



A density-functional study on the stability of anatase-type phases in the system Mg–Ta–O–N

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ABSTRACT

Magnesium-doped tantalum oxynitrides, which were prepared by ammonolysis of amorphous mixed oxides, have been investigated using quantum-theoretical methods. For small magnesium amounts (5 cat%), density-functional total-energy calculations indicate an anatase-type structure consisting of stretched, corner-sharing TaO₃N₃ octahedra with a tetrahedrally distorted equatorial plane. The calculated structural parameters are in excellent agreement with those obtained using X-ray powder diffraction and synchrotron radiation. Additionally, the quantum-chemical results show a clear preference for an ordered anionic distribution (space group *I4₁md*, no. 109) of the host lattice, which is locally disturbed around Mg²⁺. For thermodynamical reasons, the excess oxygen anions, which replace nitrogen on account of the lower charge of the dopant cation, segregate next to magnesium, thus forming local MgO “domains”. For higher magnesium contents (≥10%), minor phases of rutile-type structure have to be expected, which is in good agreement with experimental data.

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1. Introduction

Oxynitride materials have been increasingly studied in the past few years. The idea of fine-tuning the properties of such compounds via the amount of nitrogen incorporated has caused the investigation of their applicability for various concerns, such as photocatalysis [1–4] or ionic conduction [5–7]. Transition-metal oxynitrides have been tested as dielectrics [8–10] in microelectronic devices or as chemical gas sensors [11]. The substitution of cadmium-based pigments by non-toxic transition-metal and rare-earth oxynitrides [12,13] is widely studied because of its environmental benefit. It turns out that, among the many synthetic candidates, doped tantalum oxynitride appears as especially suitable for this purpose. Pure β-TaON is yellow [14], which is in reasonable agreement with the theoretically calculated bandgap of 2.2 eV [15]. It crystallizes in the monoclinic baddeleyite-type structure with an ordered anion arrangement [16]. Another metastable polymorph of light-brown color, crystallizing in the VO₂(B)-type structure and dubbed γ-TaON, has recently been reported [17,18]. It has been confirmed and structurally refined by theoretical methods [19], while a former hexagonal polymorph dubbed α-TaON, reported to be red, could be falsified [20] and does not exist. Since TaON decomposes above 1100 °C, ZrO₂-like phase transitions from the monoclinic

baddeleyite-type to tetragonal or cubic fluorite-type phases at higher temperatures have not yet been detected. Nonetheless, such phases can be stabilized at room temperature by doping TaON with aliovalent oxides. The systems Sc–Ta–O–N [21] and Y–Ta–O–N [22,23], for example, form cubic phases related to the aristotypic fluorite structure. As known from ZrO₂, MgO-doping also leads to the stabilization of fluorite-type structures.

Recently, we have reported the synthesis of a single-phase sample of nominal composition Mg_{0.05}Ta_{0.95}O_{1.15}N_{0.85} showing a brilliant orange color [24]. Astonishingly, it appeared to be the first example of an anatase-type compound without titanium. The phase is metastable and undergoes a phase transformation to a baddeleyite-type phase between 900 and 1000 °C.

Theoretical methods have already been used successfully to analyze the stability and electronic structure of several thinkable polymorphs (baddeleyite, anatase, rutile and fluorite) of TaON [25]. Therefore, we decided to augment the fundamental experimental results by means of computational chemistry, aiming for a better understanding of the structural properties, in particular in terms of local structures being invisible for X-ray diffraction techniques.

2. Experimental

2.1. Synthesis

Amorphous ternary phases in the system Mg–Ta–O were prepared using a modified Pechini method [26]. Tantalum

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chloride (Alfa Aesar, 99.99%) was dissolved in ethanol containing citric acid in an excess of 12 times the TaCl_5 amount. Any dispersed Ta_2O_5 can be removed by centrifugation. The resulting tantalum citrate complexes are insensitive to water. A stock solution with a defined content of tantalum citrate was obtained. Magnesium chloride (99.9%, Alfa Aesar) was dissolved in ethanol which contained citric acid in an excess of 12 times the MgCl_2 amount. Appropriate quantities of the two citrate solutions were mixed together and ethylene glycol in an excess of 17 times the metal's content was added. The solvent and HCl were evaporated and the citrate complexes together with ethylene glycol had been polymerized at $\approx 150^\circ\text{C}$. The organic residues of the polymer were burnt off at 600°C for 16 h to give white X-ray amorphous powders. A series of mixed oxides $\text{Mg}_x\text{Ta}_{1-x}\text{O}_{2.5-1.5x}$ with $x = 0.05, 0.10, 0.15$ and 0.20 was prepared this way.

The amorphous mixed oxides were converted into oxynitrides by ammonolysis with either dry ammonia (3.8, Messer–Griesheim) or moist ammonia (bubbled through saturated ammonia solution) at a constant flow rate of 25 L/h at temperatures of 800 or 900°C for 16 h.

2.2. N/O analysis

Nitrogen and oxygen contents were determined using a LECO TC-300/EF-300 N/O analyzer (hot gas extraction). Ta_2O_5 and Si_3N_4 were used as standard materials for calibration. The accuracy is $\approx 2\%$ of the present N/O.

2.3. Powder diffraction

Synchrotron X-ray diffraction measurements were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB, beamline B2). The computer program POWDER CELL 2.4 [27] was used for quantitative phase analysis and lattice parameter determination and the program FULLPROF2000 [28] for Rietveld refinements. Peak profiles were fitted using a pseudo-Voigt function. Structural details concerning the crystal symmetry and the positional parameters can be found in Tables 1 and 2.

2.4. Computational details

The electronic-structure calculations were performed within the framework of density-functional theory (DFT) with the Vienna *ab-initio* simulation package (VASP) [29,30], applying plane-wave basis sets and ultra-soft pseudopotentials of Vanderbilt type [31]. Contributions of correlation and exchange to the total energies were treated in the generalized-gradient approximation (GGA) as described by Perdew and Wang [32]. All results rely on well-converged structures with respect to the energy-cutoff (500 eV) and the pseudopotential. With respect to the k point sampling,

Table 1

Structural parameters for anatase-type $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$ as obtained using X-ray powder diffraction and synchrotron radiation

Structure type	Anatase
$a = b$	3.91986(6) Å
c	10.1119(3) Å
Z	4
Space group	$I4_1/amd$
V_0	155.373(6) Å ³
Calculated density	8.71 g/cm ³
Formula weight	203.42 g/mol
Diffractometer	B2/HASYLAB
Wavelength	70.990 pm

Table 2

Atomic positions for anatase-type $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$ in space group $I4_1/amd$ (no. 141) on the basis of X-ray powder diffraction using synchrotron radiation

Atom	Wyck.	x	y	z	Occ.	B_{iso} (Å ²)
Ta/Mg	4b	0	1/4	3/8	0.95/0.05	0.34(3)
O/N	8e	0	1/4	0.584(1)	0.575/0.425	1.8(3)

Note that a distinction between Ta and Mg (and also O and N) cannot be made.

self-consistency was achieved with a $12k$ point mesh in the irreducible Brillouin zone and with six irreducible k points for the undoped structures. In the calculations both the atomic positions and the cell parameters were allowed to relax until the maximum residual force was smaller than 0.02 eV/\AA .

3. Results and discussion

In the anatase-type structure of undoped, stoichiometric TaON three different distributions of the anions are thinkable if the anionic sublattice is assumed to be ordered. From the regular anatase space group ($I4_1/amd$, no. 141) with two non-equivalent anionic sites, the three maximal non-isomorphic subgroups $I\bar{4}m2$ (no. 119), $I4_1md$ (no. 109) and $Imma$ (no. 74) evolve (see Fig. 1). The $I\bar{4}m2$ and $I4_1md$ structural variants contain alternating N–Ta–N and O–Ta–O chains within the entire lattice, while in the $Imma$ structure these chains differ between the a and b directions due to the orthorhombic symmetry. In all the three structures, the local environment of the tantalum cations is of a distorted octahedral shape, with four short Ta–(O,N) bond lengths (2.00 Å) framing the equatorial plane and two longer bonds (2.14 Å) connecting the octahedral tops. The four nearest neighbors are slightly tilted out of the equatorial plane ($\pm 17^\circ$), thereby resembling a distorted tetrahedron. While in the $Imma$ and the $I4_1md$ variant, the coordinating anionic positions are equally occupied by oxygen and nitrogen, leading to TaO_3N_3 octahedra—more precisely, $\text{Ta}(\text{O}_2\text{N}_2)\text{ON}$ octahedra—as local structural attributes, there are two different tantalum environments in $I\bar{4}m2$, namely, TaO_4N_2 and TaN_4O_2 (see Fig. 2). Density-functional total energy calculations show that this is accompanied with a significant destabilization of the $I\bar{4}m2$ structure, as can be seen in Fig. 3. The most stable anion distribution turns out to have $I4_1md$ symmetry, and it is 15 kJ/mol more stable than the $I\bar{4}m2$ arrangement and 5 kJ/mol more stable than the $Imma$ variant.

To allow for a comparison with a completely *disordered* structural variant, we also generated unit cells that were doubled in all three spatial directions, leading to structural models consisting of a total of 96 atoms. The nitrogen and oxygen atoms were then manually distributed over all anionic sites, leading to structures with an anatase-type framework but without any apparent leftover symmetry in the anionic sublattices. To make sure that we came close to a fully disordered anionic setting, we performed calculations for three alternative and seemingly disordered geometries, resulting in a total energy difference of merely $\pm 1 \text{ kJ/mol}$. Given the limited accuracy of the computational approach, all three calculated disordered structural models are energetically identical and therefore serve as representatives for the multitude of all possible ways to distribute the oxygen and nitrogen anions. As Fig. 3 visualizes, a disordered anionic arrangement is about 25 kJ/mol less favorable than the $I4_1md$ ordered variant. Even assuming synthesis conditions of about 1000 K, the resulting entropical term $T\Delta S$ which may result from N/O site mixing does not overcome this energy penalty. If, as it has been done in former contributions on related systems such as Zr_2ON_2 [33] or Y-doped TaON [23], the mixing entropy S_{con} for

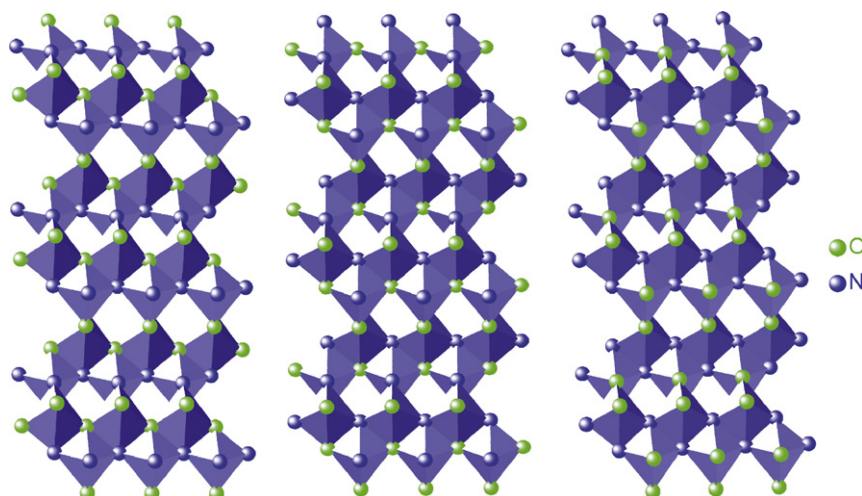


Fig. 1. Three different distributions of O and N in anatase-type tantalum oxynitride: $I\bar{4}m2$ (no. 119, left), $I4_1md$ (no. 109, middle) and $Imma$ (no. 74, right).

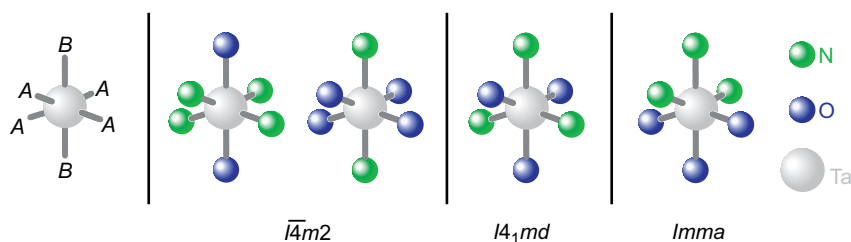


Fig. 2. Local $Ta(O,N)_6$ octahedra in three different anatase-type tantalum oxynitrides: $I\bar{4}m2$ (no. 119, left), $I4_1md$ (no. 109, middle) and $Imma$ (no. 74, right). Note that there are two different bond lengths, Ta–A (2.00 Å) and Ta–B (2.14 Å).

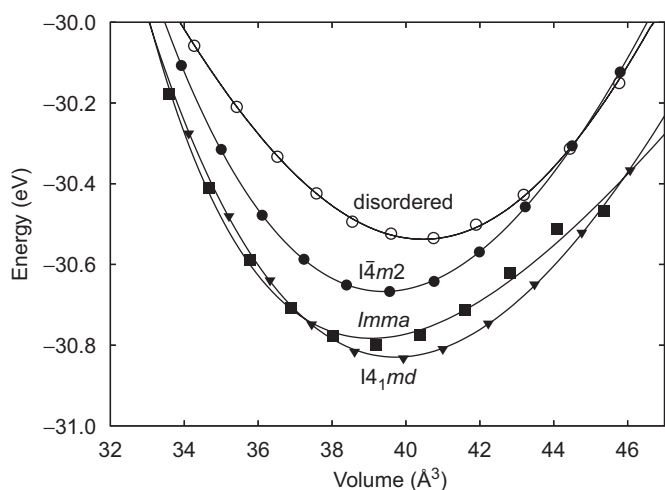


Fig. 3. Total energy and volume of a disordered and three different ordered arrangements of anatase-type TaON.

interchange of O and N is estimated with the simple formula

$$S_{\text{con}} = R \sum_i x_i \ln x_i \quad (1)$$

with R being the ideal gas constant and x_i the molar fraction of the anion i , an energetic gain of $T\Delta S \approx -5$ kJ/mol results. This is clearly insufficient to allow full anionic disorder. We may therefore summarize that DFT unambiguously predicts that anatase-type TaON is most stable in the $I4_1md$ structure type with an ordered anionic sublattice and distorted TaO_3N_3 octahedra as local structural attributes.

While such a prediction is easy to make for pure TaON, the situation changes quite dramatically upon doping with magnesium. Due to the charge difference between Ta^{5+} and Mg^{2+} , three nitrogen anions have to be replaced by oxygen anions whenever one magnesium cation is incorporated. As a result, both cationic and anionic sublattices are severely disturbed. The question arises whether the dopant ions are incorporated as “misfits” within the $I4_1md$ structure of the undoped compound, or if a completely different structural arrangement—either ordered or disordered—is formed. In earlier studies, dealing with doped tantalum oxynitrides [22,23], it has been demonstrated that the charge difference between the host and dopant cations can also be compensated by anion vacancies which eventually leads to fluorite-type structures. In the present case, however, there are no experimental indications whatsoever for such defect structures.

It has to be mentioned that, in such doped compounds, the assignment of a space group is only meaningful to depict the structural motive, irrespective of a distinction between O and N (or Ta and Mg, respectively). In order to describe the real symmetry, such distinction would be inevitable to be made. In principle, the entire symmetry is lost if one has to distinguish between the different anions and the different cations, respectively. Using an experimental method such as synchrotron X-ray scattering for structural characterization (which lacks this distinction), the ionic ordering cannot be resolved and the structure appears in the anatase supergroup $I4_1/amd$ (see Tables 1 and 2).

By using DFT and therefore being able to compare different anion/cation distributions, it turns out that, also in Mg-doped TaON, the $I4_1md$ -related structure is the most stable one (compare Fig. 4). Moreover, quantum-chemical calculations provide evidence that, in the framework of the anatase-type structure, the

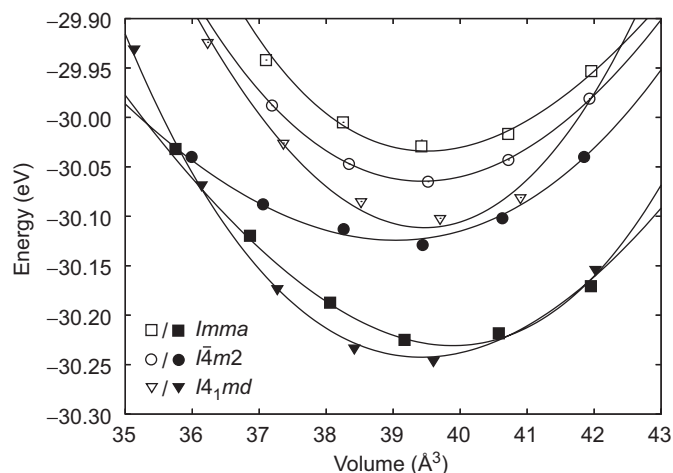


Fig. 4. Total energy and volume of different arrangements of $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$ with anatase-type structure, with the excess oxygen anions located next to Mg (filled circles, boxes and triangles) and statistically distributed within the anionic sublattice, respectively (empty symbols). For the structures with a statistical distribution of the anions, we present the average values for three different disordered anionic setups which were calculated for each structural model.

Table 3

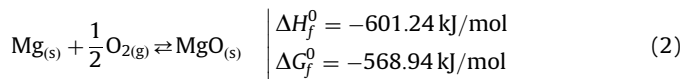
Structural parameters for anatase-type $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$ in space group $I4_1md$ (no. 109) as deduced from X-ray diffraction using synchrotron radiation and as obtained with density-functional theory (see also text)

	Atom	Wyck.	x	y	z	Occ.	
<i>Synchrotron</i>							
$a = b$	3.91986(6) Å	Ta/Mg	4a	0	0	0.95/0.05	
c	10.1119(3) Å	O/N	4a	0	0	0.575/0.425	
Z	4	O/N	4a	0	1/2	0.042(1)	0.575/0.425
V_0	155.373(6) Å ³						
<i>DFT-GGA</i>							
$a = b$	3.933 Å	Ta/Mg	4a	0	0	0.95/0.05	
c	10.269 Å	O	4a	0	0	0.208	1.0
Z	4	O/N	4a	0	1/2	0.042	0.15/0.85
V_0	158.4 Å ³						

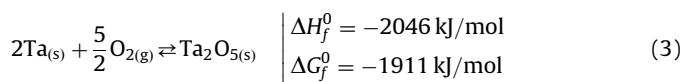
oxygen anions prefer to be located in the direct neighborhood of the lower-valent Mg^{2+} cations, which can be concluded from the course of the total energies in Fig. 4. With respect to the entire structure, this is accompanied by only a *local* perturbation around the dopant cations, while the surrounding lattice sticks to the symmetry of space group $I4_1md$. The resulting structural parameters for $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$ obtained by our quantum-chemical calculations are summarized in Table 3 (lower entries) together with the data that were derived from the diffraction experiment with synchrotron radiation (upper entries). In order to allow for a better comparison with the theory—and thereby being able to easily distinguish between O and N—the structural data for space group $I4_1md$ (no. 109) as shown in Table 3 (left) have been deduced from those for space group $I4_1/amd$ (no. 141, Table 2) just by splitting the $8e$ anion site into two distinguishable positions $4a$ and performing an origin shift of $(0, -\frac{1}{4}, -\frac{3}{8})$. Apart from that, the experimental structure data in Tables 2 and 3 are identical. The agreement between theory and experiment is exceptionally good with the theoretical atomic positions being identical within *one* standard deviation of the experiment. The theoretical volume per formula unit is a little larger (1.9%) than the experimental number, but this slight overestimation of the volume is a well-known feature of the GGA functional.

The coordination polyhedron around Mg^{2+} is shown in Fig. 5, while the resulting bond lengths are summarized in Table 4. It is obvious that the Mg–O bond lengths are elongated while the adjacent Ta–O bond becomes shorter, which may be looked upon as a simple consequence of the stronger Coulomb interaction between Ta^{5+} and O^{2-} .

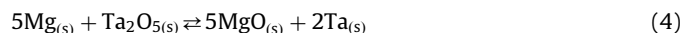
The surprising result of a “clustering” of oxygen anions around the magnesium cations requires an explanation, which is not too difficult to derive, even in quantitative terms. Quite on the contrary, it is easy to see that the formation of local Mg–O “domains” is thermodynamically favorable. If we consider the standard heats of formation ΔH_f^0 and the standard Gibbs energies of formation ΔG_f^0 [34] for the reactions



and



the Gibbs reaction energy ΔG_R^0 of the redox reaction



amounts to

$$\Delta G_R^0 = 5(-569 \text{ kJ/mol}) + 1911 \text{ kJ/mol} = -934 \text{ kJ/mol} \quad (5)$$

Thus, the highly exergonic nature of reaction (4) indicates a higher affinity of Mg to O (compared with Ta to O) such that, even at the atomistic level, the formation of MgO “domains” in Mg-doped TaON appears to be very plausible. Alternatively, the affinity of oxygen and the low-valent Mg^{2+} ion is consistent with crystal-chemical wisdom, in particular Pauling’s second rule [35,36].

Astonishingly enough, the above thermochemical argument also holds whenever nitrogen is competing with oxygen for bonding to either Mg or Ta. We then have to consider the standard

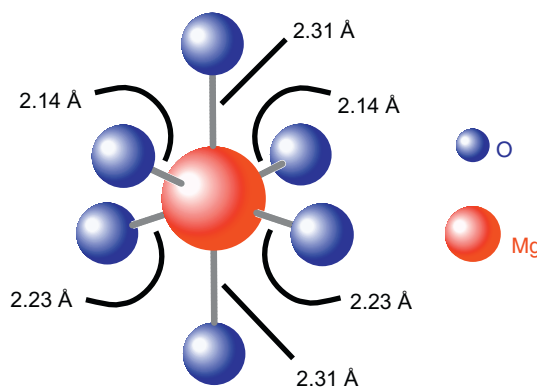


Fig. 5. Local coordination of Mg^{2+} in $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$ with anatase-type structure; all excess oxygen anions are located next to Mg.

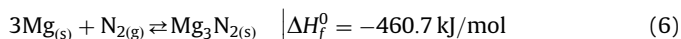
Table 4

Bond lengths (Å) in anatase-type $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$

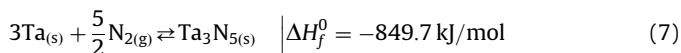
Bond	Bond length
Ta–O(–Mg)	1.83–2.00
Ta–O	2.00 (2×), 2.14 (1×)
Ta–N	2.00 (2×), 2.14 (1×)
Mg–O	2.14 (2×), 2.23 (2×), 2.31 (2×)
Mg–N	–

The Ta–O bonds in the vicinity of the dopant cation are shortened (top line).

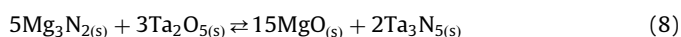
heats of formation ΔH_f^0 [34,37]—unfortunately, the Gibbs energies are unknown to us—for the nitridation reactions



and



such that the reaction enthalpy ΔH_r^0 of the N/O metathesis reaction



amounts to

$$\Delta H_r^0 = -2276 \text{ kJ/mol.} \quad (9)$$

This is so strongly exothermic that, quite clearly, the formation of MgO “domains” is thermodynamically favorable. Here we can safely trust on the cancellation of (numerically insignificant) entropic contributions to the Gibbs energies of educts and products because only solid-state materials are involved. Summarizing, O is attracted by Mg, and N is attracted by Ta.

It is easy to understand that a small perturbation of the host lattice, as described before, is only possible for small dopant amounts. Upon bringing more and more magnesium into the compound, the structure shifts away from the ideal $I4_1md$ symmetry, and other arrangements may become more favorable. In Fig. 6 the calculated total energies of three thinkable polymorphs—anatase, rutile and baddeleyite—are shown as a function of different Mg^{2+} -contents. Not too surprisingly, baddeleyite is the most stable polymorph for undoped TaON, but even a small amount of magnesium leads to an $\approx 50 \text{ kJ/mol}$ stabilization of the anatase structure, thereby becoming the energetically more favorable structure type. With an increase of the dopant concentration the rutile-related structure type also becomes more and more stable, and the energetic difference to the anatase-type structure slowly vanishes: at a dopant amount of 20%, this energy difference is merely 5 kJ/mol. In agreement with our thermodynamical perceptions, a local arrangement of O around Mg is also favored in the rutile polymorph, while the remaining anions are ordered according to space group $Cmmm$ (no. 65).

This tendency for the energetic course of the polymorphs, which was predicted by DFT, is very well reproduced in the experiment. Fig. 7 shows the yields of the above mentioned polymorphs as they are obtained in the experimental synthesis.

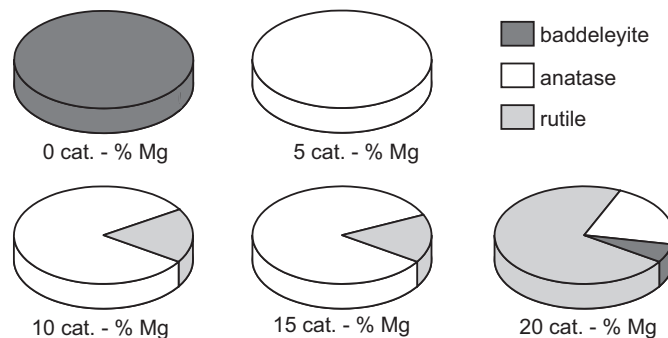


Fig. 7. Relative polymorph amounts of Mg-doped TaON phases as obtained via synthesis.

Pure TaON adopts the baddeleyite structure. For a magnesium content of 5 cat%, the anatase-type structure is exclusively formed. Upon inserting more dopant cations into the structure, and thereby decreasing the relative energetic benefit of the anatase polymorph, a rutile-type structure appears as a minor phase. The rutile polymorph becomes the majority at a magnesium content of 20 cat%, and even a small amount of baddeleyite can be identified. Note that there is no theoretical evidence for the formation of a baddeleyite-type phase, which was calculated to be increasingly less stable the more magnesium is incorporated. We believe that such small deviations between theory and experiment may go back to kinetic effects upon synthesis and crystal growth.

The stabilization of the anatase-type phase in the system Mg–Ta–O–N cannot be explained by simple arguments touching upon ionic radii, since Mg^{2+} is larger than Ta^{5+} ($r_{\text{Mg}^{2+}} = 0.72 \text{ \AA}$, vs. $r_{\text{Ta}^{5+}} = 0.64 \text{ \AA}$, both for c.n. = 6) and, thus, the cation coordination number should increase. Instead, it decreases from 7 (baddeleyite type) to 6 (anatase type). Nonetheless, the crystal chemistry of the binary magnesium and tantalum oxides unambiguously proves that such size criterion must fail. In MgO, Mg^{2+} is sixfold coordinated whereas the supposedly smaller Ta^{5+} experiences a mixed coordination between six and seven already in $\beta\text{-Ta}_2\text{O}_5$. Similar failures of qualitatively predicting coordination numbers or structure types based on ratios of ionic radii are very well known [38]. In the present case, however, the presence of Mg^{2+} clearly induces the anatase type with sixfold coordination because the latter is the only reasonable coordination pattern for Mg^{2+} .

4. Conclusions

A single-phase sample $\text{Mg}_{0.05}\text{Ta}_{0.95}\text{O}_{1.15}\text{N}_{0.85}$ with anatase-type structure was synthesized by ammonolysis. Anion ordering patterns of AXY compounds in the anatase type can be described in three of the *translationengleich* subgroups of $I4_1/amd$ — $I\bar{4}m2$, $I4_1md$ and $Imma$ —leading to three different structural variants. Density-functional total energy calculations indicate an ordered anionic arrangement in space group $I4_1md$ for the host lattice. With each Mg^{2+} cation incorporated, three nitrogen anions have to be replaced by oxygens. Because of thermodynamical reasons, the excess oxygen segregates next to magnesium, thereby forming local MgO “domains”. As a consequence, the perturbation of the anionic sublattice is limited to the nearest neighborhood of the dopant, such that, for small dopant amounts, the statement of anionic ordering appears to be sustainable. For Mg contents $>5 \text{ cat\%}$, a rutile-type structure appears as a minor phase due to a decreasing energy difference between the two structural variants.

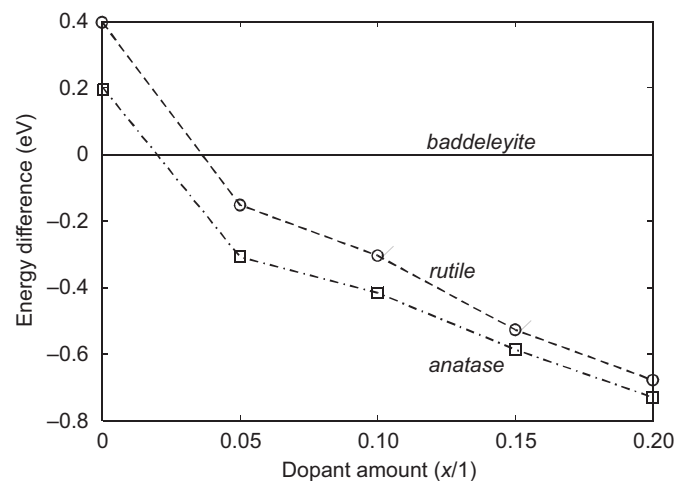


Fig. 6. Differences in total energy for Mg-doped TaON in several polymorphs, each in its most stable arrangement.

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