



## Band structures and nitrogen doping effects in zinc titanate photocatalysts

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### ABSTRACT

The electronic structure of  $\text{ZnTiO}_3$ ,  $\text{Zn}_2\text{TiO}_4$  and  $\text{Zn}_2\text{Ti}_3\text{O}_8$  is investigated using a hybrid DFT method in which the exchange mixing coefficient is obtained through its relation with the dielectric constant (also computed at the hybrid DFT level). Bandgaps higher than those of the simple oxides are predicted, in agreement with some experimental data; but in the case of spinel structures bandgaps also appear to depend significantly on the (dis)ordering of the cations at octahedral sites, implying a strong influence of the preparation details on the final gap values. The change in the electronic structure of the spinel titanates which occurs when they are nitrated can lead to photocatalytic activity with visible light, as is known to happen with  $\text{TiO}_2$  and other oxides; but here the cation vacancy suppression effect which accompanies the transformation makes the nitridation process much more favourable, as shown by total energy DFT calculations. These zinc titanate spinels are thus promising candidates to achieve via nitridation efficient and robust photocatalysts active with visible light. All these compounds show a lower conduction band edge constituted mainly by Ti-centred orbitals; this may have influence on the details of the photocatalytic reaction mechanisms.

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### 1. Introduction

The best known and most used photocatalyst is titanium dioxide, especially in its anatase form that is considered to be the most photoactive one [1,2]. Its advantages lie in its relatively low cost, good chemical stability, low toxicity and high efficiency in separating photogenerated charges and transferring them to other substances at its interface. Zinc oxide, normally in the wurtzite structure, is another photocatalytically active simple material [3] which, although less frequently used than anatase due to its lower stability, shares most of the other advantages. Both oxides share one main disadvantage: a relatively large bandgap width (in both oxides it is around 3.2 eV at ambient temperature), which causes that only ultraviolet light can be absorbed and used to drive chemical changes, preventing the use of these oxides for an efficient harvesting of solar energy.

Still, the properties of these two oxides have led a number of authors to examine photocatalysts which combine them, either in form of biphasic composites or as single-phase mixed oxides. In the first case a number of studies report improvements in the photocatalytic activity [4–6] which are usually ascribed to a better electron–hole separation at the interface between both oxides in a similar way as proposed for the anatase–rutile interface [7], although some authors state that the bands of ZnO lie at higher levels than those of anatase [4,8] while others claim the contrary

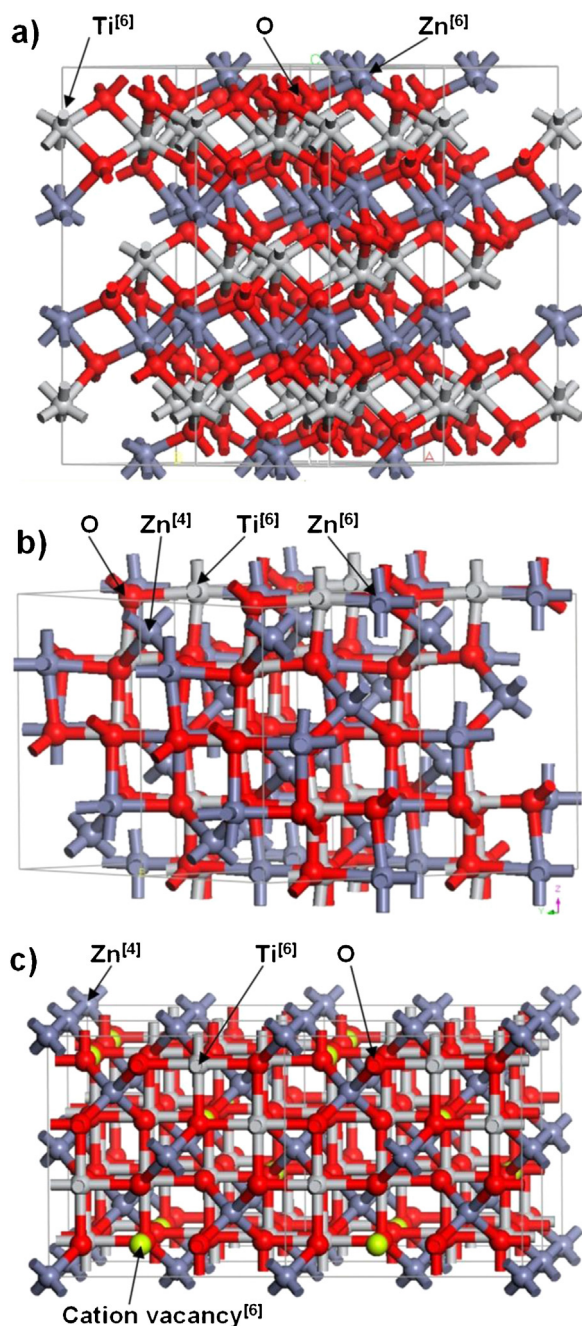
to be true [5,9]; recent work by this author based on hybrid DFT calculations [10] indicates that the second interpretation is the correct one. In the case of the mixed oxides photocatalytic activity has been found as well [11–13], although it is not clear whether improvement over the individual simple oxides is obtained; on the other hand some authors claim that the bandgaps of these photocatalysts are close to those of ZnO or  $\text{TiO}_2$  [12] while others report that the bandgap is pushed to higher values [11,14]. Of particular interest is that these mixed oxides seem able to admit significant levels of nitrogen doping, an alteration that brings the range of active wavelengths into the visible region of the spectrum leading to interesting photocatalytic properties [15]; in these works it is worth noting that relatively high amounts of N atoms could be inserted in these systems (up to ca. 1/8 of the anions), and that the thermal nitriding treatment seems to favour the crystallization of the cubic spinel structure. This further justifies the interest of studying and understanding the properties of these compounds.

Two crystal structure types are known for mixed titanium–zinc oxides (normally described as zinc titanates). The first one is rhombohedral (trigonal)  $\text{ZnTiO}_3$ , with an ilmenite-type structure [16] which is derived from that of corundum by ordering both cations in alternating layers perpendicular to the trigonal symmetry axis (Fig. 1a); in this structure both cations have a more or less distorted octahedral coordination.

Other zinc titanates are known which have spinel-type structure. The best known one is  $\text{Zn}_2\text{TiO}_4$ , an inverse spinel in which the Zn and Ti cations that populate in 1:1 ratio the octahedral sites have, in the most stable state of the compound, a specific ordering which leads to a supercell with the primitive tetragonal space

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**Fig. 1.** Structures of (ordered) zinc titanates: (a) ilmenite-type  $\text{ZnTiO}_3$ ; (b)  $\text{Zn}_2\text{TiO}_4$  inverse spinel; (c)  $\text{ZnTi}_3\text{O}_8$  cation-defective spinel, in which octahedral cationic vacancies are represented by unconnected spheres. The superindices in brackets designate the cation coordination number.

group  $P4_122$  [17] and in which the unit cell contents has the formula  $\text{Zn}_8\text{Ti}_4\text{O}_{16}$  (Fig. 1b), i.e. it is twice as large as in the primitive cell of the parent spinel lattice. It should be noted here that a recent study of a  $\text{Zn}_2\text{TiO}_4$  single crystal [18] reports a rather high bandgap value ( $E_g = 5.05$  eV). Another known zinc titanate with spinel-type structure is  $\text{Zn}_2\text{Ti}_3\text{O}_8$ . In this case all Zn ions have tetrahedral coordination (the preferred one for Zn in most oxides) and all Ti ions occupy octahedrally coordinated sites but do not populate all of them: 25% of the octahedral sites are empty, and in the most stable configuration of this oxide these cation vacancies are ordered in a specific way [19] leading to a cubic primitive lattice with space group  $P4_332$  and volume four times larger than the primitive cell

of the spinel lattice, i.e. with a total contents of  $\text{Zn}_8\text{Ti}_{12}\text{O}_{32}$  in the crystal cell (Fig. 1c).

Both  $\text{Zn}_2\text{TiO}_4$  and  $\text{Zn}_2\text{Ti}_3\text{O}_8$  are obtained frequently with full cation disorder in the octahedral sites, so that their diffractograms display only features typical of the parent fcc spinel structure. It is not surprising therefore that spinel-type zinc titanate materials with Zn:Ti atomic ratios intermediate between the mentioned 2:1 and 2:3 values can be prepared in which the octahedral positions contain Ti, Zn and vacant sites in a disordered manner; indeed “cubic  $\text{ZnTiO}_3$ ” has been reported more than once in the literature [11b,12b,20], but it is metastable and transforms to the trigonal form at high temperature [12a]. Of these spinel-type structures the  $\text{Zn}_2\text{TiO}_4$  inverse one seems to be most stable, and indeed  $\text{Zn}_2\text{Ti}_3\text{O}_8$  decomposes upon annealing at high temperature giving  $\text{Zn}_2\text{TiO}_4$ , rutile-type  $\text{TiO}_2$  and other phases [21]. This might be related to the fact that zinc titanate spinels with lower Zn:Ti ratios have necessarily cation vacancies, which implies less compact structures and smaller Madelung energies (or, from a more chemical point of view, a smaller number of cation–anion bonds) so that their cohesive energy will be lower. It may be mentioned finally that some of these titanates have found practical use as ceramic components for microwave applications [22] or as sulphur absorbents in chemical plants [23].

These mixed oxides have only scarcely been studied with quantum methods. To this author’s knowledge, there is one modelling of  $\text{Zn}_2\text{TiO}_4$  [24], carried out at the standard GGA level, which was concerned only with energetics and order/disorder aspects of the structure, without any consideration for the bandgap; another publication exists (in Chinese), using also a GGA functional, on ilmenite-type  $\text{ZnTiO}_3$  [25], and yields a bandgap of 3.1 eV (which will be an underestimation as happens always when using this theory level). On the other hand, no reports exist using DFT on N-doped Zn titanates. This contrasts with the very extensive literature on theoretical studies of the electronic structure of both  $\text{TiO}_2$  and ZnO that has been developed during several decades. For the former, besides earlier tight-binding studies of rutile-type  $\text{TiO}_2$  in the seventies [26] more advanced calculations were started in the nineties for rutile using LDA [27] and for anatase using Hartree–Fock theory [28]; for ZnO empirical pseudopotential-based calculations go back as far as 1973 [29]. Concerning N-doped photocatalysts for use in the visible light range, which will be addressed also here, a number of calculations exist for  $\text{TiO}_2$ ; restricting ourselves to the charge-balanced case (i.e. without unpaired electrons), which has been evidenced by theoretical studies [30] to be the most realistic one for the best characterized preparations which use  $\text{NH}_3$  as source of nitrogen, extensive work besides the said Ref. [30] has been carried out among others by Pacchioni et al. [31]. For N-doped ZnO less theoretical work has been done (mostly dealing with uncompensated doping); it has been focused mainly on the possibilities of the doped material in spintronics or electronic devices [32], but photocatalysis-oriented studies also exist [33]. Among N-containing mixed oxides involving Ti or Zn (but not both together) the calculations by Domen’s group on (Zn,Ge), (Zn,Ga) and (La,Ti) oxynitrides active in visible light-sensitive photocatalysis [34] can be mentioned.

All these calculations, when using a DFT-type approach, do it either at the LDA or GGA level or with one of the standard hybrid DFT functionals which use a fixed degree of Hartree–Fock exchange ( $\alpha = 0.25$  in the PBE0 or HSE functionals, the value being based on theoretical considerations, although HSE introduces an additional screening effect; and  $\alpha = 0.20$  in the B3LYP functional, the value being obtained by fitting to experimental thermochemical data). As will be shown here, the value  $\alpha = 0.25$  is close to the best-suited one for ZnO, so it is not surprising that relatively good results can be found for the bandgap of this oxide with the PBE0 functional,

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