Tailoring of an unusual oxidation state in a lanthanum tantalum(IV) oxynitride via precursor microstructure design

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Perovskite-type oxynitrides hold great potential for optical applications due to their excellent visible light absorption properties. However, only a limited number of such oxynitrides with modulated physical properties are available to date and therefore alternative fabrication strategies are needed to be developed. Here, we introduce such an alternative strategy involving a precursor microstructure controlled ammonolysis. This leads to the perovskite family member LaTa(IV)O2N containing unusual Ta4+ cations. The adjusted precursor microstructures as well as the ammonia concentration are the key parameters to precisely control the oxidation state and O:N ratio in LaTa(O,N)3. LaTa(IV)O2N has a bright red colour, an optical bandgap of 1.9 eV and a low (optically active) defect concentration. These unique characteristics make this material suitable for visible light-driven applications and the identified key parameters will set the terms for the targeted development of further promising perovskite family members.
In spite of the growing interest in perovskite materials, the number of oxynitride members is still limited. Most oxynitrides contain metal cations in $d^0$ or $d^{10}$ electronic configuration\textsuperscript{4–8}, whereas alternative materials with B-site cations in e.g. $d^1$ configuration such as Ta$^{4+}$ are largely lacking. However, the latter could allow access to different electronic band structures, thus, expanding the applicability of perovskite-type oxynitrides in visible light-driven processes. The negligible number of known perovskite-type oxynitrides might be attributed to the reaction protocols normally used. Currently, the most widely used synthesis technique for this material class is the ammonolysis of oxides\textsuperscript{9,10}. This procedure enables tuning of the electronic bandgap via (partial) substitution of oxygen by nitrogen. Typically, the bandgap decreases, making the formed perovskite-type oxynitrides AB(O,N)$_3$ interesting for visible light-driven applications\textsuperscript{11–14}. An important task in order to identify perovskite-type oxynitrides is the exact determination of the O:N ratio which often causes difficulties\textsuperscript{11,12}.

The precursors are often mixtures of crystalline binary oxides (e.g. La$_2$O$_3$ or Ta$_2$O$_5$)\textsuperscript{13,14,17} or ternary oxides (e.g. LaTaO$_3$)\textsuperscript{14,15}, which are either prepared by solid state reactions (SSR) or via a Pechini method. The latter allows mild reaction conditions providing excellent product homogeneity\textsuperscript{2}. In the case of LaTa(V)ON$_2$, most studies involve a high-temperature treatment of the oxide precursors prior to ammonolysis, leading to high crystallinity of the precursors\textsuperscript{13,14,16,17}. The formation of several perovskite-type oxynitrides such as LaTiO$_2$N and SrTaO$_2$N from crystalline oxide precursors has been described by a topotactic reaction scheme\textsuperscript{18}. In contrast, the reaction behaviour of amorphous/nanocrystalline oxide precursors is still unclear and the detailed ammonolysis mechanism has yet to be clarified\textsuperscript{1}. A better understanding and control of essential reaction steps might help to develop new synthesis strategies. Furthermore, a target-oriented electronic configuration of the B-site cation and the precise adjustment of the O:N ratio in oxynitrides are the key factors to generate various interesting physical properties.

In this in situ and ex situ experimental study, we override the above-mentioned strong topotactic relation between oxide precursor and resulting LaTa(O,N)$_3$ formation through a considered selection of well-characterised oxide precursors with different microstructures and an adjusted ammonia concentration. Furthermore, we demonstrate the formation of the LaTa(V)O$_2$N utilising nanocrystalline lanthanum tantalum oxide (n-LTO), which exhibits smaller primary particles (nm-range) and a higher specific surface area than microcrystalline LaTaO$_4$ (m-LaTaO$_4$). This adjusted precursor microstructure leads to a favoured Ta reduction in n-LTO. In contrast, ammonolysis of larger primary particles in the μm-range (m-LaTaO$_4$) results in conventional LaTaO(V)ON$_2$. Hence, we expand the experimental toolbox by an additional method to access further requested perovskite-type oxynitride family members.

Results

In situ ammonolysis of lanthanum tantalum oxides. First, the reaction steps of the LaTaO$_2$N (Fig. 1) synthesis were investigated by in situ ammonolysis (10 vol% Ar in NH$_3$) using thermogravimetric analysis (TGA). For a better comparability, similar measurement conditions were selected for both in situ and ex situ ammonolysis (see below). Nanocrystalline lanthanum tantalum oxide (n-LTO) and microcrystalline LaTaO$_4$ (m-LaTaO$_4$) were synthesised as precursors in order to investigate the effect of the microstructure on the reaction behaviour (synthesis and characterisation details in Supplementary Note 1, Supplementary Fig. 1–5 and Supplementary Tables 1–4).

The TGA curve of n-LTO during in situ ammonolysis (Fig. 2) reveals several mass changes, the origin of which were determined by termination experiments. The initial mass change of −0.7% in the range of 25 °C to 588 °C (region I) can be assigned to the desorption of residual water or organic contaminants, which is why the precursor remains white (Fig. 2).

The subsequent larger mass change of −2.9% (region II) is accompanied by a local mass minimum at 844 °C. At this temperature, the powder is black and the powder X-ray diffraction (PXRD) pattern shows the onset of crystallisation. In addition, hot gas extraction (HGE) reveals a composition of LaTaO$_{4.4}$N$_{0.14}$ (product of the termination experiment at 844 °C) with an assumed ratio of La:Ta=O = 1:1.4 (HGE results are listed in Supplementary Table 5). Therefore, region II (between 588 °C and 844 °C) is characterised by an oxygen vacancy formation with simultaneous nitrogen incorporation. According to literature\textsuperscript{19,20}, LaTaO$_4$ crystallises in space group $A_2$$_1$m up to around 800 °C and exhibits octahedron chains with corresponding interspace (Fig. 1). Therefore, we assume that vacancy formation and nitrogen incorporation takes place in this interstitial region.

At the same time, the colour-change of the powder from white to black indicates a reduction of the contained Ta. As can be shown by X-ray photoelectron spectroscopy (XPS), heating to 844 °C in ammonia atmosphere causes the two existing Ta(V)–O binding characters in n-LTO (Fig. 3a, n-LTO) to change their character. The evaluation of the Ta(V)–O binding characters in n-LTO and m-LaTaO$_4$ is described in Supplementary Note 4. The two new binding energies of the Ta 4f$_{7/2}$ orbitals in LaTaO$_{4.4}$N$_{0.14}$ (between 588 °C and 844 °C) is characterised by an oxygen vacancy formation in addition to ammonolysis. In this case, oxidation state and the binding energy in the point charge approximation\textsuperscript{1} concur with simultaneous nitrogen incorporation. Therefore, the oxygen vacancy formation in addition to nitrogen substitution. Therefore, the binding energy $E_B$(Ta 4f$_{7/2}$) = 25.2 eV can be allocated to a Ta(V)–O binding character since the original binding energy lowers by the expected $\Delta E_B$ = 0.3 eV. The other Ta 4f$_{7/2}$ binding energy of Ta (V), however, shifts from 26.7 eV in n-LTO to 24.4 eV in LaTaO$_{4.4}$N$_{0.14}$, the difference being much higher than $\Delta E_B$ = 0.3 eV. This might be explained by a change of the Ta oxidation state in addition to nitrogen substitution. Therefore, the binding energy $E_B$(Ta 4f$_{7/2}$) = 24.4 eV can be assigned to a Ta (IV)–O binding character. The Ta (IV)–(O,N) binding character can be determined by applying the point charge model\textsuperscript{20,21} assuming that the atomic potential of Ta remains unaffected by a change of the oxidation state. Ta(0) at $E_B$(Ta 4f$_{7/2}$) = 21.9 eV\textsuperscript{22} and Ta(V) at $E_B$(Ta 4f$_{7/2}$) = 25.3 eV in m-LaTaO$_4$ (P2$_1$/c) (instead of $E_B$(Ta 4f$_{7/2}$) = 25.9 eV in m-LaTaO$_4$ (Cc2/m)) were selected as references (Fig. 3b). The selection of the Ta(V) binding energy was based on the similar interatomic distances in and between the [TaO$_6$]$^{2-}$ octahedron together with the amount of neighbouring ions of Ta compared to the respective oxynitride ([Ta(O,N)$_4$]$^{2-}$ octahedron). Thus, due to the linear relationship between the oxidation state and the binding energy in the point charge model, a Ta oxidation state of 4 + ($d^0$ electronic configuration) at $E_B$(Ta 4f$_{7/2}$) = 24.4 eV was determined (Fig. 3b).

A further mass change of +1.0% occurs in the temperature range of 844 °C to 891 °C (region III). Simultaneously, the colour of the powder changes from black to ochre. The weight fractions at 891 °C determined by HGE amount to 13.7 wt% O and 6.7 wt% N (compared to 14.4 wt% O and 1.5 wt% N at 844 °C).
However, the total mass increase due to the strong nitrogen enrichment accompanied by only a small oxygen loss cannot be explained by a simple refill of the previously generated oxygen vacancies in “LaTaO₄”, since the total anionic weight fraction substantially exceeds the calculated maximum value of 16.7 wt% for “LaTaO₄” (Supplementary Table 5). Evaluation of the respective powder pattern shows that the ochre-coloured phase is not fully crystallised (Supplementary Note 6 and Supplementary Fig. 6) suggesting the formation of a nitrogen-rich intermediate (proposed composition: LaTa(O,N,□)₄:(N₂)ᵢ). Such intermediates are well-known from reoxidation experiments of several other oxynitrides including LaTiO₂N. The XPS measurement (Fig. 3a, n-LTO, NH₃/ 891 °C) again reveals a chemical shift of the Ta 4f7/2 binding energy from 24.4 eV (Ta(IV)–(O,N)) to 24.0 eV (Ta(IV)–N). This indicates an increased nitrogen content in the chemical environment of Ta and, hence, in the whole sample. The other Ta(V)–(O,N) binding character at Eₚ(Ta 4f7/2) = 25.1 eV (previously 25.2 eV) remains unchanged. A further temperature increase to 950 °C (region IV) leads to an abrupt mass change of −6.9%. During the following 10 h ammonolysis prior to cooling to 25 °C the mass remains near-constant. The respective termination experiment indicates a colour change from ochre to red after the 10 h ammonolysis. HGE of the red phase reveals a composition of LaTaO₁.₄₄(1)N₁.₆₃(9). This phase is further transformed to red LaTaO₁.₂₆(9)N₁.₈₃(4) by a second heating cycle under ammonia at 1000 °C for 14 h. Such intermediate compositions during the synthesis of LaTa(O,N)₃ are often reported in literature when large amounts of oxide precursors are used or the applied precursor has been crystallised at around 1000 °C before the ammonolysis. Additionally, a large sample amount can cause inhomogeneous exposure to the reducing species during ammonolysis. The positive and negative mass changes observed during the heating and cooling steps seem to be caused by desorption and adsorption of gaseous species (e.g. H₂O and/or NH₃). The nitrogen content of both red phases falls short of that of LaTaON₂, revealing that n-LTO is susceptible to the reduction of tantalum (Ta⁵⁺ to Ta⁴⁺). The usage of m-LaTaO₄ as a...
precursor for in situ ammonolysis results in LaTaON$_2$, neither involving intermediate phases nor reduction of Ta(V) to Ta(IV) (no black powder indicating a reduction). Instead, the initial formation of oxygen vacancies (yellow LaTaO$_{3.87(7)}$)$^\square_{0.12(3)}$i s followed by a one-step mass change of $\Delta m = -5.5\%$ (onset at 820 °C) indicating the conversion to LaTaON$_2$ (Fig. 4).

To be more precise, the in situ ammonolysis of m-LaTaO$_4$ starts with a mass change of $-0.5\%$ between 25 °C and 820 °C (Fig. 4). According to the PXRD results of termination products, the crystal structure of m-LaTaO$_4$ remained unchanged in this temperature range. However, a colour change from white (25 °C) to yellow (820 °C) indicated the conversion to LaTaON$_2$ (Fig. 4).

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During oxygen vacancy formation and subsequent nitrogen incorporation they connect to the neighbouring chains in a “zipper-type” manner\(^1^8\). However, the microstructure of n-LTO is different and exhibits thereby a “soft” topotactic relation to the resulting oxynitride along the interspace of the octahedron chains (Fig. 1) inducing a faster reduction of Ta(V) to Ta(IV). Afterwards, a “soft” topotactic reaction with a simultaneous “zipper-type” octahedral connection\(^1^8\) enables the aforementioned filling of oxygen vacancies by nitrogen.

The lower nitrogen content of LaTa(O,N)\(_3\) in comparison to LaTaON\(_2\) when using n-LTO for in situ ammonolysis can be explained by the specific surface area and the primary particle size and, thus, the microstructure of the oxide precursors. The specific surface area of n-LTO is \(S_{\text{BET}} = 7\ \text{m}^2/\text{g}\) (primary particle size: nm-range) and that of m-LaTaO\(_4\) \(S_{\text{BET}} = 2\ \text{m}^2/\text{g}\) (primary particle size: \(\mu\text{m}-\text{range}\)). Further details about the oxide precursors can be found in Supplementary Note 1. The higher surface area and the smaller primary particle size of the nanocrystalline precursor compared to m-LaTaO\(_4\) makes it more susceptible to Ta reduction, since the diffusion of reducing agents is simplified (at higher temperatures NH\(_3\) decomposes into nitrogen- and hydrogen-containing species and molecular hydrogen\(^9\)). A detailed explanation of the interaction of the reducing species with n-LTO can be found in the Supplementary Note 7: Reduction of Ta. This is confirmed by the finding that in situ ammonolysis of n-LTO that has been previously converted to m-LaTaO\(_4\) also leads to LaTaON\(_2\) (Fig. 5 and Supplementary Note 2).

Moreover, scanning electron microscopy (SEM) images of the termination products of the annealing process of n-LTO in syn.
air prior to in situ ammonolysis (Fig. 6a) show a continuous microstructural change with increasing temperature leading to a morphology very similar to m-LaTaO₄ (Fig. 6c).

In parallel, the onset temperature of the ammonolysis reaction steadily increases from 588 °C to 820 °C with increasing primary particle size and crystallinity (n-LTO to m-LaTaO₄, Figs 2, 5 and 6). Hence, a well-designed microstructure allows to enable or suppress significant Ta reduction.

**Ex situ ammonolysis of lanthanum tantalum oxides.** Eventually, in situ ammonolysis of n-LTO did not deliver LaTaO₂N which might be attributed to the less reductive atmosphere caused by the 10 vol% Ar in NH₃ needed to protect the device. The application of nearly 100 vol% instead of 90 vol% NH₃ in a classical thermal gas flow ammonolysis setup turned the in situ into an ex situ ammonolysis. The ex situ ammonolysis only slightly differs from the in situ setup with respect to the sample environment. Using the same temperature profile as in the in situ ammonolysis and an NH₃ flow rate of 300 mL/min we finally converted n-LTO into bright red LaTaO₁.₉₈(₇)N₀.₉₈(₅) (SBET = 25 m²/g) after 10 h at 950 °C via ex situ ammonolysis (anionic composition obtained by HGE, Supplementary Table 6). However, when using the microcrystalline instead of the nanocrystalline precursor for ex situ ammonolysis with the same temperature profile and ammonia flow as in in situ ammonolysis, purple-coloured LaTaO₁.₀₅(₃)N₂₀₂(₃) is obtained (very similar to the in situ ammonolysis product). This indicates a very similar parameter selection in ex situ and in situ ammonolysis. Considering the results of all in situ and ex situ ammonolysis

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**Fig. 6** SEM images of the termination products of all in situ ammonolysis studies. a Precursor conversion from n-LTO to m-LaTaO₄ in synthetic (syn.) air prior to ammonolysis. b SEM images of the termination products of in situ ammonolysis of n-LTO and c SEM images of the in situ ammonolysis of m-LaTaO₄. The temperatures mark the termination temperature at which the products were observed. Scalebar of the SEM images: 1 µm.
experiments, we have identified the reduction sensitivity due to structural differences and the ammonia concentration as main parameters to adjust the O/N ratio in LaTaO(N)3.

The aforementioned red LaTaO1.98(7)N0.98(5) and the purple LaTaO1.06(3)N2.02(3) phases prepared by ex situ ammonolysis are subjected to a second ex situ ammonolysis cycle (same temperature profile as in situ ammonolysis) with KCl flux addition in order to heal possible defects. After the second cycle the compositions slightly change to a bright red LaTaO1.97(3)N1.02(5) (5µE= 8 m²/g) and to purple LaTaO0.99(1)N2.00(9) (5µE = 3 m²/g), respectively. LaTaO1.97(3)N1.02(5) (LaTaO(N)) reveals less vacancies compared to LaTaO1.98(7)N0.98(5) (obtained from first cycle) indicating a defect healing effect via KCl flux. Additionally, a reoxidation study (Supplementary Note 8, Supplementary Fig. 7 and Supplementary Table 7) validated the formation of LaTaO2N.

Table 7) validated the formation of LaTaO2N. XPS measurements of LaTaO1.97(3)N1.02(5) and LaTaO0.99(1)N2.00(9) obtained by ex situ ammonolysis (Fig. 3c, survey spectra cf. Supplementary Note 9, Supplementary Fig. 8) show significant differences of the Ta oxidation states between both compounds. The data reveal a Ta(IV)–d differenced orbital character with a certain amount of Ta(III)–(O,N) in LaTaO1.97(3)N1.02(5) and a Ta(V)–(O,N) and a Ta(III)–(O,N) binding character in LaTaO0.99(1)N2.00(9) (Fig. 3b and Supplementary Table 8). Since the binding energy at E_B(Ta 4f2/3) = 24.4 eV in LaTaO1.97(3)N1.02(5) corresponds to that in LaTaO4.44(0)N0.41(2) [114.10(9)], the same binding character due to a similar chemical environment ([Ta(ON)x]16– octahedron) can be assumed. However, the fitted binding energy E_B(Ta 4f2/3) = 25.0 eV in LaTaO0.99(1)N2.00(9) reveals a Ta(V)–(O,N) binding character which can be explained by a simple chemical shift of 0.3 eV to lower binding energies due to nitrogen substitution (m-LaTaOx, E_B(Ta 4f2/3) = 25.3 eV (P2/3/c)). The Ta(III)–(O,N) binding character is the result of the reducing conditions during ammonolysis favoring the reduction of Ta on the surface compared to the bulk. XPS is highly surface-sensitive owing to the small mean free path of photo-emitted electrons. Therefore, the concentrations of Ta(IV)–(O,N) and Ta(V)–(O,N) in the bulk are assumed to be higher than on the surface. The Ta(III)–N binding character in LaTaO0.99(1)N2.00(9) at E_B(Ta 4f2/3) = 22.9 eV is attributed to the secondary phase TaN since the reference binding energy of this nitrride is E_B(Ta 4f2/3) = 23.0 eV. Additionally, XPS measurements of LaTaO2N (LaTaO1.97(3)N1.02(5)) also confirmed the absence of Ta(III)–(O,N) in LaTaO2N (LaTaO1.97(3)N1.02(5)) which also confirmed the absence of Ta(III)–N (observed, however, in LaTaO2N (LaTaO1.99(1)N2.00(9))) eliminating the possibility of a 1:1 mixture of Ta3+ and Ta5+ in LaTaO2N.

Investigations of the magnetic properties of LaTaO2N and LaTaO2N by superconducting quantum interference device (SQUID) measurements were carried out in order to confirm the presence of Ta4+ although challenging due to the presence of magnetic impurities such as Ta3+ as observed from XPS analysis (Fig. 3) and the in general limited knowledge about the magnetism of 5d transition metal compounds (compared to their 3d counterparts). The respective zero field cooled (ZFC) curves at 500 Oe down to 2 K are shown in Supplementary Note 10 and Supplementary Fig. 9. The low temperature regions (below ~70 K) can be described by a paramagnetic Curie–Weiss-like behaviour with very small effective moments (1.3 × 10−5 µB/Ta at 2 K for the LaTaO2N sample and 9.8 × 10−5 µB/Ta for the LaTaO2N sample, respectively) pointing to an activation of magnetic impurity states rather than an intrinsic materials property. The effective magnetic moment is further drastically reduced at increasing temperature. Overall the observed magnetisation is much lower than 1 µB/Ta as expected from the simplest paramagnetic model. The small magnetic moment and the fact that Ta is a 5d element suggests that the largely extended 5d orbitals in LaTaO2N are strongly hybridised and overlapping with the O/N 2p orbitals leading to weakly localised electrons hampering the up-built of a significant magnetisation. It is well-known for 3d transition metal containing perovskites AB03 and ABF3 that with decreasing electronegativity of the anion the hybridisation (or in other words the covalency of the B–X bond) is enhanced resulting in the aforementioned stronger delocalisation of the electrons and hence the spin. We believe the same is valid for 5d transition metal containing perovskites. Besides, two further factors could contribute diminishing the effective magnetic moment: (i) the spin–orbit coupling being expected to be much stronger in 5d than in 3d materials, (ii) the experimentally observed presence of stretched octahedra (Supplementary Note 11 and Supplementary Table 9e) results in a splitting of the initially degenerated t2g levels. This splitting leads to the formation of four-fold degenerated 5d-orbital states lower in energy than the initial state only occupied by one electron, making it difficult to develop magnetic ordering.

Phase purity of LaTaO2N is proven by high resolution (HR)-PXRD. LaTaO2N has already been reported in the space groups Imma and C2/m,27,32,33 and both are considered for LaTaO2N as well. Since we have observed no clear evidence for a monoclinic distortion and the Imma space group gives a slightly higher magnetic moment than C2/m, we propose Imma as space group for LaTaO2N. The same applies to LaTaON2 (Supplementary Fig. 10 and Supplementary Table 9 for complete crystal structure analysis). The unit cell volumes of LaTaO1.97(3)N1.02(5) (Vcell = 264.78(3) Å3) and LaTaON2 (Vcell = 264.68(2) Å3) are very similar. The slightly larger unit cell of LaTaO2N can be explained by the increase of the effective ionic radius of Ta from 0.64 Å (Ta5+) to 0.68 Å (Ta4+), leading to a contraction of the unit cell. Furthermore, LaTaO2N is phase pure, while in LaTaON2 a small amount of Ta2N5 (Cmcm) was detected through HR-PXRD (Supplementary Fig. 10b and Supplementary Table 9d). Since XPS reveals TaN on the surface and HR-PXRD Ta2N5 in the bulk, a nitrogen gradient combined with a decreased susceptibility for the reduction of Ta from Ta5+ to Ta3+ can be assumed. However, TaN can also be amorphous or the amount below the HR-PXRD detection limit.

Scanning electron microscopy gives insight into the morphology of the oxynitrides synthesised by ex situ ammonolysis. LaTaO2N shows primary particles in the nm-range, while LaTaON2 exhibits porous and sintered particles in the µm-range (Fig. 7a).

In addition to the determination of the specific surface area (Supplementary Table 10), an increased pore formation in LaTaO2N during ammonolysis can also be confirmed by comparing the SEM images of the oxides with its respective oxynitride. Furthermore, the particle size increases during ammonolysis of n-LTO, whereas m-LaTaO4 the particle size remains constant (Fig. 6c). The respective SEM images of the oxides can be found in the SI (Supplementary Fig. 2c).

As the colours of the obtained oxynitrides differ from each other, diffuse reflectance spectroscopy (DRS) measurements were performed. The data – converted to Kubelka–Munk curves (Fig. 7b) – show a difference of ΔEg = 0.1 eV between the optical bandgaps of the LaTaO2N (1.9 eV) and LaTaON2 (1.8 eV). Detailed investigation shows that the Kubelka–Munk curve of LaTaO2N converges to zero in contrast to that of LaTaON2, indicating a much lower optically active defect concentration. In addition, after the optical bandgap of Eg = 1.8 eV an intensity increase as observed for LaTiO3N36, which exhibited undesired defects was not detected for LaTaO2N. LaTaO2N possess an unusual colour (bright red), which has been expected to be darker (bluish) due to the reduction of Ta5+ to Ta4+. Additionally, the larger optical bandgap of LaTaO(IV)2N compared to LaTa(V)ON2 is noticeable. Based on both observations, we assume a larger
crystal field splitting for LaTaO$_2$N caused by the $d^1$ state of Ta$^{4+}$, since Ta is coordinated in a distorted octahedral environment (Jahn–Teller effect$^{31}$) indicated by bond length analysis via Rietveld refinements. Specific visible light-driven applications require materials with appropriate defect concentrations$^{38-40}$ and suitable bandgaps$^{41-43}$. Therefore, LaTaO$_2$N could be an interesting candidate for further investigations in this application field.

Discussion

In this in situ and ex situ ammonolysis study the key parameters to tailor the oxidation state and to synthesise a perovskite family member LaTa(IV)O$_2$N containing unusual Ta$^{4+}$ were identified. The oxynitride has an optical bandgap of 1.9 eV, a bright red colour, and a low optically active defect concentration providing promising physical properties for light-driven applications. The formation of LaTa(IV)O$_2$N is boosted by the oxide precursor’s microstructure (primary particle size, specific surface area and crystallinity) and the ammonia concentration (nearly 100%). In previous studies, the ammonolysis mechanism was already investigated and mostly clarified for the topotactic case. The findings shown here make a substantial contribution to the elucidation of the ammonolysis mechanism in general and to that of amorphous/nanocrystalline oxide precursors in particular. This opens up new perspectives and possibilities for the synthesis of further perovskite-type oxynitrides.

Methods

Synthesis of LaTaO$_2$N and LaTaON$_2$. The oxynitrides LaTaO$_2$N and LaTaON$_2$ were prepared from the respective nanocrystalline and microcrystalline oxide precursors (cf. Supplementary Methods) via thermal ammonolysis (synthesis of the respective oxides is described in the SI). The precursor oxides (200 mg) were transferred to an alumina boat and ammonolysed at 950 °C for 10 h with a NH$_3$ gas flow rate of 300 mL/min (Westfalen AG, > 99.98%). A second ammonolysis step together with KCl flux (Roth, ≥ 99%, Ph. Eur.) was carried out in a 1:1 weight ratio of sample and flux at 1000 °C for 14 h.

Sample characterisation. In order to clarify the phase purity and crystal structure of the produced oxides and oxynitrides, powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku Smartlab powder X-ray diffractometer using Cu-K$_\alpha$$_2$ radiation. To avoid a contribution of Cu-K$_\beta$ radiation a thin nickel foil as filter was used (efficiency is ~90%). The continuous scan covered an angular range of 10° ≤ 2θ ≤ 90° with an angular step interval of 0.02°. For selected oxide and oxynitride samples additional high-resolution synchrotron radiation PXRD measurements were performed at the beam line ID22 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The powders were filled into 0.7 mm diameter Kapton® capillaries (wavelength, see specific refinements). The collected diffraction data were evaluated via Rietveld refinements$^{44,45}$ using FullProf$^{2}$$^{46}$. A pseudo-Voigt function was selected to describe the reflection profile and the background was linearly interpolated between a set of background points with refinable heights. The anionic composition of the oxynitrides were fixed according to the respective compositions determined by HGE because the virtually equal form factors make it impossible to discriminate between O$^2-$ and N$^3-$ by means of X-rays. O and N were statistically assigned to the two independent crystallographic sites.

The chemical composition of the produced samples was investigated via inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Spectro Ciros CCD ICP-OES instrument for cations and hot gas extraction technique (HGGE) using an Eltra ONH-2000 analyser for the anions.

The investigation of oxynitride formation from nanocrystalline and microcrystalline oxides and the reverse reaction of LaTaO$_2$N to the corresponding oxide was performed by thermogravimetric analysis (TGA) using a Netzsch STA 449 F3 Jupiter. In situ ammonolysis experiments were carried out under flowing NH$_3$ (80 mL/min NH$_3$ + 8 mL/min Ar) on an alumina plate with a heating rate of 10 °C/min up to 1000 °C. To protect the TGA device from corrosion the measurements were performed in 10 vol% Ar in NH$_3$. A fast cooling rate of 40°C/min was used to successfully quench the intermediates since the mass changes observed by TGA and HGE were in good agreement. Reoxidation was carried out on an alumina plate under flowing synthetic air (20.5 vol% O$_2$ in N$_2$, Westfalen AG, 50 mL/min) to study the anionic composition of LaTaO$_2$N. The sample was first heated up to 200 °C and maintained at this temperature for half an hour to remove surface adsorbed water. Thereafter, heating was continued up to 1400 °C at a heating rate of 10 °C/min. The temperature was maintained for 2 h in order to achieve full conversion of oxynitride to respective single-phase oxide. TGA-MS to determine possible organic residues in n-LTO was carried out with a Netzsch STA 409 Jupiter coupled with a GAM 200 (InProcess Instruments) mass spectrometer. The oxide was heated to 1200 °C at a rate of 10 °C/min in a crucible under syn. air. (20.5 vol% O$_2$ in N$_2$, Westfalen AG, 50 mL/min) and then cooled down to 25 °C.

X-ray photoelectron spectroscopy (XPS) on LaTaO$_2$N, LaTaON$_2$, n-LTO, m-LaTaO$_4$ and termination products was carried out to investigate the oxidation states using a Thermo VG Theta Probe 300 XPS system from Thermo Fisher Scientific. The incident beam provided monochromatic and micro-focused Al K$_\alpha$ radiation and a spot size of 400 μm. The powders were fixed on a carbon tape and a flood gun was used to avoid charging effects. For background subtraction a Shirley-type inelastic background was utilised and the zero-shift correction was done by normalizing the measured C 1s peak to 284.5 eV. The peak fitting was implemented by carefully considering quantum mechanical requirements for the intensity and energy relations of Ta 4f$_{7/2}$ and Ta 4f$_{5/2}$ orbitals with $\Delta E_F$= 1.91 eV$^{25}$ and identical full width at half maximum (FWHM) for both orbital contributions.

The morphology of the produced oxynitrides and oxides was analysed via scanning electron microscopy (SEM) (ZEISS GeminiSEM 500, 5 kV). The ienis-detector was used for imaging.

UV-visible diffuse reflectance spectra (DRS) were obtained using a Carry 5000 UV–VIS NIR spectrophotometer. The baseline was measured with BaSO$_4$. The spectra were recorded in the range of 200–800 nm. The Kubelka–Munk$^{35}$ conversion was applied to the obtained reflectance spectra and the optical bandgap was estimated by extrapolating the onset of absorption to the abscissa.

The specific surface area was obtained via nitrogen sorption, first annealing the sample at 120 °C to remove adsorbed water. Adsorption and desorption isotherms were collected at liquid nitrogen temperature using an Autosorb-1-MP (Detection limit: $S_{BET} > 1$ m$^2$/g) from Quantachrome Instruments. The specific surface area was determined via the Brunauer–Emmett–Teller$^{47}$ (BET) method.

SQUID measurements to investigate the magnetic behaviour of Ta in LaTaO$_2$N and LaTaON$_2$ were carried out with a commercial VSM MPM3S Superconducting Quantum Interference Device (SQUID) from Quantum Design. For zero field cooling (ZFC) measurements the magnetic field was set to 500 Oe.

Fig. 7 SEM images and Kubelka–Munk curves of ex situ-prepared LaTaO$_2$N and LaTaON$_2$. a SEM images of LaTaO$_2$N and LaTaON$_2$ show the different morphologies of the materials in the μm-range. Scalebar of the SEM images: 1 μm. b Kubelka–Munk curves of LaTaO$_2$N and LaTaON$_2$ together with the respective powder images. The bright red colour indicates a much lower optically active defect concentration compared to LaTaON$_2$.

LaTaO$_2$N

LaTaON$_2$
Data availability
The authors declare that all other data supporting the findings of this study are available within the paper and its Supplementary Information.

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Competing interests
The authors declare no competing interests.

Additional information
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