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Tantalum Oxynitride

γ-TaON: A Metastable Polymorph of Tantalum Oxynitride**

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Recently, materials based on tantalum oxynitrides have become a focus of interest, for example, as nontoxic color pigments[1,2] or as photocatalysts.[3] The archetypal solid-state tantalum oxynitride TaON was first described by Brauer and Weidlein.[4] This polymorph, β-TaON, which is the only confirmed polymorph of TaON, crystallizes isotypically to ZrO_2 in the monoclinic baddeleyite structure type, in which the metal atoms are seven-coordinate. Powder neutron diffraction experiments later revealed that the oxygen and nitrogen atoms of β-TaON have an ordered arrangement.[5] β-TaON is typically synthesized by treating the starting material β-Ta_2O_5 with flowing ammonia gas at 800 °C. The existence of a hexagonal polymorph, α-TaON, which was proposed by Buslaev et al.,[6] has been refuted on the basis of quantum-chemical calculations.[7]

In the Ta–O–N system, we have now prepared a new phase, as a light brown powder, through the ammonolysis of β-Ta_2O_5 with dry ammonia gas flowing at a rate of 10 L h^{-1}. A maximum yield of 85 wt % was obtained at a reaction temperature of 850 °C and a reaction time of 5 h. More severe reaction conditions (higher flow rate, higher temperature) resulted in only the known phases β-TaON and Ta_3N_5. As the new phase could only be obtained as a powder, the structure determination was performed with powder X-ray diffraction (PXRD) data. Although the optimized reaction conditions yielded the maximum phase fraction of the new TaON polymorph, the product could not isolated as a pure phase: a number of competing phases such as β-TaON, Ta_3N_5, and a yet unidentified compound, possibly an oxynitride, were also produced. The large number of side products led to severe difficulties in the structure determination. Therefore, samples produced in reactions with shorter ammonolysis times, which contained a smaller fraction of the new phase, but only β-Ta_2O_5 as a side phase, were used for the structure determination.

Quantitative analysis of the oxygen and nitrogen contents of several samples (by hot-gas extraction), taking into account the phase fractions of the side products (determined by Rietveld refinement), gave values of 8.3 wt % oxygen and 6.0 wt % nitrogen. The resulting composition of $TaO_{1.1}N_{0.9}$ is in good agreement with the formula TaON, within experimental error.

In situ temperature-dependent PXRD experiments in a nitrogen atmosphere provided additional evidence for the stoichiometric composition. As can be seen in Figure 1, the new phase transforms into the known β-TaON phase at high temperature (ca. 900 °C). Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) revealed that no weight is lost during the phase transition. The phase fraction of β-Ta_2O_5 is identical before and after the transition. We conclude that the new phase is, indeed, an unknown, metastable polymorph of TaON and propose that it be designated as γ-TaON.

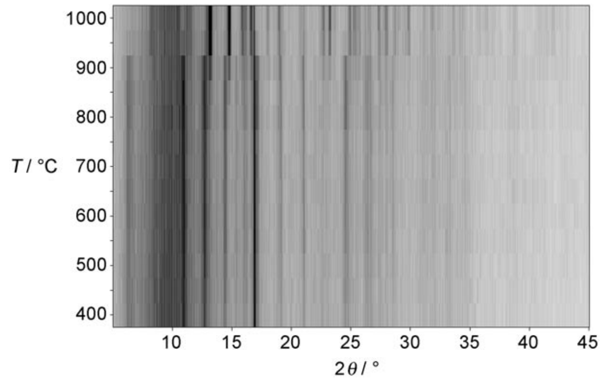

Figure 1. In situ PXRD patterns of γ-TaON upon heating in a nitrogen atmosphere. At approximately 900 °C, γ-TaON transforms into baddeleyite-type β-TaON.

The reflections of γ-TaON were indexed to a *C*-centered monoclinic cell, and the space group *C*2/*m* (no. 12) was chosen. Rietveld refinements in all the *translationengleich* subgroups of *C*2/*m* did not lead to any improvement in the residual factors. The integrated intensities were numerically extracted. The structure was solved by direct methods and then refined by the Rietveld method ($a = 12.9862(9)$, $b = 3.8909(2)$, $c = 6.7254(3)$ Å, $\beta = 107.413(5)°$; $R_{wp} = 0.089$, $R_p = 0.055$, $R_F = 0.039$). Figure 2 presents the experimental PXRD pattern, as well as the pattern simulated from the results of the Rietveld refinement.

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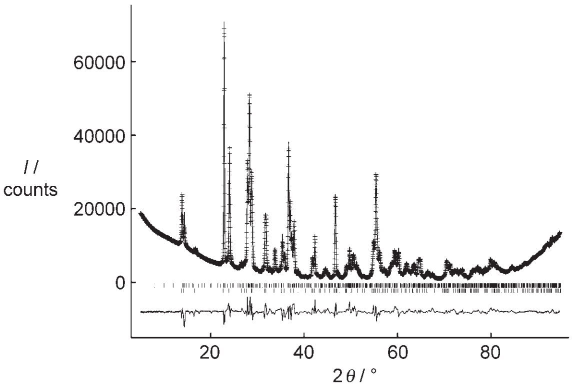

Figure 2. Rietveld refinement of the crystal structure of γ-TaON. The upper curves correspond to the experimental PXRD pattern (+++) and the pattern simulated from the results of the refinement (——); the lower curve corresponds to the difference. The vertical bars indicate the reflection positions for γ-TaON (lower) and for the side phase β-Ta_2O_5 (upper).

Examination of the unit-cell metrics and crystal structure indicates that γ-TaON is structurally related to $VO_2(B)$,[8] $TiO_2(B)$,[9] and the ternary compounds $MNbO_4$ ($M = Al^{3+}$, Ga^{3+}, Fe^{3+}, Co^{3+}),[10–13] $AlTaO_4$,[14] and FeV_3O_8.[15]

The crystal structure of γ-TaON consists of $Ta(O,N)_6$ octahedra, which share edges to form layers parallel to (001). These layers are connected through shared octahedral vertices to form a three-dimensional framework that contains small voids (Figure 3). There are two different types of $Ta(O,N)_6$ octahedra, which are connected to the neighboring octahedra in different ways. The octahedron around Ta1 shares five edges and four vertices with neighboring octahedra, while the octahedron around Ta2 shares only four edges and four vertices. In structurally related compounds with two types of cations, the higher-valent cations preferentially occupy the octahedra with fewer shared edges.

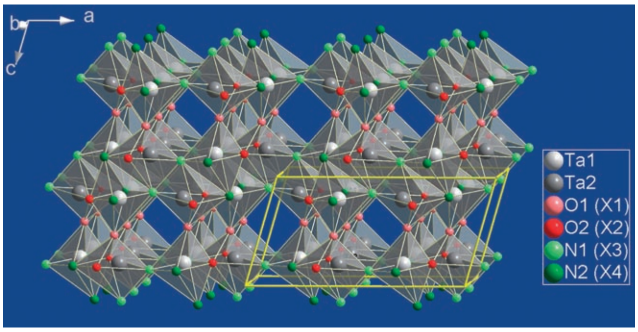

Figure 3. The crystal structure of γ-TaON. The monoclinic unit cell is outlined by yellow lines. The $Ta(O,N)_6$ octahedra are outlined by white lines to highlight their connectivity.

The $VO_2(B)$ structure type includes four different anion sites, which we label as X1–X4. One anion site has a coordination number of two (X1), two sites have a coordination number of three (X2 and X3), and the remaining site has a coordination number of four (X4). The average coordination number of the anions in the $Ta1(O,N)_6$ octahedron is 3.33, while that of the $Ta2(O,N)_6$ octahedron is 3.

With PXRD data and with β-Ta_2O_5 as a side phase, it was impossible to determine the anion positions of γ-TaON precisely, given the proximity of the heavily scattering tantalum atoms, or to distinguish between the nitrogen and oxygen anions. Although neutron diffraction would be the most appropriate method to resolve these problems, our sample size was unfortunately insufficient. However, the atomic positions are easily determined by quantum-chemical calculations. Furthermore, such calculations allow the investigation of the total energies of various anion distributions. Accordingly, the stabilities of all six possible distributions of two nitrogen and two oxygen anions over the four available sites of the primitive cell were investigated at the density functional theory (DFT) level. As a fundamental stability criterion, we chose the atomization energy E_a with respect to the free gas-phase atoms. The calculations were performed with optimized atomic positions and lattice parameters in all cases. As shown in Figure 4, the atomization energies of the six configurations are substantially different. The stability decreases with decreasing coordination number of the nitrogen anions. This trend is a clear indication that in γ-TaON an ordered anion distribution is preferred over a random distribution, as is also the case in β-TaON. A detailed calculation of disordered γ-TaON structures was beyond the scope of the present work and will be addressed in future studies.

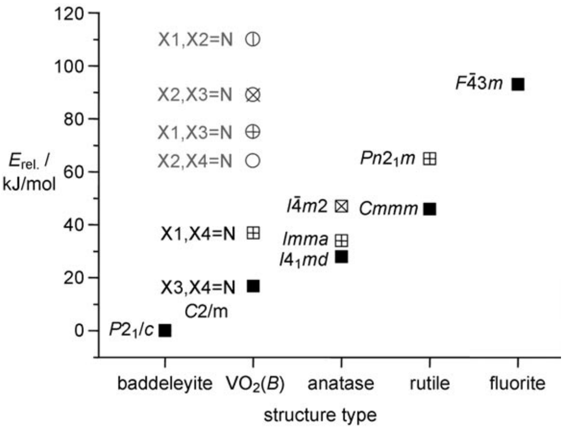

Figure 4. Calculated relative energies E_{rel} (PW1PW method; normalized to one formula unit) of TaON in different AX_2 structure types and with different anion orderings. The energies of $VO_2(B)$-type γ-TaON are given for all possible anion distributions (see Table 1).

The optimized fractional atomic coordinates of the most stable structure (with X3, X4 = N) are given in Table 1. The calculations, independent of the basis sets or functionals used, support the experimental findings. Attempts to distort the lattice symmetry did not lead to more-stable structures. The theoretical results confirm that $VO_2(B)$-type γ-TaON is a metastable polymorph. For TaON, the $VO_2(B)$ structure type is even more stable than some of the previously investigated structure types, such as anatase and rutile. Further investigations focusing on the electronic properties of the new phase

Table 1: Fractional atomic coordinates for γ-TaON (space group *C*2/*m*), with the most stable anion distribution, calculated by four different quantum-chemical methods (see Experimental Section).

Site	Wyckoff	*x*				*y*	*z*			
		PW1PW	USPP-PW	PAW-PW	PAW-PBE		PW1PW	USPP-PW	PAW-PW	PAW-PBE
Ta1	4*i*	0.3115	0.3110	0.3116	0.3120	0	0.1968	0.1942	0.1938	0.1940
Ta2	4*i*	0.6026	0.6024	0.6024	0.6020	0	0.2080	0.2063	0.2080	0.2080
O1 (X1)	4*i*	0.3624	0.3586	0.3604	0.3600	0	0.4934	0.4931	0.4928	0.4930
O2 (X2)	4*i*	0.1364	0.1347	0.1343	0.1340	0	0.2135	0.2109	0.2110	0.2110
N1 (X3)	4*i*	0.4452	0.4458	0.4460	0.4460	0	0.1338	0.1372	0.1373	0.1370
N2 (X4)	4*i*	0.7576	0.7586	0.7585	0.7590	0	0.1464	0.1475	0.1477	0.1480

and the differences between the theoretical methods used are in progress.

Figure 5 presents the Ta(O,N)$_6$ octahedra corresponding to the positional parameters given in Table 1. For all the calculations, the average bond lengths are slightly larger for the Ta1(O,N)$_6$ octahedron, because of the higher average coordination number of the anions. A similar situation is found in VO$_2$(*B*) and TiO$_2$(*B*).

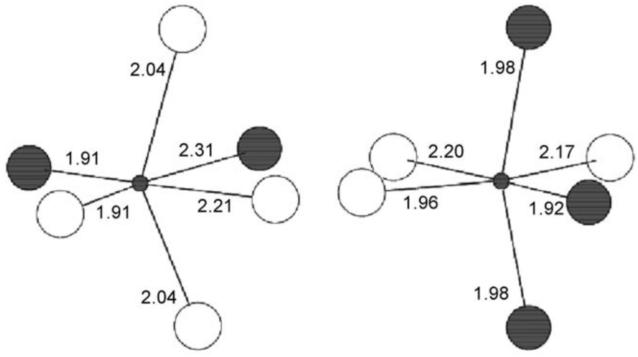

Figure 5. The Ta1(O,N)$_6$ (left) and Ta2(O,N)$_6$ (right) octahedra of γ-TaON. The optimized Ta—O and Ta—N distances [Å] are indicated. Ta small filled circle, O larged filled circles, N large empty circles.

In Figure 4, the relative energies of γ-TaON with different anion distributions are compared with those of the most stable phase, baddeleyite-type β-TaON, and of TaON in other common AX$_2$ structure types. As indicated above, oxygen atoms prefer to occupy the two-coordinate site, and nitrogen atoms the four-coordinate site. The three-coordinate anion sites are occupied by nitrogen and oxygen atoms. This anion distribution is in good accordance with Pauling's second rule.[16]

Comparison with other possible polymorphs of TaON makes it clear that the baddeleyite-type structure is more stable than the VO$_2$(*B*)-type structure. However, the VO$_2$(*B*) structure type is more favorable than the feasible and often-encountered anatase, rutile, and fluorite structure types. The new VO$_2$(*B*)-type γ-TaON phase has a calculated density of 8.6 $\mathrm{g\,cm^{-3}}$, whereas β-TaON has a density of 11.0 $\mathrm{g\,cm^{-3}}$. Consequently, γ-TaON cannot be synthesized under high pressure. The lower density of γ-TaON is mainly due to the voids between the densely packed layers of octahedra. Note that, according to the Ostwald–Volmer rule, metastable polymorphs prepared under mild synthetic conditions (low temperature) are characterized by low densities and transform into stable polymorphs with higher densities at higher temperature.[17] This scenario is confirmed by the temperature-dependent in situ diffraction experiments (Figure 1). The temperature-dependent behavior of γ-TaON is similar to that of VO$_2$(*B*), a metastable polymorph of VO$_2$, which undergoes a phase transition at 400–500 °C to rutile-type VO$_2$(*R*).[8] The metastable modification TiO$_2$(*B*) can also be obtained under mild reaction conditions.[9]

Experimental Section

The ammonolysis reactions were performed in a conventional tube furnace equipped with a corundum tube (50-mm inner diameter). The flow rate of the ammonia gas (3.8, Messer-Griesheim) was regulated with a needle valve. β-Ta$_2$O$_5$ (200 mg; 99.99 %, Sigma-Aldrich) was placed in a small alumina boat inside the tube and was heated under flowing ammonia gas for 1–10 h at 600–1000 °C.

The products were characterized by PXRD (Siemens D5000) with Cu$_{K\alpha1}$ radiation ($\lambda = 1.5405$ Å) and by in situ temperature-dependent PXRD (STOE STADI-P, graphite-heated furnace) with Mo$_{K\alpha}$ radiation ($\lambda = 0.7093$ Å). The crystal structure was solved by direct methods, using the program EXPO,[18] and refined by the Rietveld method, using the program GSAS.[19] Quantitative analysis of the nitrogen and oxygen contents was performed by hot-gas extraction (LECO TC-300/EF-300). The samples were heated under helium in graphite crucibles to approximately 2700 °C; the amount of oxygen was then detected as CO$_2$ by IR spectroscopy, and the amount of nitrogen as N$_2$ by heat-conductivity measurements.

Quantum-chemical calculations were performed with the crystal-orbital program CRYSTAL03[20] and with the plane-wave (PW) code VASP.[21] Details of the basis sets and computational setup were described in our previous study of TaON.[22] On the basis of our experience, we selected two quantum-chemical methods, the Hartree–Fock/DFT hybrid method PW1PW,[23] as implemented in CRYSTAL03, and the DFT method, using a PBE-GGA functional[24] as it is implemented in VASP. In the PW calculations, core electrons were described either by ultrasoft pseudopotentials (USPP) or by projector-augmented waves (PAW).[25]

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