Theoretical calculations meet experiment to explain the luminescence properties and the presence of defects in $m\text{-ZrO}_2$

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Abstract

The present article is a thorough quantum mechanics investigation based on DFT method targeting the opto-electronic properties of the $m\text{-ZrO}_2$ material issuing from the presence of defects. Herein, we conclude that the luminescence observed around 477 nm (~ 2.60 eV) corresponds to the charge transfer between Ti_{Zr} and oxygen atoms (*i.e.*, $\text{Ti}^{3+} + \text{O}^- \rightarrow \text{Ti}^{4+} + \text{O}^{2-}$), and not from oxygen vacancies or $d\text{-}d$ transitions at Ti^{3+} sites. Namely, based on constrained DFT calculations, an emission at 2.61 eV (475 nm) was calculated that matches perfectly with experiments (around 2.60 eV / 477 nm). Moreover, in order to demonstrate the propensity of the ZrO_2 host lattice to entrap titanium, intrinsic and extrinsic point defect formation energies on $m\text{-ZrO}_2$ were computed.

13 Introduction

14 In the last decades, zirconia (ZrO_2) material became particularly appealing due to its po-
15 tential incorporation into a wide variety of technological devices. Thanks to its chemical
16 and mechanical stabilities, biocompatibility, wide bandgap, high refractive index and high
17 dielectric constant, one may find the following potential applications: semiconductor sub-
18 strates, solid electrolytes, thermal barriers, sensors, gate dielectric stacks, catalysts, etc.¹⁻⁶
19 ZrO_2 may also display luminescent properties as discussed hereafter.

20 Formally, even though luminescent properties of ZrO_2 compound have been widely re-
21 ported in the literature for the different crystallographic phases (*i.e.*, cubic, tetragonal and
22 monoclinic),⁷⁻¹⁷ the origin of its intense white-blue emission at 470-490 nm in pure mon-
23 oclinic phase ($m\text{-ZrO}_2$) is still a matter of debates. A tentative explanation ascribed this
24 band to the electronic relaxation from oxygen vacancies,¹⁰ comforted by the observation of
25 the decrease in photoluminescent intensity by increasing the partial oxygen pressure.¹⁷⁻¹⁹
26 This proposition is supported by i) EPR analyzes which confirm the existence of F^+ colour
27 centers (*i.e.*, single charged oxygen vacancies),^{16,17} and ii) point defect calculations.²⁰

28 Another model suggests the blue emission is induced by on-site d - d transitions of im-
29 purity titanium ions Ti^{3+} .^{12,13} Ti impurities may be naturally present as traces in ZrO_2
30 and unintentionally substitute zirconium, since zirconium element is commonly extracted
31 from Ti ores (e.g. ilmenite or rutile). Also, it was evidenced that the photoluminescence
32 intensity significantly increases with titanium doping.^{12,16,21} Here, oxygen vacancies are as-
33 sumed to participate to the reduction of titanium species ($\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$), explaining the
34 close connection with the enhancement of the luminescence band for crystal growths with
35 the presence of a reducing agent.¹⁶ Surprisingly, Ti^{3+} species have not been identified by
36 EPR measurements¹⁶ except at the surface of the samples.²²

37 Other sources for the luminescence at ≈ 2.6 eV can be found within the literature. For
38 instance, a self-activated emission by Zr^{4+} sites has been pointed to be possibly responsible
39 for.²³ Another experimental study by Pan *et al.* concluded the charge transfer $\text{Ti}^{3+} + \text{O}^-$

→ $\text{Ti}^{4+} + \text{O}^{2-}$ could indeed be the main cause.²⁴

From the theoretical side, Density Functional Theory (DFT) is usually used for inorganic solids in optics to determine band gaps, identify electronic transitions at work in a given material and get access to the complex refractive indexes. More recently, DFT has been employed to provide information on charge transition levels within the bandgap,^{25–35} enabling one to characterize the presence and the nature of defects in the studied structure. To our knowledge, such simulations have been reported for (only) intrinsic point defects in $m\text{-ZrO}_2$.^{20,36–44} Consequently, this prompted us to revisit in-depth the impact of defects (*i.e.*, native defects and substitution of Zr by Ti) in $m\text{-ZrO}_2$ on its electronic structure.

Moreover, *ab initio* calculations should be capable to shed light on transitions at work and anticipate the emission characteristics of solids. Unfortunately, at the opposite of molecular *ab initio* simulations for which the methodology is mature and (almost) routine to simulate luminescence spectra,^{45–52} the *ab initio* simulation of emission spectra in solid state materials remains still challenging and a matter of some debate. Recent works demonstrated the efficiency of the ΔSCF method (an efficient alternative to TD-DFT) based on the *constrained* DFT (cDFT) to predict transition energies of Ce^{3+} or Eu^{2+} doped phosphor compounds.^{53–55} In these studies, authors applied the so-called constrained DFT methodology (cDFT) as commonly used in molecular simulations.⁵² In that context, we embarked on a tentative elucidation of the luminescence properties of Ti doped $m\text{-ZrO}_2$ via DFT calculations.

Herein, we report a computational study to provide more clues on the origin of the white-blue luminescence of $m\text{-ZrO}_2\text{:Ti}$. Our calculations strongly advocate that Ti_{Zr} is at the origin of the white-blue emission in $m\text{-ZrO}_2$ at ≈ 477 nm (2.6 eV). To do so, we combined cDFT to model excited state together with the estimation of defect formation enthalpies (DFEs) and charge transition levels (CTLs) of point defects. Also, we demonstrated that titanium center is stable at the oxidation state +IV even with the presence of oxygen vacancies.

Methods

Ground and Excited States Modelling for the cDFT approach

Accurate Bulk Structure

We performed first-principles simulations based on the Density Functional Theory (DFT) within the projector augmented wave (PAW) method, as implemented in the VASP software.^{56–58} Excited state simulations have been conducted using the PBE functional⁵⁹ with a cutoff energy set to 550 eV. Full geometry relaxation of the unitcell was performed considering a $4 \times 4 \times 4$ Monkhorst-Pack k -mesh (16 irreducible k -points).⁶⁰ Atomic forces and total energy were minimized until threshold values of 1 meV/Å and 10^{-6} eV, respectively. Accurate energy calculations were carried out with a $6 \times 6 \times 6$ Γ -centered k -points sampling (80 irreducible k -points).

Ground and Excited States

A $2 \times 2 \times 2$ supercell was built in which the V_O and Ti_{Zr} were evaluated. Structural relaxations were performed on all geometries for both GS (Ground State) and ES (Excited State), together with accurate energies determined with a smaller density k -mesh (Γ point only) to reduce the (already) heavy computational cost. We kept strong threshold values during the optimizations (5 meV/Å and 10^{-6} eV).

On these grounds, we computed the emission wavelengths using the Δ SCF procedure as reported in Ref 53–55. Here, the emission energy expression is given by the formulae

$$E_{em} = E(A_1^*) - E(A_1) \quad (1)$$

where $E(A_1^*)$ is the total energy of the relaxed excited state (Q_{ES} in Figure 1), and $E(A_1)$ is the total energy of the ground state enforcing the excited state geometry. The energy difference corresponds to the electronic vertical emission.

Figure 1: Schematic representation of the absorption and emission processes with respect to the configuration coordinate Q .

Point Defects Modelling

For point defect calculations, in order to reduce the computational time and after careful checks, the plane waves basis expansion was set with a cutoff energy of 500 eV. We considered the meta-GGA SCAN (Strongly Constrained and Appropriately Normed) approach to describe the exchange-correlation potential.⁶¹ Full geometry relaxations were done on the unit-cell until atomic forces were lower than 5 meV/Å and with a $12 \times 12 \times 12$ Γ -centered k -mesh (518 irreducible k -points).

Faulted structures with isolated (complex) point defects were built based on a $2 \times 2 \times 2$ ($3 \times 3 \times 3$)-supercell of the fully relaxed ZrO_2 primitive unit cell. Atomic relaxations were conducted until forces on atoms are below 10 meV/Å. A $4 \times 4 \times 4$ Γ -centered k -mesh (36 irreducible k -points) was used. For complex defects, geometry relaxations were done considering a $1 \times 1 \times 1$ Γ -centered k -mesh, and a $2 \times 2 \times 2$ Γ -centered k -mesh was used for accurate energy calculations.

Defect formation enthalpies were estimated using the supercell approach and assuming point defects are sufficiently diluted in it. In such a situation, interactions between periodic

boundary images are minimized and the volume of the supercell does not suffer any changes.

Thus, DFEs may be computed with the following formula:

$$\Delta_f H^{D,q}(\mu_{E_F}) = \left(E_{DFT}^{D,q} - E_{DFT}^{host} \right) + \sum_i n_i \mu_i + q \left(E_{VBM}^{host} + \mu_{E_F} \right) + E_{corr} \quad (2)$$

where $\Delta_f H^{D,q}$ is the DFE of a defect D in a charge state q , $E_{DFT}^{D,q}$ is the DFT total energy of the faulted structure, E_{DFT}^{host} is the DFT total energy of the host structure, n_i is the number of atoms of the i^{th} specie added ($n_i < 0$) or removed ($n_i > 0$) from the ideal material, μ_i is the chemical potential of the related species, μ_{E_F} is the Fermi level, E_{VBM}^{host} corresponds to the valence band maximum (VBM) of the host material, and E_{corr} is associated to various corrections of spurious effects (see SI for more details).

The charge transition levels $\epsilon(q/q')$ for probed defects were also calculated. CTLs correspond to the Fermi level position for which the two charge states q and q' of a same point defect D are involved in a thermodynamic equilibrium, *i.e.*, both species are in equal amount. This quantity is expressed as:

$$\epsilon(q/q') = \frac{\Delta_f H^{D,q}(\mu_{E_F} = 0) - \Delta_f H^{D,q'}(\mu_{E_F} = 0)}{q' - q} \quad (3)$$

All defect post-treatments were performed using the development version of the PyDEF software.^{62,63}

Results

Host structure

The primitive cell of the m -ZrO₂ phase is given in Figure 2. The structure crystallizes in the $P2_1/c$ space group and contains three atoms symmetrically nonequivalent, all of them being positioned in a $4e$ Wyckoff site. The first oxygen atom (hereafter labelled O(3)) is located

at the centre of a trigonal plane formed by three Zr atoms. The second (hereafter labeled O(4)) is inside a Zr₄ tetrahedron. The Zr atom is coordinated to four O(4) and three O(3).

Figure 2: (a) View of the primitive cell of *m*-ZrO₂ along the [001] crystallographic direction. Zr atoms are represented by green spheres. O(3) and O(4) species are distinguished by red and orange spheres, respectively. (b) O(4) tetragonal, (c) O(3) trigonal plane and (d) Zr 7-coordinated environments.

Emission and Excited State Electronic Structures

Computed Electronic Emission

Most of previous experimental studies attributed the origin of blue luminescence in zirconia to the presence of titanium. Following these conclusions, a doped system was built with the substitution of one zirconium by a titanium atom. The faulted structure was relaxed at both the GS and ES, followed by accurate energy calculations. Then the vertical electronic

emission energy was computed following the protocol given in the computational section. Our simulated $\text{Ti}^{3+} + \text{O}^- \rightarrow \text{Ti}^{4+} + \text{O}^{2-}$ electronic emission ($\simeq 2.61$ eV) is in outstanding agreement with the observed one (≈ 2.6 eV).^{13,15,16} Therefore, with respect to the level of accuracy used herein, the luminescence measured at around 477 nm is very likely due to the presence of Ti^{4+} substituting Zr^{4+} cations. We now discuss in more details the structure and electronic structure for this doped material. The calculated bond lengths around the metal at both GS and ES are given in Table 1. As expected, there is a strong local rearrangement around the metal upon the excitation process. Indeed, the five short Ti-O distances ($1.86 < d_{\text{Ti-O}} < 2.12$ Å) become larger ($2.02 < d_{\text{Ti-O}} < 2.19$ Å) when going from the A_0 ground to the A_1^* excited states, and the largest ones ($2.35 < d_{\text{Ti-O}} < 2.43$ Å) at the ground state become shorter ($2.28 < d_{\text{Ti-O}} < 2.32$ Å) at the excited state. In average, the Ti-O distances are ≈ 2 % larger in the excited state than in the ground state. Finally, one must say that all the Ti-O(3)-type bonds (O(3)= O1, O2 and O3) are elongated when going from the ground to the excited state, while Ti-O(4)-type bonds gain in homogeneity with a mean value decreasing.

Table 1: (left) Ti environment. Ti, O(3) and O(4) atoms are depicted by blue, red and orange spheres, respectively. (right) Ti-O distances at both ground and excited states together with their respective variations $\Delta(r)$ (in Å).

Bond	A_0	A_1^*	$\Delta(r)$
Ti-O ₁	1.868	2.027	0.159
Ti-O ₂	2.032	2.065	0.033
Ti-O ₃	1.940	2.050	0.110
Ti-O ₄	2.355	2.311	-0.044
Ti-O ₅	2.113	2.188	0.075
Ti-O ₆	2.118	2.185	0.067
Ti-O ₇	2.427	2.281	-0.146

The projected density of states (see Figure S1 in SI) of this compound evidences that, as expected, the valence band is built upon the oxygen atoms and the bottom of the conduction band is constituted by (mainly) titanium, the d -block of Zr being higher in energy than the d -block of Ti. We can therefore characterize the charge transfer occurring during the excitation

151 process, which corresponds to a transfer from oxygen orbitals to titanium ones. We can also
 152 go further and assign the charge transfer occurring during the emission process by comparing
 153 the charge densities of the last occupied states at both A_1^* ($ES@ES$, *i.e.*, the electronic
 154 excited state at the excited state geometry) and A_1 ($GS@ES$, *i.e.*, the electronic ground
 155 state at the excited state geometry) states represented in Figure 3. As one can see, for the
 156 A_1^* state, the charge density is unambiguously located around the titanium site and presents
 157 a d orbital-like shape. Concerning the A_1 state, the charge density is strongly delocalized
 158 over O(3) atoms, *i.e.*, O atoms with a pseudo lone pair that contributes to the uppermost
 159 levels of the valence band (see Figure S2 in SI). Thus, this calculated emission at ≈ 2.6 eV
 160 is clearly assigned to a $Ti-3d \rightarrow O-2p$ charge transfer, supporting a recent proposition based
 161 on experimental investigations.²⁴

Figure 3: Projected charge densities on the last occupied electronic state at the (a) initial
 and (b) final step of the emission process within the Ti-doped ZrO_2 system. Zr, Ti, O(3)
 and O(4) atoms are represented by green, blue, red and orange spheres, respectively.

162 In addition, our findings are in good agreement with different experimental works that
 163 commonly assign the broad blue luminescence band of titanium doped materials to the pres-
 164 ence of Ti^{4+} ions and report that Ti^{3+} lead to emission at lower energies (red/orange/yellow).^{64–66}
 165 More particularly, the emission band located at 490 nm (2.53 eV) in $MgAl_2O_4:Ti$ crystals was
 166 shown to be due to the presence of Ti^{4+} involved in a CT mechanism.⁶⁴ Based on ESR mea-
 167 surements, an experimental study performed on Ti-doped low-silica calcium aluminosilicate

glass (LSCAS) evidenced that visible luminescent bands at 640 nm (1.94 eV) and 480 nm (2.58 eV) originate from Ti^{3+} ($d-d$ transition) ions and Ti^{4+} , respectively.⁶⁵ An experimental study conducted on aluminophosphate glass and sapphire assigned the 840 nm (1.48 eV) and 747 nm (1.66 eV) luminescent bands to Ti^{3+} ions.^{67,68} Thus, on many different materials, the luminescence at about 2.5-3.0 eV can be attributed to Ti^{4+} and not to Ti^{3+} ions in good agreement with our calculations on Ti doped ZrO_2 .

To go deeper in the analysis, we estimated defect formation enthalpies and the position of charge transition levels for intrinsic and extrinsic point defects. Such study turns out to be necessary to prove that Ti^{4+} are easily formed through zirconium substitution and the emission at about 2.60 eV indubitably originates from a $\text{Ti}^{3+}/\text{O}^{2-}$ charge transfer.

Investigation of point defects

Here, we considered the SCAN functional to estimate defect formation enthalpies (DFEs) for intrinsic defects and Ti impurities. This functional was chosen since it is cost affordable, accurate for structure predictions and reliable for point defect properties as demonstrated by some of us.³⁵ The lattice parameters of the ideal $m\text{-ZrO}_2$ unitcell were calculated at $a = 5.146$ Å, $b = 5.226$ Å, $c = 5.315$ Å, and $\beta = 99.32^\circ$, close to the experimental values ($a = 5.14422(4)$ Å, $b = 5.20969(5)$ Å, $c = 5.31120(5)$ Å, and $\beta = 99.220(1)^\circ$).⁶⁹ The band gap was estimated at 4.14 eV, while a HSE06⁷⁰ approach gave 5.28 eV close to already reported GW_0 ⁷¹ (5.34 eV), HSE⁴⁰ (5.22 eV) and EELS⁷² (5.3 eV) data. For a HSE06@SCAN calculation (*i.e.*, HSE06 band gap estimated on the fully optimized SCAN structure), we found 5.23 eV in great agreement with the HSE06 value. Thus, in the following, we considered the SCAN approach for all first-principles calculations concerning point defects, and HSE06@SCAN correction was introduced for a better description of the band gap requested to access more accurate calculated DFEs.

DFE calculations were carried out on intrinsic defects of $m\text{-ZrO}_2$, *i.e.*, vacancies (V_{O} and V_{Zr}), interstitials (Zr_i and O_i , the initial position corresponds to the one labelled P1

in Ref 73) and antisites (Zr_O and O_{Zr}) under oxygen-poor (titanium-rich) and oxygen-rich (titanium-poor) atmospheres. The computational study was extended to Ti doped ZrO_2 with Ti located at the Zr site (Ti_{Zr}) and at the interstitial position (Ti_i).

In the experimental literature, zirconia samples intentionally doped by titanium have been widely prepared by heating manufactured TiO_2 and ZrO_2 powders mixed together and varying the atmosphere of synthesis.^{10,21,74} On the computational side, we set the synthesis conditions by fixing the chemical potentials of the species in presence, such values being determined with the procedure already reported by some of us.³³ Synthesis boundary conditions for the m - ZrO_2 phase doped by titanium were determined on the basis of formation enthalpies of 12 competitive phases, leading to 8 extreme limits for the stability domain of zirconia (see Figure S3 and Table S2 in SI for more details). For the sake of clarity, we considered hereafter the extreme i) O-rich atmosphere (point A in Table S2, associated to the competition with O_2 and TiO_2 phases) and ii) O-poor atmosphere (point H in Table S2, associated to the competition with Ti_3O and Zr phases). We mention that being under O-rich atmosphere will naturally prevent the formation of oxygen vacancies and titanium easily replaces zirconium. In O-poor conditions, an opposite behavior is expected. It is worth to underline that the increase of the oxygen vacancy content should inevitably lead to the formation of the tetragonal or cubic phases for ZrO_2 .⁷⁵⁻⁷⁷ In that sense, this extreme O-poor synthesis condition constitutes a negative control for our point defect investigation targeting the Ti_{Zr} substitution.

DFEs are reported under each atmosphere for isolated point defects in Figure 4. Computed defect concentrations are presented in Figure 4.

For intrinsic defects, charge transition levels were found in good agreement with those already reported in the literature estimated using hybrid functionals.^{42,43} Briefly, we show that zirconium vacancies create both shallow and deep transition levels up to 1.43 eV above the VBM with high DFEs under both atmospheres, unlikely to access for hole trapping/de-trapping processes at room temperature. In the case of V_O species, deep donor transition

Figure 4: (a) Defect formation enthalpies *vs.* μ_{E_F} for O-rich (point A in Table S2) and (b) O-poor (point H in Table S2) synthesis conditions. (c) Defect concentrations *vs.* crystal growth temperature T_{gr} for O-rich and (d) O-poor synthesis conditions.

levels are located between 1.19 and 2.05 eV below the CBM, which drastically limits the direct thermal release of trapped electrons to the conduction band. For antisites, *i.e.*, Zr_O and O_{Zr} , the large computed DFEs evidence the impossibility to form such entities under both atmospheres. In the case of interstitials, deep transition levels are reported for both Zr and O species, but also with too high DFEs for potentially acting as charge carrier traps.

Concerning titanium interstitials, donor transition levels are found between 0.72 and 2.68 eV below the CBM with important DFEs whatever the synthesis conditions are. This let us suggest that such species are hardly created within $m\text{-ZrO}_2$. In contrast, Ti_{Zr} entities present DFEs lower than 2 eV for both synthesis conditions. Thus, titanium impurities

prefer to substitute Zr atoms than occupy interstitial positions. Here, formal $\text{Ti}^{4+}/\text{Ti}^{3+}$ ($\epsilon(-1/0)$) and $\text{Ti}^{3+}/\text{Ti}^{2+}$ ($\epsilon(-2/-1)$) transition levels for Ti_{Zr} are lying within the gap and are respectively calculated at 0.98 and 0.30 eV below the CBM.

More specifically to the O-rich limit, the dopability domain is set by $V_{O(3)}$ and V_{Zr} intrinsic species for which DFEs are crossing the μ_{EF} axis at 0.40 and 2.70 eV above the VBM, respectively. The predominant defects are titanium impurities substituting zirconium at defect charge state $q = 0$ within the whole region, as indicated by their low DFEs of 0.45 eV. Defect concentrations estimated for different growth temperatures confirm that this atmosphere of synthesis is ideal to stabilize Ti_{Zr} species. Typically, for $T_{gr} = 1100$ K, we computed $[Ti_{Zr}] \approx 10^{20} \text{ cm}^{-3}$, the other point defects being found more than eight order of magnitude less concentrated. Also, we found $E_F^{gr} = 1.80$ eV, which reveals the preferential presence of formal Ti^{4+} during the synthesis. At working temperature $T_w = 300$ K, the Fermi level moves to $E_F^w = 0.45$ eV which emphasizes that titanium remains at the oxidation state +IV at room temperature.

In O-poor conditions, $V_{O(3)}$ still pins the p -type limit but this time at 1.90 eV below the CBM. Under this atmosphere, oxygen vacancies exhibit the lowest DFEs, leading to $[V_{O(3)}] = 1.5 \times 10^{18} \text{ cm}^{-3}$ and $[V_{O(4)}] = 2.7 \times 10^{18} \text{ cm}^{-3}$ for $T_{gr} = 1100$ K, while Ti species are significantly less concentrated ($[Ti_{Zr}] = 2.2 \times 10^{13} \text{ cm}^{-3}$ and $[Ti_i] = 3.2 \times 10^9 \text{ cm}^{-3}$). Here, we found $E_F^{gr} = 4.07$ eV, which indicates that $V_{O(3)}^0$, $V_{O(3)}^{+1}$ and $V_{O(4)}^0$ are strongly favoured during the synthesis. At $T_w = 300$ K, only oxygen vacancy entities at charge states $q = 0$ coexist due to the position of E_F^w at 4.65 eV. In these conditions, Ti^{3+} cations at Zr sites are expected in much larger concentrations than Ti^{4+} , $\epsilon(-1/0)$ transition level of Ti_{Zr} defects being located at 4.25 eV.

To sum up, the extreme synthesis conditions of choice for the stabilization of Ti_{Zr} species is an O-rich atmosphere (point A), which notably favours the existence of Ti^{4+} in place of Zr^{4+} . Thus, the luminescent properties in $m\text{-ZrO}_2$ are particularly favoured for such synthesis conditions, except if the concentration of Ti impurities is too large and leads to concentration

quenching phenomena. In contrast, an extreme reduced atmosphere (point H) will tend to promote the formation of oxygen vacancies, while titanium impurities appear significantly less concentrated with an oxydation state lower than +IV. For this last case, experimentally, oxygen vacancies are so prompt to be formed that they may irresistibly induce a phase transition to the tetragonal or cubic forms,⁷⁵⁻⁷⁷ (usually stabilized with the help of Y^{3+}).^{9,78} This clearly means that calculations on $m\text{-ZrO}_2$ in O-poor conditions have to be regarded as an unrealistic solution⁷⁵⁻⁷⁷ that nevertheless shed light on the reactivity of the system to a stimulus, the deprivation of oxygen.

Experimental analyzes pointed that V_O entities may coexist with titanium impurities and could impact the photoluminescence intensity.^{15,16} Regarding the luminescent properties, the most commonly adopted mechanism^{12,41} which involves intra-site $d-d$ electronic transitions at Ti^{3+} explains the changes in the photoluminescence intensity by the reduction of Ti^{4+} species due to the presence of neighboring V_O species. This supposition is notably weakened by the absence of Ti^{3+} species into ESR spectra.¹⁶

From our theoretical investigations on point defects, we demonstrated that isolated Ti^{4+} are preferred to Ti^{3+} species under O-rich synthesis conditions, and are not supposed to be formed under O-poor conditions. Obviously, such extreme synthesis conditions might be not comparable with realistic (intermediate) atmospheres and their study would require more computational efforts. To go beyond this first attempt, we extended the point defect calculations to intermediate atmosphere limits located at the frontier of the $m\text{-ZrO}_2$ stability domain. For fixed growth and room temperatures respectively at $T_{gr} = 1100$ K and $T_w = 300$ K, we followed the evolution of the charge state for Ti_{Zr} species for different atmospheres of synthesis.

For O-rich atmospheres (*i.e.*, high $\Delta\mu_O$ values), we found that Ti^{4+} species are preferentially present within $m\text{-ZrO}_2$, as observed in the extreme case at the A point ($\Delta\mu_O = 0$ eV). By reducing more and more the atmosphere of synthesis (*i.e.*, by decreasing $\Delta\mu_O$), the concentration of oxygen vacancies increases and the charge balance is displaced to stabilize

Figure 5: Nature of Ti_{Zr} species in m - ZrO_2 as a function of synthesis conditions. These atmospheres correspond to the frontier of the m - ZrO_2 stability domain between the A and E points (see Figure S3 and Table S2 in SI). The related chemical potential deviations (in eV) of oxygen ($\Delta\mu_O$) and zirconium ($\Delta\mu_{Zr}$) are only reported for clarity. Results were obtained considering the growth and room temperatures arbitrarily set at 1100 and 300 K, respectively.

Ti^{3+} species (see Figure 5). Here, the change in oxidation state for Ti from +IV to +III is observed at $\Delta\mu_O = -2.05$ eV ($\mu_O = -8.07$ eV). While $\Delta\mu_O$ values are decreasing, $\Delta\mu_{Zr}$ is enhanced due to the constraint imposed by $\Delta H_f(ZrO_2) = \Delta\mu_{Zr} + 2\Delta\mu_O$. The synthesis conditions become more and more Zr-rich which tends to disfavour the substitution of Zr by Ti, favour the formation of oxygen vacancies and thus the transition to cubic or tetragonal phases. In that sense, the point E ($\Delta\mu_O = -4.85$ eV) constitutes a reasonable limit for our analysis to form Ti_{Zr} defects within monoclinic zirconia.

Under O-poor conditions, in a more realistic picture, both species, Ti_{Zr} and V_O , may coexist at (slightly) different ratios *vs.* the oxygen atmospheres. Because the clustering of point defects might not be avoided, we attempted to estimate first accessible transition levels for $Ti_{Zr} - V_O$ based complex entities by considering a $3 \times 3 \times 3$ supercell of 324 atoms. Three combinations were considered: coexistence of V_O with i) one Ti impurity (labelled $(Ti_{Zr} - V_O)$), ii) two Ti (labelled $(2Ti_{Zr} - V_O)$), and iii) one Ti plus another isolated Ti (labelled $(Ti_{Zr} - V_O) + Ti_{Zr}$). Corresponding transition levels are presented in Table 2 and compared to levels of isolated defects in Figure 6.

Here, the calculated transition levels $\epsilon(0/+1)$ appear slightly shifted toward the middle

Table 2: Position of the $\epsilon (+1/0)$ transition level (in eV) within the band gap for complex defects under O-poor synthesis conditions

Defect species	$\epsilon (+1/0)$
$(Ti_{Zr} - V_{O(3)})$	3.88
$(Ti_{Zr} - V_{O(4)})$	3.58
$(2Ti_{Zr} - V_{O(3)})$	3.86
$(2Ti_{Zr} - V_{O(4)})$	3.62
$(Ti_{Zr} - V_{O(3)}) + Ti_{Zr}$	3.89
$(Ti_{Zr} - V_{O(4)}) + Ti_{Zr}$	3.59

Figure 6: Charge transition levels for point defects of interest, *i.e.*, oxygen vacancies, zirconium substituted by titanium and complex defects.

of the gap, moving below previous E_F^{gr} values. The investigations on the electronic properties reveal null spin densities for all complex defects at charge state $q = 0$, confirming the stabilization of Ti^{4+} species after doping.

Discussions

We undertook a computational investigation to provide new insights concerning the blue emission process of $m\text{-ZrO}_2$, for which several investigations proposed different mechanisms. Based on conclusions from the ΔSCF calculations, the origin of luminescence at ≈ 2.6 eV is explained by the charge transfer (CT) from Ti impurities substituting zirconium, in the lines of previous works.²⁴ Indeed, we demonstrated the de-excitation from Ti electronic states is characterized by an energy transition of 2.61 eV.

Other arguments can be brought to support the fact that the presence of Ti^{4+} ions are responsible for the blue band. For instance, transition metal oxides containing nd^0 ions such as titanates (or vanadates) are known to present such CT luminescence, associated with an intense absorption band in the UV region, a high Stokes shift ($\approx 1.5\text{-}2.5$ eV) and a very broad ($\approx 0.5\text{-}0.6$ eV) emission band.⁷⁹ These particular features have been reported experimentally for $m\text{-ZrO}_2$.^{15,16}

To argue that the blue luminescence is due to the presence of Ti^{4+} ions and not to intra-site $d\text{-}d$ transitions for Ti^{3+} in bulk $m\text{-ZrO}_2$, one can also consider the result from pDOS represented in Figure S1 (in SI). Titanium d states that appears inside the gap just below the conduction band are separated in an energy range smaller than 2.6 eV. A large splitting of d orbitals would be required to allow $d\text{-}d$ transition and provide blue light.

In the lines of these studies, our point defect calculations demonstrated that Ti^{4+} species are preferentially formed for most of the synthesis conditions, especially under O-rich atmospheres. In the extreme O-rich limit, the defect formation enthalpies for Ti_{Zr} are so small that Ti doping can be easily done and thus increase the photoluminescence intensity. Nevertheless, quenching phenomena have been reported when the concentration in titanium impurities increases above ≈ 1 wt%,¹⁶ and one may wonder if intermediate situations are preferable to avoid such a situation.

It is worth to note that different experimental studies argue that the blue luminescence might find its origin from the presence of Ti^{3+} ions inside ZrO_2 ,^{13,80} notably created by the

coexistence with lattice defects.¹⁶ More specifically, Wang *et al.* observed that the intensity of the blue band rises with the annealing temperature. The authors proposed that the oxygen vacancy content is enhanced accordingly, which reduces titanium in Ti^{3+} due to the charge compensation. This assumption can be rebutted by the fact that annealing has been done under air which could bring oxide ions in the material and thus oxide ions modifying Ti^{3+} in Ti^{4+} .

At the end, one may notice that the transition levels of Ti_{Zr} defects and (Ti_{Zr}, V_O) complexes are separated by about 0.4-0.7 eV according to the nature of the oxygen vacancies ($V_{O(3)}$ or $V_{O(4)}$). Consequently, to account for the long lasting luminescence observed at ≈ 2.6 eV for $\text{ZrO}_2:\text{Ti}$ compounds after excitation at ≈ 2.6 eV,¹⁶ it is quite possible that electron resulting from an $\text{Zr}^{4+} + \text{O}^{2-} \rightarrow \text{Zr}^{3+} + \text{O}^-$ (or $\text{Ti}^{4+} + \text{O}^{2-} \rightarrow \text{Ti}^{3+} + \text{O}^-$) energy transfer is trapped by an oxygen vacancy located nearby Ti_{Zr} substituted site. This electron might be subsequently released at room temperature via a thermal assisted process (the ideal experimental activation energy is estimated around 0.6 eV),⁸¹ with the de-excitation at a Ti_{Zr} site according to the CT $\text{Ti}^{3+} + \text{O}^- \rightarrow \text{Ti}^{4+} + \text{O}^{2-}$. Thus, complex defects might be at the origin of luminescence properties in $m\text{-ZrO}_2$ but also of the long persistent luminescence reported in $m\text{-ZrO}_2$.¹⁵

Conclusion

We reported a computational study to determine the origin of the blue emission band of the monoclinic zirconia phase. Based on the ΔSCF method for the first time on such material, we clearly demonstrate that the luminescence arises from a charge transfer between titanium substituting Zr atoms and oxygen atoms from the lattice, and remove the uncertainty concerning oxygen vacancies. To confirm the easy Ti doping, defect formation enthalpies were estimated for intrinsic and extrinsic species. We notably evidenced that Ti^{4+} are easily created within Zr sites.

Acknowledgement

This work was performed using HPC resources from GENCI-TGCC (Grant 2020-A0080911491) and CCIPL (Centre de Calculs Intensifs des Pays de la Loire). CL thanks the CNRS and "Région Pays de la Loire" to support the "CLIC" project. The authors thanks the French National Research Agency (ANR) for its financial support (ANR-18-CE08-0012 PERSIST project) and the CNRS. Crystal structures were represented using the VESTA software.⁸²

Supporting Information Available

Details on the ground state structure used for excited state calculations, the unitcell structure considered for point defect simulations, stability phase diagram of Ti-doped ZrO₂, defect formation enthalpies, concentrations of point defects

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Table of Contents (TOC) graphic

We performed point defect calculations using DFT to demonstrate the easy stabilization of Ti^{4+} on Zr sites within the $m\text{-ZrO}_2\text{:Ti}$ compound and its major role in luminescent properties.