JOURNAL OF Materials CHEMISTRY

The electronic structure of tantalum (oxy)nitrides TaON and Ta_3N_5

C. M. Fang,*[a] E. Orhan,[b] G. A. de Wijs,[c] H. T. Hintzen,[a] R. A. de Groot,[c] R. Marchand,[b] J.-Y. Saillard[d] and G. de With[a]

[a]*Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology, Postbox 513, 5600 MB Eindhoven, The Netherlands*
[b]*Laboratoire "Verres et Céramiques" UMR CNRS 6512, Institut de Chimie de Rennes, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France*
[c]*Electronic Structure of Materials, Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*
[d]*Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 65 11, Institut de Chimie de Rennes, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France*

Received 17th July 2000, Accepted 19th December 2000
First published as an Advance Article on the web 23rd February 2001

Detailed results of *ab initio* band structure calculations for tantalum (oxy)nitrides (TaON and Ta_3N_5) are reported. The calculations are performed within the framework of density functional theory (DFT). We compare results obtained with the molecular dynamics pseudopotential (PP) approach of the Vienna *Ab initio* Simulation Program (VASP) and the Full Potential Linearized Augmented Plane Waves method (FP-LAPW) using the WIEN97 program. In agreement with neutron diffraction measurements, we show an ordering of the anions in TaON. The calculations also show that the valence band is composed mainly of the anion 2p orbitals hybridized with Ta 5d states. For TaON the top of the valence band is dominated by N 2p states. The bottom of the conduction band is mainly composed of Ta 5d states. Both TaON and Ta_3N_5 are semiconductors with calculated indirect band gaps of respectively 1.8 and 1.1 eV (VASP calculations) and 2.0 and 1.2 eV (WIEN97 calculations). Optical diffuse-reflectance spectra show an energy gap of 2.08 eV for Ta_3N_5.

1. Introduction

In recent years, oxynitrides have become a rapidly growing field of interest.[1–3] Many oxynitrides are formed by introduction of nitrogen into the anionic (oxygen) network. The consequent increase of negative charge can be compensated with cationic substitutions.[4] These materials may have new physical properties. For example, the replacement of O by N may adjust the colour of some oxynitrides containing 4d and 5d transition metals and these oxynitride materials have potential as safe pigment materials to replace the currently used toxic metal containing pigment materials.[5–8] One question that arises for many oxynitrides is the ordering of the O/N anions.[9] Most of the oxynitrides have completely or partially random distributions of the O/N anions.[4–9] For only a few of the oxynitrides is an ordered O/N arrangement assumed. TaON is one of them.[10,11]

Two phases have been reported for tantalum oxynitride (TaON).[12] Buslaev *et al.* reported a low-temperature form with a complex hexagonal structure[11,13] (α-phase). At about 800 °C the low-temperature modification transforms to a high-temperature phase[14,15] (β-form). Neutron diffraction investigations performed by Armytage and Fender[15] showed that β-TaON is monoclinic, isostructural with ZrO_2. They also concluded that the anions O and N are ordered in the structure (Table 1). In this structure, shown in Fig. 1, every Ta atom is coordinated to four N atoms and three O atoms with Ta–N(O) distances ranging from 1.99 to 2.15 Å. Every N atom is coordinated to four Ta atoms, while the O atoms are coordinated to three Ta atoms.

Tantalum nitride (Ta_3N_5) has also been proposed as a pigment material.[16] It has an orthorhombic structure determined by Brese and O'Keeffe using time-of-flight neutron diffraction,[17] as shown in Table 2. The structure of Ta_3N_5 is shown in Fig. 2. It is composed of irregular octahedra of N atoms centered by Ta atoms.[17,18] Both N1 and N3 atoms have four Ta atoms as the nearest neighbors, while N2 is coordinated to three Ta atoms. The Ta–N distances range from 1.96 to 2.24 Å and are similar to those in TaON.

Until now there has been no report on the electronic and optical properties of tantalum oxynitride. This paper presents the results of self-consistent first-principles calculations for the crystal structure and electronic structure of β-TaON within DFT. Calculations are also performed for the tantalum nitride Ta_3N_5 for the sake of comparison. Knowledge of the electronic structure of both compounds is very useful to gaining an understanding of the colour and the corresponding optical transition for these and related materials.

2. Details of the calculation method

For the sake of comparison, two types of calculations, both within the Density Functional Theory (DFT) approach, were carried out. On the one hand, we used the *ab initio* total-energy and molecular dynamics program VASP (Vienna *Ab initio* Simulation Program), developed by the Institut für Theoretische Physik of the Technische Universität Wien (who also supplied the pseudopotentials).[19–21] Vanderbilt-type ultra-soft pseudopotentials[22] were used for Ta, O and N and non-linear core corrections[23,24] were applied for Ta. The Kohn–Sham orbitals were expanded in plane waves with a kinetic energy cutoff of 36 Ry while exchange and correlation were treated in the generalized gradient approximation (GGA) using the functional of ref. 25. The Brillouin zone (BZ) was sampled with a $6\times6\times6$ Monkhorst–Pack grid,[26] resulting in 80 $\boldsymbol{k}$-points in the irreducible part centered at Γ. Tests on denser $\boldsymbol{k}$-point meshes showed that this sampling is adequate. Calculations were first carried out at fixed volume with only relaxation of the atomic positions. Then, they were performed with relaxation of both atomic positions and lattice parameters. Cell relaxation was always small and thus the quality of the $\boldsymbol{k}$-point

 DOI: 10.1039/b005751g

Table 1 Calculated parameters and coordinates of the atoms in β-TaON using the PP method as compared with the experimental results. The calculated bulk modulus is also included

		Lattice parameters				
	B/GPa	*a*/Å	*b*/Å	*c*/Å	*β*/°	Volume/Å^3
Calculated	278	4.9878	5.0569	5.2063	99.50	129.46
Expt.[15]		4.9581	5.0267	5.1752	99.640	127.16

		Calculated coordinates			Expt. coordinates[15]		
Atom	Wyckoff site	*x*	*y*	*z*	*x*	*y*	*z*
Ta	4(e)	0.2939	0.0461	0.2153	0.292	0.046	0.213
A1(N)	4(e)	0.4437	0.7565	0.4863	0.4449	0.7566	0.4810
A2(O)	4(e)	0.0627	0.3264	0.3464	0.064	0.324	0.345

β-TaON: space group: $P2_1/c$.

sampling is not affected. This procedure was repeated several times in order to give a set of total energies as a function of cell volume. From this the equilibrium volume and bulk modulus were obtained by a fit to a Murnaghan equation of state.[27] Only electronic structure calculations have been performed for the tantalum nitride Ta_3N_5 using the experimental lattice parameters and coordinates of atoms, as shown in Table 2.[17] For the oxynitride TaON, structure optimizations are performed and the electronic structure is calculated using the optimized lattice parameters and coordinates of atoms.

On the other hand, calculations were also carried out with the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method implemented in the WIEN97 code.[28] In the LAPW method[29,30] the unit cell is divided into two types of regions, the atomic spheres centered upon nuclear sites and the interstitial region between the nonoverlapping spheres. Inside the atomic spheres, the wave functions are replaced by atomic-like functions, while in the interspheres region the wave function of a Bloch state is expanded in plane waves. The local density approximation of Perdew and coworkers was used[31] together with the Perdew–Burke–Ernzerhof GGA potential.[32] The maximum *l* value in the expansion of the basis set inside atomic spheres was 10 for the computation of the muffin-tin matrix and 4 for the nonmuffin-tin matrix element. The convergence of the basis set is controlled by a cutoff parameter $R_{mt}k_{max}=8$ where R_{mt} is the smallest atomic sphere radius in the unit cell and k_{max} is the magnitude of the largest $\boldsymbol{k}$ vector. Self consistency was carried out on a 72 $\boldsymbol{k}$-point mesh in the irreducible Brillouin zone for Ta_3N_5 and a 112 $\boldsymbol{k}$-point mesh for TaON. All the WIEN97 calculations were performed with the experimental crystal structures of Ta_3N_5[17] and TaON.[15]

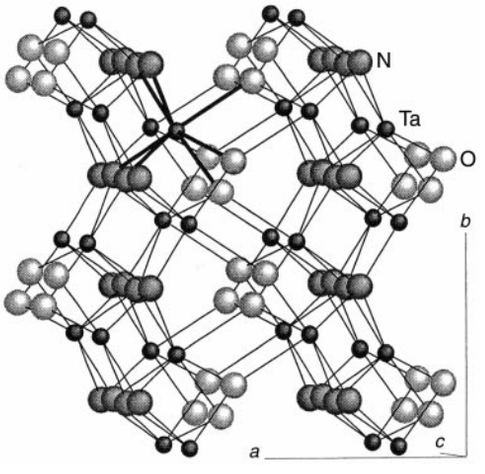

Fig. 1 The crystal structure of β-TaON.

Table 2 Lattice parameters and coordinates of the atomic position for tantalum nitride (Ta_3N_5)

Atom	Wyckoff	*x*	*y*	*z*
Ta1	4(c)	0	0.1971	¼
Ta2	8(f)	0	0.13455	0.55906
N1	4(c)	0	0.76322	¼
N2	8(f)	0	0.04701	0.11949
N3	8(f)	0	0.30862	0.073378

Ta_3N_5:[17] space group *Cmcm*, $a=3.8862$, $b=10.2118$, $c=10.2624$ Å.

3. Results and discussion

3.1. Electronic structure of Ta_3N_5

We begin by considering tantalum nitride Ta_3N_5. Fig. 3a shows the Brillouin zone (BZ) for Ta_3N_5 with space group *Cmcm*. The dispersion of the electron bands calculated with the VASP and the WIEN97 codes are shown in Fig. 4a and b, respectively. Clearly, both types of calculations provide very similar results. The partial and total density of states (DOS) computed with both methods are almost identical. Therefore, only the VASP DOS curves are shown in Fig. 5.

The lowest bands, with energy in the range from −15.4 to

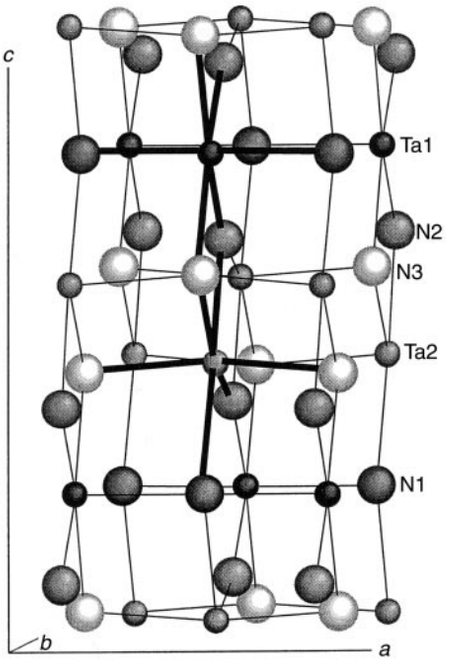

Fig. 2 The crystal struture of Ta_3N_5.

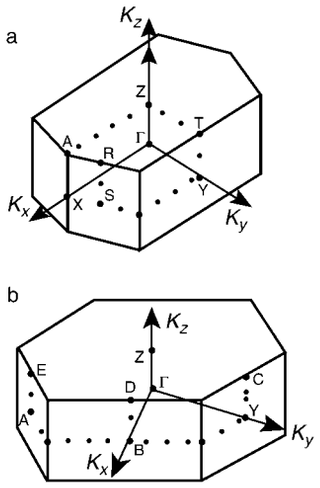

Fig. 3 The Brillouin zones and high symmetry points of Ta_3N_5 with a single-faced orthorhombic lattice (a) and TaON with a monoclinic lattice (b).

−12.6 eV (the Fermi level is set at the top of the valence band), are mainly composed of N 2s states. The 2s states of the N2 ions, with a peak at the upper part of the band, are different from the other two N ions (N1 and N3). This is due to the different coordination: every N2 ion has three Ta neighbors while N1 and N3 ions are coordinated by four Ta atoms.[17] There is a gap of about 5.6 eV between the N 2s states and the bottom of the valence band. The valence band is mainly composed of N 2p states (Fig. 4b and 5). However, the density of Ta 5d states is high all over the valence band, which indicates a strong covalent interaction between Ta and N. The bottom of the conduction band is mainly composed of Ta 5d states. The

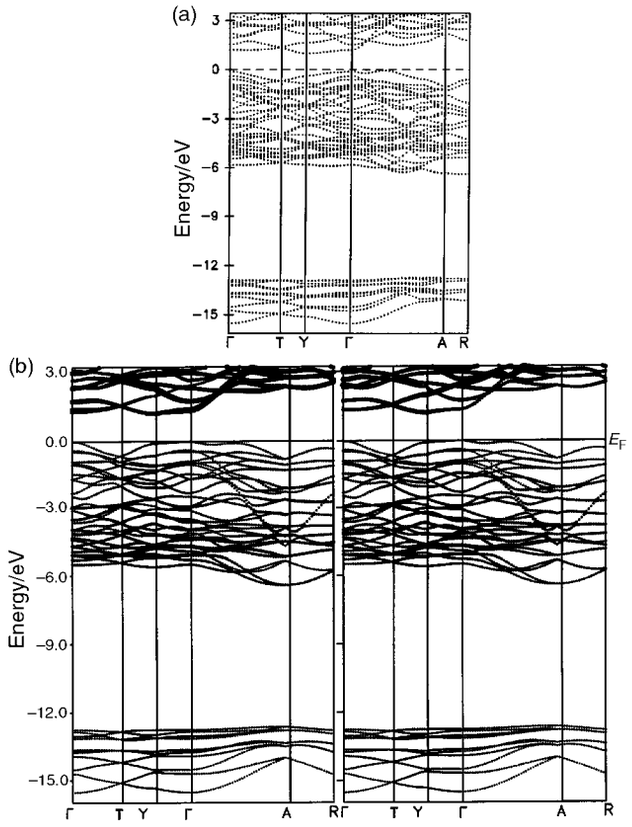

Fig. 4 Dispersion of the energy bands for Ta_3N_5: (a) VASP calculations; (b) WIEN97 calculations. The thickness of the lines is proportional to the contribution of the 5d Ta1 states (left) and the 5d Ta2 states (right).

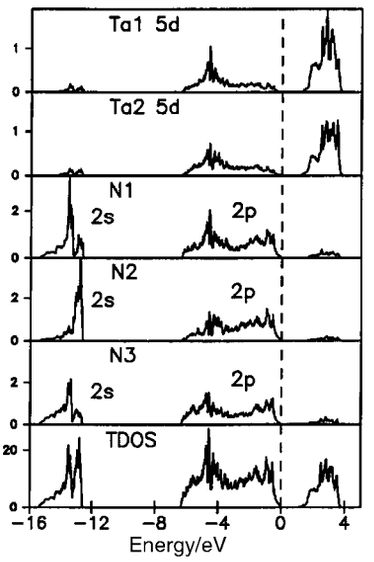

Fig. 5 Partial and total density of states for Ta_3N_5 (VASP calculations). The Fermi level is at 0 eV.

Table 3 Comparison between the calculated indirect gaps and experimental (optical) values for the tantalum compounds (* = estimated value). The calculated values in parentheses are the direct energy gap at Γ

			Calculated results/eV	
Compound	Exp./eV	Colour	VASP	WIEN97
Ta_2O_5	4.1–4.4[37,38]	white		—
TaON	>2.1*	green	1.8 (2.0)	2.1 (2.2)
Ta_3N_5	2.1[33]	bordeaux red	1.1 (1.4)	1.2 (1.4)

top of the valence band is along the Γ–X line and the bottom of the conduction band is at Y in the BZ. Therefore, the compound is an indirect semiconductor with an energy gap of about 1.1 eV (VASP) and 1.2 eV (WIEN97) as shown in Table 3. The direct energy gap at Γ is about 1.4 eV for both programs.

Samples of Ta_3N_5 have the colour of bordeaux wine red.[8,16–18] From the measured optical diffuse-reflectance spectra an energy gap of about 2.1 eV is obtained.[33] This is in reasonable agreement with the calculated value of the direct gap, as it is well known that electronic structure calculations within GGA generally underestimate the energy gap.[34]

3.2. Crystal structure of TaON

The first question about the structure of TaON is the occupation of the O/N anions at the sites A1 and A2, *i.e.* the distribution of O/N in the structure as suggested in the literature.[10,11] VASP calculations with the same lattice parameters and a relaxed symmetry (space group *P*1) were performed for four different kinds of occupations: (a) 4 N at A1 and 4 O at A2; (b) 3 N and 1 O at A1, and 3 O and 1 N at A2; (c) 2 O and 2 N at A1 and A2; and (d) 4 O at A1 and 4 N at A2. The calculations include optimization for both lattice parameters and coordinates of atoms for every configuration. The VASP calculations confirmed the ordered O/N occupation for TaON, that is, A1 is fully occupied by N atoms and A2 fully occupied by O atoms, which has an energy about 1 to 2 eV lower than the other kinds of occupations. This is understandable because nitrogen ions prefer to be four-coordinated, while oxygen ions would prefer to have three neighbors. This result is in agreement with the refinement of the structure with neutron diffraction measurements.[15] Table 1 lists the results of

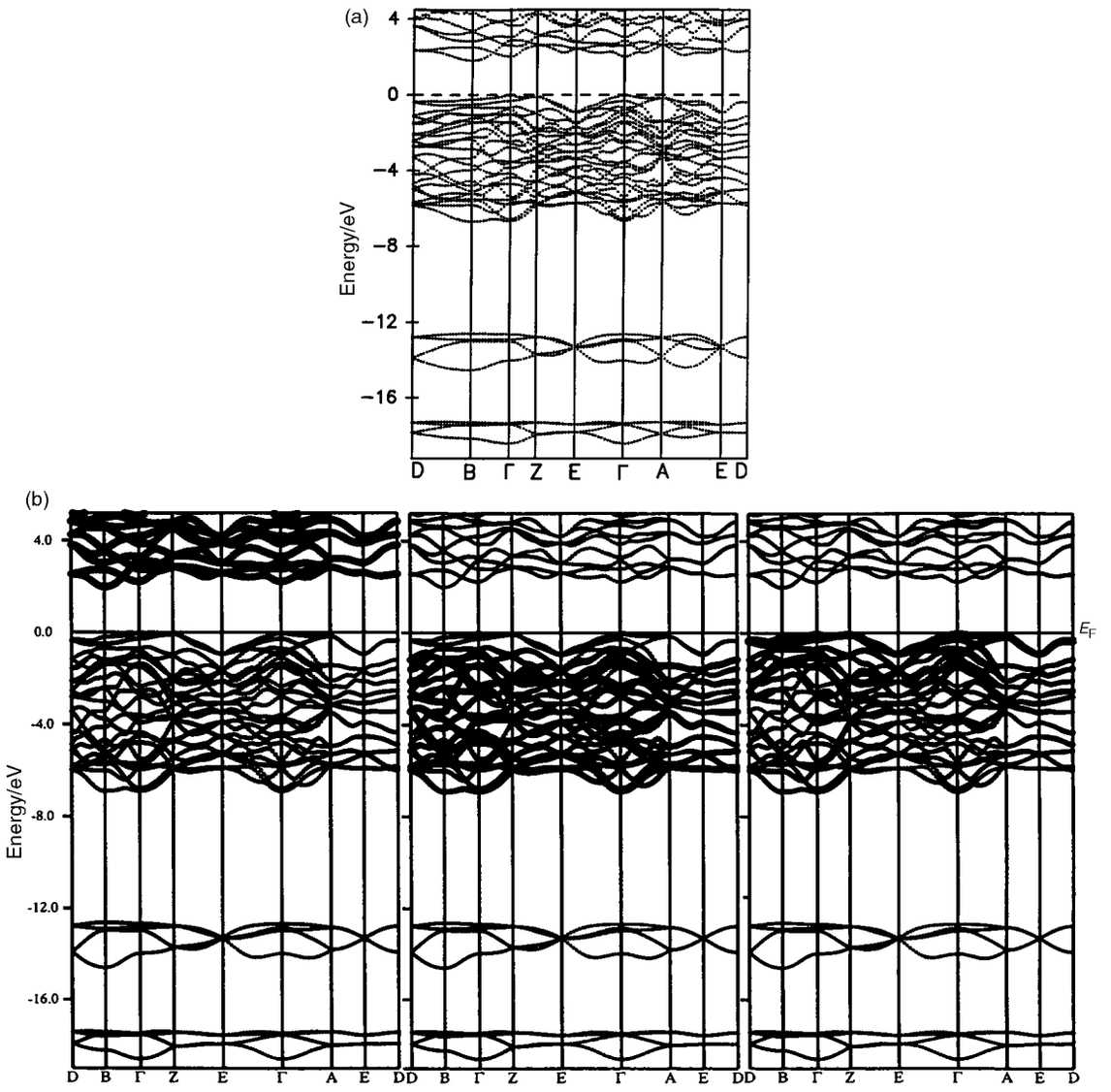

Fig. 6 Dispersion of the energy bands for TaON: (a) VASP calculations; (b) WIEN97 calculations. The thickness of the lines is proportional to the contribution of the 5d Ta states (left), 2p O states (middle) and 2p N states (right).

optimization of lattice parameters and coordinates of the atomic positions. The agreement between the calculated coordinates of the atoms and the experimental results is excellent. The minimum in the total energy curve gives an equilibrium volume of 129.46 $Å^3$, close to the experimental data (127.16 $Å^3$). Such results are typical for the GGA approximation.[34] By fitting the calculated data points to the Murnaghan equation of state,[27] we obtained a bulk modulus of 278 GPa. This value is larger than the experimental value of 185 GPa of the partially stablised (monoclinic) zirconia ZrO_2.[35] There are no data about the bulk modulus for the tantalum oxides and (oxy)nitrides. The only experimental value we found is 575.8 GPa for TaN.[36]

3.3. Electronic structure of TaON

Fig. 3b shows the BZ for β-TaON. The dispersions of the electron bands calculated with the VASP and the WIEN97 codes are shown in Fig. 6a and b, respectively. As in the case of Ta_3N_5, both types of calculations give very similar results and therefore, only the VASP DOS curves are shown in Fig. 7.

The lowest bands, with energy in the range from −18.4 to −17.3 eV (the Fermi level is set at the top of the valence band), are mainly of O 2s states. At the upper part of the O 2s band, there are two bands, which are very localized with a bandwidth of less than 0.2 eV, as shown in Fig. 6 and 7. A gap of about 2.7 eV exists between the O 2s and the next (N 2s) band. The N 2s states have a splitting with a bandwidth of about 2.0 eV, which is narrower than that in Ta_3N_5 (about 3.0 eV), but broader than the O 2s band (about 1.0 eV). The gap between the N 2s band and the valence band (band near the Fermi level) is about 6 eV, close to that of Ta_3N_5 (Fig. 5). The valence band is mainly composed of O 2p and N 2p states (Fig. 6b) hybridized with Ta 5d states. Both the O 2p and N 2p states are

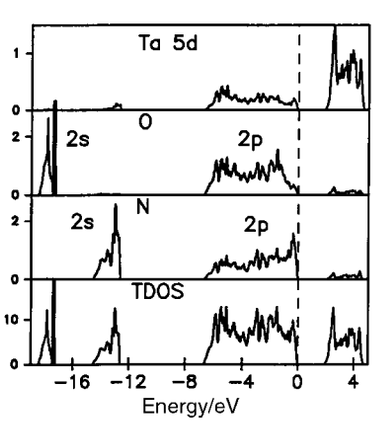

Fig. 7 Partial and total density of states for TaON (VASP calculations). The Fermi level is at 0 eV.

all over the valence band. But the top part of the valence band is dominated by N 2p states. The top of the valence band is at Γ of the BZ, while the bottom of the conduction band is not at Γ, but at B. Therefore, the compound is an indirect-gap semiconductor with a calculated energy gap of 1.8 eV (VASP) and 2.1 eV (WIEN97). The direct gap at Γ is about 2.0 eV (VASP) and 2.2 eV (WIEN97). The lower part of the conduction band is mainly composed of Ta 5d states.

There is no report about experimental determination of the energy gap of TaON. This compound is generally reported to be green coloured.[10–13] Assuming that this colour does not originate from impurities or non-stoichiometry, this colour indicates the existence of several absorption peaks in the visible spectrum. From the comparison of the experimental and theoretical band gaps of Ta_3N_5 (see above), we suggest the TaON experimental band gap to be significantly larger than 2.1 eV. Further experimental investigations on the physical properties of TaON are in progress.

The experiments showed an energy gap of 4.1 to 4.4 eV for the white oxide Ta_2O_5.[37,38] Table 3 compares the calculated results and experimental (optical) gaps for the tantalum compounds. It is shown that with increasing content of nitrogen the energy gap of the tantalum compounds decreases.

4. Conclusions

First-principles calculations were performed for TaON and Ta_3N_5 by using two different computer codes within DFT (the molecular dynamics VASP program and the FP-LAPW WIEN97 program). Both types of calculations provide very similar results. The VASP calculations show that the O/N atoms in TaON are ordered, in agreement with the neutron diffraction results. Both types of calculations show that with increasing the content of nitrogen the energy gap of tantalum compounds decreases. The calculated indirect energy gap is 1.1/1.2 eV for Ta_3N_5 and 1.8/2.1 eV for TaON. The calculated direct gap at Γ is 1.4 eV for Ta_3N_5 and 2.0/2.2 eV for TaON as shown in Table 3. The optical diffuse reflectance spectra show an energy gap of about 2.1 eV for Ta_3N_5.

References

1 R. Marchand, Y. Laurent, J. Guyader, P. l'Haridon and P. Verdier, *J. Eur. Ceram. Soc.*, 1991, **8**, 197.
2 R. Metselaar, *Pure Appl. Chem.*, 1994, **66**, 1815.
3 A. Simon, *Coord. Chem. Rev.*, 1997, **163**, 253.
4 R. Marchand, F. Pors, Y. Laurent, O. Regreny, J. Lostec and J. M. Haussonne, *J. Phys. C*, 1986, **47**, C1–901.
5 N. Diot, L. Le Gendre, R. Marchand, P. Macaudière and P. Maestro, in *ISNT II abstracts, International Symposium on Nitrides II*, ed. S. Hampshire, 1998, Limerick, Ireland, p. 17.
6 F. Pors, R. Marchand, Y. Laurent, P. Bacher and G. Roult, *Mater. Res. Bull.*, 1988, **23**, 1447.
7 X. Gouin, R. Marchand, Y. Laurent and F. Gervais, *Solid State Commun.*, 1995, **93**, 857.
8 L. Le Gendre, B. Piriou and R. Marchand, *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 973.
9 P. E. D. Morgan, *J. Mater. Sci.*, 1986, **21**, 4305.
10 M. Weishaupt and J. Strähle, *Z. Anorg. Allg. Chem.*, 1977, **429**, 261.
11 Yu. A. Buslaev, M. A. Glushova, M. M. Ershova and E. M. Shustorovich, *Neorg. Mater.*, 1966, **2**, 2120.
12 G. Brauer and J. R. Weidlein, *Angew. Chem.*, 1965, **77**, 218.
13 Yu. A. Buslaev, G. M. Safronov, V. I. Pakhomov, M. A. Glushova, V. P. Repko, M. M. Ershova, A. N. Zhukov and T. A. Zhdanova, *Neorg. Mater.*, 1969, **5**, 45.
14 G. Brauer, J. R. Weidlein and J. Strähle, *Z. Anorg. Allg. Chem.*, 1966, **348**, 298.
15 D. Armytage and B. E. F. Fender, *Acta Crystallogr., Sect. B*, 1974, **30**, 809.
16 M. Jansen and H. P. Letschert, *E. P. Patent*, No. 592867 A1, 1993.
17 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. C*, 1991, **47**, 2291.
18 J. Strähle, *Z. Anorg. Allg. Chem.*, 1974, **402**, 47.
19 G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558; G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
20 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.
21 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
22 D. Vanderbilt, *Phys. Rev. B*, 1990, **41**, 7892.
23 G. Kresse and J. Hafner, *J. Phys.: Condens. Matter*, 1994, **6**, 8245.
24 S. G. Louie, S. Froyen and M. L. Cohen, *Phys. Rev. B*, 1982, **26**, 1738.
25 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671.
26 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.
27 F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA*, 1944, **30**, 244.
28 P. Blaha, K. Schwarz and J. Luitz, *WIEN97*, Vienna University of Technology, 1997. Improved and updated Unix version of the original copyrighted WIEN code.[29]
29 P. Blaha, K. Schwarz, P. Sorantin and S. B. Trickey, *Comput. Phys. Commun.*, 1990, **59**, 399.
30 *Plane waves, pseudopotentials and the LAPW method*, ed. D. J. Singh, Kluwer Academic, Dordrecht, The Netherlands, 1994.
31 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671.
32 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 7865.
33 N. Diot, Ph.D Dissertation, University of Rennes 1, 1999, p. 127.
34 R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.*, 1989, **61**, 689.
35 P. H. J. van den Berg and G. de With, *J. Eur. Ceram. Soc.*, 1992, **9**, 265.
36 *Handbook of high temperature compounds: Properties, production, application*, ed. T. Ya. Kosolapova, Hemisphere Publ. Co., New York/Washington/Philadelphia/London, 1990.
37 C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, 1995.
38 H. Demiryont, J. R. Sites and K. Seib, *Appl. Opt.*, 1985, **24**, 490.