# Experimental and theoretical aspects of the stabilization of zirconia.

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Using the Rietveld method, phases of ceria-doped zirconia, calcined at temperatures of 600 and 900 °C, were quantitatively analysed for different concentrations of ceria. The results show that the stabilization of zirconia depends on the dopant concentration and calcination temperature. Moreover, the theoretical calculation using the *ab initio* Hartree–Fock–Roothaan method indicates that the most stable phases for ceria-stabilized zirconia are cubic or tetragonal, in accordance with experimental results. © *1999 Kluwer Academic Publishers*

## 1. Introduction

Zirconia is an important material for high-temperature applications [1]. There are three well-defined polymorphisms for this material: monoclinic, tetragonal and cubic phases. The monoclinic phase, which is stable below 1300 K, can be described as a distortion of the cubic $CaF_2$ structure [2]. Zirconium dioxide is normally monoclinic at room temperature, but undergoes a reversible martensitic phase transformation at about 1200 °C to a tetragonal structure [3]. Although this high-temperature phase cannot be quenched, it is well known that the tetragonal structure exists at room temperature in microcrystals [4].

The crystal structure of, and mechanisms of the transformations between, the monoclinic, tetragonal and cubic phases are of considerable technical interest, because they can be manipulated to provide optimized physical and chemical properties of the materials fabricated from the stabilized zirconia [5–7]. The so-called partially stabilized zirconias (PSZ), which are typically two-phase cubic and tetragonal or single-phase tetragonal, are of importance for mechanical and structural applications. The fully stabilized zirconias (FSZ), which are normally single-phase cubic, are of interest for heating elements, oxygen sensors and fuel cell applications [5]. The zirconia can be stabilized at room temperature by doping with oxides of di, tri- and tetravalent metals such as calcium, magnesium, yttrium, lanthanum, ytterbium and cerium [8].

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, and its ionicity is different for the cubic and the tetragonal phases [9]. Ching *et al*. [10] have studied the electronic levels and charge-density distribution in defect-stabilized zirconia by means of large cluster calculations. Cohen *et al*. [11] have 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 discrepant with experimental data, and it is suggested that disorder greatly affects its elastic behaviour. Furthermore, disorder and defects may be important in stabilizing the monoclinic and tetragonal structure of zirconia.

Zandiehnadem and Murray [12] studied zirconia in the cubic, tetragonal and monoclinic phases using a first principle self-consistent orthogonalized linear combination of the atomic orbital method. They obtained the band gaps of 3.84, 4.11 and 4.51 eV, respectively, for the three phases. Jansen and Gardner [13] used the full-potential linear-augmented-plane-wave (FLAPW) method for studying the tetragonal to cubic phase transition. Their results show the phase transition from tetragonal to cubic is driven by the thermal motion of the oxygen atoms. Orlando *et al*. [14] 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. The analysis of the electronic structure shows appreciable departure from a purely ionic type of bond. French *et al*. [15] 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 (orthogonalized linear combination of atomic orbital method) 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 which contained atomic defects, while the calculations were performed for undoped idealized zirconia structures without atomic defects. Reasonable agreement was found between experiment and theory at this level.

The theoretical and experimental analysis of the stabilization of zirconia leads to antagonistic results

due to the high number of parameters that should be optimized. However, it should be mentioned that at room temperature the tetragonal and cubic phases could exist when doped with alkaline earth metal oxides (MgO, CaO) or by transition metal oxide ($Y_2O_3$, $CeO_2$). Thus the theoretical studies should consider the effects of these dopants because they have not been considered so far [9–14].

In this work, an experimental study to verify the influence of dopant concentration on the stabilization of zirconia as a function of temperature was carried out and compared with the theoretical *ab initio* results on ceria-stabilized zirconia.

## 2. Experimental procedure and calculation method

The monoclinic samples were prepared from zircon by alkaline fusion (IPEN). Data for the other phases were collected on free-standing, sintering specimens of polycrystalline zirconia containing $CeO_2$ (0, 2, 4, 6, 8 and 10 mol %). The samples were characterized by X-ray diffraction using a Siemens D-5000 diffractometer. The quantitative analysis (wt %) was performed with the results of the Rietveld refinements, according to the Hill, Howard and Reichert method (Equation 1) [16]. The DBWS 9411 Rietveld program [17] was used, with the pseudo-Voigt profile function (Equation 2), in the following least squares parameters refinements: four background polynomial, unit cell, scale factor, peak-width ($U$, $V$, $W$), shape ($\eta$), asymmetry, and crystal structures for the predominant phases. The full-width at half-maximum varied according to the Caglioti, Paoletti and Ricci function [18]

$$W_j = M_j V_j S_j \Big/ \sum_i (M_i V_i S_i) \qquad (1)$$

$$p - V = \eta L + (1 - \eta)G \qquad (2)$$

where $S$ is the scale factor reached at the end of the Rietveld refinements, $V$ is the unit cell volume calculated with the refined unit cell parameters, and $M$ is the mass of all the unit cell contents, for each phase. $L$ and $G$ are the Lorentz and Gauss functions, respectively, $\eta$ is the Lorentzian fraction varying with $2\theta$ by $NA + NB\, 2\theta$, and $NA$ and $NB$ are refinable parameters.

To study the stabilization, the cluster model ($CeZr_3O_8$) was used. The *ab initio* Hartree–Fock–Roothaan was employed for the calculation with the Games program [19].

The linear combination of atomic orbitals (LCAO) method has been extensively used in the study of electronic structures of solids in the last 20 years. One of the advantages of the LCAO method is its ability to handle systems with complex structures and large unit cells because of the basis functions. In the present calculation, the orbital exponents and contraction coefficients of the atomic wave functions were determined by optimizing total energies, as was explained in detail in a previous article of Sakai *et al*. [20].

In the minimal basis set, the radial functions of the atomic orbitals are expressed as

$$R_{nx} = \sum_{i=1}^{N} C_{nx,i} X_i(r) \qquad (3)$$

Where $X = s$, $N = 2$ for O; $N = 5$ for Zr, and $N = 6$ for Ce; $X = p$, $N = 1$ for O; $N = 3$ for Zr, and $N = 4$ for Ce; $X = f$, $N = 1$ for Ce, and $n$ is the principal quantum number. This set of primitive Gaussian-type functions (GTOs) are used to construct each $s_i(r)$, $p_i(r)$, $d_i(r)$ or $f_i(r)$, which can be written as

$$s_i(r) \sum_{k=1}^{m} d_{SI}, kg_{Si}(\alpha_{Si}, k, r) \qquad (4)$$

$$p_i(r) \sum_{k=1}^{m} d_{pi}, kg_{pi}(\alpha_{pi}, k, r) \qquad (5)$$

$$d_i(r) \sum_{k=1}^{m} d_{di}, kg_{di}(\alpha\phi, k, r), \qquad (6)$$

$$f_i(r) \sum_{k=1}^{m} d_{fi}, kg_{fi}(\alpha_{fi}, k, r), \qquad (7)$$

where $g_{si}$, $g_{pi}$, $g_{di}$, and $g_{fi}$ are normalized 1s-type, 2p-type, 3d-type and 4f-type Gaussian functions, respectively. The convenient shortened notations are (432222/4222/4214) for cerium; (73, 7) for oxygen and (43333/433/43) for zirconium. The orbital exponents and the contraction coefficients have been determined by the same method reported by Huzinaga *et al*. [21], and the values are shown in Table I.

The structural parameters used in the band structure calculations are summarized in Table II and Figure 1, including unit cell parameters, volumes per molecule and bond lengths for Zr-O and Ce-O.

## 3. Results and discussion

The stabilization of zirconia should be considered both theoretically and experimentally. The experimental analyses are based on the synthesis method and the type and concentration of dopants, whereas the theoretical results are based on quantum mechanical methods and on the optimization of the crystalline structure. Due to the fundamental complexity of dopant-induced phase stabilization of zirconia, it is not possible at present to undertake experimental and theoretical studies of identical systems. A room-temperature study of the three phases of zirconia requires the use of dopants in order to stabilize the tetragonal and the cubic phase of zirconia. These materials have substantial dopant concentrations and also have high concentrations of dopant-induced oxygen vacancies. The stabilizers strongly affect the unit cell volume of the tetragonal and cubic phases, leading to larger unit-cell volumes than the idealized structure [15].

Refinements of the monoclinic, tetragonal and cubic structures were undertaken in space groups P21/c, P42/nmc and Fm3m, respectively, and the results are shown in Tables III and IV. As shown in these tables, the cubic phase of zirconia can be stabilized completely (100%) with additions of $CeO_2$, which does not induce oxygen vacancies into the zirconia structure. However, Dwivedi and Cormack [22] suggested that the cubic phase is stabilized by doping zirconia with cations such as $Ca^{2+}$ which impose a local cubic symmetry on the

TABLE I Exponents and expansion coefficients for zirconium, cerium and oxygen

| Ce | | O | | Zr | |
|---|---|---|---|---|---|
| Exponents | Coefficients | Exponents | Coefficients | Exponents | Coefficients |
| $s_1$ | | $s_1$ | | $s_1$ | |
| 7624.1049 | 0.1166973 | 10334.736 | 0.0008449 | 23631.786 | 0.0168699 |
| 50563.078 | 0.0166001 | 1500.3950 | 0.0067550 | 3562.8550 | 0.1185090 |
| 1734.6306 | 0.4306567 | 337.95497 | 0.0343071 | 808.60763 | 0.4348796 |
| 469.78702 | 0.5665720 | 96.051304 | 0.1250896 | 218.05710 | 0.5615664 |
| $s_2$ | | 31.613952 | 0.3167742 | | |
| 700.94718 | −0.1147211 | 11.423798 | 0.4533328 | $s_2$ | |
| 81.168677 | 0.6594528 | 4.3012501 | 0.2144500 | 326.01729 | −0.1118501 |
| 35.782997 | 0.4120855 | | | 37.193042 | 0.6449565 |
| $s_3$ | | $s_2$ | | 15.852335 | 0.4274608 |
| 69.370368 | 0.2784065 | 10.195221 | −0.0837570 | $s_3$ | |
| 11.019743 | −1.132336 | 0.93361357 | 0.5751097 | 29.133824 | −0.2521087 |
| $s_4$ | | 0.28587720 | 0.5103155 | 5.0468818 | 0.7860020 |
| 13.119354 | −0.3183287 | | | 2.2623576 | 0.3549481 |
| 2.1795111 | 1.1521180 | $p_1$ | | $s_4$ | |
| $s_5$ | | 117.21023 | 0.0022198 | 3.7366979 | −0.2986953 |
| 2.5787978 | −0.2682437 | 26.967137 | 0.0172064 | 0.76213451 | 0.7775379 |
| 0.33572966 | 1.1098845 | 8.3338649 | 0.0750846 | 0.32420281 | 0.3994054 |
| $s_6$ | | 2.9811654 | 0.2122762 | $s_5$ | |
| 0.01149362 | 0.1584908 | 1.1284031 | 0.3725583 | 0.43503515 | 0.1698386 |
| 0.03414466 | 0.8674480 | 0.42167369 | 0.3985842 | 0.06305064 | −0.6844755 |
| $p_1$ | | 0.15059051 | 0.1832060 | 0.02564552 | −0.4201123 |
| 2383.3398 | 0.0244934 | | | $p_1$ | |
| 563.10164 | 0.1653555 | | | 1037.5430 | 0.0264386 |
| 177.92475 | 0.4919077 | | | 244.33521 | 0.1742981 |
| 62.635045 | 0.4769569 | | | 76.352112 | 0.5001034 |
| $p_2$ | | | | 26.341227 | 0.4645667 |
| 27.047588 | 0.4739006 | | | $p_2$ | |
| 10.797621 | 0.5867927 | | | 12.091567 | 0.3419849 |
| $p_3$ | | | | 4.9777934 | 0.5656245 |
| 4.4186707 | 0.5455808 | | | 2.1315357 | 0.1858844 |
| 1.8164039 | 0.5122086 | | | $p_3$ | |
| $p_4$ | | | | 1.1983281 | 0.4371619 |
| 0.60472662 | 0.5634847 | | | 0.50580455 | 0.5167044 |
| 0.22177225 | 0.5086430 | | | 0.20176662 | 0.1393652 |
| $d_1$ | | | | $d_1$ | |
| 297.66639 | 0.0380686 | | | 99.316322 | 0.0498668 |
| 87.399204 | 0.2197978 | | | 28.232958 | 0.2570547 |
| 31.380124 | 0.5264647 | | | 9.5340582 | 0.5306913 |
| 11.655706 | 0.4193660 | | | 3.2233126 | 0.4038262 |
| $d_2$ | | | | $d_2$ | |
| 6.1047986 | 0.4958934 | | | 1.5339873 | 0.2328655 |
| 1.9558493 | 0.6259546 | | | 0.46969283 | 0.5299868 |
| $f_1$ | | | | 0.13054859 | 0.4871967 |
| 25.516484 | 0.0830548 | | | | |
| 7.5835275 | 0.3154957 | | | | |
| 2.4478786 | 0.5223007 | | | | |
| 0.70826970 | 0.4442941 | | | | |

TABLE II Crystallographic parameters and bond distances used in the structure calculation

| Parameters | Cubic | Tetragonal | Monoclinic |
|---|---|---|---|
| Lattice constant (nm) | $a = 0.5083$ | $a = 0.3584$ $b = 0.5170$ | $a = 0.5147$ $b = 0.5198$ $c = 0.5314$ $\beta = 99.21$ |
| Volume ($10^{-3}$ nm$^3$) | 131.60 | 66.40 | 140.36 |
| Space group | F$m3m$ | P4$_2$/$nmc$ | P2$_1$/$c$ |
| Zr-O bond (nm) | 0.2072 | 0.2102 | 0.2210 |
| Ce-O bond (nm) | 0.2072 | 0.2102 | 0.2090 |

TABLE III Phase percentages obtained by the Rietveld method for the zirconia–ceria system at 600 °C

| Ceria (%) | Monoclinic (%) | Tetragonal (%) | Cubic (%) | Total stabilized (%) |
|---|---|---|---|---|
| 0 | 54.8 ± 0.5 | 0 | 45.2 ± 0.6 | 45.2 ± 0.6 |
| 1 | 91.0 ± 0.4 | 9.0 ± 0.9 | 0 | 9.0 ± 0.9 |
| 2 | 24.0 ± 0.7 | 76.0 ± 0.6 | 0 | 76.0 ± 0.6 |
| 4 | 16.5 ± 1.0 | 66.9 ± 0.7 | 16.6 ± 1.0 | 83.5 ± 1.7 |
| 6 | 0 | 0 | 100 | 100 |
| 8 | 0 | 0 | 100 | 100 |
| 10 | 0 | 0 | 100 | 100 |

**TABLE IV** Phase percentages obtained by the Rietveld method for the zirconia–ceria system at 900 °C

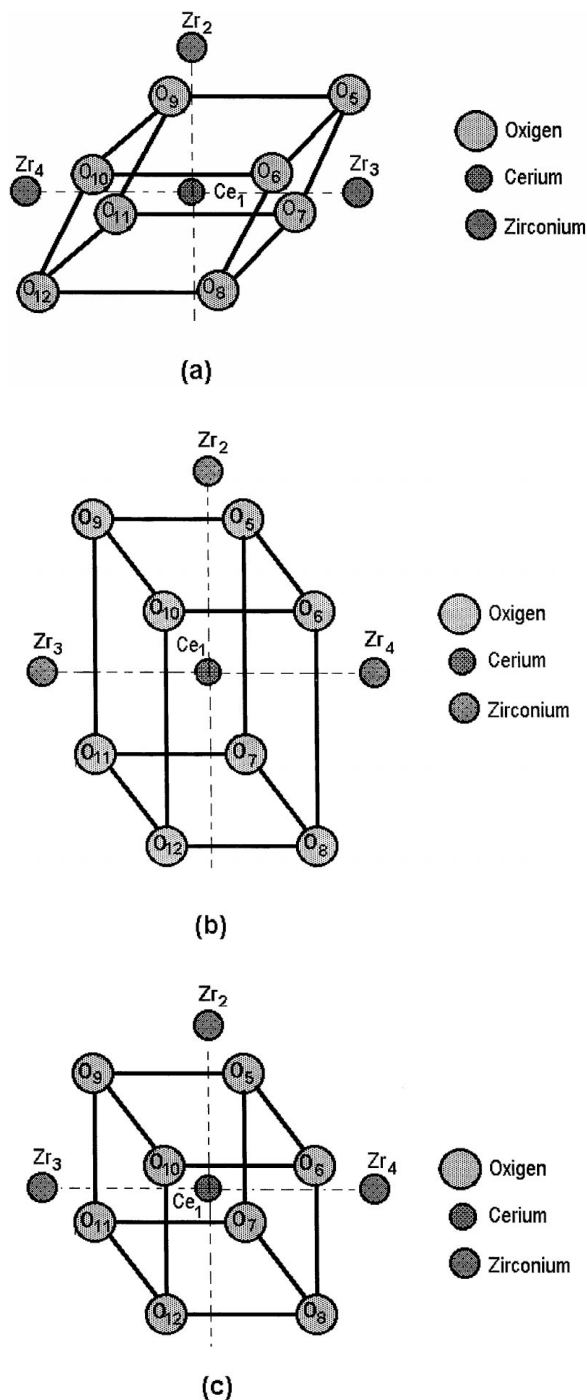| Ceria (%) | Monoclinic (%) | Tetragonal (%) | Cubic (%) | Total stabilized (%) |
|---|---|---|---|---|
| 0 | 94.8 ± 0.3 | 0 | 5.2 ± 0.9 | 5.2 ± 0.9 |
| 1 | 95.4 ± 0.2 | 1.0 ± 0.9 | 3.6 ± 0.8 | 4.6 ± 1.7 |
| 2 | 93.7 ± 0.2 | 0 | 6.4 ± 0.8 | 6.4 ± 0.8 |
| 4 | 60.7 ± 0.6 | 39.3 ± 0.8 | 0 | 39.3 ± 0.8 |
| 6 | 8.0 ± 0.8 | 92.0 ± 0.4 | 0 | 92.0 ± 0.4 |
| 8 | 7.3 ± 0.8 | 92.7 ± 0.4 | 0 | 92.7 ± 0.4 |
| 10 | 0 | 91.7 ± 0.4 | 8.3 ± 0.9 | 100 |



*Figure 1* Schematic representation of the zironia–ceria structures: (a) monoclinic, (b) tetragonal, (c) cubic.

anion sublattice. The defect energy of a vacancy is lower in cubic zirconia than in tetragonal zirconia. Therefore, the presence of vacancies makes the cubic phase more stable. The importance of oxygen vacancies for the cubic phase stabilization has been emphasized by Hillert and Sakuma [23] and Hillert [24]. Cormack and Parker [25] calculated the phonon spectra of pure and doped cubic zirconia crystals. They obtained an imaginary frequency for the $X^{2-}$ mode in the pure crystal and concluded that the cubic phase does not correspond to a local minimum of the adiabatic free energy surface (AFES). By adding impurities they calculated that the frequency of this mode becomes positive, which was interpreted as a creation of a local minimum of the AFES corresponding to the cubic phase. Stefanovich and Shluger [26] proposed that the calculations clearly reveal an important effect of dopants on the dynamics and hence the free energy of the solid. However, the existence of the total energy minimum does not necessarily imply that the cubic phase has lower free energy than the tetragonal phase and, therefore, does not prove its relative thermodynamic stability. They have identified some of the basic factors controlling the relative stability of the tetragonal and cubic zirconia such as the ionicity, vacancies, defect–defect interactions and electronic configuration of cations. However, the studies of Li *et al.* [27, 28] using X-ray diffraction showed that the coordination of the cerium ion with oxygen in the zirconia matrix is significantly different to that of the host cation. $CeO_8^{4-}$ polyhedrons of a large size were observed in tetragonal zirconia with a Ce—O bond length greater than that of a Zr—O bond, but smaller than that of the Ce—O bond length in pure ceria.

On further analysis of Tables III and IV, it is observed that a higher amount of stabilized zirconia with the cubic structure was obtained at 600 °C than at 900 °C, showing clearly the effect of crystallite size. The crystalline size, measured by XRD using the Rietveld method, did not change substantially with cerium concentration. The mean value of crystalline size for powders calcined at 600 °C was 35 nm while for powders calcined at 900 °C it was 55 nm. According to Garvie [4] the existence of the tetragonal phase in monocrystals at temperatures well below the normal monoclinic-to-tetragonal transformation temperature can be explained by a crystallite size effect. The experimental results are therefore coherent because there is an association of crystallite size and dopant concentration on the phase formation. For a low calcination temperature (600 °C) there is a predominance of tetragonal (2 and 4 mol % ceria) and cubic (6, 8 and 10 mol % ceria) zirconia. An increase in calcination temperature to 900 °C results in less-stabilized zirconia being formed for compositions containing 0–2 mol % ceria. The increase in calcination temperature therefore destabilizes the low ceria-concentration-doped zirconia (0–2 mol % Ce). Moreover the increase in ceria concentration (4–10 mol %) produces the transformation of zirconia from monoclinic to predominantly tetragonal phase.

The structure energies formed by substitution of a zirconium atom by a cerium atom are listed in Table V. These data are in accordance with the experimental

TABLE V Total energy, $E_T$, high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO)

| Parameters | Cubic | Tetragonal | Monoclinic |
|---|---|---|---|
| $E_T$ (arb. units) | −19765.3405 | −19764.7775 | −19759.1837 |
| HOMO (arb. units) | −0.1773 | −0.2135 | −0.2765 |
| LUMO (arb. units) | −0.0387 | −0.0628 | −0.0124 |

TABLE VI Atomic charges (arb. units) of the $(ZrO_2)_3CeO_2$ structure

| Atom | Cubic | Tetragonal | Monoclinic |
|---|---|---|---|
| $Ce_1$ | 2.69 | 2.64 | 2.49 |
| $Zr_2$ | 1.26 | 0.82 | 0.21 |
| $Zr_3$ | 1.26 | 0.82 | 1.16 |
| $Zr_4$ | 1.02 | 1.36 | 0.15 |
| $O_5$ | −0.90 | −0.81 | −0.55 |
| $O_6$ | −0.90 | −0.81 | −0.55 |
| $O_7$ | −0.66 | −0.60 | −0.57 |
| $O_8$ | −0.66 | −0.60 | −0.57 |
| $O_9$ | −0.90 | −0.81 | −0.44 |
| $O_{10}$ | −0.90 | −0.81 | −0.44 |
| $O_{11}$ | −0.66 | −0.60 | −0.44 |
| $O_{12}$ | −0.66 | −0.60 | −0.44 |

TABLE VII The electronic energy gaps (eV) for zirconia

| Reference | Monoclinic | Tetragonal | Cubic |
|---|---|---|---|
| [26] (theor.) | 5.25 | 3.05 | 2.88 |
| [12] (theor.) | 4.51 | 4.11 | 3.84 |
| [14] (theor.) |  | 12.3 | 13.3 |
| [15] (theor.) | 4.46 | 4.28 | 4.93 |
| [15] (exper.) | 5.83 | 5.78 | 6.10 |
| [15] (exper.) | 7.09 | 6.62 | 7.08 |
| [30] (exper.) | 4.70 |  | 5.73 |
| present work (theor.) | 7.18 | 7.51 | 3.77 |

crystallite growth can generate stresses that destabilize cubic or tetragonal phases to the monoclinic phase. Vacancy concentration is an important, but not fundamental, factor for zirconia stabilization.

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

results listed in Tables III and IV, where the tetragonal and cubic structures are more stable at room temperature after stabilization. In this case there is no formation of oxygen vacancies, which are considered as fundamental for the stabilization of zirconia [23, 24]. The stabilization of zirconia is therefore promoted by the action of dopant ions at a molecular level. This fact is emphasized in Table VI where the electron population on the cerium ion has a decreasing value from the cubic phase to the monoclinic phase (less stable). The same effect is observed for the mean value of electron populations on the zirconium ion. The role of a dopant would be to generate a centre of polarization and attraction that would decrease the unit-cell volume of zirconia. The repulsive forces would then overcome the attractive forces in the monoclinic structure, resulting in the formation of the cubic and tetragonal structures at ambient temperature and consequently destabilizing the monoclinic structure. The calculation of Modelung potentials for MgO and $Y_2O_3$ stabilized zirconia [29] indicated that the cubic structure of these crystals are metastable. These structures transform without an energy barrier to a pseudomonoclinic or tetragonal structure. However, these calculations have neglected important effects such as short-range interactions, covalent bond, etc. In the present work, the theoretical model considers these effects by using the *ab initio* HFR method.

The results listed in Table VII show that there is a good reproducibility in the determination of the energy gap for zirconia, although the *ab initio* self-consistent field Roothaan–Hartree–Fock methods overestimate the calculated values [14]. This fact emphasizes the strong dependence of the base choice with relation to this property, because the *ab initio* calculation made by Orlando *et al.* [14] resulted in values up to three times higher than the experimental values.

## 4. Conclusion
The experimental results show that the stabilization of zirconia is dependent on the dopant concentration but

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