic conductivity thus confirming its major characteristic as a refractory material.

4. Conclusion

Using the first principles calculations, the properties of $cZrO_2$ were investigated. The calculated lattice parameters showed conformity with available experimental data. The computed properties based on elastic constants

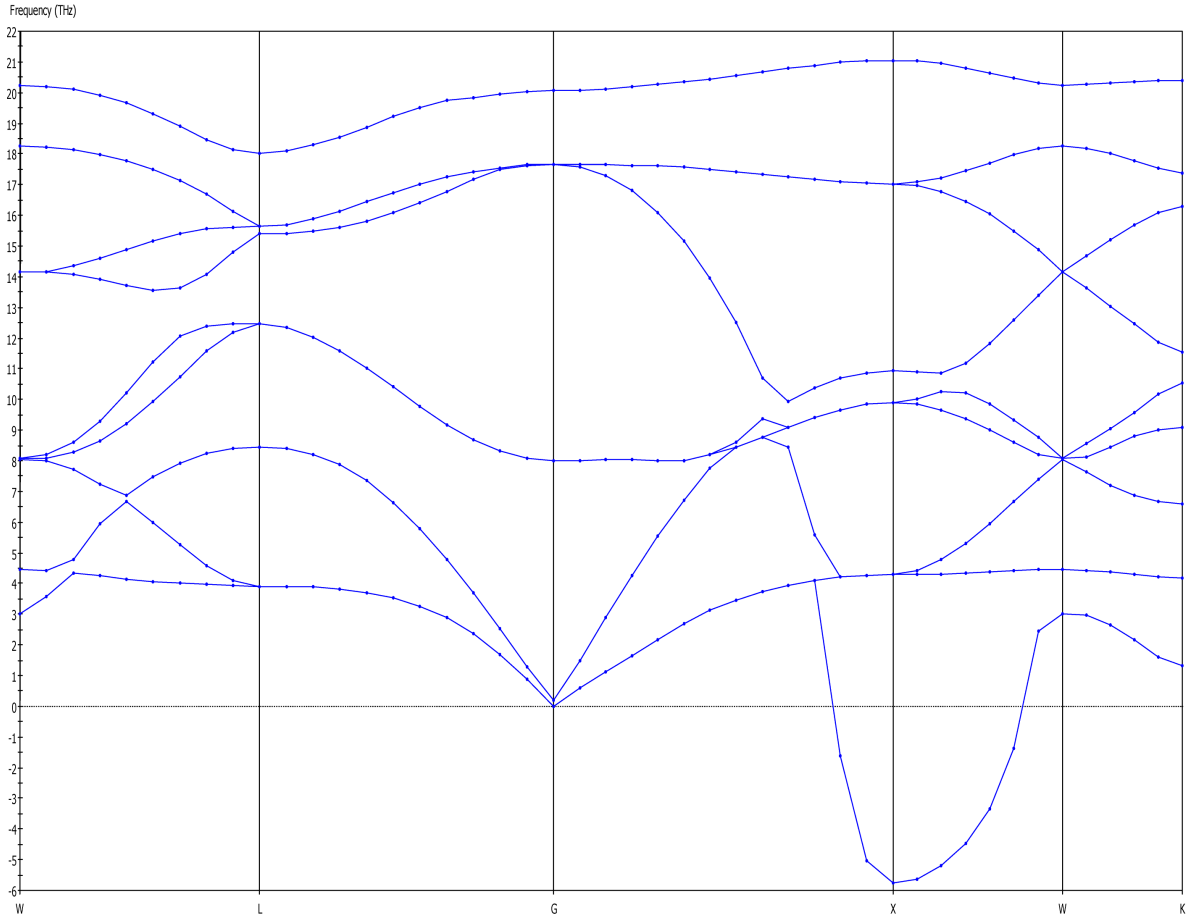


Figure 2. Phonon dispersion curves of $cZrO_2$.

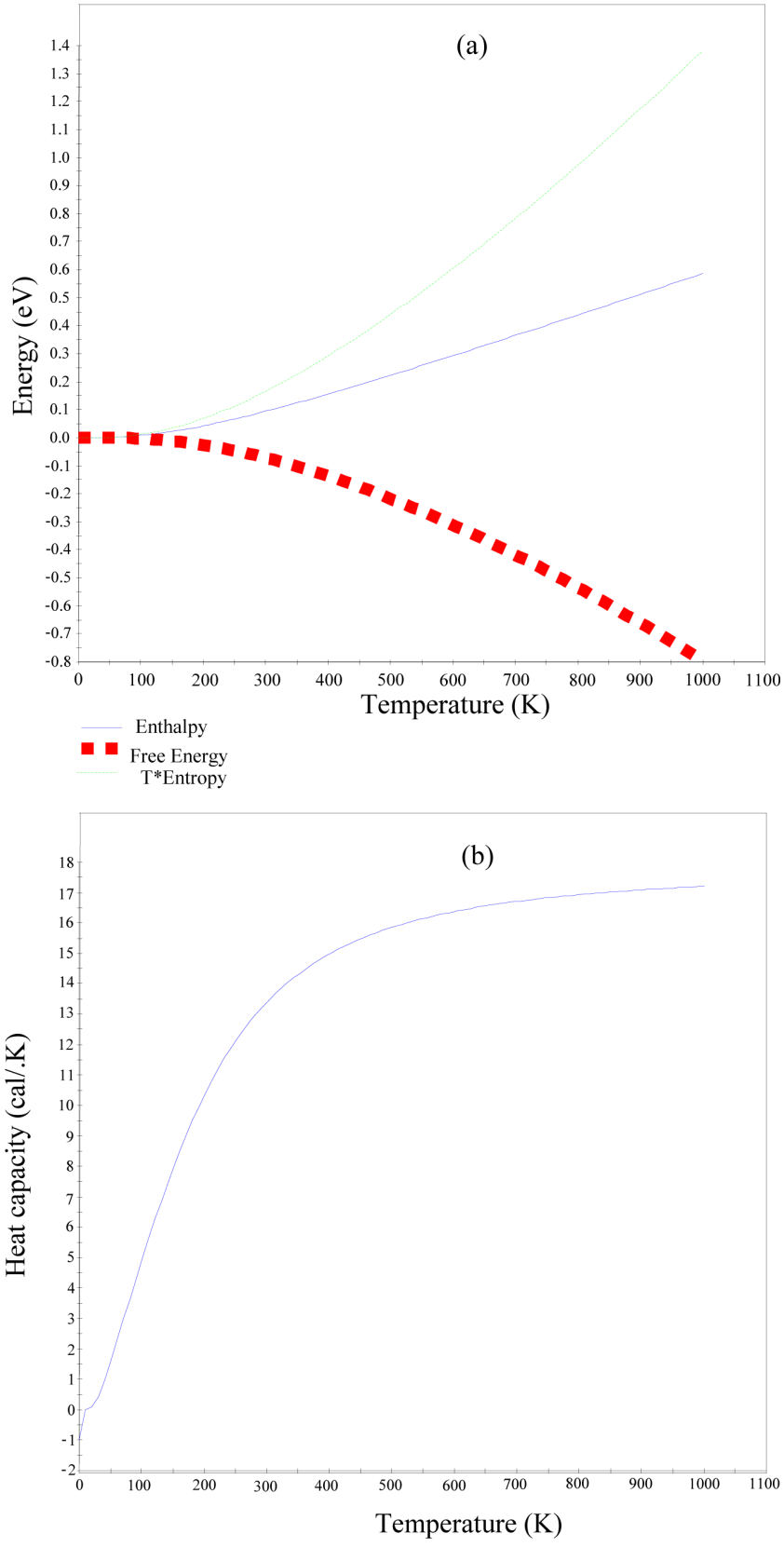


Figure 3. Enthalpy, free energy and entropy (a) and heat capacity of $cZrO_2$.

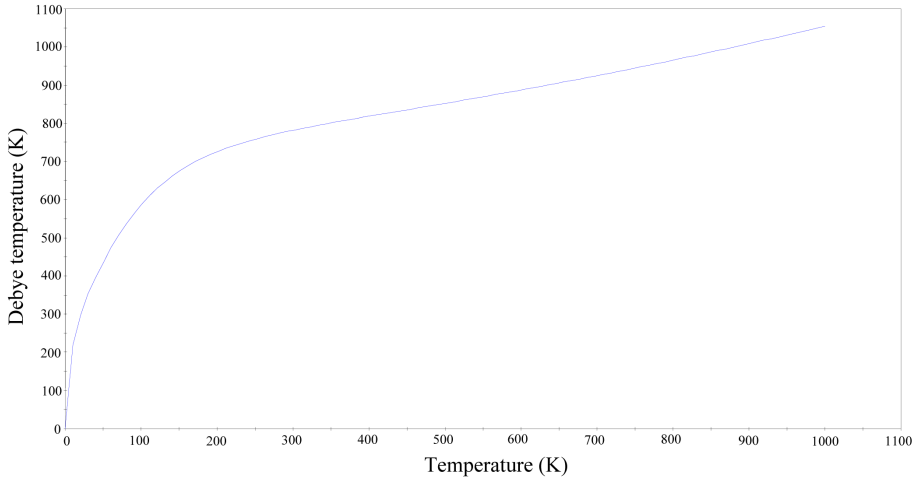


Figure 4. Debye temperature graph of $cZrO_2$.

indicate that $cZrO_2$ has satisfied the mechanical stability requirements; however, the young's modulus and hardness are high when compared to similar material such as cerium oxide. As expected, the thermodynamic properties obtained confirmed the ceramic characteristics of $cZrO_2$. The data obtained may further be used to predict properties in relation to defects and/or dopants and setting parameters for processing nanocomposites related to $cZrO_2$.

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