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Supposed Versatile  $\beta$ -Ta<sub>x</sub>O<sub>y</sub>N<sub>z</sub> structures: DFT studiesLuigi Abbondanza<sup>a</sup>, Laura Meda<sup>a\*</sup><sup>a</sup> *Istituto ENI Donegani , Via Fauser 4, NOVARA 28100, Italy*

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**Abstract**

In the last decade, tantalum oxynitride material has been proposed as an interesting photo-catalyst for its spectral response extension in the visible light and good efficiency in water splitting process [1]. The electronic and structural properties of crystalline materials based on  $\beta$ -TaON (baddeleyite-type) have been theoretically investigated (PBE, B3LYP) in the density functional theory (DFT). The effects of Ta-vacancies, together with changes of the stoichiometry ratio Ta:O:N, suggested from experimental literature, are investigated. The electronic properties are valued by changing N and O atom positions in the crystallographic TaON, to reach the most stable form. The  $\beta$ -form of TaON is an n-type semiconductor when O prevails, while is a p-type semiconductor when N prevails. Consideration was given on the formation of acceptors or donors states related to the energetic positions. A structure with the best stability has also been found when a Ta-vacancy is formed in conjunction to an O increase. A model of the crystal structure that fully meets the experimentally observed properties (optical, structural and stoichiometric ratio) is proposed.

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*Keywords:* hydrogen; photo-electrochemical ; solar; TaON; semiconductor; density functional theory

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**1. Introduction**

The study of oxynitrides as photocatalysts has found some interest in the literature for water photo splitting activation [1, 2]. The photoanode differently made, or nanotube of TaON on Ta or porous film of TaON loaded with the IrO<sub>2</sub> on transparent conductor FTO, gets out almost high quantum efficiency with very low applied potential at visible light in mild electrolyte solution compared with other most diffusely studied materials (TiO<sub>2</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or WO<sub>3</sub>) [3]. Adequate band gaps (around 2.4 eV), absorption extension towards the visible range (550 nm) [4] and good stability in aggressive environments, make Ta-based oxynitrides quite interesting. By considering the crystalline  $\beta$ -form of TaON, the most stable one after treatments at T > 1123 K [5] is a monocline baddeleyite-like structure, with space group P 21/c [6, 7]. Cell parameters and atomic positions were elucidated by synchrotron radiation and neutron scattering to be: a=4.9498 Å; b=5.0179 Å; c=5.152 Å;  $\alpha=90^\circ$ ;  $\beta=99.61^\circ$ ;  $\gamma=90^\circ$ ; V=126.48 Å<sup>3</sup>; density 11.077 g/cm<sup>3</sup>) and the stoichiometry is supposed to be TaON 1:1:1 [5], with an optical bandgap of 2.4 eV.

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However, in experimental data taken from the literature different stoichiometries were also reported [4, 8]. In fact, by nitridation of  $\text{Ta}_2\text{O}_5$  under  $\text{NH}_3$  flow, at 1123 K, intermediate phases of  $\text{TaO}_x\text{N}_y$  can be obtained [8], and the species TaON is rather metastable, resulting from the substitution of two  $\text{N}^{3-}$  ions for three  $\text{O}^{2-}$  ions, to maintain the charge balance. As a consequence, it is quite fortuitous to find a homogeneous material, rather than a distribution of randomly ordered anions [9], so that the study of occupancies requires a statistical approach. Unfortunately, it is impossible to distinguish O and N atoms on the basis of XRD data, so that DFT calculations can give indication on what happens when both site occupancies and stoichiometry are changed [9, 10]. The reason for this study in depth is the suspicious that real TaON it is not simply the one ideally extrapolated by experimental and theoretical investigations obtained until now, and therefore further investigations about the stability of the crystal with different stoichiometries have to be considered.

## 2. Calculation Method

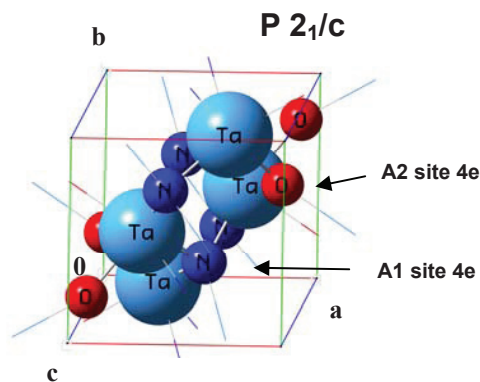
DFT calculations by CRYSTAL09 [12] code on all crystals are executed with two type of functional approximation (the bare DFT like Perdew-Burke-Ernzerhof (PBE)[13] and the hybrid DFT + Hatree-Fock, Becke's 3 parameter functional Lee, Yang, Parr (B3LYP)[14]), and Gaussian function basis set, as Pople-Boys scheme set, for full electrons shells of Oxygen (8-41G) and Nitrogen (7-31G) and only for outer 13 electrons valence shell of Ta (-31+G). Core electrons are replaced by an effective core potential [15] named HAWSC, to obtain band structures and density-of-states for different configurations. Band-gap values, effective masses in CB and VB, and binding energies, to evaluate the stability, have also been obtained for different configurations. It will be noted that the basis sets of anions were reduced by one uncontracted and polarized Gaussian, with respect to the present literature, taking care not to loose the quality of numerical results. The electronic calculations were defined into the reciprocal sample space, with Monkhorst shrink factor 8.

The geometry optimizations of all following crystals are executed starting by the bulk structure of  $\beta$ -TaON, site and crystal parameters from neutron diffraction data refinement [5], and within  $10^{-5}$  Hartree tolerance are relaxed.

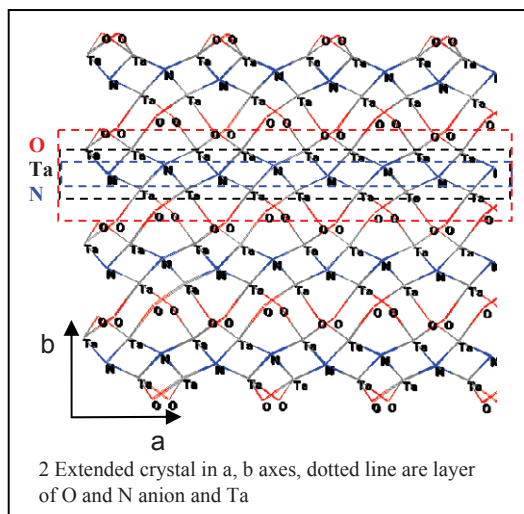
## 3. Results and discussion

Crystal baddeleyite base, in figure 1, have four sites for each Ta, N and O. In an ideal structure,  $\beta$ -TaON sites of the first tetra-coordinated anion (A1) are occupied by nitrogen atoms and second tri-coordinated anion (A2) by oxygen atoms. Ta-atoms are surrounded by four tetrahedral N and three planar O in seven coordinate configurations. The crystal bulk is characterized (fig. 2) by parallel planes (c, a) where each element lies on different layers. It is easy to find plates made of two neighboring layers of nitrogen bonded to layers of tantalum, which are in turn linked by layers of oxygen.

When different stoichiometries are considered the minority anion layer is contaminated by an excess of the other type anion. In this way, by studying different stoichiometry the best stability is found and could be compared with original  $\beta$ -TaON crystal.



1 Crystal cell of  $\beta$ TaON has different site 4 folded with symmetry operations, correspond to Ta:O:N=1:1:1 shoichiometry. They are the site occupaed only by Tantalum, the site A1 occupied by anions N and A2 occupiaed by O.



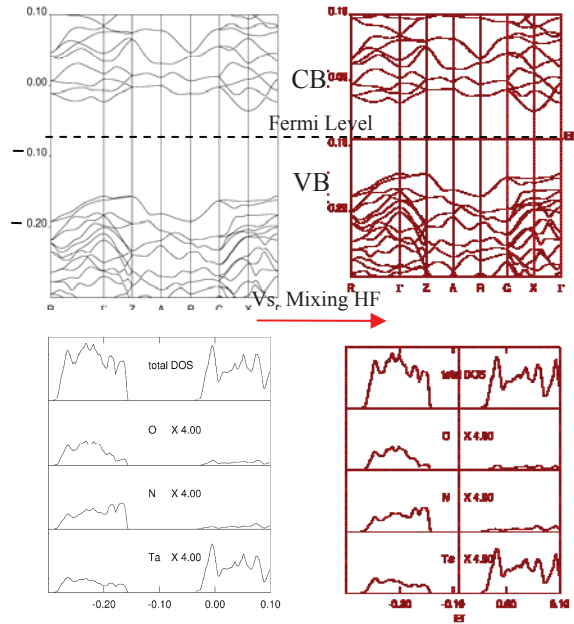
2 Extended crystal in a, b axes, dotted line are layer of O and N anion and Ta

In a first step with a relaxed geometry only, DFT calculated parameters result very closed to the experimental ones, with nominal stoichiometry Ta:N:O=1:1:1. The percent variations were as in the following:  $\mathbf{a} = 0.4\%$ ,  $\mathbf{b} = -0.2\%$ ,  $\mathbf{c} = 0.4\%$ ,  $\mathbf{\beta} = -0.2\%$ , Volume = 0.7% (density = 10.998 g/cm<sup>3</sup>). Nevertheless the indirect band gap (Lowest Unoccupied Band State or Conduction Band – Highest Occupied Band State or Valence Band) was 3.2 eV in B3LYP, can be refined without variation with the evaluation of energy gap in frame of  $\Delta$ -SOLV method [17]. Other calculations in B3LYP functional, with different mixing [16] of HF (standard 20% vs 10% HF mixing, in figure 3) and PBE approximation, result respectively 2.59 eV and 1.97 eV closer to the experimental one (2.4 eV). The PBE can be refined to 2.2 eV by the  $\Delta$ -SOLV method.

The good dispersion of the bands, along the path in first Brillouin zone of the reciprocal lattice, is shown in figure 3. From the curvature of conduction and valence band the effective mass of both charge carriers were estimated. The electron effective mass was calculated at X point (figure 3) at the bottom of the conductive band and results 0.88 (a.u.) (electron mass unit) (the same curvature was found in different directions C-X and  $\Gamma$ -X). The hole effective mass was calculated at  $\Gamma$  point and results 0.85 (a.u.). The density of states (DOS), with its projection on oxygen, nitrogen and tantalum bands, are shown around energy gap to confirm the same results as reported in the literature [5, 6].

As a final verification of the validity of the calculations an atomic exchange of one O with one N per cell was performed and the energy stability was checked with literature data [9]. In this case, the increase ( $E_{ex} = 1.6 \cdot 10^{-2}$  au) in energy of the cell is directly related to the amount of the reduction of the band gap (2.9 eV). It evidence that the order of anions closely depends on thermal treatment cycles and is related to the exchange energy ( $E_{ex}$ ) needed to exchange N with O in statistical thermodynamic framework. Than it is possible to take a useful relation of the occupation probability of an N anion in A1 site ( $occ_{N-A1}$ ), can be a definition of the “order parameter” of the anions in the crystal, with the temperature in following equation (figure 4); where  $g$  is the number of ways to realize the N-O anions exchange in the cell. If the  $occ_{N-A1}$  is 1, all nitrogen atoms are in A1 and the anions in the crystal are completely ordered, for that the temperature has to be low, otherwise the order with  $occ_{N-A1}$  value is decreased by increasing the temperature. For example the temperature to realize the exchange in previous case  $occ_{N-A1} = 0.75$  has to be around 1297 K.

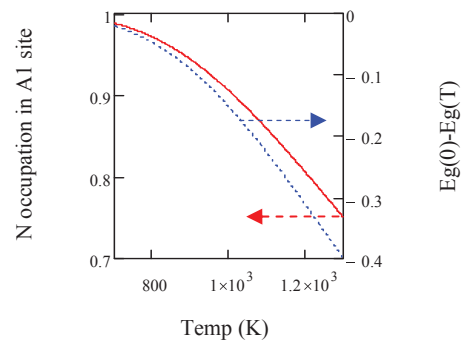
Moreover, the linear interpolation model about the decrease of gap energy ( $\Delta E_{g_{ex}}$ ) versus the temperature can be established as in figure 4. This result is in trend with experimental evidence in pigment properties based on  $\beta$ -TaON particles [4].



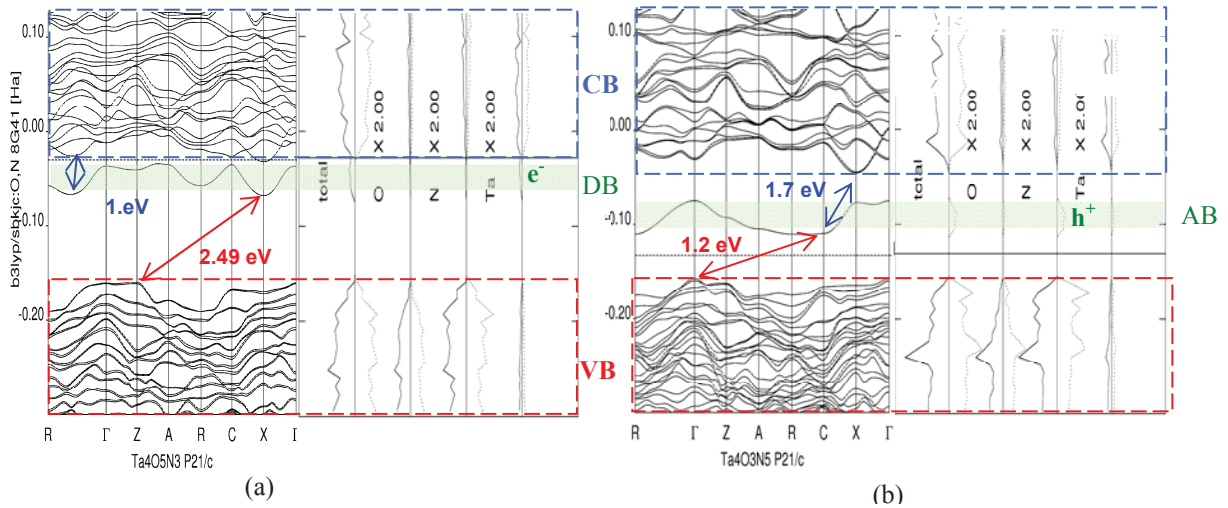
3 Band plot and DOS for different HF mixing B3LYP calculation. DOS shows also its projections on each element

$$occ_{N-A1}(T) = \frac{1}{1 + g \exp\left(-\frac{E_{ex}}{RT}\right)}$$

$$\Delta E_{g_{ex}}(T) \equiv E_g(0) - E_g(T) \cong [(occ_{N-A1}(T) - 0.75) \cdot 1.6 + 0.4] eV$$



4 plot of  $occ(N-A1)$  versus temperature



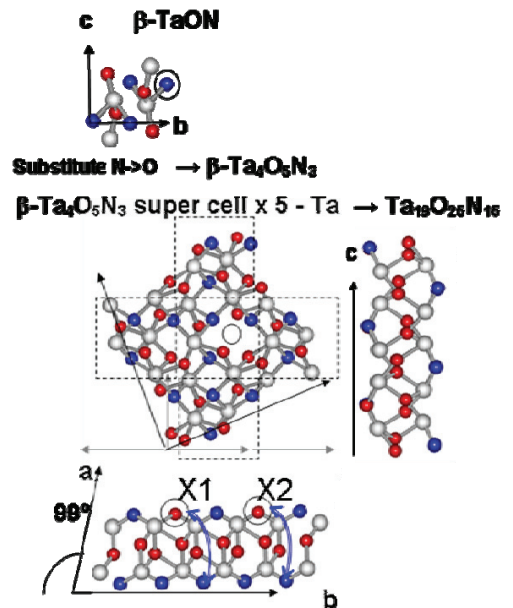
6. Band and DOS plots of two anion modified stoichiometry of  $\beta$ TaON. (a) O:N=5:3 the extra  $e^-$  is in donor band (DB) close to CB and localized on Ta orbital, (b) O:N=3:5 the extra  $h^+$  is acceptor band (AB) close to VB and localized on N orbital.

In a second step, the behavior with stoichiometry changes is considered. In particular, two limit O:N ratios, consistent to Ta oxidation states, considered in a single cell, of 5:3 and 3:5 are considered. For the 5:3 ratio ( $N/O=0.6$  is closer to value 0.7 stable form in water or air [5]), the A1 sites are partially occupied by N with O in excess and A2 sites are always occupied by O, to minimize the cell energy. For the 3:5 ratio, the A2 sites are partially occupied by O with N in excess and A1 sites are always occupied by N to minimize the energy cell too.

In principle, the occupancies are supposed to be statistically distributed, however in the following calculations just one ordered situation is considered. In the case 5:3 ratio the formal charge of anions can be considered unchanged, then the total number of formal charges on all four Ta-atoms in a single cell is 19. It can result from three  $Ta^{5+}$  and one  $Ta^{4+}$ . Therefore, the bottom of CB is expected to be filled (donor band) and an n-type semiconductor results, as shown in the band plot (a) of figure 6.

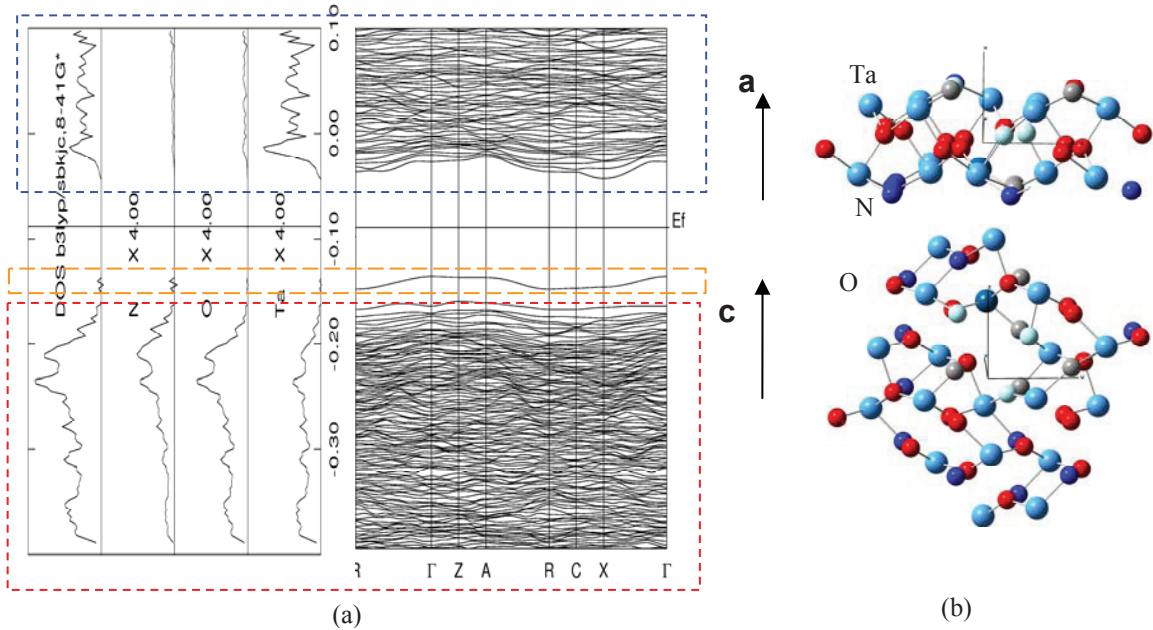
Conversely, by increasing N occupancy with 3:5 ratio, the formal charge state of cations can be considered unchanged and therefore the total number of formal charges can be composed by three  $O^{2-}$ , one  $N^{2-}$  and four  $N^{3-}$ . In this case, the top of the VB is empty (acceptor band) and a p-type semiconductor results, as shown in figure 6 (b).

The cell parameters and atomic positions in previous cases were not changed with respect to the previous geometrical optimization procedure to optimize  $\beta$ -TaON (the percent variations are less than 0.6% for  $a, b, c$ , Volume and 1.1% for  $\alpha, \beta, \gamma$ ). The relative stability of these configurations is described by the bond energies evaluated for Ta. By considering the O:N ratios equal to 5:3, 1:1 and 3:5 these energies result to be -1.055 au (density 11.009 g/cm<sup>3</sup>); -1.048 au (10.998 g/cm<sup>3</sup>); -1.011 au (10.804 g/cm<sup>3</sup>)



5 Building scheme of superstructure based on  $\beta$ TaON cell to make a vacancy site for Ta at the right stoichiometry ratio. X1 and X2 indicate the possible exchange tested.

respectively; so confirming the better stability of the system oxygen rich. To make a comparison, the  $Ta_2O_5$  (group

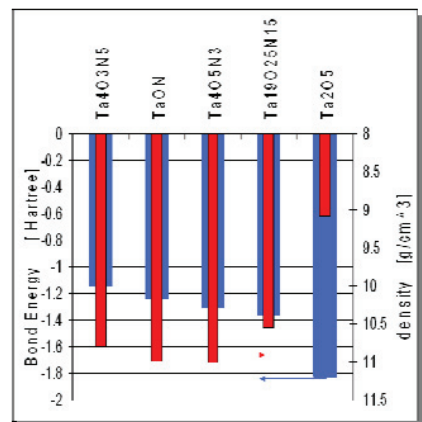


8 (a) DOS and band plots of new stoichiometry. The dotted lines are the Conduction (blue) and Valence (red) range of ideal  $\beta$ -TaON and top valence band is box line (orange). (b) The structure of the supercell with component the top valence band projected on atom coloured (Dark sky Ta, light sky O, grey N).

$C2/c$  and density  $8.828 \text{ g/cm}^3$ ) results to have bond energy of  $-1.281 \text{ a.u.}$  and calculated density around  $9.09 \text{ g/cm}^3$ . Moving from this consideration an extended supercell, of 5 original cells (60 atoms) with 20 Ta-atoms, was chosen to simulate a stoichiometry ratio  $O:N=5:3$ , with different position of O in A1 site. In addition, to get a new anion/cation ratio  $(O+N):Ta = 2.1:1 = 40:19$ , as given in experimental elementary analysis formula  $TaO_{1.24}N_{0.84}$  [2], a super-cell with one position among twenty Ta-atoms statistically vacant (as shown in figure 5) was built. The resulting stoichiometry is therefore  $Ta_{19}O_{25}N_{15}$  which has formula  $(TaO_{1.31}N_{0.79})$  very near to previous one. In figure 5 orthogonal projections of supercell are shown, and new crystallographic axes are defined:  $a \rightarrow a$ ,  $2b-c \rightarrow b$ ,  $b+2c \rightarrow c$ , with new cell parameters:  $a = 4.9498$ ,  $b = 11.287$ ,  $c = 11.48462$ ,  $\alpha = 91.3$ ,  $\beta = 98.63$ ,  $\gamma = 85.62$ ;

The cell parameters resulting from fully optimized geometry are even closer to experimental  $\beta$ -TaON data, than the ones calculated with 1:1:1 stoichiometry. The percentage of deviations are  $a = 0.4\%$ ,  $b = 0.0\%$ ,  $c = 0.4\%$ ,  $\alpha = 0.2\%$ ,  $\beta = -0.2\%$ ,  $\gamma = 0.2\%$  and  $V = 0.7\%$ . The calculated density is  $10.555 \text{ g/cm}^3$ .

The energy band gap for this new structure, obtained by using standard B3LYP, results to be  $2.49 \text{ eV}$  in agreement to the experimental estimation [18] and equal to the indirect energy gap, as found between VB and Donor Band in the case of 5:3 ratio, fig.6 (a). The bond energy related to 19:25:15 stoichiometry is lower ( $-1.089 \text{ au}/(Ta)$ ) than the one for 20 Ta-



7. Summary of bond energy and density result by B3LYP calculations on the different stoichiometry TaON beta form.

atoms and a ratio O/N 25:15 (-1.048 au/(Ta)). This energy stability is also preserved by exchanging the anions in A1 from two position lying in two planes (a,b) with labels X1 and X2 showed in figure 5, in facts the cell energy results varied from 0.003 to 0.0063 a.u. only (super-cell unit).

The band structure relative to this new stoichiometry shows that upper VB has risen and a new band is present in the upper-VB DOS. This new band is not intersecting other ones and it is supposed to improve the holes transport. The effective masses are around 1.12 (a.u.) for electrons and 1.84 (a.u.) for holes, estimated by band plot at bottom CB (X-point) and at the top VB ( $\Gamma$ -point). Nevertheless transport properties of electrons are only slightly worse while the effective mass of hole is doubled, with respect to 1:1:1 case.

At  $\Gamma$ -point, the top VB wave function is mainly composed of N2p orbital, while there are a little components of the three O2p (light sky) orbital and one Ta-d (dark sky) orbital near vacant site (fig. 8 (b)). This means that the wave function extends in the space along the crystallographic direction 'a' to form a cylinder around the Ta vacant sites. In the other hand, the wave function around the bottom of CB is diffused on all Ta-d orbitals (different dark sky Ta in fig.8 (b)), therefore the electrons can travel along d-orbital of Ta lying in the same plane (b, c).

#### 4. Conclusion

Tantalum oxynitride  $\beta$ -TaON material presents very interesting characteristic mainly due to susceptibility in changing both composition and positions of anions in crystal occupation sites. A new stoichiometry Ta:O:N=19:25:15 (with formula  $Ta_{0.95}O_{1.25}N_{0.75}$ ) is found to have better stability and the same  $\beta$ -TaON crystallographic parameters but less atomic density than the 1:1:1, at the moment considered as a model in interpretation of experimental data. On the other hand, an oxygen enriching is observed by elemental analysis data from samples used in early experiments, by Domen et al.[1], used for photo-catalysis experiment. The lower density in the new material (19:25:15), compared with both TaON and  $Ta_4O_5N_3$  is in agreement to the formation route: starting from  $Ta_2O_5$ , a nitridation at high temperature. The energy gap corresponding to the optical absorption of  $Ta_{19}O_{25}N_{15}$  is in better agreement with the experimental value (2.4 eV) and it is relatively lower than TaON (around 0.8 eV). The disorder by exchanging of the anions decreases the energy band gap  $\Delta E_{g_{ex}}$  too (around 0.4 eV one exchange per cell). This material is considered a versatile pigment from green to yellow [4]. The order of the anions, with the occupancy of N in site A1 ( $occ_{N-A1}$ ), and difference gap energy ( $\Delta E_{g_{ex}}$ ) versus temp are estimated, for 1:1:1 case are 0.943, -0.09 eV at 900 K; 0.846 -0.25 eV at 1123 K and 0.75, -0.4eV at 1297K.

The types of majority carriers depend on the O/N ratios. For example, starting from intrinsic 1:1:1 composition, a ratio > 1 brings to an n-type semiconductor material, while a ratio < 1 brings to a p-type. In the new stoichiometry case 19:25:15, the ratio results 5:3 and the behavior is intrinsic.

The carrier mobility for this most stable structure resulted worse, with respect to the 1:1:1 TaON structure; in particular holes in the new structure are less interacting with crystal phonons.

From this study a large versatility is possible for this material; however this characteristic can strongly modify the properties expected from the design. Good performance in photo-electro catalysis application could be obtained only by controlling the order and the stoichiometry homogeneity of this material.

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