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On the stabilizing behavior of zirconia: A Combined experimental and theoretical study

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Reactive zirconia powder was synthesized by the complexation of zirconium metal from zirconium hydroxide using a solution of 8-hydroxiquinoline. The kinetics of zirconia crystallization was followed by X-ray diffraction, scanning electron microscopy and surface area measured by the nitrogen adsorption/desorption technique. The results indicated that zirconia with a surface area as high as 100 m^2/g can be obtained by this method after calcination at 500°C. Zirconia presents three polymorphic phases (monoclinic, tetragonal and cubic), which are reversibly interconversible. The cluster model Zr_4O_8 and $Zr_4O_7^{+2}$ was used for a theoretical study of the stabilization process. The *ab initio* RHF method was employed with the Gaussian94 program and the total energies and the energy gap of the different phases were calculated and compared with the experimental energy gap. The theoretical results show good reproducibility of the energy gap for zirconia.

1. Introduction

Zirconia is an important material for high temperature applications [1] and it has four well-defined polymorphic forms: the monoclinic (m), tetragonal (t), orthorhombic (o) and cubic (c) phases [2]. Only the monoclinic form is stable at room temperature, although both the tetragonal and orthorhombic phases can be quenched to the ambient condition. The addition of appropriate dopants, however, is known to stabilize the tetragonal and cubic phases [3].

The crystal structure and transformation mechanisms of the monoclinic, tetragonal and cubic phases are of considerable technical interest since they can be manipulated to optimize the physical and chemical properties of materials produced from stabilized zirconia [4–7].

So-called partially stabilized zirconia (PSZ), which can typically consist of two phases (cubic and tetragonal) or a single phase (either tetragonal or cubic), is important in mechanical and structural applications. Fully stabilized zirconia (FSZ), normally single phase cubic, is useful for applications such as heating elements, oxygen sensors, fuel cells, electrolytes, coatings, structural and wear components, and toughening agents in many ceramic composites [8–10].

Increasing interest has been evinced in the synthesis of submicrometric powders owing to the need for high performance products in the ceramic industry [11]. These powders are characterized by their high purity (>99.9%), controllable and reproducible chemical composition (including dopants addition), chemical homogeneity at the atomic level and controllable particle size and shape.

Colloidal particles can be obtained by several methods in liquid or vapor phases [12–15], but the techniques that involve chemical solutions are more convenient to prepare highly pure fine powders. Using this method, the solid phase can be obtained from a solution containing the desired cations by precipitation, evaporation or solvent extraction. Segregation is reduced by combining the ions in a gel phase or by means of quick (milliseconds) solvent extraction. The solid phase is usually a salt that can be calcined at low temperatures. This calcined powder is porous and brittle, enabling it to be easily ground to submicrometric size.

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Previous investigations of the zirconia polymorphs have been limited primarily to X-ray, neutron, and electron diffraction studies [4, 5, 7, 8, 16–25]. Although diffraction data are highly reliable for pure ZrO_2 polymorphism, they cannot provide definitive and specific information concerning the dopants and host cations for the two-alloy phases [3]. Several investigations of zirconia systems using X-ray-absorption spectroscopy (XAS) that have been reported in recent years have begun to offer new insights [26–32]. These studies have helped to draw a comprehensive picture of the host and doping environments in various solid solutions. Li *et al.* [3] studied zirconia using the XAS method. They showed that the Zr cation network in t-Zr_4O_8 is nearly fcc, but some evidence points to incoherent distortion beyond a correlation length (∼ unit cell size), even at 10 K, because of phase instability. Zr—O bonding is similar in m-, t-, or c-Zr_4O_8, with sevenfold coordination and comparable bond distance. Despite its fluorite-type symmetry, the Zr-cation network in c-Zr_4O_8 is severely distorted to accommodate the sevenfold Zr—O polyhedra.

The electronic structures of both cubic and tetragonal zirconia were calculated by the discrete variational (DV) X alpha method. The results show that zirconia is fairly ionic, with differing ionicity in the cubic and the tetragonal phases [33]. Cohen *et al.* [34] calculated the phase transitions and elasticity in zirconia using the potential induced breathing (PIB) model. The elastic constants and pressure derivatives for cubic zirconia are inconsistent with experimental data, suggesting that disorder strongly affects the elastic behavior. Furthermore, disorder and defects may be important factors in stabilizing the tetragonal and cubic structures of zirconia.

Zandiehnadem *et al.* [35] studied zirconia in the cubic, tetragonal and monoclinic phases using a method of first principle self-consistent orthogonalized linear combination of atomic orbitals and obtaining band gaps of 3.84, 4.11 and 4.51 eV, respectively, for the three phases. Jansen and Gardner [36] used the full-potential linear-augmented-plane-wave (FLAPW) method to study the tetragonal to cubic phase transition. Their results show that the phase transition from tetragonal to cubic is driven by the thermal motion of oxygen atoms. Orlando *et al.* [37] proposed the use of a periodic *ab initio* Hartree-Fock method to investigate the structural stability and electronic structure of the two high temperature phases of zirconia. An analysis of the electronic structure shows an appreciable departure from a purely ionic type of bond. French *et al.* [38] examined the optical properties of the three phases of zirconia with vacuum ultraviolet and valence band X-ray photoemission spectroscopies combined with *ab initio* band structure calculations (method of orthogonalized linear combination of atomic orbitals) in an attempt to understand the complex interaction of the stabilizing dopants and associated atomic defects with the crystal structures of zirconia and their phase transitions. The experimental samples were single or polycrystalline stabilized materials containing atomic defects, while the calculations were performed for undoped idealized zirconia structures with no atomic defects. Reasonable agreement was found between experimental and theoretical results at this level.

2. Experimental procedure

2.1. Experimental

An aqueous solution of zirconium ions was prepared by the dissolution of $Zr(OH)_4$ in an acid medium. 8-hydroxiquinoline (Q) 12% in acetic acid was added to this solution, followed by neutralization with a concentrated ammonium hydroxide solution to produce the precipitate. The precipitate was collected by filtration in a Büchner funnel, washed with hot water to remove possible excess of 8-hydroxiquinoline, air dried at room temperature for 24 h and stored in a desiccator.

The dry powder was then subjected to simultaneous thermal analysis, TG-DTA (Model Mettler TA-4000). A heating rate of 20°C/min, with 90 ml/min air flux, was applied on 6 mg of the sample in alumina crucibles.

The resulting powders were calcined at different temperatures from 300 to 1200°C. Characterization was carried out by X-ray diffraction (XRD) (Model D5000, Siemens, Karlsrushe, Germany), using Cu K_α radiation and a graphite monochromator for the phase formation study. Specific surface areas for the zirconia powders were measured by the BET multipoint method (ASAP 2000, Mecromeritics, Norcross, GA), using N_2 as the adsorption/desorption gas.

2.2. Calculation method and models

Our calculations for the m, t and c of the perfect Zr_4O_8, and the vacancy $Zr_4O_7^{+2}$ structures were based on the parameters presented in Table I. The most severe restrictions on the unit cell dimensions were imposed for the c structure ($a = b = c$; $\alpha = \beta = \gamma = 90°$). The representation of the stabilized c structure was calculated using frozen and optimized geometries for comparison. The *ab initio* Roothaan-Hartree-Fock (RHF) method included in the Gaussian94 package [40] was employed in our calculations using the basic functions of Huzinaga *et al.* [41].

TABLE I Crystallographic parameters and bond distances (Å) used in the structure calculation

Parameters	Cubic	Tetragonal	Monoclinic
Lattice constant (Å)	$a = 5.083$	$a = b = 3.584$ $c = 5.170$	$a = 5.147$ $b = 5.198$ $c = 5.314$ $\beta = 99.21°$
Space group	Fm3m	$P4_2/nmc$	$P2_1/c$
d_{Zr-O}			
Exp. [ZrO_2]	2.28 ± 0.00 Ref. [20]	2.260 ± 0.208 Ref. [18]	2.160 ± 0.085 Ref. [2]
Theor. [Zr_4O_8][a]	2.422	2.102	2.267 2.243
Theor. [$Zr_4O_7^{+2}$][a]	2.076	2.273	2.094 2.069

[a] Geometry obtained through the optimization of Zr_4O_8 and $Zr_4O_7^{+2}$ clusters.

The method of linear combination of atomic orbitals (LCAO) has been extensively used to study the electronic structures of solids over the past twenty years. One of the advantages of the LCAO method is its ability to handle systems with complex structures and large unit cells because of its basic functions. In our calculations, the orbital exponents and contraction coefficients of the atomic wave functions were determined by optimizing total energies, as explained in detail by Huzinaga *et al.* [41].

The convenient shortened notation is (43/3) for O and (43333/433/43) for Zr. The orbital exponents and contraction coefficients were determined using the same method reported by Huzinaga *et al.* [41].

The structural parameters used in our band structure calculations are summarized in Table I and Fig. 1, including unit cell parameters and bond lengths for Zr—O.

3. Results and discussion

Thermal decomposition studies of the complex obtained after drying were carried out by thermogravimetric analysis. Fig. 2 shows a simultaneous analysis of TG-DTA curves at 200°C, indicating the material was dry since no weight loss was observed. A continuous weight loss of about 40% and two exothermal reactions occurring in the 250–550°C range were attributed to decomposition with the formation of 5-quinolonol N-oxide (Q'_2) and volatile organic compounds. This led to the formation of carbon, which started to burn out at about 550°C in air. Complete decomposition of the complex occured at around 600°C with the formation of zirconium oxide, according to the following equation:

$$\mathrm{Zr(OH)_4{\cdot}Q'_2{\cdot}1H_2O} \xrightarrow{600^\circ\mathrm{C}} \mathrm{ZrO_2} + \mathrm{Q'_2} + 3\mathrm{H_2O} \qquad (1)$$

X-ray diffraction (XRD) (Fig. 3) results revealed that zirconia is formed after nucleation from the amorphous precursor, with no intermediate phases, at a low temperature (300°C). XRD showed the formation of the tetragonal/cubic phase of zirconia after calcination of the amorphous dry phases in the 300 to 500°C range. Crystallization into the metastable tetragonal/cubic zirconia occurred between 300–500°C, while transformation to the stable monoclinic phase, seemingly related to the burnout of carbon, started at about 600°C. Calcination at 1000°C caused sharpening and increasing intensity of the monoclinic peaks and a further decrease of tetragonal/cubic zirconia.

An analysis of the particles obtained showed two distinct stages. In the first step, the powders were formed from amorphous zirconia in the presence of organic materials in a decomposition phase consisting mainly of carbon. The next step consisted of the crystallization of zirconia and the total elimination of organic materials. The particles showed a large, highly reactive surface area, indicating their suitability for application in catalyzers (Table II). Particle size, which was measured by X-ray peak broadening analysis, was found to be 8 to 12 nm after heat treating between 300 and 600°C.

According to Garvie *et al.* [5], zirconium stabilized in the tetragonal structure arranges itself into small crystallites. However, with increased temperature and, thus, increased crystallite size, zirconium destabilizes, changing from the tetragonal to the monoclinic phase at temperatures above 600°C, as illustrated by Fig. 3. Fig. 4 shows the nitrogen adsorption/desorption curve, demonstrating that, at higher sintering temperatures, the nanoparticles become rearranged through particle coarsening, which was observed by the decrease in the volume of adsorbed gas.

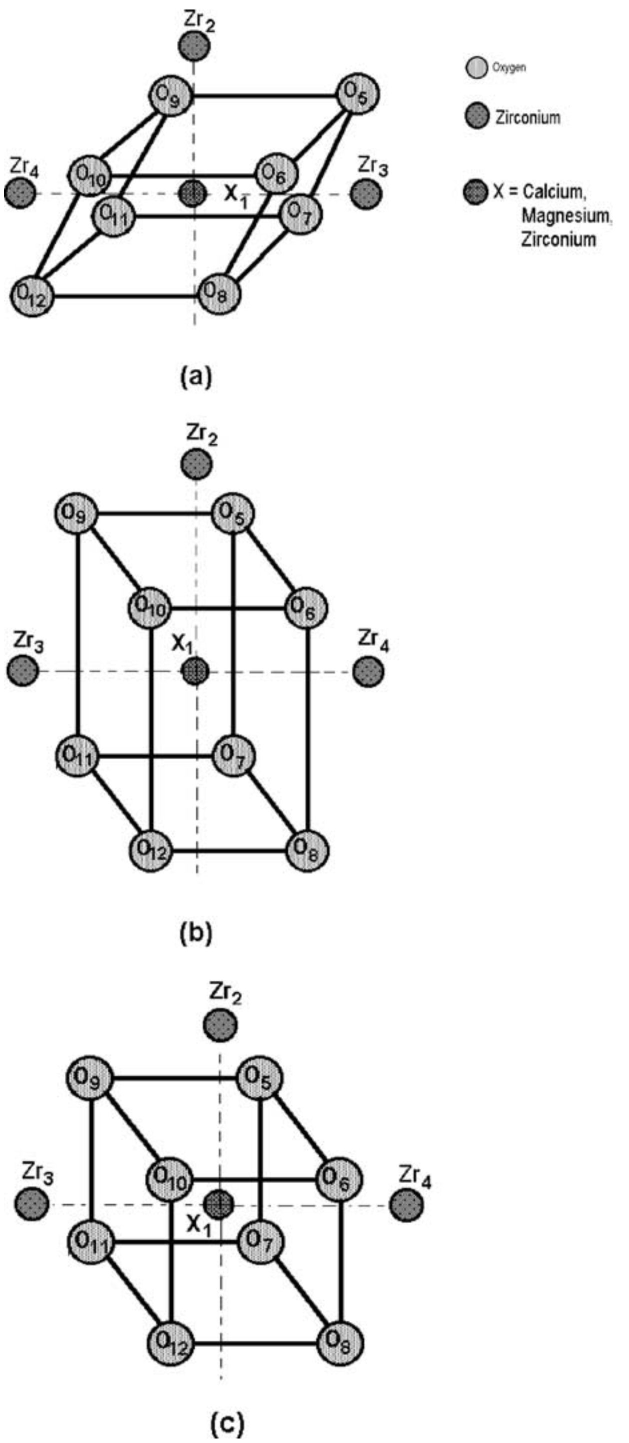

Figure 1 Schematic representation of the zirconia structures: (a) monoclinic, (b) tetragonal and (c) cubic.

The SEM micrograph (Fig. 5) shows the different agglomerate structures, i.e., very fine powders with particle sizes under 100 nm, obtained after calcination at 600°C.

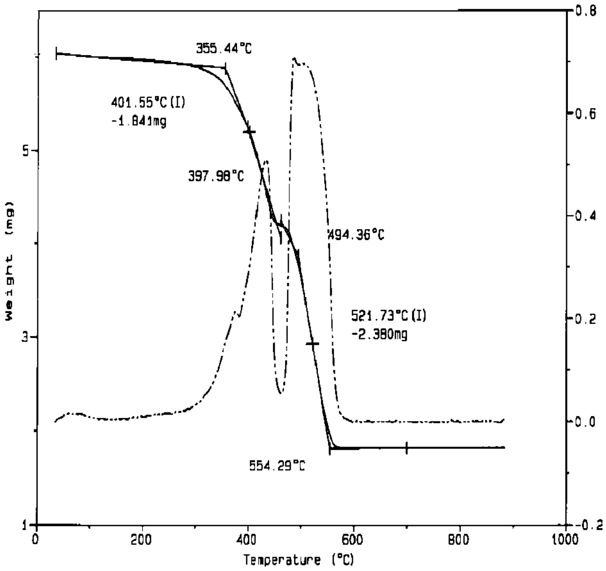

Figure 2 DTA/TG for the zirconia powders dried at room temperature.

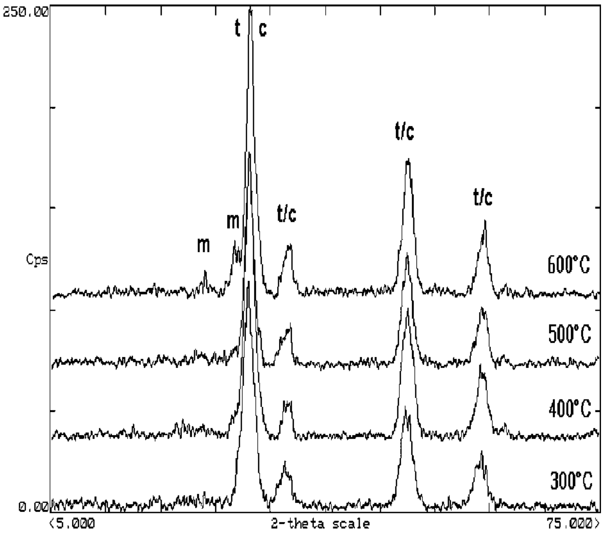

Figure 3 X-ray diffraction of zirconia powders calcined in the range of 300 to 600°C for 1 h.

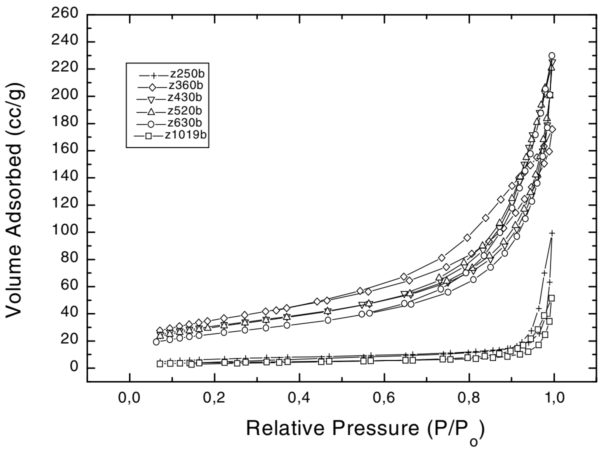

Figure 4 Nitrogen adsorption/desorption of calcined zirconia powders in the range of 250 to 1020°C for 1 h.

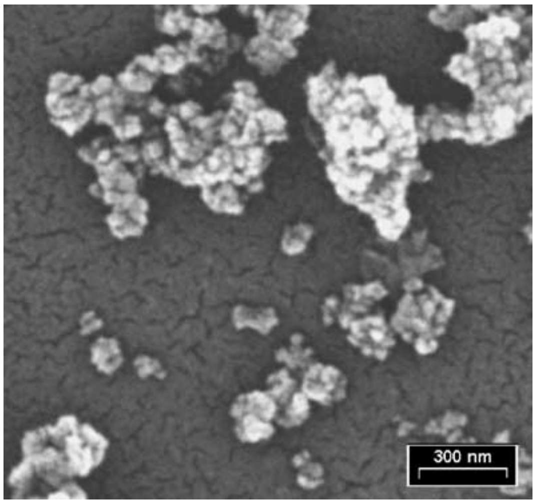

Figure 5 SEM micrograph of the zirconia powder calcined at 600°C for 1 h (1 cm corresponds to 0.2 μm).

The method of organic synthesis was used to obtain powdered zirconia, whose crystallization temperature started at ≈300°C, producing a fairly weak arrangement of the agglomerates after calcination and resulting in quite highly reactive powders due to the large surface area of approximately 100 m^2/g at this calcination temperature.

The stabilization of zirconia should be considered from both the theoretical and the experimental points of view. The experimental analysis is based on the method of synthesis and the type and concentration of vacancies, whereas the theoretical results are based on quantum mechanical methods and on the optimization of the crystalline structure. The generation of vacancies strongly affects the unit cell volumes of the tetragonal and cubic phases, promoting the stabilization of these phases at room temperature.

TABLE II BET surface areas of zirconia powders calcined in the range of 250 to 1020°C

Temperature (°C)	Surface area (m^2/g)
250	22
360	127
430	109
520	107
630	89
1020	11

The total energy, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the energies of the structures formed by the molecules with and without oxygen vacancies obtained in this work are listed in Table III.

The RHF technique, using the basic functions of Huzinaga *et al.* [41], qualitatively reproduces the main geometrical parameters of the m, t and c phases of zirconia (Table III). A full theoretical explanation of the stabilization of m, t and c-phases requires calculation of the RHF values for different crystalline modifications or, more precisely, the O- and Zr-relaxation with the RHF technique, using the basic functions of Huzinaga *et al.* [41]. As determined by Dwivedi and Cormack [42], the defect energy of a vacancy is lower in c-Zr_4O_8 than in t-Zr_4O_8. Therefore, the presence of vacancies increases the stability of the c phase. The symmetrical relaxation of the nearest oxygen atoms around the

TABLE III Total energy (E_T), highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the energy differences for the three zirconia polymorphs

Parameters	$[Zr_4O_8]$	$[Zr_4O_8]^a$	$[Zr_4O_7^{+2}]^a$
Monoclinic			
E_T (u.a.)	−14,604.1248	−14,738.6412	−14,663.7384
HOMO (u.a.)	−0.1089	−0.2103	−0.5584
LUMO (u.a.)	0.0880	0.0378	−0.3203
Tetragonal			
E_T (u.a.)	−14,603.4211	−14,738.6239	−14,663.7482
HOMO (u.a.)	−0.0476	−0.1300	−0.4938
LUMO (u.a.)	0.1149	0.0278	−0.2910
Cubic			
E_T (u.a.)	−14,604.0411	−14,738.4739	−14,663.7992
HOMO (u.a.)	−0.1297	−0.2173	−0.5657
LUMO (u.a.)	0.0856	−0.0158	−0.3357
$E^c - E^m$ (eV)	2.28	4.55	1.66
$E^c - E^t$ (eV)	−16.87	4.08	1.39
$E^t - E^m$ (eV)	19.15	0.47	0.27

[a] Geometry optimized of Zr_4O_8 and $Zr_4O_7^{+2}$ clusters.

TABLE IV Total atomic charges of Zr_4O_8 and $Zr_4O_7^{+2}$ optimized structures

	Monoclinic		Tetragonal		Cubic	
	Zr_4O_8	$Zr_4O_7^{+2}$	Zr_4O_8	$Zr_4O_7^{+2}$	Zr_4O_8	$Zr_4O_7^{+2}$
Zr_1	1.46	1.25	1.63	1.45	1.41	1.21
Zr_2	1.13	1.24	0.94	1.18	1.00	1.37
Zr_3	1.20	1.48	1.36	1.22	1.00	1.70
Zr_4	1.12	1.74	1.36	1.70	1.03	1.41
O_1	−0.710	−0.709	−0.770	−0.702	−0.660	−0.697
O_2	−0.710	−0.750	−0.770	−0.689	−0.660	−0.434
O_3	−0.700	−0.683	−0.770	−0.659	−0.450	−0.474
O_4	−0.700	−0.594	−0.770	−0.502	−0.450	−0.768
O_5	−0.490	−0.370	−0.550	−0.317	−0.660	−0.716
O_6	−0.490	−0.325	−0.550	−0.331	−0.660	−0.309
O_7	−0.550	−0.279	−0.550	−0.350	−0.450	−0.292
O_8	−0.550	–	−0.550	–	−0.450	–
q_{Me}	4.91	5.71	5.29	5.55	4.44	5.69

vacant site imposes isotropic negative pressure on the anionic sublattice, favoring the formation of an isotropic cubic-like structure around the vacancy and increasing the energy of the anisotropic t structure [49]. The importance of oxygen vacancies for c-phase stabilization has also been emphasized by Hillert [44] and Parker [45].

It has been proposed [46] that the valence electronic configuration of Zr ions in c-Zr_4O_8 is close to the $4d^2$ configuration. In the crystalline field having an O_h symmetry, this corresponds to the partial occupancy of the t_{2g} levels [37], resulting in sixfold degeneration. According to the Jahn-Teller theorem, this (cubic) structure around the cation site is unstable and lattice distortions should appear in order to lower the symmetry and remove the degeneration. This explains why six different (symmetry-related) tetragonally distorted structures may appear around each Zr atom [46].

As can be seen in Table III, the theoretical results for the Zr_4O_8 cluster show that the monoclinic structure has a lower energy than the tetragonal and cubic ones, which is in good agreement with experimental results and indicates that this structure is the most stable one. This effect is characteristic of ionic structures in which the atoms are bonded radially, thus destroying the directional character imposed by the covalent bonds between zirconium and oxygen, which are determined mainly by the d orbital of zirconium. In the $Zr_4O_7^{+2}$ cluster, the cubic phase has a lower energy than the tetragonal and monoclinic phases. It should be noted that the energy differences $E^c - E^m$, $E^c - E^t$ and $E^t - E^m$ are overestimated by all the calculations in relation to the experimental data (Table III). It is well known that directional covalent forces contribute substantially to the Zr—O interaction in ZrO_2. Formation of Zr(d)–O(p) hybrid orbital and increase of the electronic charge density between the Zr and O atoms have been reported in the calculated electronic charge distribution of ZrO_2 crystals [36, 37].

The stabilization of zirconia is, therefore, promoted by the oxygen vacancy at a molecular level and, at a macromolecular level, it stabilizes for the associated atomic defect in the nanoparticles. The presence of an oxygen vacancy would, thus, generate a center of polarization and attraction that would decrease the zirconia unit cell volume. The repulsive forces would then overcome the attractive forces in the monoclinic structure, resulting in the formation of the cubic and tetragonal structures at room temperature and, consequently, destabilizing the monoclinic structure. An increase in the ionic character between the Zr_4O_8 and $Zr_4O_7^{+2}$ of the m, t and c structures can be seen in Table IV through the charges over the zirconium atoms calculated by the Mulliken Population Analyses [50, 51].

Our experimental results showed that nanometric zirconia particles were stabilized into tetragonal/cubic phases. Therefore, the theoretical data lead to a concept in which zirconia is stabilized as a function of the chemical bonds formed around the zirconium ion. The higher density of defects on nanometric surface particles induces polarization of the zirconium ion, increasing its ionic character and resulting in the stabilization of cubic/tetragonal structures. These interconvertible structures are in a good agreement with the calculations of Madelung potentials [48]. There is a small barrier potential between the phases that always causes a change to occur in the covalent-ionic character of the zirconium ion during transformation.

The results listed in Table V indicate that the energy gap for the polymorphic phases of zirconia is well

TABLE V The electronic energy gaps (eV) for zirconia

Reference	Monoclinic	Tetragonal	Cubic
(Theor) (46)	5.25	3.05	2.88
(Theor) (35)	4.51	4.11	3.84
(Theor) (37)		12.3	13.3
(Theor) (38)	4.46	4.28	4.93
(Theor)(50)	7.18	7.51	3.77
(Exper) (38)	5.83	5.78	6.10
(Exper) (38)	7.09	6.62	7.08
(Exper) (50)	4.70		5.73
This work Zr_4O_8 (Theor)	4.79	4.30	5.48
This work $[Zr_4O_8]^a$ (Theor)	5.36	4.42	5.86
This work $[Zr_4O_7^{+2}]^a$ (Theor)	6.47	5.52	6.26

[a] Geometry optimized of Zr_4O_8 and $Zr_4O_7^{+2}$ clusters.

reproduced in this work, although the *ab initio* Self Consistent Field Roothaan-Hartree-Fock method overestimates the calculated values [37]. This fact emphasizes the strong dependence on the set of atomic bases used to calculate these properties, since the *ab initio* calculation made by Orlando *et al.* [37] resulted in values up to three times higher than the experimental ones.

4. Conclusions

A new method for the synthesis of zirconia particles using a complexation of zirconia ions in a solution of 8-hidroxiquinoline was developed in this study. Powders with high surface area and low degree of agglomeration were obtained by this method. The calcined powders at 630°C showed a surface area of 89 m^2/g and a crystallite size of 8 to 12 nm.

The RHF cluster method was used to calculate the electronic structures of monoclinic, tetragonal and cubic Zr_4O_8 and $Zr_4O_7^{+2}$.

The RHF technique provided a qualitative reproduction of the main geometrical parameters of m, t and c phases of the zirconia structure with and without vacancy. The c structure of zirconia vacancies was more stable than the corresponding m and t structures. Agreement with the experimental data was improved by taking into account optimized structures.

The theoretical results indicate that the oxygen vacancy acts as a local stabilizing agent by generating a crystalline field that decreases the volume of the monoclinic, tetragonal and cubic phases, causing destabilization of the monoclinic phase and resulting in the formation of the cubic or tetragonal phases.

The results also show a strong dependence of the gap energy on the atomic basis set used in the calculation.

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