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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 TaO_3N_3 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 $I4_1md$, no. 109) of the host lattice, which is locally disturbed around Mg^{2+}. 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 ($\geqslant$10%), minor phases of rutile-type structure have to be expected, which is in good agreement with experimental data.

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 $VO_2(B)$-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, ZrO_2-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 ZrO_2, 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 $\approx 150\,^{\circ}C$. 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 $Mg_xTa_{1-x}O_{2.5-1.5x}$ 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 FULLPROF 2000 [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, self-consistency was achieved with a $12\,k$ 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/Å.

Table 1
Structural parameters for anatase-type $Mg_{0.05}Ta_{0.95}O_{1.15}N_{0.85}$ 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 $Mg_{0.05}Ta_{0.95}O_{1.15}N_{0.85}$ 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	4*b*	0	1/4	3/8	0.95/0.05	0.34(3)
O/N	8*e*	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.

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, $Ta(O_2N_2)ON$) 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 ± 1 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