Tobias Lüdtke, Steven Orthmann and Martin Lerch*

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

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 $TaZrN_3$ crystallize in the cubic bixbyite-type structure (space group $Ia\overline{3}$). 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. $TaZrN_3$ can be considered as a thermodynamically stable ternary variant of metastable Ta_2N_3.

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 ZrO_2-Zr_3N_4. They are generally described by the formula $ZrO_{2-2x}N_{4x/3}$ and are structurally derived from fluorite-type ZrO_2, the high-temperature polymorph of zirconia. A series of oxygen-rich β-type phases (β: $Zr_7O_8N_4$; β′: $Zr_7O_{11}N_2$; β″: $Zr_{7.0}O_{9.5}N_{3.0}$) [5–9] are supplemented by a nitrogen-rich γ-phase (Zr_2ON_2) [5–7],

crystallizing in the cubic bixbyite-type structure. A more detailed overview concerning this system was conducted by Lerch [10]. An intergrowth of ZrO_2 and Zr_2ON_2, resulting in the formation of $Zr_4O_5N_2$ [11], and the incorporation of small amounts of Ta_2O_5 into zirconium oxide nitrides have also been investigated [12]. The hitherto reported nitrides of zirconium are ZrN [13, 14] and Zr_3N_4 [15, 16]. A cubic high-pressure polymorph of Zr_3N_4 also exists [17].

On the other hand, the ionic-covalent oxide nitride of tantalum(V), TaON, is more stoichiometrically restricted and crystallizes in various AX_2 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 ZrO_2 (m-ZrO_2). Two metastable polymorphs have been prepared so far: γ-TaON [19], which crystallizes in the monocline crystal system in the VO_2(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, Ta_3O_6N [23], has been proposed. By contrast, the variety of the nitrides is significantly higher. The compounds Ta_3N_5 [24], Ta_4N_5 [25], Ta_5N_6 [25], and Ta_2N_3 [26–29] belong to the group of nitrogen-rich nitrides. Ta_2N_3 crystallizes, comparable with Zr_2ON_2, in the bixbyite-type structure [28, 29]. High-pressure polymorphs of Ta_3N_5 and Ta_2N_3 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-Ta_2N 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-ZrO_2/β-TaON and Ta_3N_5, 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 $TaZrO_3N$

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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 $Mg_{0.05}Ta_{0.95}O_{1.15}N_{0.85}$ [47] or $Sc_{0.15}Ta_{0.85}O_{1.30}N_{0.70}$ [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 $ScTa_2O_5N$ 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. $TaCl_5$ (99.999%, Sigma Aldrich, St. Louis, MO, USA) and $ZrCl_4$ (99.99%, Sigma Aldrich) were mixed in the required ratios and dissolved in a citric acid-ethanol solution. Citric acid was used in a 12-fold molar excess to the cations. Ethylene glycol in a molar excess of 17 times the cations was added to the solutions. These mixtures were vaporized at temperatures up to 523 K. The formed gels were then calcined in a corundum crucible at temperatures up to 723 K, resulting in colorless X-ray amorphous powders of the mixed oxides.

Nitrides and oxide nitrides were synthesized *via* an ammonolysis reaction of these precursors in a tube furnace with dry ammonia at temperatures of 1073–1223 K for 3–12 h and ammonia flow rates of 10–20 L h⁻¹.

A PANalytical X'Pert MPD Pro instrument (Almelo, Netherlands) was used for XRD measurements at ambient temperature. This powder diffractometer operates with a Cu anode and without a monochromator (Cu-K_α radiation,

$\lambda_1 = 154.060$ pm, $\lambda_2 = 154.443$ pm, $I(\lambda_2)/I(\lambda_1) = 0.5$) at 40 kV and 40 mA. Additional data were collected on a RIGAKU (Tokyo, Japan) SmartLab 3 kW system equipped with a Cu anode X-ray tube (40 kV and 30 mA) and a $K_{\alpha 1}$ unit (Johansson-type Ge crystal) monochromator (Cu-$K_{\alpha 1}$ radiation, $\lambda = 154.060$ pm). Rietveld refinements were carried out using the program FULLPROF 2000 (Grenoble, France) [53]. Profiles were fitted with a pseudo-Voigt profile shape function. The backgrounds were fitted with various points with refinable heights.

A LECO TC-300/EF-300 N/O hot gas extraction analyzer (Saint Joseph, MI, USA) was used for the determination of nitrogen and oxygen contents of the samples. ZrO_2 and special steel (Saint Joseph, MI, USA) were used as standard materials. The accuracy is *ca.* 2% of the N/O contents present.

UV/Vis measurements were performed on a VARIAN (Palo Alto, CA, USA) Cary 300 Scan UV/Vis spectrophotometer in diffuse reflectance mode. Barium sulfate (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].

3 Results and discussion

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%, performed at 1073 K, resulted in phase-pure powders of oxide nitrides or nitrides with cubic bixbyite-type structure ($Ia\bar{3}$). Structural similarities to bixbyite-type Zr_2ON_2 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 Zr_2ON_2 as the final member.

The ideal bixbyite structure can be described as a $2 \times 2 \times 2$ 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 octahedrally by anions, and the anions are tetrahedrally surrounded by cations. A graphical presentation is shown in Fig. 1. One characteristic of this structure type is the possible partial occupation of the vacancies by anions, leading to $A_2X_{3+\delta}$ ($\delta \leq 1$) compositions. This observation has already been made for U_2N_3 [60, 61], Zr_2ON_2 [62], and vanadium oxide nitrides [63].

In the system Ta–Zr–O–N, compounds between Zr_2ON_2/ZrO_2 and $TaZrN_3/TaZrO_3N$ can be described with the general formula $Ta_{1-x}Zr_{1+x}O_{x+3y/2}N_{3-x-y}$ ($0 \leq x \leq 1$, $0 \leq y \leq 2$). From a formal point of view, it should be possible to prepare 1:1 phases in the range from $TaZrN_3$ ($\delta = 0$) to $TaZrO_3N$ ($\delta = 1$). For a Ta:Zr ratio of 1:2, the following range can be calculated: $Ta_{0.67}Zr_{1.33}O_{0.33}N_{2.67}$–$Ta_{0.67}Zr_{1.33}O_{3.33}N_{0.67}$. The range $Ta_{1.33}Zr_{0.67}N_{3.11}$–$Ta_{1.33}Zr_{0.67}O_{2.67}N_{1.33}$ can be expected for a ratio of 2:1, which can be generalized to the formula $Ta_{1+x}Zr_{1-x}O_{3y/2}N_{3+x/3-y}$ ($0 \leq x \leq 0.33$, $0 \leq y \leq 2 - 2x/3$). Without the x restriction (no phase-pure samples could be obtained for $x > 0.33$), the series could be continued for $x = 1$ to $Ta_{2.00}N_{3.33}$ ($y = 0$) and the corresponding phase $Ta_2O_2N_2$ ($y = 1.33$), or simply TaON. As mentioned previously, quantum-chemical calculations indeed predict a metastable polymorph of TaON with fluorite-type structure [49]. This polymorph is expected to be ca. 80 kJ·mol⁻¹ less stable compared with β-TaON, making a successful synthesis unlikely.

By variation of the synthesis parameters, it was possible to produce samples with different amounts of nitrogen and oxygen. For a 1:1 cation ratio, phase-pure phases in
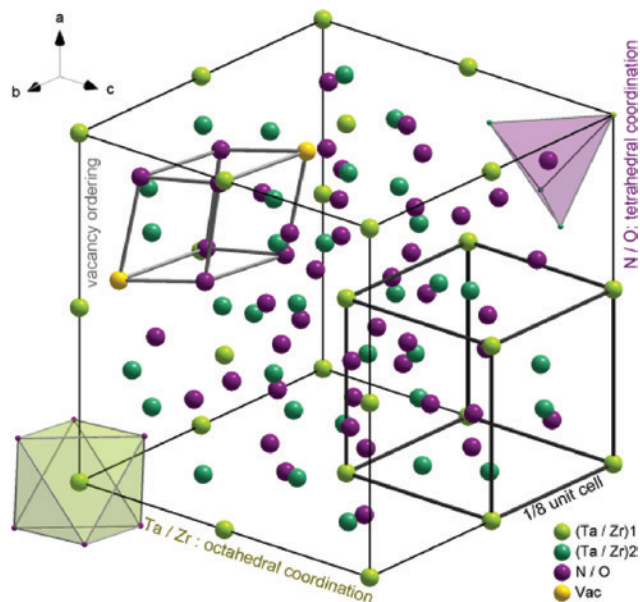
the range $Ta_{1.00}Zr_{1.00}O_{0.00}N_{3.00}$–$Ta_{1.00}Zr_{1.00}O_{1.67}N_{1.89}$ were found, corresponding to a y range of $0 \leq y \leq 1.11$. For the other two ratios, compounds $Ta_{0.67}Zr_{1.33}O_{0.42}N_{2.61}$–$Ta_{0.67}Zr_{1.33}O_{1.89}N_{1.63}$ ($0.06 \leq y \leq 1.04$) and $Ta_{1.33}Zr_{0.67}O_{0.12}N_{3.03}$–$Ta_{1.33}Zr_{0.67}O_{0.30}N_{2.91}$ ($0.08 \leq y \leq 0.20$) 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 A_2X_3 composition. Also the formation of anosovite-type side phases, which can be derived from Ta_3N_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 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 Rietveld 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_2ON_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 (Ta⁵⁺: 64 pm; Zr⁴⁺: 72 pm; N³⁻: 146 pm) [64] and is almost exactly
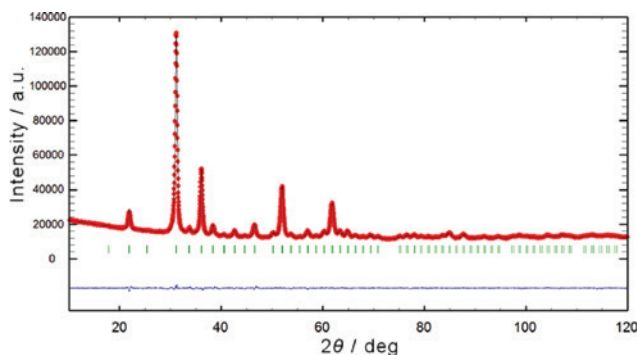

Fig. 1: Crystal structure of the bixbyite-type tantalum zirconium oxide nitrides. Only two of 16 possible vacancies (Vac) have been marked.

Fig. 2: X-ray powder diffraction pattern (Cu-K_α radiation) of $TaZrN_3$ with results of the Rietveld refinement (red: measured; black: calculated; green: Bragg-reflection positions; blue: difference between measured and calculated).

Table 1: Results of the Rietveld refinements for selected bixbyite-type phases in comparison with results for Zr_2ON_2.

Compound	Zr_2ON_2[a]	$Ta_{0.67}Zr_{1.33}O_{0.42}N_{2.61}$	$TaZrN_3$	$Ta_{1.33}Zr_{0.67}O_{0.12}N_{3.03}$
Ta:Zr		1:2	1:1	2:1
Structure type	Bixbyite			
Space group	$Ia\bar{3}$ (No. 206)			
Crystal system	Cubic			
Z	16			
a (pm)	1013.32	1001.20(4)	995.17(4)	991.50(5)
V (10^6 pm³)	1040.5	1003.62(7)	985.59(6)	974.73(8)
ρ_{calc} (g cm⁻³)	5.78	7.54	8.47	9.58
Diffractometer	P1710	PANalytical X'Pert MPD Pro		
2θ (degree)	16.5–100	10–120		
λ (pm)	154.060	154.060, 154.443		
		$I(\lambda_2)/I(\lambda_1) = 0.5$		
R_{wp}	0.073	0.0129	0.0126	0.0136
R_{exp}	0.051	0.0074	0.0080	0.0078
R_{Bragg}	0.025	0.0217	0.0146	0.0300
S	1.43	1.73	1.59	1.75

[a]Füglein et al. [62].

Table 2: Refined atomic parameters for $TaZrN_3$.

Atom	Wyckoff	x	y	z	S.O.F.	B_{iso} (10^4 pm²)
Ta1	8a	0	0	0	0.5	0.89(7)
Zr1	8a	0	0	0	0.5	0.89(7)
Ta2	24d	0.28280(7)	0	¼	0.5	0.44(4)
Zr2	24d	0.28280(7)	0	¼	0.5	0.44(4)
N	48e	0.3549(8)	0.1340(9)	0.0942(7)	1	1

S.O.F., site occupation factor.

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 48e and not on the 16c site [63, 65]. This topic has already been discussed for

Zr_2ON_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 24d cation site, which is the only cation coordinate not fixed by space group symmetry.

Table 3: Cell parameter a and cation coordinate x of selected samples with a Ta:Zr ratio of 1:1.

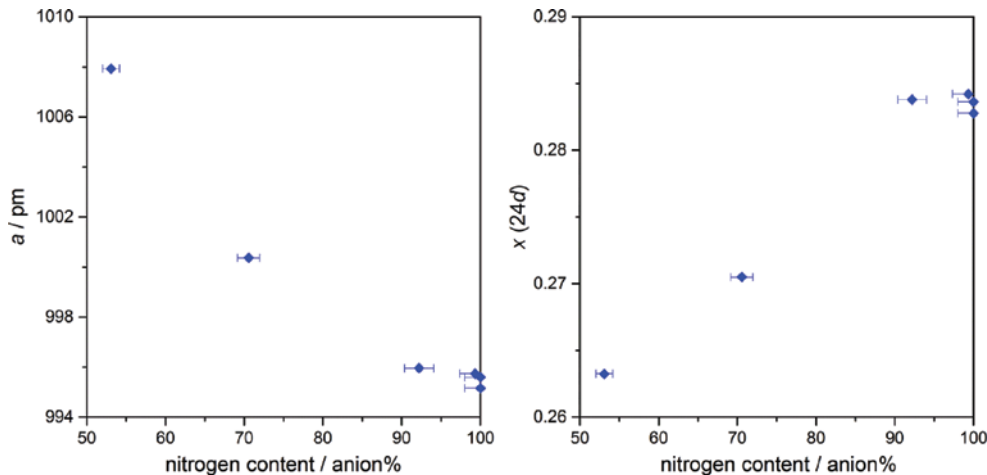| Sum formula	Nitrogen content (anion%)	a (pm)	x (24d)
$Ta_{1.00}Zr_{1.00}O_{0.00}N_{3.00}$	100	995.17(4)	0.28280(9)
$Ta_{1.00}Zr_{1.00}O_{0.00}N_{3.00}$	100	995.60(4)	0.28363(8)
$Ta_{1.00}Zr_{1.00}O_{0.02}N_{2.99}$	99.3	995.74(5)	0.28422(10)
$Ta_{1.00}Zr_{1.00}O_{0.24}N_{2.84}$	92.2	995.96(5)	0.28380(10)
$Ta_{1.00}Zr_{1.00}O_{0.98}N_{2.35}$	70.6	1000.37(6)	0.27050(16)
$Ta_{1.00}Zr_{1.00}O_{1.67}N_{1.89}$	53.1	1007.93(5)	0.26324(15)

Fig. 3: Dependency of unit cell parameter a and cation position x (24d) from the nitrogen content of the new bixbyite-type phases with an even cation ratio.

Taking a look at the present results, the y value of the general formula $TaZrO_{3y/2}N_{3-y}$ 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_2X_3 composition ($A_2X_{3+\delta}$). While δ grows, more vacancies are occupied by anions and the crystal structure becomes more and more 'fluorite-like'. Therefore, the x (24d) coordinate is approaching ¼, 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: $Ta_{0.67}Zr_{1.33}O_{2.22}N_{1.41}$.

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 $Ta_{0.67}Zr_{1.33}O_{1.89}N_{1.63}$ (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]
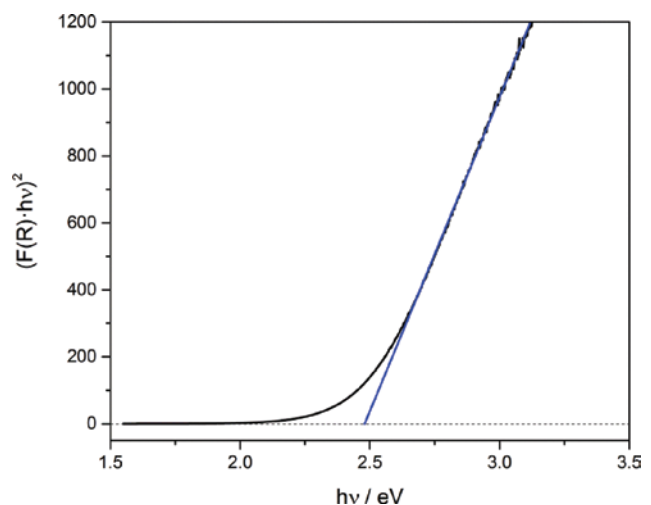

Fig. 4: UV/Vis spectrum/Tauc plot (black) of $Ta_{0.67}Zr_{1.33}O_{1.89}N_{1.63}$ with *Tauc* plot determination of the direct optical band gap (blue).

Table 4: Optical band gaps of different bixbyite-type compounds.

Sum formula	Color	Direct band gap	Indirect band gap
$Ta_{0.67}Zr_{1.33}O_{1.89}N_{1.63}$	Light-brown	2.48 eV	1.87 eV
$Ta_{0.67}Zr_{1.33}O_{1.38}N_{1.97}$	Brown	2.31 eV	1.65 eV
$Ta_{0.67}Zr_{1.33}O_{0.42}N_{2.61}$	Red-black	1.93 eV	1.32 eV
$Ta_{1.00}Zr_{1.00}O_{0.00}N_{3.00}$	Black	1.72 eV	1.30 eV
$Ta_{1.33}Zr_{0.67}O_{0.12}N_{3.03}$	Black	1.71 eV	1.27 eV

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 diffractograms 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 a and x (24d) 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 presented here [48, 71].

The corresponding mixed-valent binary tantalum nitride Ta_2N_3 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 $a = 982.05(4)$ pm [28] is consistent with our result of $a = 995.16(4)$ pm for the nitride compound, taking into account the smaller ionic radius of Ta^{4+} (68 pm) compared with the isovalent Zr^{4+} (72 pm) [64]. Most recent investigations have shown a metastable behavior of these Ta_2N_3 films [29]. Transformation to δ-TaN_x-like phases can be observed at temperatures higher than 1123 K.

Sesquinitrides of lanthanides (Tb_2N_3, Dy_2N_3, Ho_2N_3, Tm_2N_3, and Lu_2N_3 [73]) and actinides (U_2N_3 [60], Np_2N_3 [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_3N_2 [75], Mg_3N_2 [76–78], Ca_3N_2 [79], Zn_3N_2 [76, 78], and Cd_3N_2 [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_2X_3 bixbyite composition ($A_2X_{3+\delta}$), the cell parameter a, and the x coordinate of the 24d cation position. For a Ta:Zr ratio of 1:1, the ternary nitride $TaZrN_3$ 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_2N_3. Experiments with lower Zr contents did not result in new phases.

5 Supporting Information

Crystallographic data in CIF format for the structure refinement of $TaZrN_3$ are available online (DOI: 10.1515/znb-2017-0014).

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