

Effects of size on mass density and its influence on mechanical and thermal properties of ZrO₂ nanoparticles in different structures

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MS received 30 November 2015; accepted 10 March 2016

Abstract. This study investigates the effect of size on mass density and its subsequent influence on the other physical parameters of zirconia nanoparticles in the structural forms of cubic, tetragonal and monoclinic. The general equations for these calculations are established based on the variation of lattice parameter model and surface internal atoms ratio. The mass density of nanoparticles differs from the bulk value when particle size decreases. At a diameter of 4 nm, the mass density values of zirconia nanoparticles are 3.898, 3.626 and 3.488 g · cm⁻³ compared to 6.25, 6.1 and 5.87 g · cm⁻³ for bulk cubic, tetragonal and monoclinic forms, respectively. These results indicate that the variation in mass density is largely due to the differences on their boundaries and the variation in lattice parameters. The calculated results agree well with the available experimental data for the monoclinic form structure of ZrO₂ nanoparticles. The relationship between mass density and melting temperature; and Debye temperature and cohesive energy are proposed. All these parameters have the same nanosize dependence in this regard.

Keywords. ZrO₂; mass density; mean bond length; melting temperature; Debye temperature; cohesive energy.

1. Introduction

Zirconia (ZrO₂) is an important ceramic material. The crystal structures of ZrO₂ are cubic, tetragonal and monoclinic [1] with a broad range of applications and the surface properties are of high significance [2–4]. Nanoparticles (NPs) have attracted increasing attention in the ‘materials community’, because their electronic, optic, catalytic, mechanical and thermodynamic properties are significantly different from those of either the bulk or a single molecule [5,6]. There are loads of theoretical and experimental investigations showing the size-dependent properties of nanomaterials. The typical trend is that the values of thermodynamic and mechanical parameters fall with decreasing size of NPs. These parameters include mass density, melting temperature, Debye temperature and cohesive energy, and these also have huge impacts on other physical constants and play important roles in material growth, homogeneity and porosity [7–11].

Density is known to be a size-independent property for both bulk and microstructure materials. Generally, density can be altered by changing either pressure or temperature. Recently, it was observed experimentally that mass density is a size-dependent property of nanomaterials. For example, in Au nanofilms (NFs), the mass density decreased with the increase in the thickness of the layer in nanometer range [12,13], and the mass density of monoclinic ZrO₂ NPs also decreased as their size decreased, particularly for sizes lesser than 50 nm [14]. There are limited theoretical investigations reported on mass density in nanoscale materials.

The relationship between size and mass density is yet to be well developed and has different variation trends. Safaei [10] developed a model for the size-dependency of the mass density for individual elements and compound nanocrystals (NCs) based on the lattice-type-sensitive. This model proved that increase in mass density is relative to a corresponding proportional decrease in size of NCs, and Nanda [15] carried out a model based on the variation of lattice parameters according to the liquid drop model. Nanda’s model proved that the density increase with a decrease in size of NPs, while it also showed that the density can decrease as size decreases for nanostructured material. Due to the complexity of ZrO₂, only a limited number of works are available in present literature. Thus, it is necessary and important to establish a model to understand the size-dependent mass density for nanoscale size of this material. The present study investigates the mass density based on the surface/volume ratio and total volume change calculations for ZrO₂ NPs and NFs for comparison purpose in different crystal structure forms. The results of mass density were analysed and compared with the available experimental results. Furthermore, the corresponding relationship between the mass density and other physical parameters are found in the nanoscale.

2. Method of calculations

It is well known that the density of the bulk crystals with the volume is constant and expressed as [16]:

$$\rho(\infty) = \frac{M}{N_A V(\infty)}, \quad (1)$$

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where N_A is the Avogadro constant, the ratio of $M/\rho(\infty)$ the molar volume V_m , M the molar mass in the crystal, $V(\infty)$ the lattice volume which is equal to $a(\infty)$ for cubic, $a(\infty)^2$, $c(\infty)$ for tetragonal and $a(\infty)$, $b(\infty)$, $c(\infty)$, $\sin \beta$ for monoclinic structure with lattice parameters $a(\infty)$, $b(\infty)$, $c(\infty)$ and monoclinic angle $\sin \beta$.

For a low-dimensional crystal system, the excess volume is a function of both dislocation density and grain size [17,18]. The dislocations in plastically-deformed crystals are separated into geometrically-necessary and statistically-stored dislocations. Both types of these dislocations increase the volume of nanocrystalline materials and can be expressed as follows:

$$\frac{\Delta V}{V} = \frac{\Delta V_s}{V} + \frac{\Delta V_G}{V}, \quad (2)$$

where the total volume change $\Delta V/V$ is the sum of the volume change $\Delta V_s/V$ induced by statistically stored dislocations and the volume change $\Delta V_G/V$ induced by geometrically necessary dislocations. $\Delta V_s/V$ is dependent on the density of statistically stored dislocations, ρ_s as follows:

$$\frac{\Delta V_s}{V} = \beta \rho_s, \quad (3)$$

where β is the excess volume per unit length of a dislocation and $\Delta V_G/V$ is proportional to the area of grain boundary, S_{GB} :

$$\frac{\Delta V_G}{V} = S_{GB} \delta, \quad (4)$$

where δ is the (absolute) excess volume per unit area of grain boundaries. Parameter δ is equivalent to the total expansion of the crystal normal to the grain boundary, where grain is assumed to be spherical in equation (4). Thus, $S_{GB} = (\pi D^2/2)/(\pi D^3/6)$, which is equal to $(3/D)$. The theoretical volume (V^{NCs}) and mass density (ρ^{NCs}) of nanocrystalline material can be expressed as [17]:

$$\frac{V^{NCs}}{V(\infty)} = \frac{\rho(\infty)}{\rho^{NCs}}. \quad (5)$$

The volume induces a stress field and overall lattice expansion of NCs [17], the corresponding $\varepsilon(D)$ is expressed as:

$$\varepsilon(D) = \frac{\delta}{D}. \quad (6)$$

From a mechanical point of view, the hydrostatic pressure on the surface of NCs induced by the intrinsic surface stress results in lattice strain, $\varepsilon(D)$ in the form [19]:

$$\varepsilon(D) = \frac{a(D) - a(\infty)}{a(\infty)}, \quad (7)$$

where D denotes the size of NCs. Based on the Laplace-Young equation and considering the size dependence of the solid-liquid interface energy, the lattice strain or relative

change of lattice constant, $\varepsilon(D)$ at room temperature for NCs is expressed as [20]:

$$\varepsilon^{NCs}(D) = \frac{14}{3[(T_m(\infty)/T) + 6]D} \sqrt{k S_{vib} H_m D_0 h(\infty) / (R V_m)}, \quad (8)$$

where T_m is the melting temperature, T the absolute temperature, k the compressibility, $h(\infty)$ the atomic diameter, R the gas constant equal to 8.314, V_m the molar volume, H_m the molar melting enthalpy, S_{vib} the molar melting entropy, D the diameter of the NCs and D_0 the critical size (most atoms or molecules are located at the surface), which can be calculated using the equation: $D_0 = 2(3 - d)h(\infty)$, where d is the dimension which is $d = 0$ for NPs and $d = 2$ for NFs [21,22]. Combining equations (4), (6) and (7) with equation (5), the complete expression of mass density of NCs is obtained, which now depends on size and can be written as:

$$\frac{\rho^{NCs}(D)}{\rho(\infty)} = \frac{V(\infty)}{V^{NCs}(D)} = \frac{1}{1 + 3\varepsilon^{NCs}(D)}. \quad (9)$$

To have a better understanding of the physical mechanism of heat conduction in low dimensional system, Omar [23] found the relationship between the mean bonding length $d_{mean}(D)$ and lattice constant for most materials and compounds as:

$$d_{mean}(D) = \frac{\sqrt{3}}{4} a(D), \quad (10)$$

where $a(D)$ is the lattice constant, which is increased via a reduction in size which leads to a subsequent increase in the volume of NPs. The author also obtained the relationship between melting temperature change $T_m(D)/T_m(\infty)$ and the volume change $V(D)/V(\infty)$ [24] as:

$$\frac{T_m(D)}{T_m(\infty)} = \left(\frac{V(D)}{V(\infty)} \right)^{2/3} \exp \left(- \frac{2S_{vib}}{3R \left(\frac{D}{2D_0} - 1 \right)} \right), \quad (11)$$

where $T_m(\infty)$ is the bulk melting temperature and $T_m(D)$ the size-dependent melting temperature. The size dependence relationship between Debye temperature and melting temperature of NPs is illustrated below [25]:

$$\frac{\theta_D(D)}{\theta_D(\infty)} = \left[\frac{T_m(D)}{T_m(\infty)} \right]^{1/2}, \quad (12)$$

where $\theta_D(\infty)$ is bulk Debye temperature and $\theta_D(D)$ is the size-dependent Debye temperature. The cohesive energy is responsible for the atomic structure, thermal stability, atomic diffusion, crystal growth and many other properties [26,27]. It is related to melting temperature, activation energy of diffusion and vacation formation energy, which is shown in the equation below [28–30]:

$$\frac{E_{coh}(D)}{E_{coh}(\infty)} = \frac{T_m(D)}{T_m(\infty)}, \quad (13)$$

where $E_{\text{coh}}(\infty)$ is the bulk cohesive energy and $E_{\text{coh}}(D)$ is size-dependent cohesive energy.

3. Results and discussion

In this study, the necessary parameters used in calculating ZrO₂ are listed in table 1. The size-dependence on mass density $\rho(D)$ of ZrO₂ is determined using equation (9) with the values of lattice constants obtained from equations (7) and (8) for size ranging from 2 to 250 nm as shown in figure 1. In this figure, the dependences are consistent with the experimental data for the case of monoclinic form of

ZrO₂ and a sharp decrease occurs at $D < 20$ nm. For a bulk crystal, the mean bond length $d_{\text{mean}}(\infty)$ is constant, it can be seen that the $d_{\text{mean}}(D)$ increased as the size decreases as shown in figure 2. This figure shows the mean bond length variation with respect to the particle size using equation (10). The results of our calculations are much improved when we consider the lattice expansion for determining the mass density of small-sized particles. It is well known that for solids, their lattice volume have major effect on physical as well as mechanical properties such as electronic band structure, electrical, thermal and elastic properties. Hence, the actual lattice volume is of great significance for use in nanoscale range

Table 1. The parameters used in this calculation of ZrO₂ in different structures.

Parameters	Cubic	Tetragonal	Monoclinic
T_m (K)	2988 [37]	2643 [38]	3147 [39]
k (10^{-12} Pa ⁻¹)	4.975 ^a	3.472 ^a	5.494 ^a
S_{vib} (Jg atom ⁻¹ K ⁻¹)	9.82 [39]	9.82 [39]	9.82 [39]
$h(\infty)/\text{nm}$ [31]	0.225 [40]	0.206 [40]	0.204 [40]
H_m (kJ g atom ⁻¹)	29.34 ^b	26.0 ^b	31.0 ^b
$\rho(\infty)$ (g cm ⁻³)	6.29 [38]	6.1 [38]	5.87 [14]
V_m (cm ³ g atom ⁻¹)	6.53 ^c	6.73 ^c	7.0 ^c
$\theta_D(\infty)$ (K)	502 [41]	404 [41]	575 [42]
$E_{\text{coh}}(\infty)$ (eV atom ⁻¹)	11.325 [42]	11.355 [42]	11.40 [43]
Lattice parameters (nm)	$a = 0.527$ [44]	$a = b = 0.5141$ $c = 0.52609$ [44]	$a = 0.5184$ $b = 0.5207$ $c = 0.537$ $\beta = 98.8^\circ$ [44]

^a $k = 1/B$ [22,39], where B is bulk modulus which is equal to 288, 201 and 182 (GPa) for cubic, tetragonal and monoclinic, respectively [44,45].

^b $H_m = T_m S_m$ and $S_m \approx S_{\text{vib}}$ for oxides [39,46].

^cIn equation (1), $V_m = M/\rho(\infty)$ [16,39], where M is g-atom weight which is equal to 41.07 g g-atom⁻¹ [39].

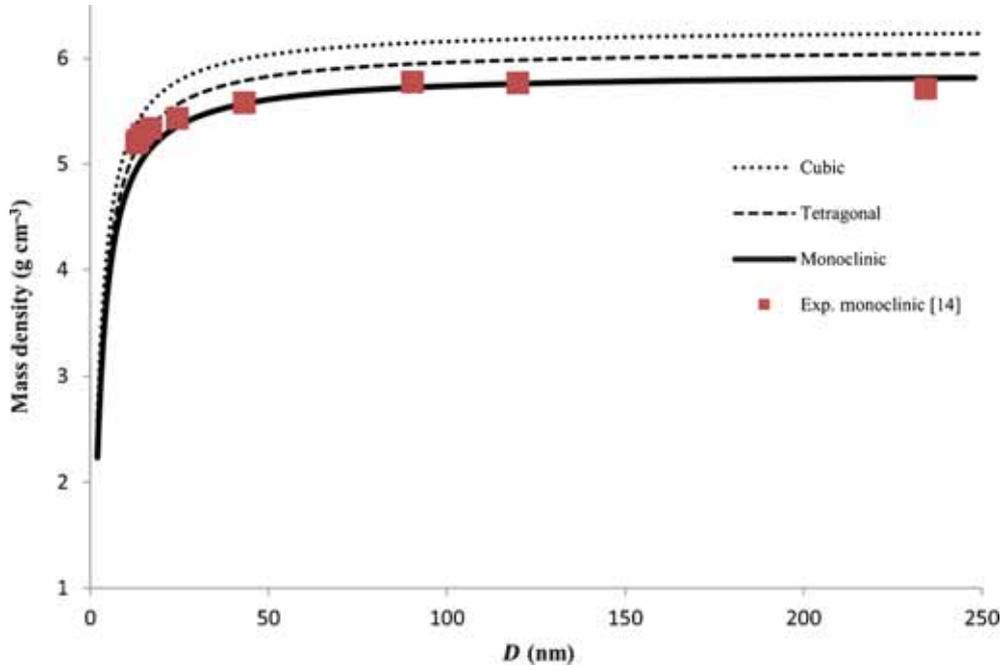


Figure 1. Size-dependent mass density of ZrO₂ nanoparticles in different structures.

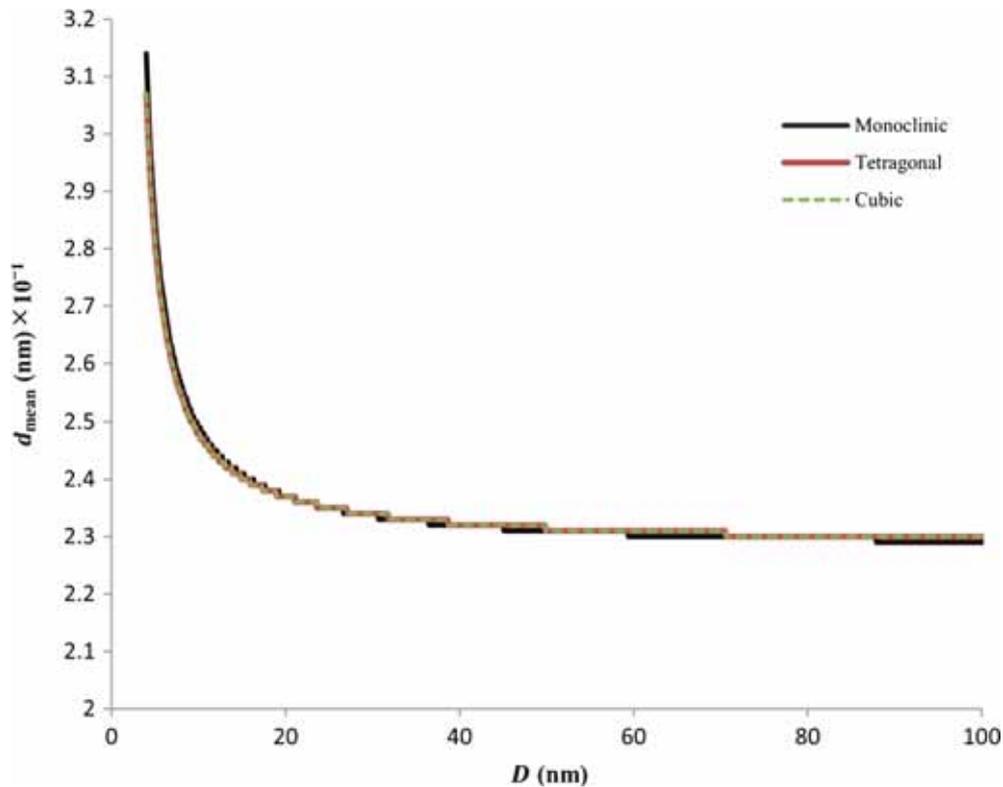


Figure 2. Size-dependent mean bond length of ZrO_2 nanoparticles in different structures.

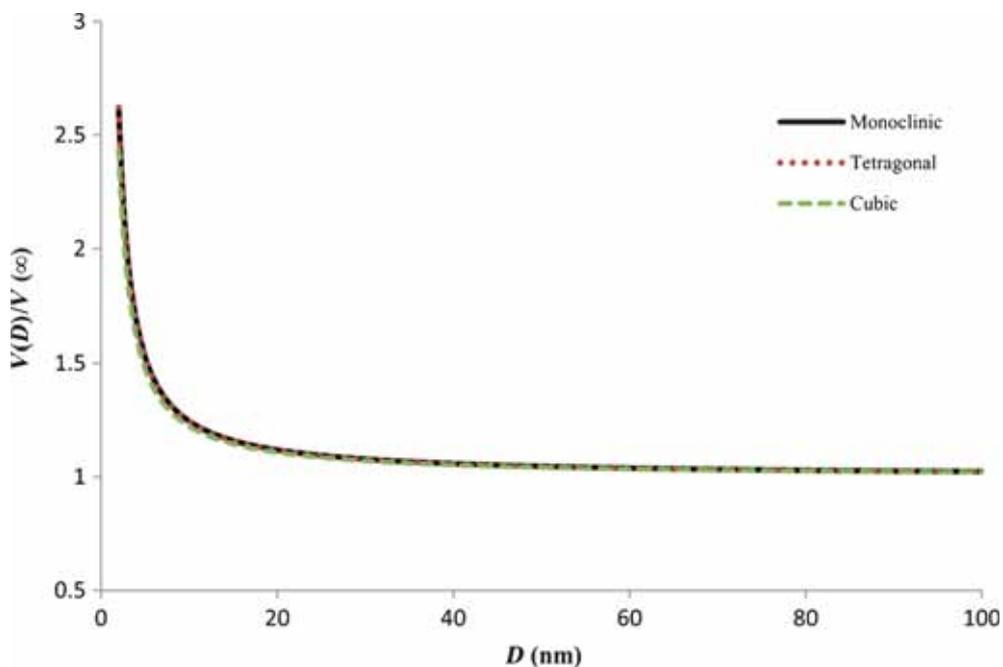


Figure 3. Size-dependent volume change of ZrO_2 nanoparticles in different structures.

materials in technology. For bulk crystals, the lattice parameter is constant; it means that the mean bond length is constant. Mass density and lattice volume have no effect on bulk and microstructure due to the existence of more core atoms compared to the surface and the effects appeared in size less

than 50 nm for NPs. Thus, any change in lattice volume leads to change in material's properties. For nanoscale range, the lattice parameter is size-dependent and it increases with size reduction, it leads to variation in volume ratio $V(D)/V(\infty)$ as shown in figure 3.

The increase in lattice constant in nanoscale size was reported by Zhu *et al* [17] and it is due to the relative disordered arrangement of the atoms and the volume induces a stress field and overall lattice expansion. Also, Siegel *et al* [12] have reported that Au thin films with the reduced mass density of thinner structure is probably due to the higher fraction of free volume. The same results are obtained by Shen *et al*

[17] from their theoretical prediction calculation on Si nanostructures. From the structural viewpoint, nanostructured materials are often visualized as consisting of two components; the grain interior and a large volume fraction of grain boundary. Nanostructures Niobium (Nb) exhibit a significantly large lattice expansion with reduction in crystalline size below 10 nm [31,32]. The grain boundary separates the

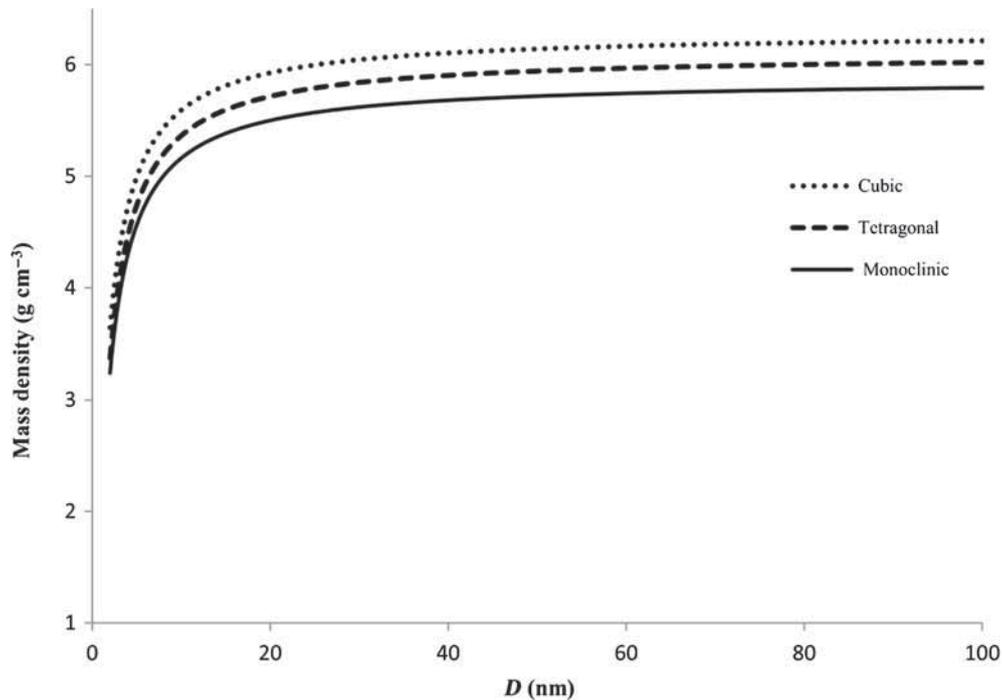


Figure 4. Size-dependent mass density of ZrO₂ nanofilms in different structures.

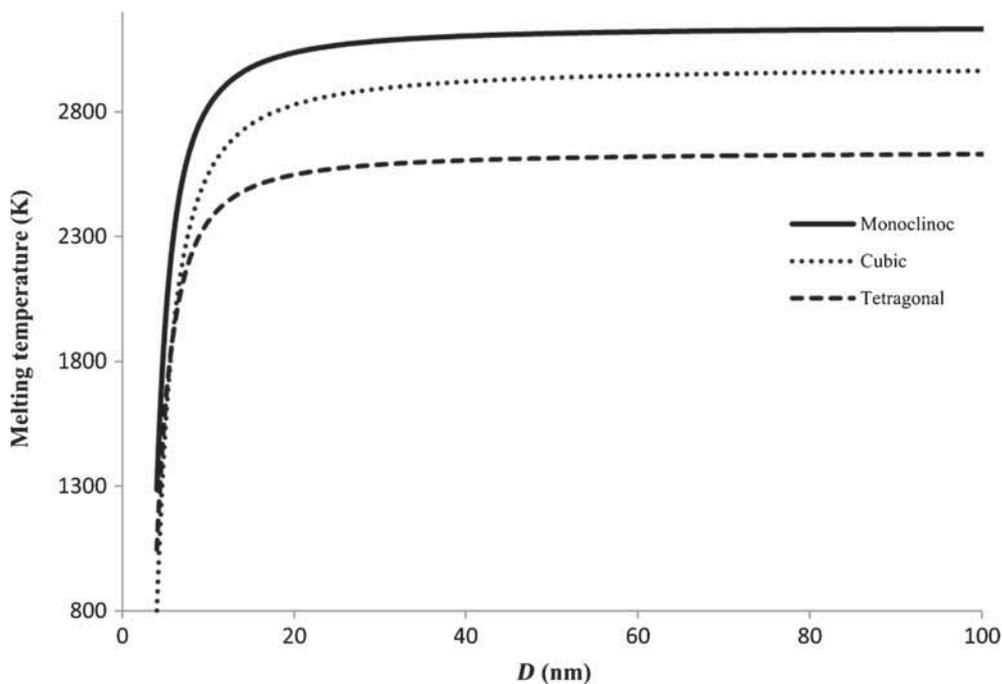


Figure 5. Size-dependent of melting temperature of ZrO₂ nanoparticles in different structures.

interiors of one grain from its adjacent one. With reduction in the average grain or crystalline size, there appears to be changes in the crystal lattice of nanomaterials with the lattice expansion increases with reduction in the crystalline size [33,34]. Furthermore, it has been reported [35] that

nanostructures Nb, prepared by high-energy ball-milling, exhibits a lattice expansion with decreasing grain size, eventually, undergoing an allotropic phase transformation from body centre cubic to face centre cubic when the average crystalline size is reduced below 10 nm.

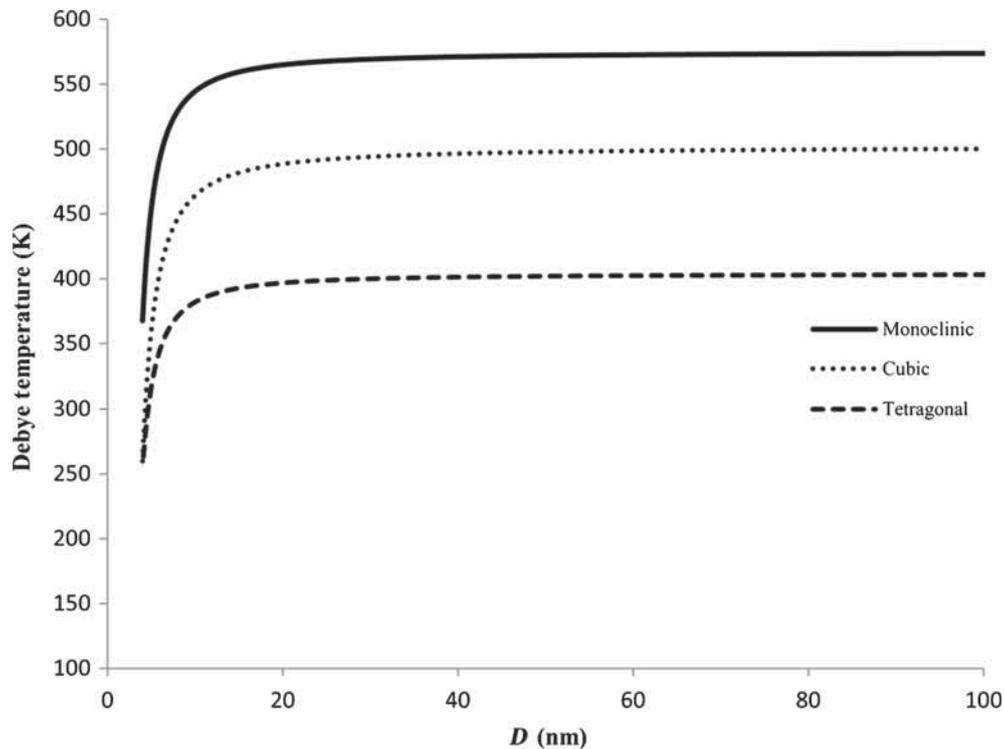


Figure 6. Size-dependent of Debye temperature of ZrO_2 nanoparticles in different structures.

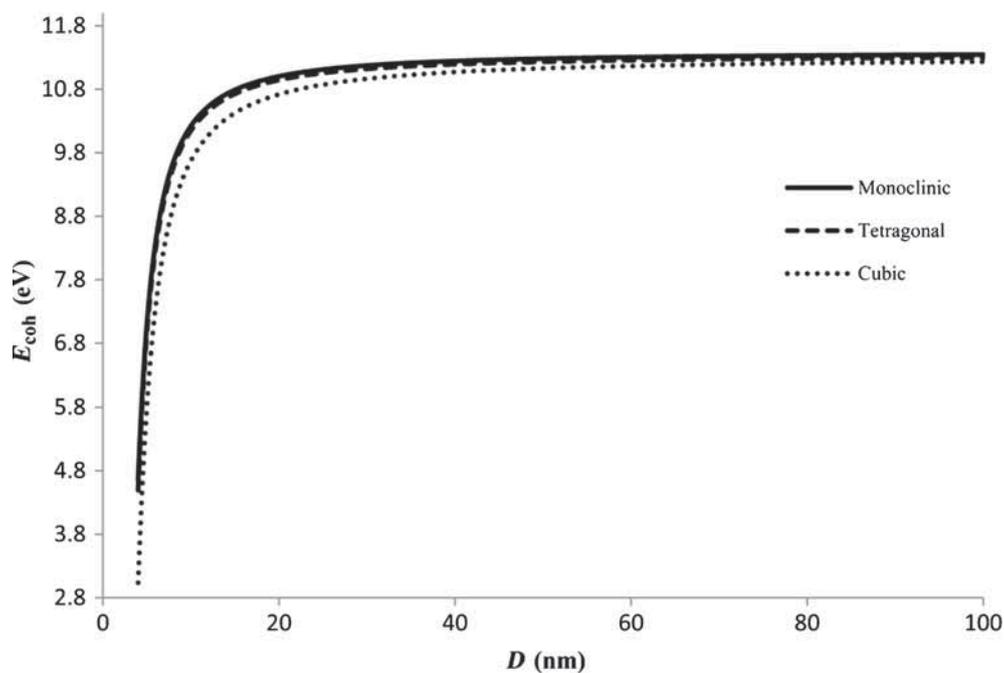


Figure 7. Size-dependent of cohesive energy of ZrO_2 nanoparticles in different structures.

Moreover, one of the most critical characteristics of NPs is their very high surface-to-volume ratio, i.e., large fractions of surface atoms. According to the shape of crystallites, three categories of NC materials may be distinguished: layer-shaped crystallites, rod-shaped crystallites and NC materials composed of equiaxed nanometer-sized crystallites [36]. In the present study, grain is assumed to be spherical in equation (4). According to ref. [14], in SEM images, it has also been observed experimentally that the grains were predominately spherical and tended to form agglomerates when grain size was reduced to that of monoclinic ZrO₂ NPs. In addition, the mass density of NFs is calculated for comparison purpose by taking $d = 2$ in equation (8) as shown in figure 4. As a result, the mass density of NFs has higher values than that of spherical NPs of ZrO₂ for the same size. The weaker dropping of mass density of NFs than that of NPs is induced by the fact that $d_{\text{mean}}(D)$ NFs $<$ $d_{\text{mean}}(D)$ NPs due to the difference in the surface to volume ratio.

In this work, the obtained values of $V(D)/V(\infty)$ are used for calculating $T_m(D)$, $\theta_D(D)$ and $E_{\text{coh}}(D)$ in equations (11)–(13) as shown in figures 5–7. The calculation results indicated that the above parameters are size-dependent and the results were dropped as the size decreased. These figures indicate the dependence of these parameters on the volume change of ZrO₂ NPs in different structures. In light of the above discussion, the new correlation relationship between the mass density and these phenomena are proposed for NPs as:

$$\frac{\rho(D)}{\rho(\infty)} = \frac{E_{\text{coh}}(D)}{E_{\text{coh}}(\infty)} = \frac{T_m(D)}{T_m(\infty)} = \left[\frac{\theta_D(D)}{\theta_D(\infty)} \right]^2. \quad (14)$$

4. Conclusions

The different structures of ZrO₂ NPs and the effects of size on mass density and the resultant influence on its mechanical and thermal properties were studied. The $\rho(D)$ function of ZrO₂ NPs in different structures was established by considering the effect of volume change due to an increase in the ratio of number of surface atoms to that of its internal atoms with size reduction. It was found that ρ decreases as D decreases for both NPs and NFs. The calculated results were consistent with the available experimental data of monoclinic ZrO₂ NPs. The advantage of this improvised model is its ability to calculate the mass density for low-dimensional materials. The calculated values of $V(D)/V(\infty)$ are successfully used to determine $T_m(D)$, $\theta_D(D)$ and $E_{\text{coh}}(D)$, which play important roles in sizes lesser than 50 nm.

Acknowledgement

We gratefully acknowledge the financial support from the University of Salahaddin-Erbil, Iraq (grant no. 540-1762013) and cooperation from Jilin University, Changchun, China.

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