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Bixbyite-type phases in the system Ta-Zr-O-N

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Abstract: Phase-pure tantalum/zirconium oxide nitrides and nitrides were synthesized by the ammonolysis of amorphous oxide precursors. The nitrogen-rich oxide nitrides with variable anion composition and the nitride TaZrN₅ crystallize in the cubic bixbyite-type structure (space group Ia₃). The nitrogen content of these compounds has a significant influence on the cell parameters, the atomic positions, and the optical band gap. The results extend the already well-studied Ta–Zr–O–N system by new oxide nitrides in addition to the already known baddeleyite- and anosovite-type phases. TaZrN₅ can be considered as a thermodynamically stable ternary variant of metastable Ta₂N₃.

Keywords: bixbyite; nitride; oxide nitride; tantalum; zirconium.

1 Introduction

Ternary transition metal oxide nitrides are interesting materials with relatively low complexity and therefore predestinated for investigations of structure-property correlations. In addition, they offer a wide range of applications. For example, tantalum- or zirconium-based oxide nitrides are promising photocatalysts [1, 2], nontoxic color pigments [3], and fast ion conductors [4]. Consequently, the investigation of phases, including both metals, oxygen, and nitrogen, may offer a wider range of interesting materials.

Ionic-covalent zirconium oxide nitrides belong to the quasi-binary system ZrO₂-ZrN. They are generally described by the formula ZrO₂-Nₓ and are structurally derived from fluoride-type ZrO₂, the high-temperature polymorph of zirconia. A series of oxygen-rich β-type phases (β: ZrO₂N₄; β’: ZrO₂N₃; β”: Zr₂O₅N₃₀) [5–9] are supplemented by a nitrogen-rich γ-phase (Zr₂ON₃) [5–7], crystallizing in the cubic bixbyite-type structure. A more detailed overview concerning this system was conducted by Lerch [10]. An intergrowth of ZrO₂ and Zr₂ON₃, resulting in the formation of ZrO₂Nₓ [11], and the incorporation of small amounts of TaO₂ into zirconium oxide nitrides have also been investigated [12]. The hitherto reported nitrides of zirconium are ZrN [13, 14] and Zr₂N₅ [15, 16]. A cubic high-pressure polymorph of Zr₂N₅ also exists [17].

On the other hand, the ionic-covalent oxide nitride of tantalum(V), TaON, is more stoichiometrically restricted and crystallizes in various AX₃ structure types. The thermodynamically stable polymorph is called β-TaON, crystallizing in the monoclinic baddeleyite-type structure [18]. Sometimes it is referred to be a nitrogen-rich analogue to monoclinic ZrO₂ (m-ZrO₂). Two metastable polymorphs have been prepared so far: γ-TaON [19], which crystallizes in the monocline crystal system in the VO₂(B)-type structure, and δ-TaON, which exhibits the tetragonal anatase type [20, 21]. A high-pressure polymorph with cotunnite-type structure has been synthesized as well [22]. In addition, the existence of a further tantalum(V) oxide nitride, Ta₂O₂N, has been proposed. By contrast, the variety of the nitrides is significantly higher. The compounds Ta₉N₅ [24], Ta₇N₇ [25], Ta₅N₉ [25], and Ta₅N₇ [26–29] belong to the group of nitrogen-rich nitrides. Ta₂N₇ crystallizes, comparable with Zr₂ON₃, in the bixbyite-type structure [28, 29]. High-pressure polymorphs of Ta₅N₇ and Ta₇N₇ are also described in literature [30, 31]. Additional nitrides can be separated into two different categories: solid solutions of nitrogen in tantalum metal (α phase) with a correlated superstructure of this type [32–34], the β-Ta₅N₇ phase [32–36], and three different mononitrides (δ-, ε-, θ-TaN) [37–39].

It is remarkable that the quaternary system Ta–Zr–O–N has also been investigated in detail. The first publication about this topic was presented by Schönberg in 1954 [40], and the most comprehensive work was presented by Grins et al. [41]. They reported on synthesis and characterization of phase-pure baddeleyite- and anosovite-type phases, which can be derived from m-ZrO₂/β-TaON and Ta₂N₅, respectively. In addition, a cubic and an orthorhombic phase, both obtained as side phases, have also been reported. Unfortunately, a detailed description of those phases was not possible. Investigations regarding the optical properties of the phase-pure baddeleyite- and anosovite-type compounds were presented later [42, 43]. The existence of a high-pressure polymorph of TaZrO₂N₅...
was studied theoretically [44]. Literature about ternary nitrides of tantalum and zirconium is restricted to (Ta, Zr) N thin films or alloys with an even lower nitrogen content (for example, see [45, 46]). To our knowledge, ternary ionic-covalent nitrides have not been reported so far.

Obviously, a more detailed investigation of the system Ta–Zr–O–N should be worth the efforts. In particular, the search for new metastable compounds was one of the main intentions for the present work. Our synthesis of metastable δ-TaON powder was based on the preparation of partly cation-substituted compounds such as Mg0.05Ta0.95O1.15N0.85 [47] or Sc0.15Ta0.85O1.30N0.70 [48] with a similar crystal structure type. The preparation of these quaternary compounds was much easier compared with the ternary phase because the anatase structure is stabilized by small amounts of incorporated aliovalent cations. The development of synthesis routes to these quaternary phases has to be considered as an indispensable prerequisite for the successful preparation of TaON in the anatase type. Results of quantum-chemical calculations suggest the existence of at least two more polymorphs with rutile- and fluorite-type structures, respectively [49]. Rutile-type ScTa2O5N has already been synthesized and might be a first step to the ternary analogue [50]. Consequently, we expand this approach to zirconium as an additional cation, in a search of new ionic-covalent phases in the system Ta–Zr–O–N.

2 Experimental section

Precursors were prepared by a modified Pechini sol-gel route [51, 52]. This method allows the synthesis of amorphous Ta–Zr oxides by using metal-citrate solutions and ethylene glycol as gelling agent. TaCl5 (99.999%, Sigma Aldrich, St. Louis, MO, USA) and ZrCl4 (99.99%, Sigma Aldrich) was used as reference. The measured diffuse reflectance spectra were converted by the Kubelka-Munk function to absorbance spectra. The optical band gaps were determined by the Tauc plot method [54, 55].

As generally described in the experimental part, mixed amorphous Ta/Zr oxides consisting of 95, 85, 66.6, 50, or 33.3 cation% Ta were prepared. The cation ratios of these precursors were confirmed by X-ray fluorescence spectroscopy. Although the ammonolysis of precursors with low Zr contents resulted only in the formation of already known baddeleyite- and anosovite-type phases, some samples with low Ta contents show crystal structures yet unknown for this system.

The ammonolysis of precursors with Ta contents of 33.3, 50, or 66.6 cation% were performed at 1073 K, resulting in phase-pure powders of oxide nitrides or nitrides with cubic bixbyite-type structure (Ia3). Structural similarities to bixbyite-type Zr2ON2 are apparent. Samples synthesized at lower temperatures contain side phases with baddeleyite-type structure. Additional tests with 70 cation% Ta were performed as well, but an anosovite-type phase was an unavoidable byproduct. It can be assumed that this series can be expanded to Ta contents lower than 33.3 cation% with Zr2O2 as the final member.

The ideal bixbyite structure can be described as a 2×2×2 superstructure of the fluorite type where one quarter of the anions is removed [56–59]. Cations are located on 8a and 24d sites, anions on a 48e site (and the
vacancies on a 16c site). The cations are coordinated octa-
hedrally by anions, and the anions are tetrahedrally sur-
rrounded by cations. A graphical presentation is shown in
Fig. 1. One characteristic of this structure type is the possi-
bile partial occupation of the vacancies by anions, leading
to \( \text{A}_2X_3^{(1−δ)} \) (\( δ ≤ 1 \)) compositions. This observation has already
been made for U\(_2\)N\(_3\) [60, 61], Zr\(_2\)ON\(_2\) [62], and vanadium
oxide nitrides [63].

In the system Ta–Zr–O–N, compounds between
Zr\(_2\)ON\(_2\)/ZrO\(_2\) and TaZrN\(_3\)/TaZrO\(_3\)N can be described
with the general formula Ta\(_{1−x}\)Zr\(_x\)O\(_{3y/2}\)N\(_{3−y}\) (0
≤ \( x \) ≤ 1, 0 ≤ \( y \) ≤ 2). From a formal point of view, it should be possi-
ble to prepare 1:1 phases in the range from TaZrN\(_3\) (\( δ = 0 \)) to
TaZrO\(_3\)N (\( δ = 1 \)). For a Ta:Zr ratio of 1:2, the following range
can be calculated: Ta\(_{0.67}\)Zr\(_{1.33}\)O\(_{0.42}\)N\(_{2.61}\)–Ta\(_{0.67}\)Zr\(_{1.33}\)O\(_{1.89}\)N\(_{1.63}\)
(0.06 ≤ \( y \) ≤ 1.04) and Ta\(_{1.33}\)Zr\(_{0.67}\)O\(_{0.12}\)N\(_{3.03}\)–Ta\(_{1.33}\)Zr\(_{0.67}\)O\(_{0.30}\)N\(_{2.91}\)
(0.08 ≤ \( y \) ≤ 0.20) were obtained. For simplicity, we mainly
concentrate the following structural discussion on the
compounds with a cation ratio of 1:1. Several reasons
favor this choice: For Ta:Zr ratios larger than 1, it is not
possible to prepare phases of the ideal \( \text{A}_2X_3 \) composition.
Also the formation of anosovite-type side phases, which
can be derived from Ta\(_3\)N\(_5\), is favored by high amounts
of tantalum. We do not focus on Ta-poor phases because
exclusively the 1:1 series principally allows the synthesis
of a pure nitride bixbyite-type compound with ideal \( \text{A}_2X_3 \)
composition (TaZrN\(_3\)). This nitride was indeed obtained
in addition to various oxide nitrides. The X-ray powder
pattern of TaZrN\(_3\) together with the results of the Riet-
veld refinement is depicted in Fig. 2. Refined structural
parameters for the nitride and the phases with the highest
nitrogen content obtained for the other investigated cation
ratios (Ta:Zr) of 2:1 and 1:2 are presented in Table 1. For
comparison, some details for Zr\(_2\)ON\(_2\) are also implemented
in Table 1 [62]. The corresponding atomic parameters for
TaZrN\(_3\) are presented in Table 2.

Further details of the crystal structure investigation
may be obtained from FIZ Karlsruhe, 76344 Eggenstein-
Leopoldshafen, Germany (fax: +49 7247 808-666; e-mail:
crysdata@fiz-karlsruhe.de), on quoting the deposition
number CSD-432434.

In TaZrN\(_3\), the octahedra around (Ta/Zr)1 have cation-
anion bond lengths of 217.3(8) pm. By contrast, the (Ta/
Zr)2(O,N)\(_6\) polyhedra show values between 204.9(8) and
221.4(8) pm. The average bond length of 214.2 pm agrees
with the sums of the ionic radii of the elements (Ta\(^{5+}\):
64 pm; Zr\(^{4+}\): 72 pm; N\(^{3−}\): 146 pm) [64] and is almost exactly

![Fig. 1: Crystal structure of the bixbyite-type tantalum zirconium oxide nitrides. Only two of 16 possible vacancies (Vac) have been marked.](image1.jpg)

![Fig. 2: X-ray powder diffraction pattern (Cu-K\(_\alpha\) radiation) of TaZrN\(_3\) with results of the Rietveld refinement (red: measured; black: calculated; green: Bragg-reflection positions; blue: difference between measured and calculated).](image2.jpg)
the average of the common Ta–N (210 pm) and Zr–N bonds (218 pm). It should be mentioned that no indication for Ta/Zr ordering was found. Consequently, a statistical distribution of the cations is assumed, and the site occupation factors have been fixed for the refinements. N/O ordering in oxide nitrides cannot be investigated using X-ray diffraction. Calculations on anion-excess vanadium oxide nitrides with bixbyite-type structure (V$_{2.000}$O$_{3.000}$N$_{0.125}$, V$_{2.000}$O$_{3.125}$N$_{0.125}$, and V$_{2.000}$O$_{3.067}$N$_{0.133}$) have shown that nitrogen is preferably located on the 48\(e\) and not on the 16\(c\) site [63, 65]. This topic has already been discussed for Zr$_2$ON$_2$ with respect to neutron diffraction investigations [62, 66] and based on quantum-chemical calculations [67]. The only possible maximal nonisomorphic translationengleiche subgroup allowing an ordered arrangement of oxygen and nitrogen is \(Ibca\). However, an ordered anion arrangement was not found by both methods.

An overview of the prepared 1:1 samples is given in Table 3. The N/O ratio has a significant effect on the cell axis \(a\) and the \(x\) parameter of the 24\(d\) cation site, which is the only cation coordinate not fixed by space group symmetry.

### Table 1: Results of the Rietveld refinements for selected bixbyite-type phases in comparison with results for Zr$_2$ON$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ta:Zr</th>
<th>Ta$<em>{0.67}$Zr$</em>{1.33}$O$<em>{0.42}$N$</em>{2.61}$</th>
<th>TaZr$_3$</th>
<th>Ta$<em>{1.33}$Zr$</em>{0.67}$O$<em>{0.12}$N$</em>{3.03}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure type</td>
<td>Bixbyite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>(Ia\bar{3}) (No. 206)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Z)</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (pm)</td>
<td>1013.32</td>
<td>1001.20(4)</td>
<td>995.17(4)</td>
<td>991.50(5)</td>
</tr>
<tr>
<td>(V) (10$^6$ pm$^3$)</td>
<td>1040.5</td>
<td>1003.62(7)</td>
<td>985.59(6)</td>
<td>974.73(8)</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) (g cm$^{-3}$)</td>
<td>5.78</td>
<td>7.54</td>
<td>8.47</td>
<td>9.58</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>P1710</td>
<td>PANalytical X’Pert MPD Pro</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2\theta) (degree)</td>
<td>16.5–100</td>
<td>10–120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\lambda) (pm)</td>
<td>154.060</td>
<td>154.060, 154.443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I(\lambda_2)/I(\lambda_1))</td>
<td>= 0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R_{\text{wp}})</td>
<td>0.073</td>
<td>0.0129</td>
<td>0.0126</td>
<td>0.0136</td>
</tr>
<tr>
<td>(R_{\text{exp}})</td>
<td>0.051</td>
<td>0.0074</td>
<td>0.0080</td>
<td>0.0078</td>
</tr>
<tr>
<td>(R_{\text{Bragg}})</td>
<td>0.025</td>
<td>0.0217</td>
<td>0.0146</td>
<td>0.0300</td>
</tr>
<tr>
<td>(S)</td>
<td>1.43</td>
<td>1.73</td>
<td>1.59</td>
<td>1.75</td>
</tr>
</tbody>
</table>

*Füglein et al. [62].

### Table 2: Refined atomic parameters for TaZr$_3$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>S.O.F.</th>
<th>(B_{\text{iso}}) (10$^4$ pm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta1</td>
<td>8(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.89(7)</td>
</tr>
<tr>
<td>Zr1</td>
<td>8(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.89(7)</td>
</tr>
<tr>
<td>Ta2</td>
<td>24(d)</td>
<td>0.28280(7)</td>
<td>0</td>
<td>(\frac{1}{4})</td>
<td>0.5</td>
<td>0.44(4)</td>
</tr>
<tr>
<td>Zr2</td>
<td>24(d)</td>
<td>0.28280(7)</td>
<td>0</td>
<td>(\frac{1}{4})</td>
<td>0.5</td>
<td>0.44(4)</td>
</tr>
<tr>
<td>N</td>
<td>48(e)</td>
<td>0.3549(8)</td>
<td>0.1340(9)</td>
<td>0.0942(7)</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

S.O.F., site occupation factor.
Taking a look at the present results, the $y$ value of the general formula $\text{TaZrO}_{3-y/2} \text{N}_{3y}$ has the range of $0 \leq y \leq 1.11$. As it can be easily understood by reasons of charge neutrality, a consequence of increasing oxygen content is the increasing deviation from the ideal $A X_2$ composition ($A X_2$). While $\delta$ grows, more vacancies are occupied by anions and the crystal structure becomes more and more 'fluorite-like'. Therefore, the $x$ (24$d$) coordinate is approaching $\frac{1}{4}$, which is the value for the cubic fluorite type. This is accompanied by lower intensities of the superstructure reflections in the X-ray diffraction patterns. With an increasing number of atoms inside the unit cell, the lattice parameter expands by ca. $12.75$ pm. All this is depicted in Fig. 3.

Phase-pure samples are predominantly nitrogen-rich. At higher oxygen contents, the formation of more than one phase is likely. It was not possible to cover the whole composition range up to the ideal fluorite-type ($AX_2$), as practiced for uranium nitride [60, 61]. Fluorite-type phases of tantalum oxide nitrides containing yttrium are known [68]. In the present system, the baddeleyite type is the favored crystal structure for an $AX_2$ composition. The maximal $16c$ occupation in all our experiments ($\delta = 0.63$) was found for a sample with a Ta:Zr ratio of 1:2: $\text{Ta}_{0.67} \text{Zr}_{1.33} \text{O}_{2.22} \text{N}_{1.41}$.

A reamorphization of the samples can be observed at temperatures higher than $600$ K in air. Under nitrogen atmosphere, the sample is stable at least up to $1273$ K.

It can be expected that the nitrogen content should have an influence on the optical band gap. Products with an Ta:Zr ratio of 1:2 and a high oxygen content have a yellowish light-brown color and become darker with increasing nitrogen content. Five different samples were analyzed by UV/Vis spectroscopy (diffuse reflectance geometry) in order to determine the optical band gaps. As an example, the Tauc plot of the absorbance spectra for the direct optical band gap of $\text{Ta}_{0.67} \text{Zr}_{1.33} \text{O}_{1.89} \text{N}_{1.63}$ (lowest nitrogen content) is depicted in Fig. 4. The results for all investigated samples are summarized in Table 4.

A band gap of $E = 2.48$ eV should correspond to a yellowish product. Therefore, the direct band gaps are probably the most reliable values. Higher contents of nitrogen reduce the gap between valence and conduction band, which nicely corresponds to the theory of Phillips and Van Vechten [69, 70].

These bixbyite-type phases are most likely the cubic side phases, which have been reported by Grins et al. [41]...
No or only small superstructure reflections were observed in their powder XRD measurements. They excluded the bixbyite type as the adequate crystal structure. However, those superstructure reflections are clearly observable in the diffrafograms presented here (see Fig. 1).

Bixbyite-type phases containing tantalum are already known. Quaternary tantalum oxide nitrides with scandium also exhibit a dependency of the α and x (2αd) parameters on the nitrogen content [48]. Because of the lower-valent scandium, the nitrogen content was far smaller (30–59 anion%) than in the Ta–Zr compounds and the corresponding mixed-valent binary tantalum nitride TaN₃ can only be realized by plasma-enhanced chemical vapor deposition at temperatures of 873–973 K [28] or sputter deposition [29] and has probably been synthesized several times before a definite phase identification was successful [26, 27, 72]. The cell parameter of α = 982.05(4) pm [28] is consistent with our result of α = 995.16(4) pm for the nitride compound, taking into account the smaller ionic radius of Ta⁺⁺⁺ (68 pm) compared with the isovalent Zr⁺⁺ (72 pm) [64]. Most recent investigations have shown a metastable behavior of these TaN₃ films [29]. Transformation to δ-TaN₃-like phases can be observed at temperatures higher than 1123 K.

Sesquinitrides of lanthanides (Tb,N₃, Dy,N₃, Ho,N₃, Tm,N₃, and Lu,N₃ [73]) and actinides (U,N₃ [60], Np,N₃ [74]) are listed in databases. It should be noted that the final compositions of the lanthanide nitrides were not determined in the publication. Nitrides of other metals, for example, Be,N₃ [75], Mg,N₂ [76–78], Ca,N₂ [79], Zn,N₂ [76, 78], and Cd,N₂ [80], exhibit the anti-bixbyite structure.

### 4 Conclusions

It was possible to complement the already well-studied system Ta–Zr–O–N by bixbyite-type compounds. The N/O ratio has a significant influence on the deviation δ from the ideal $A_{\alpha}X_{\beta}$ bixbyite composition ($A_{\alpha}X_{\alpha}$), the cell parameter a, and the x coordinate of the 2αd cation position. For a Ta:Zr ratio of 1:1, the ternary nitride TaZn₃ could be prepared. Contrary to the main intention of this work, the search for metastable compounds, this new nitride phase can be considered as a stable analogue of the already known metastable Ta,N₃. Experiments with lower Zr contents did not result in new phases.

### 5 Supporting Information

Crystallographic data in CIF format for the structure refinement of TaZrN₃ are available online (DOI: 10.1515/znb-2017-0014).

**References**


