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Perovskite-related oxynitrides – Recent developments in synthesis, characterisation and investigations of physical properties

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ABSTRACT

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Since the first investigations of perovskite type oxynitrides with the generalised composition $ABO_{3-x}N_x$ about twenty years ago, these compounds have become of growing interest. The incorporation of nitride ions in the perovskite lattice results in distinct changes in the electronic structure leading to unusual physical properties. In this article we report on new synthesis techniques, different analytical methods, progress in the structural characterisation by comprehensive diffraction techniques and local spectroscopic methods like XAS and NMR as well as state of the art theoretical investigations. Various physical characteristics like electrical and thermal transport parameters and dielectric properties are described. The thermal and chemical stability of oxynitride perovskites are investigated and their applications in different photocatalytic reactions are discussed.

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1. Introduction

The effect of substitutions on structure, physical and (thermo-) chemical properties of perovskite-related oxides has been studied intensively since decades. Most of the work focuses on cationic substitutions. Changes in the anionic (i.e. oxygen) sub-lattice mostly refer to vacancies. These oxygen vacancies may be randomly distributed or may lead to new ordered structures like the well-known Brownmillerites $ABO_{2.5}$. Anionic substitutions, i.e. the replacement of oxygen ions by other anions are by far less well examined. Such substitutions can, on the other hand, strongly alter the properties of perovskites due to different charges and differences in the ionicity of the metal–anion bond. For geometrical reasons only a limited number of elements may substitute oxygen ($r_{O^{2-}} = 1.4 \text{ \AA}$), namely fluorine ($r_{F^-} = 1.3 \text{ \AA}$) and nitrogen ($r_{N^{3-}} = 1.5 \text{ \AA}$). The introduction of larger anions like Cl^- usually results in layered compounds of, for example, the Ruddlesden–Popper type, in which the large anions occupy an interlayer position.

Perovskites (and other oxides) in which parts of the oxygen is replaced by nitrogen are commonly called *oxynitrides* and therefore this term will be used throughout this contribution. Within the last two decades oxynitride perovskites have been identified as a highly fascinating class of new materials. To the best of our knowledge, nitrogen-substituted perovskites were first reported by Marchand and co-workers in 1986 [1] although the same group already described the preparation of the Ruddlesden–Popper type oxynitride Nd_2AlO_3N in 1982 [2]. A review of early reports on these materials is given in [3]. The general preparation route for oxynitrides is the reaction of oxides with ammonia gas at temperatures around 1000°C .

Oxynitride perovskites are known for some main group metals like magnesium or aluminium and for the early transition metals Ti, V, Zr, Nb, Ta, Mo and W. At the required preparation temperatures the late transition element cations are reduced to the corresponding metals. In fact the reducing potential of ammonia, which can partly be explained by the decomposition to nitrogen and hydrogen, is a serious problem even for many of the early transition metals like titanium.

Most of the known oxynitride perovskites possess (distorted) cubic structures. In addition, some Ruddlesden–Popper type oxynitrides are known. Examples of the $A_2B(O,N)_4$ structure type ($A_{n+1}B_nO_{3n+1}$ with $n = 1$) are $A/B = Sr/Ta, Ba/Ta, Sr/Nb$ and Nd/Al [2,4–6]. To the best of our knowledge the only $n = 3$ oxynitrides are $Sr_3Nb_2O_5N_2$ [7] and $Li_2LaTa_2O_6N$ [8]. A list of known oxynitride perovskites is given in Table 1 (see also [9]).

Besides the academic interest, oxynitride perovskites are interesting for several potential technical applications. While oxide perovskites are generally either black or colourless, many oxynitrides exhibit bright colours. In addition oxynitride perovskites are often very stable towards chemicals like acids. Many of them can even be treated with boiling aqua regia without noticeable degradation. Furthermore, they are temperature-stable in air up to

several hundred degrees Celsius. The intense colour of oxynitride perovskites together with their chemical and thermal stability has led to the suggestion of using these materials as inorganic pigments [10]. For example the solid solution of $CaTaO_2N$ and $LaTaO_2N$ was found to exhibit colours ranging from yellow to red. To date cadmium-based pigments are generally used for such colours. Although these pigments are not toxic due to their very low solubility, their use has lately been strongly restricted in the European Union, based on the precautionary principle, taking into account that the toxic cadmium may become bio-available for instance during waste combustion. For this reason there exists an increasing demand for new, non-toxic pigments. Although oxynitrides based on tantalum are too expensive for mass-products, the above-mentioned $Ca_{1-x}La_xTaO_{2-x}N_{1+x}$ compounds clearly show the feasibility of this approach.

Another possible application for oxynitrides is their use as photocatalysts. It has, for example, been shown that $LaTiO_2N$ can be used in photocatalytic water splitting reactions [11]. Although the activities of the so far investigated compounds were rather low, it seems likely that a systematic screening may recover more active oxynitrides. Especially the fact that their colour can easily be tuned by suitable substitutions makes perovskite-based oxynitrides highly interesting for such applications.

Within the Priority Research Program *Substitutional Effects in Ionic Solids*, funded by the *Deutsche Forschungsgemeinschaft* (DFG) in the period 2002–2008, different groups investigated experimental and theoretical aspects of this fascinating class of compounds. This work aims at giving a summary of the obtained results in the context of recent international research activities.

2. Synthesis methods

2.1. General aspects

Since the nitride ion (N^{3-}) has a higher charge than the oxide ion (O^{2-}), the incorporation of the former in the anionic lattice must be accompanied by a charge compensation process. The following possibilities come to mind:

- generation of oxygen vacancies, e.g. $ABO_3 \rightarrow ABO_{3-3x/2}N_x$
- co-substitutions in the anionic sub-lattice, e.g. $ABO_3 \rightarrow ABO_{3-2x}N_xF_x$
- co-substitutions of cations, e.g. $A^{+2}BO_3 \rightarrow A^{2+}_{1-x}A'^{3+}_xB^{3+}_xO_{3-x}N_x$ or $AB^{3+}O_3 \rightarrow AB^{3+}_{1-x}B'^{4+}_xO_{3-x}N_x$
- oxidation of one of the cations (generally B), e.g. $AB^{3+}O_3 \rightarrow AB^{3+}_{1-x}B'^{4+}_xO_{3-x}N_x$
- reduction of the number of anions, e.g. $ABO_{3+x/2} \rightarrow ABO_{3-x}N_x$

Please note that (iv) becomes identical with the second line of (iii) if $B' = B$.

While (i)–(iv) preserve the perovskite structure, in (v) the perovskite is formed during the reaction from a complex oxide

Table 1

Perovskite-related oxynitrides reported in the ICSD and Scopus databases, their space groups and synthesis methods.

Compound	Space group	Synthesis method	Ref.
LaZrO ₂ N	<i>Pnma</i>	La ₂ Zr ₂ O ₇ (citrate), NH ₃ , 1273 K	[12]
LnTiO ₂ N (<i>Ln</i> = La ³⁺ , Nd ³⁺)	$\bar{1}\bar{1}$ (La ³⁺), <i>Pnma</i> (Nd ³⁺)	Ln ₂ Ti ₂ O ₇ , NH ₃ , 1223 K	[12,13]
Sr _{1-x} La _x TiO _{3-x} N _x	<i>Pm</i> $\bar{3}$ m – $\bar{1}\bar{1}$	Sr _{1-x} La _x TiO _y , NH ₃ , 1223 K	[14]
Ba _{1-x} La _x TiO _{3-x} N _x	–	Ba _{1-x} La _x TiO _y , NH ₃ , 1223 K	[14]
LaVO _{3-x} N _x (<i>x</i> = 0–0.9)	–	LaVO ₄ , NH ₃ , 1973–1073 K	[15]
LaNbON ₂	–	La ₂ Nb ₂ O ₈ , NH ₃ , 1223 K	[13]
CaNbO ₂ N	<i>Pnma</i>	Ca ₂ Nb ₂ O ₇ (citrate), NH ₃ , 1003 K	[16]
SrNbO ₂ N	<i>I4/mcm</i>	SrCO ₃ –Nb ₂ O ₅ –flux, NH ₃ , 1223 K	[17]
Sr ₂ NbO ₃ N	<i>I4/mmm</i>	SrCO ₃ –Nb ₂ O ₅ , NH ₃ , 1173–1323 K	[6]
Sr ₃ Nb ₂ O ₅ N ₂	–	SrCO ₃ –Nb ₂ O ₅ , 1173–1323 K	[6]
BaNbO ₂ N	<i>Pm</i> $\bar{3}$ m	BaCO ₃ + Nb ₂ O ₅ , NH ₃ , 1273 K	[18]
Ba _{1-x} Sr _x TaO ₂ N	<i>Pm</i> $\bar{3}$ m	BaTaO ₂ N–SrTaO ₂ N, NH ₃ , 1123 K	[19]
LnTaON ₂ (<i>Ln</i> = La ³⁺ → Dy ³⁺)	–	Ln ₂ Ta ₂ O ₈ , NH ₃ , 1223 K	[13,20]
LaTaON ₂	<i>C2/m</i>	La ₂ Ta ₂ O ₈ –flux, NH ₃ , 1173–1273 K	[21]
Ca _{1-x} La _x TaO _{2-x} N _{1+x}	<i>Pnma</i> – <i>C2/m</i>	CaCO ₃ –La ₂ O ₃ –Ta ₂ O ₅ –flux, NH ₃ , 1123 K	[10]
CaTaO ₂ N	<i>Pnma</i>	CaCO ₃ –Ta ₂ O ₅ –flux, NH ₃ , 1173–1273 K	[21]
SrTaO ₂ N	<i>I4/mcm</i>	SrCO ₃ –Ta ₂ O ₅ –flux, NH ₃ , 1173–1273 K/SrO–TaON, N ₂ , 1773 K	[22,4]
Sr ₂ TaO ₃ N	<i>I4/mmm</i>	SrCO ₃ –Ta ₂ O ₅ , NH ₃ , 1173–1223 K/SrO–TaON, N ₂ , 1773 K	[4,5]
BaTaO ₂ N	<i>Pm</i> $\bar{3}$ m	BaCO ₃ –Ta ₂ O ₅ , NH ₃ , 1173–1223/TaON + BaO, N ₂ , 1773 K	[4,18]
Ba ₂ TaO ₃ N	<i>I4/mmm</i>	BaCO ₃ –Ta ₂ O ₅ , NH ₃ , 1173–1223 K/BaO–TaON, N ₂ , 1773 K	[4]
LnWO _{3-x} N _x (<i>Ln</i> = La, Nd)	–	Ln ₂ W ₂ O ₉ , NH ₃ , 973–1173	[23]
LaWO _{0.4} N _{2.6}	$\bar{1}\bar{4}$	La ₂ W ₂ O ₉ , NH ₃ , 973–1173	[24]
EuWO _{1.58} N _{1.42}	<i>Pm</i> $\bar{3}$ m	Eu ₂ W ₂ O ₉ , NH ₃ , 1073–1173	[25]
SrWO _{1.7} N _{1.3}	<i>Pm</i> $\bar{3}$ m	SrWO ₄ , NH ₃ , 1223 K	[26]
SrWO ₂ N	<i>Pm</i> $\bar{3}$ m	SrWO ₄ , NH ₃ , 1173 K	[27]
SrMoO _{2.6} N _{0.4}	<i>Pm</i> $\bar{3}$ m	SrMoO ₄ , NH ₃ , 1073 K	[28]
SrMoO _{2.5} N _{0.5}	<i>Pm</i> $\bar{3}$ m	SrMoO ₄ , NH ₃ , 1123 K	[27]
AZr _x Ta _{1-x} O _{2+x} N _{1-x} (<i>A</i> = Ba ²⁺ , Sr ²⁺ , Ca ²⁺)	<i>Pm</i> $\bar{3}$ m, <i>Pcmn</i>	A–Ta–Zr sol–gel, NH ₃ , 1273 K	[29]
A _{0.5} La _{0.5} TaO _{1.5} N _{1.5} (<i>A</i> = Ca ²⁺ , Sr ²⁺ , Ba ²⁺)	<i>Pnma</i>	La ₂ O ₃ ACO ₃ , Ta ₂ O ₅ , NH ₃ , 1273 K	[30]
BaSc _{1/3} Ta _{2/3} O _{8/3} N _{1/3}	<i>P2₁/n</i>	BaCO ₃ –Sc ₂ O ₃ –Ta ₂ O ₅ , NH ₃ , 1273 K	[9]
LaMg _{1/3} Ta _{2/3} O ₂ N, LaMg _{1/2} Ta _{1/2} O _{5/2} N _{1/2}	<i>P2₁/n</i>	La ₂ O ₃ –MgO–Ta ₂ O ₃ , NH ₃ , 1143 K	[9]
Ln ₂ AlO ₃ N (<i>Ln</i> = La ³⁺ , Ce ³⁺ , Pr ³⁺ , Nd ³⁺ , Sm ³⁺ , Eu ³⁺)	<i>I4mm</i> (La ³⁺)	Ln ₂ O ₃ –AlN, N ₂ , 1623 K	[2,31]

precursor, which typically already has a perovskite-related layered structure. A typical example is the formation of LaTiO₂N from LaTiO_{3.5}, which will be described in more detail below.

The different electronegativities of the anions (3.50 for oxygen and 3.07 for nitrogen) lead to differences in the covalency of the cation–anion bond. As will be discussed in the following, the more covalent metal–nitrogen bonding results in reduced band gap, changing both the optical and electrical properties.

In the above-listed reaction schemes (i)–(v), complex oxides act as reaction educts. These oxides may be crystalline or amorphous. In addition, the formation of oxynitrides may also start from mixtures of binary oxides or carbonates, like in the following example

Whether the direct reaction from oxides/carbonates or the two-step reaction from preliminary obtained complex oxides is more advantageous needs to be checked in every case. Furthermore, the addition of low-melting alkali halides as mineraliser was often found to be helpful [21,22,32,33].

A suitable nitriding agent is required to synthesise oxynitrides. Molecular nitrogen (N₂) would be an ideal reagent. However, its triple bond (N≡N) is one of the strongest in nature ($\Delta H_{\text{diss}}^0 = 946 \text{ kJ mol}^{-1}$). Therefore, in most of cases the direct reaction between N₂ and oxides requires a too high activation energy. It was also shown experimentally that H₂/N₂-mixtures do not promote effective nitridation [3].

Ammonia (NH₃) is the most widely used nitriding reagent. The corresponding reaction between a suitable solid precursor and gaseous ammonia is usually referred to as (thermal) ammonolysis. It is normally carried out at atmospheric pressure and temperatures of 600 °C < *T* < 1200 °C.

A partial decomposition of ammonia takes place at the surface of the oxides, forming active nitriding species (N, NH, NH₂) and

molecular hydrogen [34]. The latter reacts with the lattice oxygen to form water, while nitrogen is introduced into the lattice.

The formation of thermodynamically stable molecules such as water ($\Delta G_f^0(1000) = 192.603 \text{ kJ mol}^{-1}$) and carbon dioxide ($\Delta G_f^0(1000) = -395.865 \text{ kJ mol}^{-1}$) (in the case of carbonates as agents) as well as the overall entropy increase are the main driving forces of the ammonolysis. H₂O and CO₂ are removed from the reaction equilibrium by the gas flow in the reactor thus preventing the back reaction.

At equilibrium conditions, the ammonia formation equilibrium constant K_f^0 can be expressed by partial pressures (*p*) or mole fractions of N₂, H₂ and NH₃:

$$K_f^0(T) = \frac{p(\text{NH}_3)}{p^{3/2}(\text{H}_2)p^{1/2}(\text{N}_2)} = \frac{16}{\sqrt{27}} \frac{x}{(1-x)^2} \quad (1)$$

where *x* is the mole fraction of undissociated NH₃.

The solution of this equation allows obtaining a temperature dependence of partial pressures of N₂, H₂ and NH₃.

Above 300 °C (the temperature region, where most of the oxynitrides have been synthesised) ammonia is mostly dissociated into N₂ and H₂ (Fig. 1), which are not effective nitriding sources. Therefore, it is important to work under non-equilibrium conditions by increasing the ammonia flow with temperature. Another advantage of a high ammonia flow is the faster water removal (reducing the partial pressure of water) and the renewal of active nitriding species over the sample.

The kinetics and reaction mechanism of the ammonolysis have not yet comprehensively been explored. We investigated the nitridation by thermal analysis under different heating and stationary temperatures by thermogravimetry (TG).

From the TG signals shown in Fig. 2 it can be concluded that the ammonolysis proceeds via reaction intermediates, the formation and composition of which differs depending on the cationic

Fig. 1. Temperature dependence of equilibrium partial pressures of gaseous NH_3 , H_2 and N_2 .

composition of the compounds. A first weight loss at temperatures below 1000°C is probably caused by local reduction processes. An intermediate, formed in the following weight increase, was quenched for *ex-situ* spectroscopic examination. Raman scattering experiments depicted in Fig. 3 revealed the presence of dinitrogen ($\text{N}\equiv\text{N}$) bonded to Ti, similar to the situation observed in the reoxidation of oxynitrides [16].

For perovskite type oxynitrides synthesis methods other than the ammonolysis have quite rarely been reported. $\text{Sr}_2\text{TaO}_3\text{N}$, SrTaO_2N , $\text{Ba}_2\text{TaO}_3\text{N}$ and BaTaO_2N were prepared by reaction of TaON and the alkaline earth oxides under nitrogen [4]. Nitrogen-doped $\text{NaTaO}_{3-x}\text{N}_x$ was obtained from $\text{Ta}_2\text{O}_5-x\text{N}_x$ and NaOH under hydrothermal conditions [35]. $\text{Nd}_2\text{AlO}_3\text{N}$ was prepared by the reaction of AlN and Nd_2O_3 [2]. A high-pressure reaction of BaO_2 and NbN resulted in BaNbO_2N [36].

Although the thermal ammonolysis was successfully applied for most of the known perovskite oxynitrides this reaction has some serious disadvantages. Like all solid-state reactions the ammonolysis requires a large number of diffusion steps and high temperatures to activate the diffusion. At these high temperatures ammonia partly decomposes to nitrogen and hydrogen, leading to reductions as undesired side-reactions. In addition, gas exchange between the solid and the ammonia is a limiting factor, sometimes resulting in samples, which have reacted at the surface only. In turn several ammonolysis steps with intermediate regrindings have to be done.

The obvious way to improve the ammonolysis is therefore to reduce the required diffusion steps and to enhance the exchange

Fig. 3. Raman spectra of reaction intermediates formed during ammonolysis of $(\text{La,Ca})\text{TiO}_{3+\delta}$ compounds at 950°C .

rate between the solid and the gas atmosphere. The latter problem was successfully addressed by the construction of rotating tube furnaces. Such rotating tube furnaces can be based on rotary evaporators that (instead of the usual flask) rotate a quartz or alumina reactor. This reactor is placed in a furnace and cold ammonia gas is injected by a smaller inner tube directly onto the powder, which is effectively mixed by the rotation of the reaction cavity. The use of the rotating tube furnace was found to be advantageous in many cases and helped to significantly reduce the reaction time [33,37–39].

2.2. Soft-chemistry reactions

The problem of diffusion can be reduced by different *soft-chemistry* approaches. This term (adopted from the French *chimie-douce*) generally covers all methods to prepare solids under mild conditions [40,41].

2.2.1. Citrate route

One synthetic procedure that has widely been used in recent years is the so-called *Pechini*-method. Its basic idea is to stabilise an (aqueous) solution of the desired cations by citric acid or other hydroxy-carboxylic acids. Due to the high complexing potential of these acids the dissolved metal salts are prevented from precipitation when the solvent is evaporated. In many cases diols are added as network builders, resulting in stable polymerised organic

Fig. 2. Ammonolysis reaction of (La,Ca) titanates studied by thermogravimetry.

Fig. 4. XRD patterns of an amorphous La/Ti oxide before and after ammonolysis. The latter has been shifted for clarity.

Fig. 5. Selected area electron diffraction of LaTiO_2N obtained by the citrate precursor route.

gels, which contain the metal cations. After drying of the gels the organic matrix is burned, yielding amorphous oxides. These oxides are often highly reactive since they contain the different metals already mixed on an atomic scale, making extended diffusion steps obsolete. In addition, no stable crystal lattice is formed, easing the movement of the different ions. In Ref. [16] we have compared the classical ammonolysis of oxide/carbonate mixtures with the ammonolysis of amorphous oxides prepared by a modified Pechini-method. It was found that for oxynitrides of the type ABO_2N ($A = \text{Ca}, \text{Sr}, \text{Ba}$; $B = \text{Nb}, \text{Ta}$) the nitridation takes place at lower temperatures and/or is completed after a shorter time when amorphous oxides are used. Fig. 4 shows as an example the formation of LaTiO_2N from an amorphous oxide precursor prepared by the Pechini-method. From the X-ray diffraction data it can be seen that the single phase is already obtained after one ammonolysis step of 24 h at 950°C . Applying the Scherrer equation, typical particle sizes of roughly 20 nm are found. Similar results were also obtained for other compounds, proving that oxynitrides with small particles sizes and considerable surface areas are obtained when the ammonolysis of the amorphous oxide precursors is carried out at mild temperatures. Such materials are interesting in the (photo-) catalytic investigations described later.

To prove that the peak broadening really results from small crystallite sizes and not from a low crystallinity of the material selected area electron diffraction (SAED) measurements were performed. Fig. 5 shows the diffraction patterns of the above-discussed LaTiO_2N along different zone axes. The high local crystallinity is evident.

The specific surface area of these nanocrystalline oxynitrides was investigated by the BET method with nitrogen as adsorbed gas.

In the left frame of Fig. 6 the adsorption isotherm for LaTiO_2N is shown. The middle frame gives the BET surface calculated from five data points with $0.05 < p/p_0 < 0.3$. The obtained value of roughly $40 \text{ m}^2/\text{g}$ is typical for many samples we prepared by the Pechini-method. From the BET isotherm a hysteresis between the adsorption and desorption branch can also be seen. Such a hysteresis is characteristic for porous materials. The pore size distribution function shown in the right frame of Fig. 6 indicates a maximum pore radius of 100 Å, showing that the obtained samples are mesoporous. Again, similar values were also found for other samples. The porous structure of LaTiO_2N sample can also be seen from the scanning electron micrograph depicted in Fig. 7. The large surface area and high porosity of the amorphous oxide precursors favour the gas exchange and in turn contribute to the enhanced reactivity of these materials.

To study the nature of the amorphous oxide obtained from the decomposition of the citrate precursor, X-ray absorption spectroscopy was used. Due to the proximity of the Ti–K and La– L_{III} edges no EXAFS evaluation could be carried out. Nevertheless, the XANES region of the material already provided valuable information. Comparing the edge structure of the amorphous precursor with the binary titanium oxides rutile and anatase remarkable differences are evident (Fig. 8). In contrast, the XANES structure of the decomposed precursor closely resembles the one of the crystalline $\text{LaTiO}_{3.5}$ obtained by a classical solid-state synthesis. The only considerable difference between the two spectra is a broadening and a slight energy shift of the post-edge features for the precursor. From this finding it can be concluded that the thermal decomposition of the La/Ti-citrate precursor leads to a material in which

Fig. 6. BET isotherm of LaTiO_2N prepared by a soft-chemistry reaction (left), calculated BET surface (middle) and pore radii distribution (right).

Fig. 7. SEM micrograph of LaTiO_2N prepared by a modified Pechini-synthesis.

titanium already possesses a similar local surrounding as in crystalline $\text{LaTiO}_{3.5}$. On the other hand, the intermediate formation of binary titanium oxides can be ruled out. This finding is in remarkable contrast to other systems like (substituted) LaCoO_3 , for which our EXAFS investigations clearly proved the formation of the binary oxide Co_3O_4 upon decomposition of a La/Co-citrate gel.

2.2.2. Polyol-assisted co-precipitation

In contrast to the Pechini-method, in which precipitation is suppressed by the strongly chelating citric acid, the polyol synthesis uses less-strongly binding ligands that allow a controlled co-precipitation of the dissolved metal cations.

The polyol route has widely been used for the synthesis of metal nanoparticles but is by far less well established for the formation of complex oxides [42,43]. It starts from dissolving metal salts in a chelating polyalcohol ("polyol") at elevated temperatures. A hydrolysis agent is used to initiate the co-precipitation leading to amorphous or crystalline oxide nanoparticles. The polyol approach allows a size control, because the alcohol acts as a surface-capping agent avoiding agglomerations. On the other hand, it is in many cases difficult to adjust the final composition of the precipitated oxide when complex stoichiometries are desired because the different cations usually differ in their hydrolysis behaviour. Therefore, the composition of the precipitate does not always match the one of the solution. Also the choice of the appropriate hydrolysis agent is not trivial. In some cases atmospheric moisture is already sufficient, while in other cases larger quantities of water or even HNO_3 or KOH have to be added. A flow chart of the synthesis of LaTiO_2N nanoparticles by a polyol-assisted co-

Fig. 8. Ti–K XANES of a La/Ti-containing citrate precursor decomposed at 600°C in comparison to reference compounds.

precipitation is given in Fig. 9. The corresponding samples were used for photocatalytic investigations described in [44].

In a typical experiment 2 mmol of the A-cation nitrate (e.g. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and an equimolar amount of the B-alcoide (e.g. $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) were dissolved in 30–50 ml diethylene glycol (DEG) in a closed reaction flask under dry nitrogen atmosphere [44]. The mixture was heated to 120 – 130°C and stirred at this temperature for 1 h. To the obtained clear solution 0.5–2 ml of an appropriate precipitation solution (water, HCl - or NaOH -solution) was added. Afterwards the temperature was raised to 180°C and the reaction mixture was stirred for several hours until the hydrolysis of the DEG complexes was completed. After cooling the precipitate was separated from the diethylene glycol by centrifugation and washed with acetone several times. The obtained amorphous precipitate was heated to typically 800°C to burn the organic component and to form the crystalline oxide, which was afterwards ammonolysed.

While the primarily obtained amorphous particles showed little aggregation, a significant sintering was observed after calcination and ammonolysis. Fig. 10 shows a sample after nitridation at 1000°C for 3 h, presenting strong agglomeration. Nevertheless, this procedure resulted in samples with BET surface areas between 15 and $50\text{ m}^2/\text{g}$ and high crystallinity as can be seen from the high resolution TEM depicted in Fig. 10.

2.3. Microwave induced plasma reactions

A third possibility to improve the ammonolysis reaction is to increase the reactivity of ammonia. For this purpose nitridation reactions were carried out in an ammonia plasma. The corresponding device was developed in cooperation with R. Douthwaite from the University of York. A plasma is a high energetic gas containing ions, electrons and energetically excited particles. An ammonia plasma can easily be generated using a domestic microwave oven as demonstrated in [45,46]. It will be referred to as MIP (microwave induced plasma) in the following. Fig. 11 shows

Fig. 9. Flow chart of the polyol-assisted co-precipitation in the case of $\text{LaTiO}_{3.5}$ [44].

Fig. 10. TEM image of a LaTiO_2N sample obtained by the polyol route (reacted at 1000°C). The right of the figure shows a high resolution image of a sample ammonolysed at 800°C (modified from [44]).

a photograph of the experimental set-up. This set-up was later modified by introducing a brass wave guide similar to the one described in [45]. Such wave guides focus the microwave radiation and in turn lead to a more intense plasma. The output power was varied between 600 W and 900 W and a pressure of roughly 50 mbar was adjusted. The plasma is ignited when ammonia gas interacts with the electric component of the microwave field in the quartz reactor. A chain reaction is resulting in ionisation of a large mole fraction of the neutral species, leading to a violet plasma, which fills the reactor after 1–2 s.

The advantage of the MIP nitridation was demonstrated for different oxynitrides like LaTiO_2N , SrNbO_2N and SrTaO_2N . The preparation of LaTiO_2N from $\text{LaTiO}_{3.5}$ by MIP is depicted in Fig. 12. From the XRD pattern of the products after different reaction times it can be seen that already after three hours the nearly single phase oxynitride was obtained. The classical ammonolysis, on the other hand, requires at least one day to yield a product of comparable purity. The MIP nitridation can therefore help to strongly shorten the required reaction times and in turn helps to reduce the amount of ammonia gas needed. We are currently working on further improvements of the MIP set-up and an optimisation of the reaction conditions like gas flow, pressure and microwave power. Details of the results will be reported elsewhere.

2.4. Preparation of thin films

For technical applications like coloured or hard and corrosion resistant surface coatings or photoelectric cells etc thin films of

perovskite oxynitrides are required. To prepare such films several techniques have been reported. LaTiO_2N films were deposited by RF-magnetron sputtering in N_2/Ar , starting from $\text{LaTiO}_{3.5}$ targets [47] as well as from LaTiO_2N targets [48]. With increasing nitrogen concentration in the plasma, also the N-content in the films increase while at the same time the films become more polycrystalline [49]. By pulsed laser deposition (PLD) in ammonia, $\text{SrMoO}_{3-x}\text{N}_x$ films were successfully grown [50].

In our studies, we tried to grow thin films of $(\text{La,Sr})\text{Ti}(\text{O,N})_3$ by the PLD method directly from the corresponding oxynitrides. The desired nitrogen-substituted perovskite phases were actually obtained but the films had a coarse granular structure, did not cover the substrate homogeneously and showed inclusions of larger particles.

Because of these difficulties two alternative approaches were used to obtain thin films by PLD. On the one hand we first deposited oxide layers that were ammonolysed in a separate reaction step. On the other hand, ammonia or nitrogen were used as pulsed reactive gases to directly introduce nitrogen during the film ablation.

Thin films of $(\text{La,Sr})\text{Ti}(\text{O,N})_3$ were grown on STO and MgO substrates using the two-step procedure, i.e. deposition of oxide films with a subsequent ammonolysis. The oxide targets were pressed and sintered pellets of polycrystalline $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3+x/2}$ ($x = 0, 0.25, 0.50, 0.75, 1$) prepared by the citrate method. For the

Fig. 11. Photograph of the MIP apparatus using a domestic microwave oven.

Fig. 12. XRD pattern for the microwave induced plasma nitridation of $\text{LaTiO}_{3.5}$. After 90–120 min reaction time almost single phase LaTiO_2N was obtained.

Fig. 13. XRD pattern of a film grown by PLD indicating the highly epitaxial orientation. Asterisks mark a trace impurity of TiN.

ablation a KrF excimer laser (248 nm) was used, generating 30 ns pulses with a power of 800 mJ. 20 000 pulses were accumulated to grow films of approximately 350 nm thickness on either SrTiO₃ or MgO substrates. With a pressure of 1 mbar of N₂ the best plasma plume was achieved. The substrates were kept at 800 °C during ablation. These oxide films were afterwards nitridated at 950 °C for 3 h [51].

XRD investigations showed the films to grow highly oriented on the corresponding substrate (see Fig. 13). Small amounts of TiN as impurity phase were identified, especially when MgO substrates were used. From SEM investigations of the surface and the cross-section it was deduced that the films grown by PLD are very dense and show only a small surface roughness. The latter was quantitatively measured by AFM and found to vary between 5 and 15 nm and to decrease with increasing La/N content [51]. As one representative example Fig. 14 shows the AFM scan of the film with $x = 0.5$.

The direct deposition of oxynitrides by pulsed laser deposition of oxides in presence of a nitrogen source has been applied for SrTi(O,N)₃ films. Nitrogen was introduced by pulsed reactive crossed beam laser ablation (PRCLA). This technique is a variant of PLD, which uses a pulsed gas source synchronised with the laser. The gas pulse crosses the ablation plume, resulting in a higher plasma ionisation degree. N₂ was used as nitrogen source [52]. Epitaxial films with a roughness of a few nm and a maximum N:O concentration ratio of 3% were grown on MgO substrates.

In a modified set-up the PLD chamber was equipped with a RF plasma and pulsed reactive gas inlet to yield directly perovskite

Fig. 14. AFM image of a film with the composition Sr_{0.5}La_{0.5}TiO_{2.5}N_{0.5} prepared by pulsed laser deposition. The scanned area was 15 × 15 μm.

type titanium, and molybdenum oxynitrides [53]. N-substituted SrTiO₃ thin films were deposited in one step by PRCLA with nitrogen or ammonia gas pulses. The nitrogen content in the films deposited with ammonia was 3.5 times higher compared to the corresponding films deposited by classical PLD. The N-content in the films grown with ammonia gas pulse increased from 0.8 ± 0.3 to 4.1 ± 0.4 at.% with increasing the substrate temperature from 570 °C to 720 °C. All SrTiO₃:N films deposited by PRCLA as well as by classical PLD exhibited anionic deficiency accompanied by formation of Ti³⁺.

Nitrogen incorporation results in visible light absorption at the wavelength range of 367–460 nm. Optical absorption in this region increases gradually with increasing the N-content from 0.8 to 4.1 at.%. Films with higher UV–vis transparency in the range of 460–2000 nm were obtained for higher substrate temperatures, which is most probably due the lower Ti³⁺ content in the films. Ammonia gas pulses and high substrate temperatures (above 700 °C) were found to be favourable for deposition of SrTiO₃:N films for photocatalytic tests.

Deposition on LAO and STO substrates resulted in perfectly c-axis oriented films, whereas some of the films grown on MgO exhibit small (011) reflections, indicating imperfect out-of-plane orientation due to the relatively large lattice mismatch [54]. For the same reason, mosaicity (in-plane orientations distribution) of the studied SrTiO₃:N films increased in the following order STO < LAO < MgO. Films deposited in NH₃ gas pulse revealed a lower epitaxial quality compared to films grown with nitrogen or in vacuum.

All studied SrTiO₃:N films exhibited electronic conductivity due to the presence of Ti³⁺. The samples behave similar to SrTiO_{3-δ} single crystals, namely they reveal metallic behaviour of the resistance, and very high electron mobilities of up to 10⁴ cm² V⁻¹ s⁻¹ at temperatures below 10 K.

For deposition of films with high nitrogen contents and good crystallinity the PLD experimental conditions obtained from the model system SrTiO₃:N have been used. LaTiO_{3-x}N_x perovskite type thin films were successfully grown by PRCLA with ammonia and nitrogen gas pulses. Deposition on MgO substrates yielded films with mixed (112) and (001) out-of-plane orientations, whereas films grown on LAO exhibited only a (001) orientation along the c-axis. The N-content can be tuned within 0.47–0.72 by adjusting the deposition conditions. Ammonia gas pulses yielded films with more incorporated nitrogen. Also increasing the substrate temperature in the range of 600–700 °C resulted in an increase of the N-content.

SrMoO_xN_y perovskite type thin films were deposited by PRCLA with ammonia and nitrogen gas pulses. As for other systems, the ammonia gas pulse yielded films with more incorporated nitrogen. Increasing the substrate temperature in the range of 600–650 °C resulted in the increase of the N-content, whereas further heating above 650 °C led to a phase decomposition. The N-content could be varied from 0.54 to 1.07, while the oxygen content ranged within 1.50–2.30 depending on the used deposition conditions.

Since PLD requires a rather complex and expensive experimental set-up, we were also exploring other ways to synthesise thin films of oxynitride perovskites.

In a solution-based approach, we managed to prepare oxynitride films on SrTiO₃ substrates by the spin-coating technique, using polymeric precursor solutions of Sr_(1-x)La_xTi(O,N)₃ ($x = 0, 0.25, 0.50, 0.75, 1$) with a viscosity 5 mm²/s [55]. After deposition the films were dried at 120 °C on a hot plate and afterwards heated to 400 °C to burn out the organic component. This process was repeated several times to obtain a thickness of around 400 nm. Afterwards, the amorphous oxide films were ammonolysed at 950 °C, leading to the desired oxynitrides.

Fig. 15. SEM micrographs of oxynitride films prepared by the spin-coating technique. Left: surface of a $\text{Sr}_{0.25}\text{La}_{0.75}\text{TiO}_{2.25}\text{N}_{0.75}$; Right: Cross-section of $\text{Sr}_{0.5}\text{La}_{0.5}\text{TiO}_{2.5}\text{N}_{0.5}$ [55].

Fig. 15 shows SEM images of the surface of a LaTiO_2N film and of the cross-section of a film with $x = 0.5$. The cross-section proves a good connection between the film and the SrTiO_3 substrate, as well as a homogeneous thickness and smooth surface of the films. The latter was additionally investigated by atomic force microscopy (AFM) and was found to range from 3 to 10 nm [55]. The layered structure of the films visible in the cross-section results from the cyclic repetition of the spin-coating/burning procedure. It can additionally be seen that the oxynitride films grow as small granular particles. X-ray diffraction revealed a random orientation of the crystallites indicating that no topotactical information is transferred from the substrate to the film. While this may be undesirable for some applications, the spin-coating approach has the advantage of being cheap and applicable for large surfaces. In addition, the possibility to adjust the surface roughness is attractive for catalytical applications.

3. Chemical analysis

The precise determination of both cationic and anionic composition by complementary methods is of high importance since the physical properties of perovskite-related compounds are known to be altered by even slight modifications in the stoichiometry. Especially for oxynitrides the O/N content has a strong impact on the physical and chemical behaviour as described in the following chapters.

The anionic composition of the various oxynitrides was studied with thermal analysis methods like hotgas extraction and thermogravimetry as well as neutron diffraction (described in Chapter 4.3) and elastic recoil detection analysis (ERDA). In addition, a solution-chemical analysis method based on ion-specific electrodes has been developed. The cationic stoichiometry was investigated by energy dispersive X-ray spectroscopy (EDX) and X-ray Fluorescence Spectroscopy (XRF). Since the determination of the cationic composition is a general task and not special for oxynitrides, it will not be discussed here.

3.1. Thermochemical methods

The most commonly used analytical methods for O/N content determination are hotgas extraction and thermogravimetric (TG) analysis.

For the hotgas extraction of oxynitride powders, a commercial LECO TC500 analyser was modified to allow the accurate determination of both oxygen and nitrogen (Fig. 16). In the analyser an electrode impulse furnace rapidly heats the sample in a graphite crucible to very high temperatures, resulting in a complete carbo-thermal reduction of the oxynitride. The carbon oxide evolving during this process is measured quantitatively with an infrared

detector, while the formed nitrogen is quantified by a thermal conductivity detector.

Before the analysis, an empty, sealed and purged graphite crucible is placed between the two electrodes in the furnace. A high current passing through the crucible generates heat, which releases gases trapped in the graphite. After this out-gassing step, a small aliquot of sample (usually a few mg) is dropped from the loading mechanism into the crucible, which is heated by the high current to a temperature of approximately 3000 °C. The oxygen from the sample combines with carbon from the crucible to form carbon monoxide (CO) while nitrogen is released as N_2 . Driven by a constant gas flow of helium and/or argon the gases pass through a heated rare earth copper oxide catalyst, which converts CO to CO_2 . The sample gases then enter an infrared cell, which measures the concentration of the resulting carbon dioxide. After this first detection step, CO_2 is removed by an absorber (Lecosorb). The gas then passes through a thermal conductivity cell for the quantification of nitrogen. The hotgas extraction method allows accurate and simultaneous determination of oxygen and nitrogen in a rapid measurement procedure of around 3 min maximum. To obtain reliable results, the analyser was calibrated with SiO_2 and SiN as standards for oxygen and nitrogen, respectively [39].

In an alternative approach, thermogravimetric analysis (TG) can be used to determine the weight change of the samples during a controlled temperature program. These changes are accompanied by adsorption or evolution of various gases like O_2 , H_2O , CO_2 or N_2 . The gases can be identified by means of coupled mass spectrometry (MS) or spectroscopic methods like IR. Another advantage of the thermal analysis is that exo- or endothermic events in the samples can be detected by differential thermal analysis (DTA), i.e. measurements of the temperature difference between the sample and a reference as function of the reference sample temperature or as function of time.

Fig. 16. Sketch of the modified LECO TC500 analyser.

In most of our investigations, combined TGA/DTA/MS was used to study the thermal reoxidation of the oxynitrides in synthetic air of 5.0 purity ($\geq 99.9999\%$). These studies were performed in the temperature range of $25^\circ\text{C} < T < 1400^\circ\text{C}$ with heating rates of $2\text{--}10^\circ\text{C min}^{-1}$ with a gas flow rate of typically of 50 ml/min and using Al_2O_3 crucibles.

The perovskite type oxynitrides of transition metals with d^0 electronic configuration reoxidise upon heating in synthetic air according to equation (2):

The reoxidation process generally leads to d^0 -oxides as identified by X-ray diffraction. The amount of evolved nitrogen can be determined from the weight gain (Δm), measured during the reoxidation experiment and is used to quantify the nitrogen content (y):

$$y = \frac{\Delta m}{(3/2 M(\text{O}_2) - M(\text{N}_2))} \times \frac{M(\text{ABO}_{x+3y/2})}{m(\text{ABO}_{x+3y/2})} \quad (3)$$

where $M(\text{N}_2)$ and $M(\text{O}_2)$ are the molar masses of molecular nitrogen and oxygen. $M(\text{ABO}_{x+3y/2})$ and $m(\text{ABO}_{x+3y/2})$ are the molar mass of the formed oxide and its weight, respectively. It is to be noted that this simple formula can only be applied, if both the oxynitride and the obtained oxide are chemically well defined. As will be shown in Chapter 6, the oxynitrides in some cases contain significant amounts of chemically adsorbed CO_2 and H_2O . These species distort the results of both the hotgas extraction and the thermogravimetry and therefore should be minimised.

An extensive study on the O/N determination in oxynitride perovskites was performed on LaTiO_2N as model system [39]. The compositions $\text{LaTiO}_{2.06(2)}\text{N}_{0.96(1)}$ and $\text{LaTiO}_{2.075(3)}\text{N}_{0.95(2)}$ resulted from TGA data for the oxynitride compounds cooled in a nitrogen atmosphere and quenched in an ammonia atmosphere, respectively. This finding was in good agreement with the results obtained by hotgas extraction, leading to $\text{LaTiO}_{2.11(1)}\text{N}_{0.95(2)}$ for the cooled sample and $\text{LaTiO}_{2.10(3)}\text{N}_{0.97(3)}$ for the quenched sample.

In contrast, for samples slowly cooled under ammonia the weight gain in the TGA experiment was much smaller than expected, resulting in a value of only 0.75 for the nitrogen content. This result significantly differed from the composition $\text{LaTiO}_{2.11(2)}\text{N}_{1.10(1)}$ determined by hotgas extraction measurements. The deviations were assigned to the presence of small amounts of volatile impurities or the formation of carbonates/oxy-carbonates, which decompose in the same temperature range as the reoxidation. Another possible explanation would be a partial reduction of the transition metal. All these effects result in an underestimation of the nitrogen content, whereas the presence of transition metal nitrides leads to an overestimation of the nitrogen content.

The presence of impurities can be detected by coupling the TG system with a mass spectrometer or by applying IR or Raman spectroscopy. FTIR and Raman spectra of the LaTiO_2N samples revealed broad FTIR absorption bands in the region of $700\text{--}900\text{ cm}^{-1}$, which can be attributed either to CO_3^{2-} ($\nu_2 = 725\text{ cm}^{-1}$ and $\nu_4 = 850\text{ cm}^{-1}$) or to NO_3^- ($\nu = 800\text{--}850\text{ cm}^{-1}$). The most intense signals were observed for the samples cooled slowly under ammonia whereas the weakest signal was measured for the sample cooled under nitrogen [39]. It can therefore be concluded that phase pure oxynitrides can only be obtained by quenching rapidly to room temperature after ammonolysis or by changing the gas atmosphere at high temperatures after the reaction.

3.2. Ion beam analysis

Ion beams of particles with a kinetic energy in the MeV region were employed for the quantitative analysis of the elemental composition of oxynitrides, especially for samples prepared as thin films. Here the hotgas extraction and TGA analysis cannot be applied due to the small analyte mass. Rutherford backscattering (RBS) is a non-destructive and standardless analysis method for the surface and near surface regions ($0\text{--}2\text{ }\mu\text{m}$) of solids. It uses the recoil energies of accelerated ions (e.g. He or H) to determine the species and depth profiles of elements in a given sample. RBS is extremely useful when quantitative results are required in the absence of standards. A variation of RBS is ERDA (Elastic Recoil Detection Analysis), which also allows determining quantitatively the oxygen and nitrogen contents of oxynitride perovskites.

The RBS measurements were performed using a 2 MeV ^4He ion beam and a silicon surface barrier detector under 165° . The collected RBS data were simulated with the RUMP software [56]. The experimental uncertainty reflected in the cationic and anionic composition is $\pm 3\%$ and $\pm 5\%$, respectively. The N/O concentration ratio was obtained from elastic recoil detection analysis (ERDA). For the measurements a 12 MeV ^{127}I beam was used under 18° incident angle. The scattered recoils were identified by the combination of a time-of-flight spectrometer with a gas ionisation chamber. The experimental uncertainty in determination of the N/O concentration ratio by ERDA is ± 0.005 . ERDA was for example used for the analysis of polycrystalline $\text{La}_{1-x}\text{Ca}_x\text{O}_{2+x}\text{N}_{1-x}$ [33]. The obtained oxygen and nitrogen contents were in good agreement with the ones found by hotgas extraction.

The composition of nitrogen-doped strontium titanate ($\text{SrTiO}_3\text{:N}$) films prepared by pulsed reactive crossed beam laser ablation (PRCLA) was determined by combined Rutherford backscattering spectrometry (RBS) techniques [57]. The nitrogen content in the prepared $\text{SrTiO}_3\text{:N}$ films was determined by ERDA and normalised to the oxygen content [52]. Fig. 17 presents the relative N concentration as a function of different deposition parameters. The nitrogen-to-oxygen concentration ratio ($[\text{N}]/[\text{O}]$) increases with the laser fluence, reaching a maximum value of 0.03 ± 0.005 at a laser fluence of 6.0 J cm^{-2} , which corresponds to a nitrogen content of $\text{Sr}_{1.02}\text{Ti}_{0.98}\text{O}_{2.95}\text{N}_{0.089}$. The variation of the nitrogen content vs. the substrate temperature is presented in Fig. 17B.

As a second example for the chemical analysis of oxynitride thin films with high energetic ion beams Fig. 18 shows the SIMS (secondary ion mass spectrometry) depth profile of a $\text{La}_{0.75}\text{Sr}_{0.25}\text{Ti}(\text{O,N})_3$ film obtained by spin-coating and subsequent ammonolysis [55]. The samples were analysed by secondary ion mass spectrometry (Atomika instruments, ion microprobe 4100) applying an O_2^+ primary ion beam current of 65 nA. The interface between the oxynitride film and the SrTiO_3 substrate is clearly visible from the simultaneous sudden decrease of the La and N signals. SIMS therefore proves the incorporation of nitrogen over the entire film thickness. Similar results were also obtained for films prepared by pulsed laser deposition [51].

3.3. Wet chemical analysis

While the above-mentioned analytical methods require a considerable technical equipment, it was also found possible to determine the overall concentration of nitrogen in oxynitrides by an elegant solution-chemical analysis based on element-selective electrodes.

To measure the nitrogen content with an ion sensitive electrode it is necessary first to convert the nitrogen of the oxynitrides completely into ammonia. For this, batches of e.g. nitrogen-

Fig. 17. Variations of the relative nitrogen content in SrTiO₃:N films vs. the laser fluence (A), substrate temperature (B) [52].

containing barium titanate were heated under reflux with concentrated sulphuric acid and sodium sulphate until complete dissolution was achieved. After diluting the reaction mixtures with water, solid sodium hydroxide was added to yield a strongly alkaline medium (pH = 14). In a Kjeldahl-like distillation apparatus the reaction mixture was boiled and the ammonia containing distillate was collected in an aluminium sulphate solution. The ammonia content was measured with an ammonium ion sensitive electrode (Mettler Toledo), which was calibrated against a 1000 ppm NH₄⁺-solution. The results obtained by this procedure were compared to values from the hotgas extraction. A good agreement with a relative error of only $\pm 10\%$ was reached.

A similar approach was applied to estimate the fluorine content in BaTiO₃ powders prepared by the method of co-substitution in the anionic sub-lattice (see Chapter 2.1). Also for fluorine it is possible to use an ion sensitive electrode. To analyse fluorine- and nitrogen-containing barium titanate powders, the procedure of fluorine determination described by Tsuchiya [58] was applied. After dissolving the samples in a mixture of perchloric acid and hydrogen peroxide, phosphoric acid and hexamethyldisilazane were added. The resulting volatile trimethylfluorosilane was driven out of the reaction vessel by flowing argon and absorbed in a 1 mol/l sodium hydroxide solution. After adjusting the pH to 6–7 by sulphuric acid, the fluorine content was measured with a fluoride ion sensitive electrode (Mettler Toledo), which was calibrated using a 1000 ppm F⁻-solution. The accuracy of this method is estimated to be ± 0.03 weight%.

Fig. 18. SIMS analysis for a La_{0.75}Sr_{0.25}Ti(O,N)₃ film prepared by the spin-coating technique [55].

4. Structure

For oxynitrides the possible ordering of oxygen and nitrogen offers an additional degree of freedom compared to the pure oxides. The introduction of nitrogen reduces the local symmetry of the cations. For example, in oxynitrides of the composition ABO₂N, two out of six oxygen in each BO₆-octahedron are replaced by nitrogen. This leads to a reduction of the local symmetry from O_h to D_{4h} (trans arrangement of N) or C_{2v} (cis arrangement). The symmetry reduction may or may not be associated with changes in the local bond distances.

Furthermore, the question arises, whether the incorporation of nitrogen leads to a long-range ordered arrangement detectable by diffraction techniques or if it is averaged out. In the latter case, it is important to clarify on which length scale the ordering remains.

4.1. Theoretical studies on structure and bonding

Alkaline earth based Ta and Nb oxynitrides ABO₂N (A = Ca, Sr, Ba; B = Ta, Nb) should all form cubic perovskites because of their Goldschmidt tolerance factor being close to unity. On the other hand, different Ta–O and Ta–N bond lengths are expected due to the different nature of N and O, making tetragonal or orthorhombic distortions also possible.

The stability of BaTaO₂N in a cubic (*Pm* $\bar{3}$ *m*), a tetragonal (*I4/mcm*) and an orthorhombic (*Pnma*) polymorph was calculated using the framework of density-functional theory (DFT) using (a) the Vienna *ab-initio* Simulation Package (VASP), with plane-wave basis sets and ultra-soft pseudo potentials of Vanderbilt type and (b) the all-electron Linear Muffin-Tin Orbital (LMTO) theory in its tight-binding representation. The chemical bondings within the different possible structures were analysed by means of the Crystal Orbital Hamilton Population technique. Exchange and correlation were treated in the generalised-gradient approximation (GGA). In all plane-wave calculations, structural parameters were allowed to relax for sets of different cell volumes to give an *E*–*V* function fitted by the Birch–Murnaghan equation of state, yielding equilibrium volumes, energies and bulk moduli. Also, molecular-dynamics (MD) simulations were carried out with the aixCCAD code based on the bond-valence method and tabulated bond-valence parameters. The simulation box consisted of 1800 atoms (*T* = 300 K, 200,000 steps of 0.001 fs). Diffractional data were then simulated based on MD crystal coordinates. Further details are described in [59].

DFT showed that cubic BaTaO₂N is 30 kJ/mol less stable than tetragonal or orthorhombic BaTaO₂N (see Fig. 19). Although it has been argued that an O/N random cubic structure does gain

Fig. 19. Energy and volume per formula unit for cubic, tetragonal and orthorhombic polymorphs of perovskite type BaTaO_2N , each with an ordered O/N sub-lattice [59].

a maximum of 12 kJ/mol due to configurational entropy [60], such model would still be less stable than its orthorhombic competitor (with an ordered anionic sub-lattice) by more than 18 kJ/mol.

This striking tendency for lower symmetry was found for all oxynitride perovskites. Forcing the structure into cubic symmetry does not only lead to a massive loss in total energy but also to an increased bulk modulus. This observation reminds of similar experimental findings in the realm of oxide perovskites $\text{A}_2\text{M}^{3+}\text{TaO}_6$ and $\text{A}_2\text{M}^{3+}\text{NbO}_6$ [61]. Interestingly enough, the niobium compounds show larger cell volumes than their tantalum analogues, which is exceptional considering the almost identical ionic radii but consistent with the results obtained from experiment [22].

For a closer analysis, Fig. 20 visualises all Ta–O bonding interactions in BaTaO_2N . It is clear that the energetic ranking of the three polymorphs is simply a function of the Ta–O interactions reflected by the COHP analysis. While in *Pnma* (and also in *I4/mcm*) all occupied Ta–O states are bonding (spikes to the right), antibonding interactions (to the left) show up in *Pm3m* close to the Fermi level. This finding also explains the increased bulk moduli of the cubic model because the Fermi level will be forced even deeper into the antibonding region whenever pressure is applied.

Fig. 20. Crystal orbital Hamilton population (COHP) for the Ta–O interactions in three different possible polymorphs of BaTaO_2N . The Fermi level is given as the energy zero, and bonding/antibonding interactions are given by COHP spikes to the right/left [59].

The reason for the antibonding COHP shape is easily explained on the basis of molecular orbital calculations of a structural cut designated $[\text{Ta}(\text{OH})_4(\text{NH}_2)_2]^-$ which reflects the proper metrics of the extended cubic structure. Its HOMO is essentially Ta–O non-bonding but there are two lower, occupied orbitals just below, which are Ta–O antibonding. Even lower one finds another two orbitals with non-bonding Ta–O character but these are slightly repelling in terms of O–O interactions. Thus, the instability of the cubic model is a consequence of the Ta–O antibonding molecular (and crystal) orbitals. In contrast, all Ta–N interactions are bonding throughout the entire valence band. The extended structure is optimised in terms of Ta–N bonding, namely by allowing for short Ta–N bond lengths because the bonding of the nitrogen atom is much more covalent in character [62,63]. Alternatively expressed, the cubic *Pm3m* model forces all Ta–(O/N) bond lengths to be close to the one of Ta–N, thereby leading to an inferior Ta–O bonding. Because d^0 cations tend to prefer cis over trans metal–non-metal coordinations, it is important to emphasise that the above-mentioned COHP-based arguments also hold true for a cis type Ta–N coordination.

The energetic course of the different polymorphs also manifests from the calculated band gaps. Although it is impossible to calculate their exact size using DFT, it is perfectly reasonable to make a qualitative comparison with the experimental ones. In fact, the calculated band gaps are fairly close to the experimental ones only if based on distorted (i.e., tetragonal or orthorhombic) unit cells. Upon using cubic structures, their instabilities are mirrored by much smaller band gaps, a quasi-metallisation.

We now address the question of anionic ordering. Taking the orthorhombic *Pnma* type unit cell as the geometry to start with, there are two different anionic sites designated X1 and X2, and one may ask how O and N will distribute over these sites. DFT yields that the energetically most favourable structure is the one in which nitrogen completely moved to the X2 site. Likewise, the structural stability decreases whenever N occupies the X1 site, such that the anionic sub-lattice may be looked upon as a (partially) ordered one in which N and O share the X2 site and the X1 site is completely occupied with O. Thus, the real symmetry is even lower than *Pnma*. Symmetry investigations of the relaxed unit cell resolve three remaining symmetry elements (two mirror planes and one twofold rotation axis), which lead to space group *Pmc2₁*, a maximal non-isomorphic sub group of *Pnma*. Further supercell calculations show

Fig. 21. Calculated XRD patterns of an 1800 atom BaTaO₂N supercell with *Pmc*2₁ symmetry at absolute zero temperature (left) and after a molecular-dynamics simulation at 300 K (right) [59].

that a full anionic ordering leads to a stabilisation of more than 20 kJ/mol such that disordered structural models can be ruled out, a consequence of the fact that, once again, N prefers shorter bond lengths to Ta (or Nb) than O. Even assuming synthetic conditions of about 1000 K, the resulting entropy term $T\Delta S$ which results from N/O site mixing does not overcome this energy penalty. We may therefore summarise that DFT unambiguously predicts that perovskite type tantalum and niobium oxynitrides are most stable in the *Pmc*2₁ structure type with an ordered anionic sub-lattice. Why, however, has BaTaO₂N been described as a cubic phase on the basis of powder neutron diffraction? Adhering to the quantum-chemical result of a structure, which is locally orthorhombic and ordered in terms of O and N atoms, an explanation for the cubic appearance is offered based on a thermally averaged structural description. Such model is easily checked by a classical MD simulation of a sufficiently large supercell based on the calculated structural parameters.

After validation of the bond-valence parameterisation, total energy calculations were carried out for the quantum-chemically optimised ground-state structures of BaTaO₂N in space groups *Pm*3̄*m*, *I4/mcm* and *Pnma*. After structural relaxation at 300 K, thereby moving away from absolute zero temperature and allowing the atoms to get closer to the thermal average, the supercell and its relaxed geometry was then subjected to a Fourier transformation in order to generate an XRD pattern. The latter appears in good agreement with that of the real “cubic” compound (see Fig. 21). The

atomic vibrations appear as largely uncorrelated between different unit cells because the thermal averaging does not have to fulfill an unnecessary constraint of translational invariance. Looking at a rather larger “sample” on the order of 100 unit cells, the local orthorhombic symmetry is thus no longer maintained for the entire structure such that the material looks as if it was cubic.

4.2. X-ray absorption spectroscopy

Further evidence for a local symmetry reduction – especially for different B–N and B–O bond lengths – stems from X-ray absorption spectroscopy (XAS). As an example, the upper part of Fig. 22 depicts the absorption spectrum of SrTaO₂N in the range of the Ta–L_{III} and Ta–L_{II} edges. The extracted EXAFS function $\chi(k)k^2$ is shown in the lower panel of the figure while its Fourier transform is given in the right panel. The first coordination sphere, which corresponds to the Ta–(O,N)₆ octahedron, was fitted using various different models. In all trials the coordination number was fixed to six. In the simplest approach, the shell was described by 6 identical atoms. This resulted in an unusual large Debye–Waller factor. Including an anharmonicity (3rd cumulant) did not significantly increase the quality of the fit, indicating that the applied model was insufficient. For this reason, a two-shell model was used. Since in SrTaO₂N every Ta ion is surrounded by 4 oxygen and 2 nitrogen ions, two different distances were considered and the coordination numbers were fixed to 4 and 2, respectively. To reduce the number of free

Fig. 22. left: Normalised X-ray absorption spectrum of SrTaO₂N (top) and extracted k^2 -weighted EXAFS function (bottom). Right: Fourier transform and fit of the first coordination shell.

parameters, equal Debye–Waller factors and E_0 values were used for both shells, leading to the results listed in Table 2. The distances of the two backscattering shells differ significantly, i.e. about 0.1 Å. This finding is in excellent agreement with the theoretical calculations, which predicted Ta–N bonds to be 0.1 Å shorter than Ta–O bonds [59]. It is noteworthy that due to very similar backscattering amplitudes and phase shifts of oxygen and nitrogen the results remain basically identical regardless of the nature of the backscatterer. That is, we found two shorter and four longer bonds (with a difference of roughly 0.1 Å) for all possible atomic combinations (2 N + 4 O, 2 N + 4 N, 2 O + 4 O, and 2 O + 4 N).

The result of our EXAFS fit is in remarkable contrast to the bond distances derived from neutron diffraction. SrTaO₂N has been investigated by different groups and despite of differences in the space group and O/N ordering, almost equal Ta–(O,N) distances were found, with deviations of only 0.01 Å [4,19,21]. It can therefore be concluded that on a local scale the Ta–N distance is clearly shorter than the Ta–O distance, while on the larger scale relevant for diffraction experiments the differences average out.

Similar results were also found by Ravel et al. for BaTaO₂N [64]. In the Ta–L_{III} EXAFS, a broadening of the first coordination shell (Ta–(O,N)) was observed, which was fitted using a disordered model in which both the Ta–N and Ta–O distances have a significant spreading. On average, the Ta–N bonds were found to be roughly 0.1 Å shorter than the Ta–O bonds in accordance with our results for SrTaO₂N. The absence of any superstructure reflections in the XRD, ND and ED patterns was explained by a very short correlation length [64]. These EXAFS examinations are therefore a nice verification for the theoretical calculations of the previous chapter.

Lately, further evidence for deviations of the Ta–O and Ta–N bonds in BaTaO₂N was derived from a pair distribution function (PDF) analysis of the total neutron scattering [65]. While the Rietveld refinement of the diffraction data was in accordance with a cubic crystallographic symmetry, the PDF analysis supported a local cis arrangement in the TaO₄N₂ octahedra with a small displacement of the Ta ions towards the N atoms.

4.3. Neutron diffraction

While the above-mentioned results indicate that on an atomic scale there are significant differences between the B–O and B–N bonds, the question remains whether these differences may lead to a long-range anionic ordering, giving rise to a reduction of the crystallographic symmetry from the cubic perovskite structure (space group $Pm\bar{3}m$). Since the X-ray atomic form factors of O and N are nearly identical, the two elements cannot be distinguished by XRD. The neutron scattering lengths, on the other hand, are considerably different (5.803 fm for O and 9.360 fm for N). Therefore, neutron diffraction is the method of choice for these investigations.

The influence of synthesis parameters on the oxygen/nitrogen ordering in perovskite oxynitrides has not yet been investigated systematically. Nevertheless, contradictory results given in the literature indicate that different degrees of ordering may be achieved. For example for SrTaO₂N a complete oxygen/nitrogen

ordering was reported [21] while two other groups found a completely statistical anion distribution [4,19].

SrNbO₂N was chosen as model system for our own studies. This compound has been originally described as a cubic perovskite [11] on the basis of X-ray diffraction data. Our neutron diffraction data recorded at the HRPT at SINQ, Switzerland clearly proved a tetragonal superstructure with $a \approx 2^{1/2}a_p$ and $c \approx 2a_p$ (a_p being the corresponding cubic unit cell parameter). Three different samples were investigated. The first was obtained by ammonolysis of a mixture of SrCO₃ and Nb₂O₅ in the presence of KCl (which served as mineraliser). The second batch was prepared by ammonolysis of an amorphous oxide precursor obtained by the citric acid (Pechini) method. These two samples were allowed to slowly cool in the tube furnace. The third sample was also prepared by the citrate precursor route but quenched by quickly pulling the quartz reactor out of the rotating tube furnace and blowing a high flow of cold ammonia onto the oxynitride.

Details of the experimental procedure and the results for the flux-aided nitridation of the SrCO₃/Nb₂O₅ mixture have been reported in [17]. Rietveld refinements were carried out in space group $I4/mcm$. The metric of the unit cell was almost cubic with $c/2:a/2^{1/2} = 1.0039$ at room temperature. For this sample an additional low temperature measurement was carried out, indicating only minimal differences to the room temperature results [17].

Fig. 23 shows the Rietveld refinement for the quenched sample prepared by the citrate method. As can be seen the agreement of the fit is excellent. The tiny remaining intensity at $2\theta = 40.9^\circ$ belongs to the (110) reflection of the vanadium sample container. Selected crystallographic data are given in Table 3 and a plot of the structure is shown in Fig. 24. No restriction for the site occupation factors for oxygen and nitrogen were applied but both anionic positions were restrained to be completely occupied. The structures of the three samples under investigation are virtually identical. Their deviation from the ideal cubic perovskite mainly results from a rotation of the Nb(O,N)₆-octahedra around the c -axis and a slight anionic ordering (see Fig. 24). The axial anionic position contains more oxygen than expected. In contrast, more nitrogen than for a purely statistical distribution was obtained for the equatorial site. In this context it is noteworthy that for SrTaO₂N the opposite ordering was reported, i.e. an enrichment of nitrogen on the axial site [4].

The resulting total nitrogen content of 0.92(4) is slightly smaller than the expected value of 1 but within a 2σ limit agrees with the idealised composition SrNbO₂N. Surprisingly, the anionic ordering was found to be more pronounced for the quenched sample. One

Fig. 23. Rietveld plot of the ND refinement for a quenched SrNbO₂N sample (see text for details).

Table 2
Results of the Ta–L_{III} EXAFS fit for SrTaO₂N. Coordination numbers were fixed during the refinement.

Atom	N	R [Å]	σ [Å ²]	E_0 [eV]
O	4	2.0174(4)	0.0097(2)	4.16(5)
N	2	1.9268(26)	0.0097(2)	4.16(5)

Table 3Selected crystallographic data for SrNbO₂N. Space group *I4/mcm* (No. 140). Atomic coordinates: Nb (0, 0, 0), Sr (0, ½, ¼), O1/N1 (0, 0, ¼), O2/N2 (*x*, *x*–½, 0).

Sample	<i>a</i> [Å]	<i>c</i> [Å]	<i>x</i> (O2,N2)	Ratio O1/N1	Ratio O2/N2	N-content
Solid state reaction	5.7056(4)	8.1002(9)	0.7741(1)	0.85/0.15(2)	0.61/0.39(1)	0.93(3)
Pechini, slowly cooled	5.7091(5)	8.1065(8)	0.7742(2)	0.84/0.16(3)	0.62/0.38(2)	0.92(4)
Pechini, quenched	5.7062(4)	8.0949(9)	0.7730(1)	0.92/0.08(3)	0.58/0.42(2)	0.92(4)

would expect the rapid cooling to freeze in the random anion distribution at the high reaction temperature and thus more statistical site occupation factors. On the other hand, the total reaction time for this sample was longer than for the other two. This is a hint that rather the total ammonolysis time than the cooling speed controls the degree of anionic ordering.

Very similar results were also obtained for LaTiO₂N. For this material five batches prepared under different conditions (different starting materials, fluxes, total reaction times and cooling rates) were examined by neutron diffraction and refined in space group *Pnma*. The site occupation factors were found to be comparable for all samples. It is striking that for both SrNbO₂N and LaTiO₂N the preparation conditions apparently have no significant influence on the anionic ordering while for other oxynitrides like SrTaO₂N very different degrees of O/N ordering have been reported for samples prepared under deviating conditions.

A statistical arrangement of oxygen and nitrogen was also observed in two more systems we investigated. In SrMoO_{3–x}N_x, ammonolysis for 11, 48 and 72 h resulted in samples with *x* ≈ 1.0, 1.15, and 1.25. The cubic perovskite structure (space group *Pm3̄m*) was verified by neutron diffraction (Fig. 25) and no signs for an O/N ordering were found [37,38].

For the lately discovered CaMoO_{1.7}N_{1.3} an orthorhombic unit cell was found as shown by a splitting of the (110)_{*p*} diffraction peak (the index *p* refers to the cubic perovskite unit cell) and the presence of superstructure reflections in the ND data as well as in electron diffraction [66]. Rietveld refinement of the neutron diffraction in space group *Pbnm* indicated a random O/N distribution on the three distinct crystallographic sites. In addition, the three Mo–O/N distances were found to be very similar.

A revision of the results available in the literature shows that in the great majority of investigations complete statistical O/N distributions or only partial orderings were found. The samples investigated were oxynitrides of titanium (LaTiO₂N, NdTiO₂N [12]), zirconium (LaZrO₂N [12]), niobium (SrNbO₂N [17], BaNbO₂N [18]), tantalum (CaTaO₂N [21], SrTaO₂N [4,19], BaTaO₂N [18], Sr_{0.5}La_{0.5}TaO_{1.5}N_{1.5} [30]), molybdenum (CaMoO_{1.7}N_{1.3} [66], SrMo(O,N)₃ [28,37,38]) and tungsten (SrW(O,N)₃ [26]). There seems to be no correlation between the anionic ordering and the crystallographic symmetry since for the above-listed examples cubic (*Pm3̄m*), tetragonal (*I4/mcm*, *I4̄2m*, *I4̄*), orthorhombic (*Pnma*) or even triclinic (*I* $\bar{1}$) space groups were found.

Fig. 24. Section of the crystal structure of SrNbO₂N as derived from neutron diffraction viewed along the *c*-axis (left) and almost along the *a*-axis (right). (Anisotropic) displacement parameters are shown at the 90% probability level. The numbers indicate the fractional O/N site occupation factors for the slow-cooled and quenched samples (upper and lower values, respectively).

Complete O/N ordering was only reported for SrTaO₂N (*I4/mcm*) and LaTaON₂ (*C2/m*) [21]. The latter example is especially interesting because the anionic ordering was attributed to the preparation conditions involving large amounts of mineraliser. Our own results on LaNbON₂ (space group *Pnma*) on the other hand revealed a random O/N distribution although a similar mineraliser-assisted synthesis was used. The origin of the different ordering degrees therefore remains a puzzling question.

In this context it is interesting to note that also for the Ruddlesden–Popper type oxynitrides, different types of anionic ordering have been described. For Sr₂TaO₃N, Sr₂NbO₃N and Ba₂TaO₃N, for example, the nitride ions were reported to occupy the equatorial positions only [4,5,67], while in Nd₂AlO₃N, they were exclusively found on an axial site [2].

The question of anionic ordering is not only of academic interest but is expected to strongly alter the colour of the samples. A high degree of ordering should result in narrower electronic band structures. As a result, such samples will show sharper optical absorption edges and their colours appear purer. Therefore, further investigations should reveal possible ways to influence the anionic ordering in oxynitrides and should systematically study the influence on physical properties like colour or electrical transport.

4.4. NMR spectroscopy

While neutron diffraction is a powerful tool to study the incorporation of nitrogen in the perovskite lattice for high nitrogen contents (i.e. on the level of substitution) its use is rather limited for low nitrogen concentrations (doping level). This is especially true, when the larger scattering length of N compared to O is partly compensated by the formation of anionic vacancies as in the case of A²⁺B⁴⁺O_{3–3x/2}N_x□_{x/2} oxynitrides. In these compounds the total scattering length is almost identical to the one of the parent oxide ABO₃.

To prove the O/N exchange in such perovskite-structured oxynitrides, solid-state ¹⁴N NMR spectroscopy was shown to be an extremely useful tool [68]. This method offers the possibility to probe the nitrogen nuclei directly. The ¹⁴N isotope occurs with

Fig. 25. Rietveld refinement of the neutron diffraction data of SrMoO_{1.9}N_{1.1} [38].

Fig. 26. ^{14}N NMR spectra (5 kHz MAS) of a calcined $\text{BaTi}(\text{O},\text{N})_3$ sample (a), and titanium nitride TiN (b). Centres of the resonance peaks are at 271.0 ppm and 359.3 ppm, respectively [68].

99.63 wt% abundance and has a spin of $I = 1$, which means it possesses a nuclear quadrupole moment. The coupling of this quadrupole moment to the electronic surrounding dominates the appearance of the NMR spectra. For a highly symmetric environment (e.g. the unit cells of cubic barium titanate), the quadrupole coupling vanishes, and only a single sharp line is expected in the spectrum.

However, the appearance of a singlet is not yet a proof for the incorporation of nitrogen in the perovskite lattice, since in binary titanium nitrides the nitrogen may also occupy sites of sufficiently high symmetry to give rise to sharp lines in the ^{14}N NMR spectrum. TiN , in particular, is a likely side product of the ammonolysis of mixtures of barium carbonate and titania and in fact can often be found in the XRD pattern. In such cases, the frequency shift of the resonance line is another parameter that can be used and distinguish nitrogen nuclei in different electronic environments.

The ^{14}N NMR spectra (both static and MAS) of a barium titanate powder with a nitrogen content of 0.6 wt% were investigated [68]. The powder was prepared by ammonolysis of a mixture of barium carbonate and titanium dioxide. Although the hotgas extraction analysis proved the presence of nitrogen in the sample, it was not clear whether the N^{3-} ions indeed occupy the oxygen sites in the lattice.

The ^{14}N resonance line at 271.0 ppm in the static NMR spectrum of the nitrogen-containing barium titanate was found to be fairly narrow, indicating a high symmetry of the electronic surrounding. In addition, the shape and chemical shift were practically identical to the resonance line in the spectrum of BaTaO_2N , where the N^{3-} anions are known to occupy the oxygen position in the cubic structure [69]. In contrast, the static spectrum of TiN shows a broad line shape, the origin of which is most likely a distribution of NMR

interaction parameters because of the inherent varying stoichiometry of titanium nitride. The centre of the line appears at 359.3 ppm. In the MAS spectra shown in Fig. 26 the differences become even more pronounced. While $\text{BaTi}(\text{O},\text{N})_3$ (and BaTaO_2N alike) shows a narrow resonance line with small rotational side bands, the spectrum of TiN consists of a complex multiplet.

By comparison of resonance peak positions and line shapes it can therefore be concluded that nitrogen in $\text{BaTi}(\text{O},\text{N})_3$ in fact occupies the oxygen sites in the lattice of barium titanate and does not reside in TiN domains. Furthermore, the very narrow lines obtained for the spectra of barium titanate and BaTaO_2N imply a high site symmetry of the N^{3-} without strong local fluctuations of the composition.

4.5. Transmission electron microscopy

High resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) give important information on possible local deviations from the (averaged) crystal structure determined by X-ray and/or neutron diffraction. For example a local intergrowth of different Ruddlesden–Popper ($\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$) domains with $n = 2, 3, 4, \infty$ was observed in $\text{Sr}_2\text{NbO}_3\text{N}$ [67]. HRTEM has also been used to verify the quality of thin oxynitride films as reported in [70]. Electron diffraction has been applied to identify superstructures in oxynitrides, e.g. in EuNbO_2N [71]. The large dielectric constant of BaTaO_2N was explained by a local deviation from the cubic structure, giving rise to diffuse intensities in the ED pattern [72].

In our investigations one application of transmission electron microscopy was to analyse the quality of both the oxide reactants and the obtained oxynitrides. As an example Fig. 27(a) shows a high

Fig. 27. HRTEM of (a) LaTaON_2 and (b) LaTaO_4 .

Fig. 28. TEM micrograph and electron diffraction pattern of a $\text{LaTiO}_{3.5}$ single crystal.

resolution TEM micrograph of LaTaON_2 prepared by ammonolysis at 1050°C . The horizontal plane distance is around $2.8\text{ \AA}$, corresponding to the (200) direction while the vertical planes distance of ca. $4.0\text{ \AA}$ corresponds to the (002) direction of the orthorhombic unit cell with $a \approx b \approx 5.7\text{ \AA}$ and $c \approx 8.1\text{ \AA}$. The HRTEM image of the corresponding oxide LaTaO_4 is shown in Fig. 27(b). LaTaO_4 has a layered structure characteristic for the $A_nB_nO_{3n+2}$ with $n=2$ (See Chapter 5). The observed plane distances are in accordance with the monoclinic unit cell with $a=7.650\text{ \AA}$, $b=5.577\text{ \AA}$ and $c=7.820\text{ \AA}$.

In Chapter 5 the nitridation of single crystals with the composition $\text{ABO}_{3.5}$ is described. These oxides also belong to the $A_nB_nO_{3n+2}$ family with $n=4$. Fig. 28 shows the TEM image and the corresponding electron diffraction pattern of a $\text{LaTiO}_{3.5}$ single crystal obtained by the floating zone technique.

The horizontal spacing of approximately $13\text{ \AA}$ corresponds to the basic repetition unit of 4 octahedra layers. In the horizontal direction the distance between the planes is $5.5\text{ \AA}$, which corresponds to the b axis [73]. Both the TEM image and the sharp diffraction spots shown in the inset of the figure prove the high-quality of the crystals.

For the resulting oxynitride LaTiO_2N different space groups have been reported in the literature. Our neutron diffraction data revealed that the unit cell is at least orthorhombically distorted and possibly I - or C -centered but it was not possible to unambiguously distinguish between structural models in different space groups [39]. For this reason transmission electron microscopy was applied for complementary structure analysis. From the extinction conditions observed in the electron diffraction images (Fig. 29) taken from different LaTiO_2N samples we concluded that $I\bar{1}$ is in fact the correct space group.

Further TEM examination indicated the presence of twin-domains of different types and orientations in LaTiO_2N . The presence of domains can be explained by the small mismatch in the values of the lattice parameters a and c (0.06%) and the fact that $c^2 \approx a^2 + b^2$. These domains are a hint for possible structural transition(s) occurring between 950°C and room temperature. Beside twin-domains, also incommensurate superstructure reflections were observed in some of the ED patterns (Fig. 30C) revealing a modulation of the structure [39].

5. Physical properties

Optical, electrical and other physical properties of oxynitride perovskites are highly dependent on the electronic structure of the samples, which is strongly affected by incorporation of the nitride ions. For this reason, this chapter starts with examinations of the electronic structure.

5.1. XAS-investigations of the electronic structure

The effect of nitrogen doping on the electronic structure of the transition metal can well be examined by X-ray absorption spectroscopy. The near edge (XANES) part of spectrum corresponds to transitions of the excited core electron to unoccupied bonded states. Therefore, the transition energy is a sensitive measure for the energy of the corresponding state. For transition metals the most important features in the pre-edge structure of the absorption spectra are transitions to empty molecular-orbitals with dominating d -character. Since only transitions with $\Delta l = \pm 1$ are dipole-allowed, the direct $1s \rightarrow 3d$ transition is forbidden. Yet it can be observed as a very small feature in the absorption spectrum due to a quadrupole allowance (Fig. 31). The main peaks in the pre-edge

Fig. 29. Electron diffraction patterns of LaTiO_2N taken along the orthorhombic zone axis $[100]||[111]$ (A); $[110]||[011]$ (B); $[210]||[012]$ (C); $[201]||[102]$ (D); and $[211]||[112]$ (E). Red and white colours are used to distinguish between similar zone axes. Reflections forbidden in $Imma$ are marked by circles [39].

Fig. 30. Electron diffraction patterns showing microstructural features of LaTiO_2N . (A): Rotation twin-domains formed along $[100]||[111]$ orthorhombic zone axis; (B): Rotation twin-domains formed along $[201]||[102]$ orthorhombic zone axis (characteristic reflections splitting is marked with circles); (C): Incommensurate superstructure reflections along $[100]||[111]$ orthorhombic zone axis (rows with the superstructure reflections are marked by arrows) [39].

region result from band transitions, which are dipole-allowed because of a mixing of the metal-d and oxygen-p orbitals. Due to the crystal field splitting of the d-orbitals into sets of t_{2g} and e_g symmetry, two peaks are observed. From Fig. 31 it can be seen that for LaTiO_2N the respective peaks shift to lower energy compared to the parent oxide $\text{LaTiO}_{3.5}$. Two main effects are known to alter the energy of the transition, namely the *valence shift* and the *chemical shift*. The former reflects the influence of the formal oxidation state of the transition metal in a chemically identical surrounding (e.g. Ru^{+4} and Ru^{+5} in octahedral oxygen coordination [74]), whereas the latter corresponds to the influence of chemically different neighbours while the formal charge remains unchanged. Both in $\text{LaTiO}_{3.5}$ and LaTiO_2N the charge of titanium is +4, so a valence shift is not expected. It is well known that the chemical shift increases with the ionicity of the bonds [75,76]. Since the ionicity becomes larger with the difference in electronegativities of the binding partners, less electronegative anions will result in more covalent bonds and in turn in a reduced chemical shift. Our XANES results are therefore a direct experimental evidence for the more covalent character of the metal–N bond compared to the metal–O bond. As can further be seen from Fig. 31, the e_g -orbitals are much more affected than the t_{2g} -orbitals. This is expected since the former are in fact antibonding molecular orbitals resulting from the strong $\sigma_{(d-p)}$ interaction while the latter are basically non-bonding (apart from the weak $\pi_{(d-p)}$ overlap).

The observed chemical shift is not limited to the K-absorption edges. In fact it has been shown that the metal- L_{III} or - L_{II} XAS spectra are often better suited e.g. for the determination of oxidation states because of the very intense *white lines* observed at these edges [77,78], which result from dipole-allowed 2 p-nd transitions.

Fig. 31. Ti-K XANES of $\text{LaTiO}_{3.5}$ and LaTiO_2N . In the inset the corresponding transitions are given.

For example, for the solid solution $\text{Ca}_{1-x}\text{Eu}_x\text{Ta}(\text{O},\text{N})_3$ it was recently found that the O/N ratio is essentially 2:1 for all values of x . The charge compensation is achieved by a change in the $\text{Eu}^{3+}/\text{Eu}^{2+}$ ratio as evidenced by Eu- L_{III} XANES spectroscopy [79].

For a series of Ta containing oxynitrides and their corresponding oxides we compared the Ta- L_{III} absorption edges. As an example Fig. 32 depicts the normalised Ta- L_{III} spectra of SrTaO_2N and $\text{SrTaO}_{3.5}$. In all cases the maximum of the first derivative of the spectrum was used as energy measure. Values of the chemical shifts with respect to Ta-metal are listed in Table 4. The estimated accuracy of the values is 0.1 eV. As can be seen, the incorporation of two nitride ions in the TaO_6 octahedra leads to a shift of approximately 0.5 eV towards lower energies, in accordance with the expected behaviour. In the case of the couple $\text{LaTaO}_4/\text{LaTaON}_2$ the chemical shift is expected to be much larger since four of the oxygen ions around each Ta are replaced by nitride ions. From Table 4, it can be seen that the experimentally observed shift is in fact roughly twice as large as for the other oxynitrides.

The situation becomes more complicated when the incorporation of nitrogen leads to a change in the oxidation state of the transition metal. In such cases the valence shift and the chemical shift partly compensate each other. For the system $\text{SrMoO}_{3-x}\text{N}_x$ we were able to prepare samples with rather high nitrogen contents of $x = 1.05$ and 1.19 as established by hotgas extraction [37]. The Mo-K XAS of the oxynitrides are shown in left part of Fig. 33 in comparison to the two oxides used as Mo^{+4} and Mo^{+6} references. The arrow in the inset of the right panel marks the absorption feature used for data evaluation. The right part of the figure shows the formal Mo valence as a function of the energy shift compared to Mo-metal. The derived oxidation states of Mo in the oxynitrides

Fig. 32. Comparison of the Ta- L_{III} absorption spectra of SrTaO_2N and $\text{SrTaO}_{3.5}$.

Table 4

Energy shifts (ΔE) of the Ta–L_{III} threshold for different oxides and oxynitrides. The second row ($\Delta(\Delta E)$) gives the difference of ΔE for the oxynitrides and their parent oxides.

Sample	CaTaO ₂ N	CaTaO _{3.5}	SrTaO ₂ N	SrTaO _{3.5}	BaTaO ₂ N	Ba ₅ Ta ₄ O ₁₅ + BaTa ₂ O ₆	LaTaON ₂	LaTaO ₄
ΔE [eV]	2.8	3.5	3.0	3.5	3.0	3.5	2.5	3.6
$\Delta(\Delta E)$ [eV]		–0.7		–0.5		–0.5		–1.1

were significantly smaller than the ones calculated from the chemical composition (+4.62 vs. +5.03 for $x = 1.05$ and +4.52 vs. +5.19 for $x = 1.19$) [37]. This finding clearly illustrates the competing effects of the valence shift and the chemical shift. While the former moves the XAS features to higher energies the latter shifts it back to lower energy values. When the chemical shift of ≈ 0.5 eV per nitrogen is taken into account, the oxidation states match very well. More systematic studies are planned to quantify the influences of these two effects for other oxynitride perovskites.

5.2. Optical properties

As mentioned in the Introduction, their colouring is the most obvious property of oxynitride perovskites and has therefore been the subject of numerous investigations. Within solid solutions like $\text{La}_{1-x}\text{A}_x\text{Ti}(\text{O},\text{N})_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) the colour was found to change continuously both in polycrystalline samples [14,33] and thin films [55,80]. Similar results were already found for tantalum-based oxynitrides, leading to a proposed application for pigments [10].

The broad colour spectrum of different oxynitrides [80] covers wide areas of the CIE Lab colour room [81]. The systematic colour change in solid solutions can be explained by a combined effect of electronegativity of the B type cation and symmetry of the crystal structure. A lower electronegativity leads to an increase in the energy of the conducting band and in turn to a larger band gap. The lower-symmetric crystal structure generally results in B–O–B bond angles smaller than 180° , which corresponds to sharper conduction bands, again increasing the band gap. While these considerations were originally derived for pure oxides [82] they can be applied for nitrogen-substituted compounds as well [81].

Usually the optical properties are measured on polycrystalline samples in diffuse reflectance mode. With increasing nitrogen contents of (partly) nitrated compounds a shift of the absorption edge is observed, as we found for example in the system $\text{LaTi}(\text{O},\text{N})_3$ [44]. While all samples seemed to be pure LaTiO_2N from their X-ray diffraction pattern the incomplete reaction was revealed by ERDA.

As an alternative, the optical properties of oxynitrides may be measured in transmission mode in the case of nitrated crystal slices, which will be discussed in more detail below. Fig. 34 shows

the spectra of nitrated crystals of LaTiO_2N , SrNbO_2N and SrTaO_2N in comparison to the pure oxides. For the ammonolysed crystals the onset of absorption is dramatically shifted to longer wavelengths (roughly 480–550 nm) and clear interference fringes can be observed. Since the refractive indices of the oxynitrides and the corresponding oxides and the thickness of the reacted surface layers differ for the various samples, the interference fringes show strong variations. The optical band gaps calculated from a plot of $((A - A_{\text{background}}) h\nu)^2$ versus $h\nu$ (A being the absorbance of the samples) were in good agreement with the values of the polycrystalline samples [83].

5.3. Electric, thermoelectric and dielectric properties

Only few articles deal with the electrical resistances of oxynitride perovskites [23,48,71]. We have studied the electric properties of $\text{La}_x\text{Sr}_{1-x}\text{Ti}(\text{O},\text{N})_3$ thin films prepared by spin-coating and pulsed laser deposition (see Chapter 2.4). Samples were investigated by 2-point resistivity measurements in the temperature range 4.2–300 K. For the films prepared by spin-coating strong differences in the electrical behaviour were found with changing composition [55]. The oxynitrides with $x = 1$ and $x = 0.75$ turned out to be insulators, while for $x = 0$ and $x = 0.5$ the films showed a semiconducting behaviour, i.e. their resistances decreased with increasing temperature. For $x = 0.25$ a semiconductor/metal transition with a minimum resistance of $0.02 \Omega \text{ cm}$ at 120 K was observed as depicted in Fig. 35.

For the films grown by pulsed laser deposition deviating electric properties were found [51]. All oxynitride films showed a metal-like behaviour above 33 K (Fig. 36). For $x = 0.75, 0.5$ and 0 a semiconducting behaviour was observed below 30 K (shown in Fig. 36a), indicating a semiconductor/metal transition.

Neither for the spin-coated nor for the PLD films did the resistivities show systematic changes with x . The composition $x = 0.25$ possessed the lowest resistivity values for both SC and PLD films, while both higher and lower $\text{La}^{3+}/\text{N}^{3-}$ contents resulted in larger values. In general, the resistivities of the PLD films were by far lower than the ones of the corresponding spin-coated films, probably due to higher density of the PLD films.

Fig. 33. Mo–K X-ray absorption edge of $\text{SrMoO}_{3-x}\text{N}_x$ in comparison to oxide references (left) and calculated Mo valence (right) [37].

Fig. 34. UV-vis spectra of LaTiO_2N , SrNbO_2N and SrTaO_2N in comparison to the unreacted oxides (modified from [83]).

Completely different resistance values were observed for the oxynitride films ablated by the PLD technique on MgO substrates. All the films were insulators, except for $x = 0.25$, which showed a semiconducting behaviour [51]. Possible explanations for the discrepancies in the electrical measurements for the PLD samples deposited on STO and MgO substrates are (a) mechanical stress by the different lattice mismatch of substrate/film, (b) the presence of TiN impurities not detectable by diffraction, or (c) variations of anionic vacancies induced by small variations in the ammonolysis reaction. Further experiments are planned to examine the influences of these possible effects.

When the incorporation of nitrogen in the perovskite framework is associated with a change in the oxidation state of the transition metal, the resulting physical properties of the oxynitrides are significantly different from the parent oxides. As an example, the (thermo-) electrical and magnetic properties of $\text{SrMoO}_{3-x}\text{N}_x$ have been compared to the ones of SrMoO_3 [38]. The following discussion refers to an oxynitride sample with the composition $\text{SrMoO}_{1.95}\text{N}_{1.05}$, which will be denoted as SrMoO_2N for simplicity.

Low temperature measurements of the physical properties were performed on a Quantum Design PPMS and MPMS. Electrical transport measurements were done on bars obtained by applying an uniaxial pressure of 10 bar followed by a cold isostatic pressing at 2000 bar. The bars were sintered under flowing ammonia at 800 °C for half an hour. The measured density of the bars varied between 74% and 89% of the theoretical value. Electrical conductivity (DC four-probe method) and Seebeck coefficient were measured simultaneously for 340 K $< T < 950$ K using the RZ2001i measurement system (Ozawa science, Japan).

Fig. 35. Resistivity of thin films of $\text{La}_x\text{Sr}_{1-x}\text{Ti}(\text{O,N})_3$ with $x = 0, 0.25$, and 0.50 prepared by spin-coating (modified from [55]).

Fig. 36. Resistivity of oxynitride films of $\text{Sr}_{1-x}\text{La}_x\text{Ti}(\text{O,N})_3$ grown by PLD [51].

In SrMoO_3 the formal oxidation state of Mo is +4 ($4d^2$) while in SrMoO_2N it increases to +5 ($4d^1$), giving rise to a number of changes in the physical properties. The oxynitride SrMoO_2N shows semiconducting resistivity behaviour, i.e. at higher temperatures it becomes more conductive in contrast to the oxide (Fig. 37A). Moreover, the absolute resistivity of SrMoO_2N is almost three orders of magnitude higher than that of SrMoO_3 . The positive Seebeck values indicate that holes are the predominating charge carriers in SrMoO_2N (p type conduction) (Fig. 37B). The Seebeck coefficient of SrMoO_2N is significantly higher than that of SrMoO_3 , pointing to a lower carrier concentration in the oxynitride. Furthermore, the thermal conductivity of SrMoO_2N is one order of magnitude smaller than that of SrMoO_3 (Fig. 37C). The weak temperature dependence of the electrical resistivity together with the very low thermal conductivity of SrMoO_2N suggest that the mean free paths of both phonons and charge carriers are close to the interatomic distance.

SrMoO_2N shows a nearly temperature-independent paramagnetism down to $T = 150$ K, an anomaly at $T \sim 54$ K and an upturn at very low temperatures [38]. The temperature-

Fig. 37. Resistivity (A), Seebeck coefficient (B) and thermal conductivity (C) of SrMoO_2N in comparison to SrMoO_3 [38].

independent component is, however, smaller than that of SrMoO_3 while the low temperature increase and anomaly are enhanced. The magnetic susceptibility of SrMoO_2N can be fitted by a modified Curie–Weiss law $\chi = \frac{C}{T-\theta} + \chi_0$. The obtained Curie constant corresponds to a very small effective magnetic moment of only $\mu_{\text{eff}} = 0.05 \mu_B$ and a negative θ indicates an antiferromagnetic interaction of the moments. From the temperature-independent paramagnetic term χ_0 a density of states (DOS) at the Fermi level of $D_F \sim 25 \text{ Ry}^{-1}/\text{formula unit}$ can be estimated, while the corresponding value for SrMoO_3 is significantly higher ($\sim 55 \text{ Ry}^{-1}/\text{f.u.}$). A very similar D_F was derived from heat capacity measurements. A plot of C_p/T vs. T^2 shows a linear behaviour for $T \leq 15 \text{ K}$. A fit by $C_p = \gamma T + \beta T^3$, where γT and βT^3 are the electronic and the lattice contributions, results in a Sommerfeld coefficient γ that corresponds to $D_F = 23 \text{ Ry}^{-1}/\text{f. u.}$ [38]. A small Sommerfeld–Wilson ratio for SrMoO_2N indicates no strong electronic correlations. The observed increase of the magnetic susceptibility below 50 K is most likely due to the presence of electronic defects or a paramagnetic impurity phase that cannot be detected by the applied diffraction techniques.

With longer ammonolysis times the nitrogen contents in $\text{SrMoO}_{3-x}\text{N}_x$ were found to increase. Besides the above-mentioned sample with $x = 1.05$ two additional batches with $x = 1.19$ and 1.27 were investigated in [37]. The Seebeck coefficients (S) of the oxynitrides were found to increase with higher nitrogen contents. The values of S become larger with temperature and pass through a maximum at $T = 650 \text{ K}$, 600 K and 550 K for $x = 1.05$, 1.19 and 1.27 (Fig. 38). Further heating leads to a decomposition evidenced by the formation of metallic Mo impurities.

Electrical conductivity decreases with enhanced nitrogen content. For all samples the electrical conductivity increases with temperature, i.e. a semiconducting behaviour is observed. The measured values are one order of magnitude higher than those reported for $\text{SrMoO}_{2.5}\text{N}_{0.5}$ (2 S cm^{-1}) [27]. It is also noteworthy that the temperature dependence of the $\text{SrMoO}_{2.6}\text{N}_{0.4}$ conductivity was reported to be semiconductor-like [28] similar to our results, whereas that of $\text{SrMoO}_{2.5}\text{N}_{0.5}$ was described as metallic [27]. These deviations in the conductivity may be caused by grain boundary effects. Taking into account that the samples are moisture sensitive, the grain surfaces may become partly reoxidised during the handling and the measured slight temperature dependence of the conductivity could originate from the grain boundaries influence.

Dielectric investigations of perovskite oxynitrides so far mainly focussed on BaTaO_2N . The dielectric response of this compound was first deduced from the infrared reflection spectra of a pelletised polycrystalline sample and was found not to reach very high values

[84]. In contrast, impedance spectroscopy on sintered pellets of BaTaO_2N and SrTaO_2N led to bulk permittivities of roughly 5000 and 3000 for the two compounds [22]. These values were found to remain almost constant in the temperature range 180–300 K. The bulk conductivities were in the order of $10^{-5} \text{ S cm}^{-1}$. On the other hand, a strong influence of the grain boundaries was also observed, having permittivities of 3.2×10^5 for BaTaO_2N and 1.3×10^5 for SrTaO_2N . As the origin of the high dielectric constants, local dipole moments due to differences in the Ta–N and Ta–O distances were discussed (see also the structural section of this work). As an alternative explanation the formation of internal barrier layers was also considered. Similar values were found by a second group, who also examined Sc-substituted oxynitrides. For $\text{BaSc}_{0.05}\text{Ta}_{0.95}\text{O}_{2.1}\text{N}_{0.9}$ even larger values of 7300 were derived from impedance spectroscopy [9]. For the Eu-based oxynitrides EuNbO_2N and EuTaO_2N strongly deviating properties were observed. While EuTaO_2N shows a low temperature dielectric constant of only 37, the ϵ' values of EuNbO_2N is in the order of 10^4 for $T = 150 \text{ K}$ and low measurement frequencies. Upon lowering the temperature or increasing the frequency there occurs a dramatic breakdown of the dielectric constant [71].

One of the major problems in the measurement of any transport property of oxynitride perovskites is the fact that they have little tendency to sinter. Therefore, dense ceramic samples cannot be obtained and the measurements are always affected by influence of the grain contacts.

In addition, single crystals of perovskite oxynitrides apparently cannot be grown. We performed numerous attempts to grow crystals by the floating zone method in (diluted) ammonia atmosphere, starting both from the $\text{ABO}_{3.5}$ oxides and from the oxynitrides themselves. Additional trials were performed to melt the oxynitrides in pure nitrogen or 2% NO_2 in N_2 . None of these trials was successful; instead they resulted in the formation of (partly reduced) oxides.

One possibility to avoid the problem of grain contacts is the use of high-quality thin films. Lately, the dielectric properties of LaTiO_2N films deposited by RF-sputtering in Ar/N_2 atmospheres were investigated [49]. At room temperature and 10 kHz, ϵ' values above 1000 were observed but were found to decrease to roughly 500 with increasing N-contents of the films. Since these films become more polycrystalline with higher nitrogen amounts, the ϵ' values may strongly be altered by grain boundary contributions.

Epitaxial films of BaTaO_2N were grown by pulsed laser deposition on (100)-cut SrTiO_3 at 760°C in a N_2/O_2 atmosphere of 13 Pa [70]. In contrast to the sintered pellets of the same material, the permittivity of these films was only 200, i.e. two orders of magnitude smaller. The formation of boundary-layer capacitors in the pellets is one possible explanation for this strong discrepancy. On the other hand, dielectric constants of thin films are often significantly reduced from values obtained in bulk material.

For these reasons, measurements on thick single-crystalline films would be highly desirable. To address this problem we applied a complementary approach based on the idea to use the single crystal itself as reactant instead of growing oxynitrides on the surface of an inert substrate [83]. The obvious advantages are a minimal lattice mismatch and the already fixed correct cationic composition.

Single crystals of $\text{LaTiO}_{3.5}$, $\text{NdTiO}_{3.5}$, $\text{SrNbO}_{3.5}$, and $\text{SrTaO}_{3.5}$ were grown in synthetic air by the floating zone technique. The growth furnace (model GERO SPO) is equipped with two 1000 W halogen lamps, the radiation of which is focussed by gold-coated ellipsoidal mirrors. From the obtained crystals thin slices of some hundred micrometer thickness and several square millimeters area were cleaved. These slices were nitridated at temperatures between 900°C and 1050°C for several hours in an ammonia flow of 50 ml/min.

Fig. 39 shows single crystal slices of $\text{SrTaO}_{3.5}$ before and after ammonolysis. From the change in colour the formation of the

Fig. 38. Temperature dependence of Seebeck coefficients of $\text{SrMoO}_{3-x}\text{N}_x$ oxynitrides. The inset shows an irreversible decrease of the measured values when samples were heated above their decomposition temperature [37].

Fig. 39. Slices of a $\text{SrTaO}_{3.5}$ crystal before and after ammonolysis. The grid represents $1 \times 1 \text{ mm}^2$.

oxynitride SrTaO_2N already is evident. The incorporation of nitrogen was furthermore verified by electron probe micro analysis (EPMA) of a cross-section and can also be seen in scanning electron microscopy (SEM) as a clear change in contrast. As an example, Fig. 40 shows a SEM image of an $\text{SrNbO}_{3.5}$ crystal slice nitrated for 75 h at 950°C . For the cross-section the crystal was embedded in an organic polymer that is visible in the left and right border of the image. As can be seen, the slice consists of two surface layers of the oxynitride SrNbO_2N with thicknesses of 50 and $30 \mu\text{m}$, respectively and an unreacted inner region of $50 \mu\text{m}$ thickness. The thinner oxynitride layer was the side on which the crystal was lying during the reaction.

As expected, the thickness of the oxynitride layers was found to strongly depend on the reaction time. For nitridation times of only 24 h, layers of $2\text{--}3 \mu\text{m}$ are usually obtained. To achieve thicknesses of $50 \mu\text{m}$ and more, the ammonolysis time has to be raised to 75–120 h, depending on the material under investigation.

The crystalline quality of the oxynitride layers was investigated by X-ray diffraction using a Bragg-Brentano diffractometer for $\theta/2\theta$ scans and a four-circle diffractometer for pole figure and mosaicity measurements [83]. The $\theta/2\theta$ X-ray diffraction patterns of the nitrated crystals show peaks of both the oxynitride and the unreacted oxide as expected. For both phases only specific sets of reflections were observed as shown in Fig. 41. This can easily be understood from the crystal structures: All the studied samples are $n=4$ members of a family of perovskite-related oxides with the general

Fig. 40. SEM cross-section of a $\text{SrNbO}_{3.5}$ crystal nitrated at 950°C for 76 h.

composition $A_nB_n\text{O}_{3n+2}$. These oxides are built of perovskite type blocks with a thickness of n corner-sharing BO_6 -octahedra oriented parallel to the $[110]$ -direction of the cubic perovskite structure. Apart from details in their crystal structures like different space groups and cell parameters, the idealised crystal structure can be derived from the cubic perovskite by the relations $a=a_p$, $b=a_p \times \sqrt{2}$, and $c=2 \times s + n \times a_p \times \sqrt{2}$, where a_p is the cubic perovskite unit cell length ($\approx 3.9 \text{ \AA}$) and $s \approx 2.3 \text{ \AA}$ is the distance between neighbouring layers.

The crystals easily cleave perpendicular to the long axis and therefore only (001) reflections (with $l = \text{even integer}$) are found in Bragg-Brentano geometry. The long c -axis is oriented parallel to the $[110]$ -direction of the perovskite structure of the oxynitrides obtained from ammonolysis as shown in the right side of Fig. 41. As a consequence of this topotactical relation only $\{hh0\}$ reflections of the oxynitride phase are found in the diffraction pattern.

Pole figure measurements yield a full epitaxial relationship $\text{ABO}_2\text{N} (110)[001] \parallel \text{ABO}_{3.5} (001)[100]$. As example a $\{110\}$ pole figure plot for SrTaO_2N is shown in Fig. 42.

The mosaic spread of the epitaxial oxynitride layer was determined by ω and ϕ scans of the (110) reflections at $\chi = 0^\circ$ and $\chi = 60^\circ$, respectively. Full widths at half maximum (FWHM) between 0.3 and 1.5° for both the ω scans and the ϕ scans document a (nearly) single-crystalline character of oxynitride layers with a highly topotactical relation to the parent crystal substrate [83]. A slight broadening of the peak widths of the ω and ϕ scans is due to the fact, that the oxynitrides actually do not crystallise in the ideal cubic structure but in slightly distorted variations as discussed in the structural section of this paper.

Measurements of the electrical conductivity and the dielectric constant were performed in the frequency range from 1 Hz to 10 MHz with a Novocontrol Alpha-A frequency-response analyser. For low temperature measurements in the range from 40 to 300 K a closed cycle cryostat was used. Various ammonolysed crystals of $\text{LaTiO}_{3.5}$, $\text{SrTaO}_{3.5}$ and $\text{SrNbO}_{3.5}$ were investigated. As an example, the dielectric properties of the nitrated $\text{SrNbO}_{3.5}$ crystal shown in Fig. 40 (reacted for 76 h at 950°C) are discussed in the following and compared to the parent oxide. For simplicity, the nitrated crystal will be referred to as SrNbO_2N in the following. For the dielectric measurements co-planar silver-paint contacts were applied on the top of the crystal slices. This geometry was chosen in order to minimise the influence of the unreacted oxide layer on the results of SrNbO_2N . Fig. 43 shows the temperature dependences of the dielectric constant and conductivity of the oxide $\text{SrNbO}_{3.5}$ (left frames) and SrNbO_2N (right frames). The dielectric constant ϵ' of $\text{SrNbO}_{3.5}$ shows a frequency independent peak at $T \approx 100 \text{ K}$ with large values of ϵ' up to 1000, due to a ferroelectric transition based on atomic displacements [85,86]. The ferroelectric transition also results in an anomaly in the conductivity σ' as depicted in the lower left panel of Fig. 43. The frequency dependency of σ' at low temperatures is due to a superimposed relaxational behaviour and ac-conductivity.

The electrical properties of SrNbO_2N are completely different from the ones of $\text{SrNbO}_{3.5}$. The dielectric constant ϵ' shows a step like behaviour at high frequencies and low temperatures indicating a relaxation, the origin of which is not completely understood yet. Small anomalies in ϵ' and σ' values at high frequencies close to 110 K are caused by a remaining contribution of the underlying oxide layer. Apart from these features it is obvious that the dielectric constant of SrNbO_2N is quite high with values reaching 5000 at 300 K. Furthermore, the high- ϵ' values only show a very small dependence on temperature and frequency. This is in sharp contrast to the behaviour of the oxide, in which ϵ' reaches 1000 only at the ferroelectric phase transition and drops to below 100 at room temperature.

Fig. 41. Bragg-Brentano XRD pattern of an ammonolysed SrNbO_{3.5} crystal slice (left). The right part illustrates the structural relation between the ABO_{3.5} oxide educt and the oxynitride [83].

On the other hand, the electrical conductivity of SrNbO₂N is also strongly increased. A semiconducting behaviour is found with values increasing from $10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 30 K to maximum $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at room temperature. Compared to the parent oxide the conductivity of SrNbO₂N is thus at least three orders of magnitude higher. Furthermore, σ' of SrNbO₂N shows only a minor frequency dependence, again in sharp contrast to the oxide (please note the different scales of the plots for the oxide and the oxynitride, respectively).

The outlined results are of high interest for possible applications. Large- ϵ' materials are required in capacitive elements (e.g. for semiconductor technology and energy storage in so-called supercapacitors). Ferroelectrics as SrNbO_{3.5} or BaTiO₃, possess high- ϵ' values in the vicinity of the ferroelectric phase transition, but show strongly temperature-dependent properties and are thus not well suited for technical applications. Here we demonstrated that nitridation can result in nearly temperature-independent high- ϵ' oxynitrides, which may become of interest for electronic devices.

In addition to SrNbO₂N the (di-) electric properties of SrTaO₂N and LaTiO₂N crystals were also investigated and compared to the parent oxides. Also these oxynitride crystals were not completely reacted and were thus measured in the co-planar configuration. The dielectric properties will be published separately. Here, only the conductivity data are presented.

Fig. 42. X-ray pole figure of the SrTaO₂N{110} reflections ($2\theta = 31.19^\circ$).

Fig. 44 shows the electrical conductivity for a crystal slice of SrTaO_{3.5}. Two electric anomalies (between 78 and 95 K and at roughly 155 K) can be observed and were associated with ferroelectric phase transitions [87]. As for SrNbO₂N, the electrical properties of SrTaO₂N have not been reported yet. SrTaO₂N shows a semiconducting behaviour, with σ' values increased by 4–5 orders of magnitude compared to the non-ammonolysed crystal.

The electrical properties of LaTiO_{3.5} are plotted in Fig. 45. In contrast to the above-mentioned oxides no anomalies were observed. Its electrical conductivity varies between 10^{-9} and $10^{-7} \Omega^{-1} \text{cm}^{-1}$ depending on the applied frequency. Remarkably, the σ' are almost constant in the entire temperature range. As the other oxynitrides, LaTiO₂N presents semiconducting behaviour with electrical conductivity values in the order of $10^{-2} \Omega^{-1} \text{cm}^{-1}$, e.g. at least 5 orders of magnitude higher than the one of the corresponding oxide. In contrast to SrNbO₂N and SrTaO₂N the values of σ' only slightly changes between 30 and 300 K and shows basically no dependence on the measurement frequency.

The higher electrical conductivity of the oxynitrides compared to the respective oxides is a severe disadvantage for their application as dielectrics. On the other hand, the incomplete reaction of the crystals may offer a natural way to circumvent this shortcoming. As depicted in Fig. 40 the reacted crystals consist of top and bottom layer of oxynitride with an unreacted oxide layer in between. Thus this “sandwich” arrangement results in layers with high dielectric constants and a highly insulating layer in between. If measured in parallel arrangement (i.e. perpendicular to the layering) and not in a co-planar way, one should observe both large dielectric constants and low conductivity, which is the ideal combination for a promising dielectric material.

6. Stability and reactivity

Many oxynitride perovskites show a surprisingly high stability against oxygen, water and even acids. Together with the colouring this chemical and thermal stability opens the possibility to use oxynitrides in various technical applications.

6.1. Thermal stability

The thermal stability of oxynitride perovskites and their unusual reaction behaviour in oxygen-containing atmospheres have been the subject of several investigations. It was first observed by Marchand et al. that the reoxidation according to $ABO_2N + 3/2 O_2 \rightarrow ABO_{3.5} + 1/2 N_2$ involves an intermediate state in which the weight

Fig. 43. Temperature dependencies of dielectric constant and conductivity of SrNbO_{3.5} (left frames) and the nitrated crystal (50 μm SrNbO₂N oxynitride on 50 μm SrNbO_{3.5}) (right frames).

of the samples surprisingly is higher than expected [1]. The intermediate was later found to have a considerable thermal stability and a comparatively low density. The perovskite structure is retained with a slight increase of the cell parameters. On the other hand, the diffraction peaks are very broad indicating a low crystallinity. XPS measurements revealed the presence of N₂-entities [88]. For the reoxidation of LaTiO₂N the presence of N₂ units in the intermediate (described as LaTiO_{3.5}N_{0.67}) was later also verified by Raman spectroscopy [89]. For a series of La_{1-x}Ba_xTi(O,N)₃ oxynitrides (x = 0, 0.3) the heats of formation of the oxynitrides, their N₂-containing intermediates and the corresponding oxides were studied by drop solution calorimetry [32]. Most of the reaction enthalpy of the intermediate phases was attributed to the structure change linked with the formation of the layered perovskite LaTiO_{3.5}.

Our own investigations on the thermal reaction behaviour of oxynitride perovskites started with the reoxidation of ABO₂N compounds with A = Ca, Sr, Ba and B = Nb, Ta prepared both by

conventional solid-state reaction and by the citrate assisted soft-chemistry approach [16].

The evolution of the structure was studied by *in-situ* X-ray powder diffraction using synchrotron radiation. Samples were heated up in static air in quartz capillaries at the beamline B2 of HASYLAB/DESY. The wavelength was adjusted to Mo-K_α (0.7093 Å). With the applied position-sensitive detector complete datasets from 5 to 45 °2θ were recorded within about 3 min. Fig. 46 shows the temperature evolution of the XRD pattern of CaTaO₂N. The intensities of the oxynitride-related peaks were found to be almost constant for temperatures up to 400 °C. Above this temperature a slight decrease was observed. In the temperature range 600–850 °C a plateau was found, while between 900 °C and 940 °C the peak intensities decreased dramatically and the evolution of diffraction peaks corresponding to CaTaO_{3.5} was observed. This behaviour correlates well with the spectroscopic and thermoanalytical results presented in the following.

Fig. 44. Electrical conductivity of a SrTaO_{3.5} single crystal (a) before and (b) after ammonolysis at 1050 °C for 120 h. The thickness of the oxynitride layer is approximately 25 μm.

Fig. 45. Electrical conductivity of a $\text{LaTiO}_{3.5}$ single crystal (a) before and (b) after ammonolysis at 1050°C for 120 h. The thickness of the oxynitride layer is $25\ \mu\text{m}$.

Raman microscopy in backscattering geometry was performed using an Ar-laser ($514.5\ \text{nm}$) [16]. As an example the *ex-situ* spectra for SrNbO_2N annealed at different temperatures are depicted in Fig. 47. In the lower frequency range the evolution of the strong NbO_6 -octahedra “breathing” mode at approximately $840\ \text{cm}^{-1}$ was observed for temperatures above 450°C . At roughly 600°C this mode reaches its final intensity indicating that at this temperature the uptake of oxygen is already completed. In the high frequency region a vibrational band at $2320\text{--}2340\ \text{cm}^{-1}$ appears, which is characteristic for the stretching mode of N_2 and indicates the presence of dinitrogen in the material. This finding is similar to the observations by Le Gendre for LaTiO_2N [89] and was interpreted as the retention of N_2 molecules due to a weak interaction with the transition metal. The BO_6 breathing mode and the N_2 peak appear at the same temperature of approximately 450°C , which indicates that the sample is completely oxidised (i.e. the oxygen stoichiometry $\text{O}_{3.5}$ is reached), while the nitrogen is retained in the crystal framework, which according to the XRD pattern, is basically still a perovskite. Similar results were found for all samples investigated [16].

The temperatures at which the maximum intensity of the N_2 stretching mode is observed correspond well to the temperatures for the weight maximum. Fig. 48 shows as a typical example the weight and MS signals for the oxidation of SrNbO_2N in $20\%\text{O}_2/80\%\text{Ar}$. The sample is stable up to 400°C . Upon heating to higher temperatures, the weight increases due to the uptake of oxygen. This weight increase is partly compensated by the loss of N_2 as indicated by the pronounced $m/e = 28$ signal in the MS. At roughly

600°C the maximum of the weight is reached. Between 600 and 950°C the intermediate, N_2 -containing compound is surprisingly stable as can be seen from the small weight change and the reduction of the MS signal. Finally, at 950°C the sample suddenly loses its retained dinitrogen and the final weight is reached. Similar behaviours were also observed for other oxynitrides [16,81].

In contrast, remarkable differences in the thermal stability were observed in the system $\text{La}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ [33]. While for LaTiO_2N the intermediate phase decomposes in a sharp temperature interval around 1000°C , for $x = 0.3$ and $x = 0.5$ the decomposition temperatures were clearly higher (roughly 1200°C) and the temperature interval becomes significantly broader with increasing x . This finding can be understood taking into account the calorimetric measurements mentioned above [32], which indicate that the formation of the final crystalline layered perovskites comprises the main contribution of the released enthalpy. For the Ca-substituted samples it was observed that the reoxidation product consists of a perovskite type phase and a considerable amorphous fraction. So the missing released crystallisation enthalpy results in a higher stability of the intermediate N_2 -containing compounds.

A dramatic change in the thermal reactivity was observed on reducing the oxygen content of the atmosphere. From Fig. 48 it can be seen that the reaction in $2\%\text{O}_2/98\%\text{Ar}$ starts at a similar temperature but does not show a pronounced increase in weight. Instead there occurs a slow but continuous loss of nitrogen simultaneously to an uptake of oxygen. At 950°C a sudden release of N_2 is observed, leading apparently to an oxygen deficient compound, which slowly accumulated oxygen until at roughly 1200°C the final product $\text{SrNbO}_{3.5}$ is formed.

Fig. 46. Temperature dependence of the X-ray diffraction pattern of CaTaO_2N studied with synchrotron radiation ($0.7093\ \text{\AA}$).

Fig. 47. Raman investigation of SrNbO_2N annealed in air at different temperatures. The intermediate N_2 -adduct leads to the characteristic peak at $2330\ \text{cm}^{-1}$.

Fig. 48. Thermogravimetric investigation of the reoxidation of SrNbO_2N to $\text{SrNbO}_{3.5}$ in 20% oxygen (solid line) and 2% oxygen (dashed line).

To gain a more detailed insight in the thermal reaction behaviour, we systematically varied the oxygen content of the atmosphere [90]. Samples were heated on a thermobalance up to 1200 °C with a heating range of 10 °C/min and kept at this temperature for 30 min. A constant gas flow (40 ml/min) of O_2/Ar -mixtures with oxygen contents between 0 and 20% was applied and the gaseous reaction products were identified by mass spectrometry. A variety of m/e values were monitored in order to unambiguously identify the gases by their isotope patterns. For example a signal for $m/e = 28$ might stem from either N_2 or CO , but both gases can be distinguished upon also monitoring the channels $m/e = 29$ and 30 .

An illustrative example for the thermal behaviour is shown in Fig. 49 for SrTaO_2N . A small weight drop ($<0.5\%$) below 400 °C was attributed to the release of H_2O and CO_2 by the $m/e = 18$ and 44 signals. These chemically bonded molecules result from impurities in the ammonia gas and can be minimised by changing the atmosphere to high-purity nitrogen before cooling the oxynitrides to room temperature [39].

For all oxynitrides it was observed that the onset temperature of decomposition is independent of the oxygen content but the reaction behaviour changes dramatically. For higher oxygen contents (e.g. $\geq 3\%$ for SrNbO_2N , $\geq 10\%$ for SrTaO_2N) the thermal decomposition principally resembles the one shown in Fig. 48. With decreasing oxygen percentages the weight increases slower and the weight maximum is shifted to smaller values. For the highest oxygen concentrations traces of NO or NO_2 were detected by mass spectrometry [90]. It is not yet clear though, if the small amounts observed are artefacts generated in the ionisation unit of the spectrometer.

Fig. 49. Weight change of SrTaO_2N upon heating in O_2/Ar -mixtures. Bold values close to the curves give the oxygen contents (modified from [90]).

In an oxygen-free atmosphere deviating reaction products were found for the different oxynitrides. LaTiO_2N partly decomposes in the temperature regime 950–1200 °C. The reaction proceeds in two steps at roughly 950 °C and 1100 °C, respectively. Both weight losses are accompanied by a release of N_2 and lead to La_2O_3 , TiN and remaining LaTiO_2N as final reaction products. Similar results were also found upon heating LaTiO_2N in He [33]. The only differences compared to the heating in Ar were a shift of the first reaction step to roughly 1000 °C and a more pronounced N_2 signal in the MS.

SrNbO_2N on the other hand reacts to the complex oxide $\text{Sr}_4\text{Nb}_2\text{O}_9$ and the binary nitride Nb_4N_3 upon heating in pure Argon. Again, the reaction takes place in two steps at 950 °C and 1200 °C, respectively [90]. In contrast to LaTiO_2N and SrTaO_2N (see below) the oxynitride is apparently completely destroyed at 1200 °C.

Also for SrTaO_2N a two-step reaction was found with reaction temperatures of roughly 600 °C and 1200 °C (Fig. 49). The XRD pattern indicates the presence of unreacted oxynitride and a small fraction of a still unidentified phase.

The most interesting reaction behaviours were observed for small oxygen contents. For LaTiO_2N and SrNbO_2N concentrations above 0.5% were sufficient to obtain the layered $\text{ABO}_{3.5}$ phases as final reaction products. On the other hand, these oxides were only formed after annealing at 1200 °C for prolonged times. More interestingly, the reoxidations proceeded via a different mechanism. In high oxygen contents the oxynitrides achieve their final oxygen contents and lose some nitrogen in a first step. The retained N_2 is completely released in the above-mentioned sharp weight drop and the layered oxide forms. In low oxygen contents, on the other hand, the final oxygen content is not reached for the intermediate N_2 -containing compound, i.e. its composition is $\text{ABO}_x(\text{N}_2)_y$ ($2 < x < 3.5$, $y < 1/2$). This intermediate loses its retained nitrogen at the “usual” temperature, leading to an anion-deficient material (ABO_x with $x < 3.5$) as indicated by a drop in the weight below the one of the final oxide (see dashed line in Fig. 48). The oxygen deficient oxide is afterwards completely oxidised at highest temperatures [91].

The most diverse thermal behaviour was observed for SrTaO_2N as depicted in Fig. 49. For this oxynitride the layered $\text{SrTaO}_{3.5}$ could only be obtained in oxygen-rich atmospheres. For concentrations below 10% significant amounts of $\text{Sr}_5\text{Ta}_4\text{O}_{15}$ were found. Surprisingly, only two values close to 90/10 and 20/80 were observed for the $\text{SrTaO}_{3.5}/\text{Sr}_5\text{Ta}_4\text{O}_{15}$ ratio.

It is to be noted that for all studied samples no crystalline phases other than the starting oxynitride, the final reaction products and the “perovskite-like” N_2 -containing intermediate could be identified by *ex-situ* or *in-situ* X-ray diffraction. Especially, the structure of the oxygen deficient compounds, which are observed for low oxygen contents, remains to be solved in future investigations.

6.2. Photocatalytic activity

Photocatalysis is based on the radiation-stimulated formation of electron/hole pairs in mater. If the recombination of these pairs is sufficiently slow, they may induce reduction/oxidation reactions. Since sunlight is one of the few energy sources mankind gets for free in inexhaustible quantities, chemical reactions started by a catalyst activated by sunlight are of special interest. There exists a large variety of (technical) applications for photocatalytic active compounds like the water splitting reaction, self-cleaning surfaces, disinfection of water or air purification.

TiO_2 is a well-known photocatalyst but has the disadvantage of being activated only by UV-light, thus leaving the greater part of the sunlight spectrum unused [92]. Doping with fluoride and/or nitrogen shifts its absorption edge to longer wavelengths and enhances the photocatalytic activity under visible light irradiation

[93–95]. There is an ongoing search for new materials that are making use of a broader range of wavelengths. Due to their rich colour spectrum, nitrogen-substituted perovskites are promising candidates for photocatalytic applications.

6.2.1. Photocatalysis in solution

Photocatalysis can be applied in water purification to clean wastewater contaminated by biological matter (bacteria, germs, viruses and fungi), hazardous metals deriving from industry (e.g. by reducing Cr(VI) to Cr(III)) or by organic compounds like pesticides or solvents (aldehydes, alcohols, phenols, etc). One possible application is the decontamination of sewage water from hospitals, which is often loaded with drugs that have a strong impact on the ecosystem.

The band gap of nitrogen-containing BaTiO_3 powders is lowered to 2.45 eV, a value well within the visible light range. Since this shift may result in a photocatalytic reactivity, the activities of N-containing barium titanate powders were examined, using the photodegradation of methyl orange (MO) as model reaction. The experiments were carried out in a glass reactor using a high-pressure mercury vapour lamp source shown in Fig. 50. In a first series of experiments the UV-part of the lamp spectrum was used by inserting a filter, which cuts off all wavelength above 365 nm. In a second set of measurements only the visible light was used by applying a filter, which absorbs all wavelengths below 473 nm.

Prior to the photocatalytic experiments, methyl orange (0.05 mmol/l) and barium titanate powder (1.7 mmol/l) were well mixed and the absorbance of this starting dispersion was determined on a Shimadzu UV-3101PC UV-Vis spectrophotometer. During the photocatalytic process the irradiation was interrupted every 30 min and the absorbance was re-measured. The kinetic data of the photodegradation of methyl orange (MO) are shown in Fig. 51.

In the presence of $\text{BaTi}(\text{O},\text{N})_x$ particles alone, MO did not degrade significantly during UV irradiation ($\lambda \leq 365$ nm). We therefore tested the influence of H_2O_2 as additional oxidant. When MO mixed with 10 mmol/l H_2O_2 alone (i.e. without $\text{BaTi}(\text{O},\text{N})_x$), only a slight degradation was observed (Fig. 51). In contrast, a noticeable photocatalytic activity was found in the presence of both $\text{BaTi}(\text{O},\text{N})_x$ and H_2O_2 . The observed reaction rate was comparable to the photocatalytic activity of the TiO_2 standard P25 (Degussa). It has to be taken into account though, that the specific surface area of P25 is about 10 times larger than the one of $\text{BaTi}(\text{O},\text{N})_x$ (4–5 m^2/g as determined by BET). If normalised to the same surface area, the activity of $\text{BaTi}(\text{O},\text{N})_x$ is roughly by a factor 5 higher compared to P25.

The photocatalytic activity of the samples was also tested under irradiation with visible light ($\lambda \geq 473$ nm). The degradation rates

Fig. 50. Scheme of the set-up for the photodegradation of methyl orange (1: high-pressure mercury vapour lamp, 2: aperture, 3: cuvette filled with water, 4: filter, 5: reactor, 6: stirrer).

Fig. 51. Degradation of methyl orange (MO) upon UV irradiation ($\lambda \leq 365$ nm).

were found to be considerably different, when the UV-range of the light source is filtered out. Only the mixture of $\text{BaTi}(\text{O},\text{N})_x$ and H_2O_2 showed a noticeable activity as illustrated in Fig. 52, while P25 was less active under the same conditions.

The outlined results prove that N-doped BaTiO_3 is indeed a promising candidate for the light-induced oxidation of organic compounds, at least when the UV-part of the spectrum is not cut-off. While the use of UV-radiation might be a considerable limitation for some applications, it is not problematic for the decontamination of wastewater from organic pollutants. For this reason, N-substituted BaTiO_3 might be applicable for the photocatalysed processing of sewages, e.g. from hospitals.

6.2.2. Photocatalytic water splitting

Perhaps the most appealing application for photocatalysis is the water splitting reaction. The evolution of H_2 and O_2 from water by sunlight would be the cheapest and most convenient way to solve mankind's energy problem. Hydrogen is often referred to as a *green* or *sustainable* fuel since upon oxidation only water evolves. Unfortunately, nowadays about 99% of all hydrogen produced stems from steam reforming/converting of either natural gas or crude oil, leading to the same amount of the greenhouse gas CO_2 as the simple burning of these fossil fuels does. Because of unavoidable energy losses during fabrication and storage, the H_2 -technology is in fact even less effective and thus more polluting than the classical combustion technology.

Fig. 52. Methyl orange (MO) degradation under irradiation with visible light ($\lambda \geq 473$ nm) in the presence of H_2O_2 , P25/ H_2O_2 , and $\text{BaTi}(\text{O},\text{N})_x/\text{H}_2\text{O}_2$.

Fig. 53. Scheme of the set-up for the O_2 and H_2 evolution by photocatalysis [80].

The ideal way to produce hydrogen is the water splitting reaction photocatalysed by sunlight. Besides hydrogen, the other product of the water splitting reaction is oxygen, so hydrogen production and consumption results in a closed cycle. Against this background there has been tremendous effort to find a suitable photocatalyst for the water splitting reaction. TiO_2 is known as an effective photocatalyst for more than thirty years. The problem with titanium dioxide is that it only absorbs light in the UV-part of the light spectrum and therefore only a fraction of the available radiation can be used.

Lately, several perovskite type oxynitrides have been checked for their photocatalytic activity in the water splitting reaction. In two articles the activity of $LaTiO_2N$ prepared from an oxide precursor obtained by the citrate route and nitridated under different conditions was studied. In the first work the nitridation temperature was varied from 600 °C to 950 °C [11]. A considerable activity for both H_2 and O_2 evolution was found for a sample with a nitrogen content of 70% of the theoretical amount. Upon partial substitution of La^{3+} by Ca^{2+} an increased activity was observed. In a second investigation [96] the nitridation reaction at 850 °C was found to be finished after roughly 100 h. An incompletely reacted sample (after 75 h) showed the largest O_2 evolution. The photoactivity of $LaTiO_xN_y$ films deposited by RF-magnetron sputtering on $SrTiO_3:Nb$ substrates was recently studied [97]. The highest activity was observed for a well-crystalline film with a low nitrogen content. In solutions containing $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ or Na_2SO_4 , a photocurrent was observed at wavelengths of up to 540 nm. The photocurrent strongly increased upon modification of the oxynitride particle surfaces by colloidal IrO_2 .

Photocatalysed water splitting was also observed for the layered oxynitrides $Rb_{1+x}Ca_2Nb_3O_{10-x}N_x \cdot yH_2O$ ($x = 0.7-0.8$, $y = 0.4-0.6$)

and $Rb_{1+x}LaNb_2O_{7-x}N_x \cdot yH_2O$ ($x = 0.7-0.8$, $y = 0.5-1.0$) upon irradiation by an unfiltered Xe-lamp [98]. In contrast to $LaTiO_2N$ these compounds strongly decomposed under the reaction conditions. Also for nitrogen-doped $SrNbO_{3.5}$ the highest activity for H_2 evolution was observed for a partly substituted sample [99]. A comparison of $ATaO_2N$ ($A = Ca, Sr, Ba$) showed $SrTaO_2N$ to be the most effective catalyst for the H_2 evolution but none of these oxynitrides led to the evolution of O_2 [100]. While the formation of H_2 and O_2 are usually studied in separate reactions, a combination of Pt-loaded $ATaO_2N$ ($A = Ca, Ba$) and Pt-loaded WO_3 was very recently reported to lead to an overall water splitting (e.g. simultaneous evolution of H_2 and O_2) under visible light in the presence of I^- -ions [101].

In our own investigations selected oxynitride perovskites were studied for their photocatalytic activity [80]. The used experimental set-up is described in [11] and a schematic sketch is illustrated in Fig. 53. The set-up consists of a Pyrex reactor vessel connected to a closed gas circulation and an evacuation system. The reactor is illuminated by a 300 W Xe-lamp equipped with UV cut-off filter ($\lambda > 420$ nm) and a water-cooling system.

The two individual reactions (formation of hydrogen and oxygen, respectively) were studied applying slightly different reaction conditions. Reduction of H^+ to H_2 was examined using 0.5 wt% Pt as co-catalyst in a water solution containing 10% volume of methanol. The alcohol serves as sacrificial electron donor.

Table 5

Reaction conditions for the photocatalysed water splitting reaction.

	H_2 evolution	O_2 evolution
Catalyst	0.2 g	0.2 g
Co-catalyst	Pt 0.5 wt% ^a	None
Reaction solution ^b	200 ml aqueous solution with 10 vol% methanol	200 ml 0.01 M $AgNO_3$ aqueous solution
Additional reagents	None	La_2O_3 0.2 g ^c
Light source	300 W Xe-lamp with cut-off filter ($\lambda > 420$ nm)	300 W Xe-lamp with cut-off filter ($\lambda > 420$ nm)

^a Impregnation method from $H_2PtCl_6 \cdot 6H_2O$, followed by reduction in H_2 at 473 K for 1 h.

^b Containing sacrificial reagent for H_2 or O_2 evolution.

^c Maintaining pH of solution around 8.

Fig. 54. O_2 and H_2 evolution for selected oxynitride perovskites resulting from 5 h of reaction [80].

Fig. 55. Oxygen, hydrogen and nitrogen evolution within 5 h of photocatalytic measurements for $\text{Sr}_{(1-x)}\text{La}_x\text{Ti}(\text{O},\text{N})_3$ oxynitrides.

Oxidation of H_2O to O_2 in the presence of Ag^+ acting as electron acceptor was measured in a separate reaction step. La_2O_3 was added to maintain the $\text{pH} \sim 8$ during the complete reaction time. Prior to the experiment, the reaction solution was evacuated several times to remove air before the lamp was switched on. During the reaction time of 5 h the evolved gases were analysed by gas chromatography. A summary of the reaction conditions is given in Table 5. It is to be noted that for none of the studied compounds a significant amount of N_2 was detected. This finding indicated that the perovskites oxynitrides are stable under the chosen reaction conditions.

The photocatalytic activities of the examined samples are shown in Fig. 54. A considerable hydrogen evolution from water–methanol solutions was observed for NdTaON_2 , BaTaO_2N and LaTiO_2N with total H_2 amounts of 1, 4 and 9 μmol , respectively.

For the oxygen evolution from the Ag^+ aqueous solution the compounds SrTaO_2N , BaTaO_2N , LaTiO_2N and CaNbO_2N were found to show a noteworthy activity with a total O_2 production of 4, 6, 22 and 37 μmol , respectively.

The photocatalytic activity of CaNbO_2N was surprisingly high for the oxygen evolution. In the same reaction time almost twice as much O_2 was formed compared to LaTiO_2N , which is the so far best examined oxynitride perovskite. On the other hand, no H_2 formation was observed for CaNbO_2N while LaTiO_2N has a considerable activity for both individual reactions. The different activities most likely result from the energy positions of the valence and conducting bands. For the oxygen evolution, potential of the top of the valence band must be lower than the one of the $\text{H}_2\text{O}/\text{O}_2$ redox pair, while for the hydrogen formation the bottom of the conduction band must be lower than the one of H_2/H^+ . Therefore, not only the size of the band gap but also its absolute energy position has to be suitable for the water splitting reaction.

In Ref. [11] an increased photocatalytic activity of LaTiO_2N was observed upon partial substitution of Ca^{2+} for La^{3+} . To investigate the influence of other alkaline earths, we prepared a series of $\text{Sr}_{(1-x)}\text{La}_x\text{Ti}(\text{O},\text{N})_3$ oxynitrides from amorphous oxides synthesised by the citric acid method. The results of the photocatalytic investigations are summarised in Fig. 55. No nitrogen evolution was observed for any compound, proving that the samples do not decompose during the photocatalytic experiments.

A pronounced change in the activity with composition was observed. Hydrogen evolution was only observed for $x=0$ and $x=1$, with the largest amount for LaTiO_2N . The compounds with $x=0.25$, 0.5 and 1 led to almost the same O_2 quantities of approximately 25 μmol in 5 h. The most remarkable result is the very high oxygen evolution of 200 μmol for $x=0.75$, which is more than five times higher than the one found for CaNbO_2N , the best photocatalyst in Fig. 54.

While $\text{Sr}_{0.25}\text{La}_{0.75}\text{Ti}(\text{O},\text{N})_3$ and CaNbO_2N show a high activity for the oxidation of water, the results outlined indicate that LaTiO_2N is the only compound active in both partial reactions. It is therefore the most promising oxynitride perovskite for the photocatalytic water splitting reaction. It should be noted though, that all studied compounds were completely nitrated, i.e. no remaining oxide phases were present. From the references listed in the introduction of this chapter as well as from the results discussed in the following it seems that in fact partly reacted compounds may be much better candidates.

6.2.3. Gas phase photocatalysis

In air purification photocatalysis can be used for sterilisation and deodourisation in hospitals, hotels and homes, destroying micro organisms and/or oxidising unpleasant odour-causing organic molecules (as cigarette smoke, mould, domestic smells and pet-odour). In outdoor applications photocatalysts can serve to purify the air in cities by eliminating toxic gases and/or contaminant molecules (like NO_x , SO_x or volatile organic compounds) that are expelled as exhaust gas from vehicles.

While the photocatalytic activity of oxynitride perovskites in the water splitting has already been investigated to some extent, very little is known about the photocatalytic gas phase decomposition of organic molecules. To the best of our knowledge, the only study so far concerned the photocatalysed decomposition of formaldehyde by $\text{NaTaO}_{3-x}\text{N}_x$ [35]. The highest activity was observed for a sample with only a very small nitrogen content of $x \approx 0.05$.

To examine if oxynitride perovskites can be used for air purification, we examined the photocatalysed oxidation of simple organic molecules in the gas phase. Because of biological hazards like skin burning and eyes injury, ultra violet light cannot be employed in domestic applications e.g. to promote the photocatalytic decomposition of odour molecules. Therefore, an activation by the visible part of the light spectrum is highly desirable.

Fig. 56. Schematic sketch of the photocatalysis set-up (left). The right part shows a photo of the open spectrometer with the irradiated reactor.

Fig. 57. Typical FTIR 3D graphic obtained during photodecomposition of acetone (left). The right part of the figure shows characteristic peaks at the start and end point of the reaction (modified from [44]).

The photocatalytic activity of oxynitrides in the oxidation reaction of gaseous organic compounds was studied *in-situ* by infrared (IR) spectroscopy in a self-designed experimental set-up. It consists of a quartz reaction vessel with KBr windows mounted in an IR spectrometer. Suspensions of the oxynitrides were doctor bladed on glass slides, dried overnight and fixed in the quartz vessel, which afterwards was flushed with synthetic air to remove CO₂. A small amount of a volatile organic compound was injected through a diaphragm and allowed to evaporate for a couple of minutes. Afterwards, the reactor was illuminated by a 150 W Xe-lamp for several hours and the IR spectra were recorded continuously. The high energetic part of the Xe-lamp was cut-off by a UV-filter ($\lambda > 420$ nm). Blank measurements with the empty sample holder were carried out and subtracted from the data. Carbonyl compounds are particularly suited since the C=O group as well as the oxidation product CO₂ are easily detected by infrared spectroscopy. During the course of the research program the experimental set-up was improved several times with respect to the injection system and gas tightness. Fig. 56 shows the working principle and a photograph of the most recent version of the reactor installed in the spectrometer. In Fig. 57 the IR spectra during a typical acetone photodecomposition experiment are depicted. The left graphic is a pseudo-3D plot of the intensity change with increasing irradiation time in which the most characteristic peaks are marked. In the right part of the figure peaks related to acetone, CO₂ and water are plotted at the beginning and ending of the reaction [44].

The results of the photocatalysed acetone oxidation for different oxynitride perovskites are plotted in Fig. 58. The integrated peak intensities were normalised with respect to their values at the beginning of reaction and the blank measurement was subtracted from the data. Most of the samples showed a considerable activity and three of them revealed an even better activity than P25. This compound, which is a commercial trademark from Degussa for nanosized TiO₂ composed of ca. 30 wt% rutile and 70 wt% anatase, serves as a quasi-standard for photocatalytic investigations. The samples with the highest decomposition rate were NdTaO₂N, followed by LaTiO₂N prepared by the Pechini-method, CaNbO₂N and SrNbO₂N, respectively. The high activity of NdTaO₂N is especially noteworthy since the sample was prepared by the classical mixed oxide method and therefore possesses only a small surface area.

The pronounced influence of the specific surface area on the photocatalytic activity becomes obvious from a comparison of the three LaTiO₂N samples studied. These were synthesised by solid-state reaction, spray pyrolysis, and the Pechini-method, respectively.

BET surfaces of 3.6, 10, and 13.7 m²/g were measured. From Fig. 58 it can be seen that the oxidation rate of acetone follows this trend, i.e. with increasing BET surface an enhanced photocatalytic activity is observed. It is therefore reasonable to assume that oxynitrides with a specific surface area comparable to P25 may show much higher reaction rates than titanium dioxide.

The influence of the synthesis procedure on particle size, BET surface and photocatalytic activity was additionally studied using LaTi(O,N)₃ nanopowders ammonolysed at varying temperatures [44]. In a first step, nanoparticles of an amorphous La/Ti-oxide were synthesised by the polyol technique. Ammonolysis was carried out for 3 h at temperatures of 800, 870, 920 and 1000 °C. With increasing nitridation temperature the colour of the samples changed from orange to brown reflecting a reduction of the optical band gap from 2.6 to 2.3 eV. Although no other phases than the oxynitride were detectable in any of the XRD patterns, ERDA analysis revealed an incomplete reaction for all samples except for the one reacted at 1000 °C. The obtained N/(N+O) ratios correspond to a 28%, 71%, 95%, and 98% reaction completeness for $T = 800, 870, 920$, and 1000 °C. Simultaneously, the BET surface decreased from 44 m²/g to 16 m²/g [44]. The comparison of the carbonyl and CO₂ peak intensities shown in Fig. 59 clearly reveals that the sample reacted at the intermediate temperature 870 °C exhibits the highest catalytic activity.

Similar results were also found in a recent study on the hydrogen production from water-methanol mixtures with

Fig. 58. Normalised integrated C=O peak intensity as function of time for different oxynitride photocatalysts.

Fig. 59. Time dependence of the C=O and CO₂ IR peak intensities for the photocatalysed oxidation of acetone using LaTi(O,N)₃ samples nitridated for 3 h at 800 °C, 870 °C, 920 °C, 1000 °C (modified from [44]).

nitrogen-doped SrNbO_{3.5} as photocatalyst. For this compound the highest photocatalytic activity was observed for an intermediate nitrogen concentration, i.e. an incomplete nitridation [99]. SrNbO_{3.5} possesses the same $n = 4$ layered perovskite structure as LaTiO_{3.5}. In layered perovskites the interlayer space can act as reaction sites while the electron-hole pair recombination is hindered by the separation of the slabs. The nitrogen substitution decreases the band gap leading to an absorption of visible light. A complete reaction, on the other hand, leads to a collapse of the layered structure. Therefore, the highest activity may be found for a medium nitrogen doping level, which shifts the absorption edge to the visible light region but remains the layered structure. An optimised photocatalytic activity may thus be obtained by a large surface area, an adjusted optical band gap and a considerable remaining fraction of the layered parent oxide.

7. Conclusions and outlook

Oxynitride perovskites are highly interesting both for their structural challenges and their physical properties, which offer the possibility of applications as pigments, dielectrics or photocatalysts. The known perovskite oxynitrides are based on electro-positive metals. Under conventional nitridation conditions transition metals with intermediate electronegativities like V, Mo, W often undergo partial reduction while the late transition metals and many main group metals like Sn, Sb or Pb are usually reduced to the corresponding metals. One interesting task for the future is therefore to explore new synthesis methods that allow preparing oxynitrides of such elements. One possibility is the reaction of amides with oxides [102]. Other alternative synthesis routes are the reaction of binary nitrides with oxides, the controlled oxidation of nitrides and the reaction of oxides with solid ammonia sources such as urea or amines. Furthermore, we were able to demonstrate that plasma-assisted nitridations show various advantages compared to the conventional thermal analysis.

Oxynitride perovskites are usually obtained as polycrystalline samples. A number of soft-chemistry approaches have been recently developed to also prepare nanoscopic particles. In addition, various methods like spin-coating, PLD or RF-sputtering were successfully applied in the synthesis of thin films. The ammonolysis of oxide single crystals leads to thick oxynitride films in the micrometer range, which possess a very small mosaic spread, a fixed epitaxial relationship to the oxide material and are well suited for measurements of various physical properties. These samples may also be used to study the reaction kinetics of the nitridation and give information on the nitrogen mobility. The growth of oxynitride perovskite single crystals remains a challenging task. It seems not to be possible to grow crystals directly, because oxynitrides cannot be melted but decompose at high

temperatures. Therefore the nitridation of oxide crystals seems to be a more promising approach. Such completely reacted single crystals are desired for measurements of physical properties.

For the comprehensive investigation of the chemical composition and crystal structure of oxynitride perovskites a variety of complementary methods need to be applied. The chemical analysis based either on hotgas extraction or on ion-selective electrodes provides the total nitrogen content. To verify the incorporation of N³⁻ in the anionic sub-lattice and for structural investigations neutron diffraction can be used for high N-contents while ¹⁴N solid-state NMR was successfully applied for low concentrations. Finally, spectroscopic methods like EXAFS yield information on the local structure. State of the art computational methods were found to be highly useful for *ab-initio* predictions of the local symmetry. While X-ray and neutron diffraction yield information on the average crystal structure, local deviations can better be detected by transmission electron microscopy in combination with electron diffraction.

The introduction of nitrogen leads to strong changes in the electronic structure of perovskites as for example seen in X-ray absorption spectroscopy. Many compounds exhibit interesting modified physical properties, like an intense colouring. In addition, the electrical conductivity is highly affected by nitrogen substitution. While oxynitrides with d⁰-configuration usually have a higher conductivity than related pure oxides, for transition metals with partly occupied d-states this is not generally the case. On the other hand, e.g. for SrMo(O,N)₃ improved thermoelectric properties have been observed, compared to the parent oxide.

Some perovskite oxynitrides were reported to have unusually high dielectric permittivities making them interesting e.g. for capacitors. On the other hand, the enhanced electric conductivity is a severe disadvantage for this application. The “sandwich” structure of partly nitridated single crystals may be beneficial here, since it provides a combination of the large dielectric constant of the oxynitride and the low conductivity of the oxide.

Many oxynitride perovskites show astonishing stabilities. In some cases they can even be boiled in concentrated oxidising acids without any detectable reaction. In addition their thermal stability is also surprisingly high. This point is of special interest for possible application e.g. as pigments since these are usually submitted to heat treatments when incorporated in commodities like polymers, enamels or ceramics. Our investigations indicated that perovskite oxynitrides of Nb, Ta and Ti are thermally stable up to approximately 400 °C, regardless of the oxygen concentration. In the presence of at least small quantities of oxygen the respective ABO_{3.5} oxides are found as reaction products. In oxygen-free atmospheres, quite deviating reaction products were observed for the different oxynitrides. These comprise binary oxides and nitrides or complex oxides. Both on heating in oxidising and inert atmospheres, the

thermal decompositions involve complex intermediates. It is noteworthy though, that none of these intermediates seem to be crystalline, i.e. they could not be detected by *ex-* or *in-situ* XRD. Apart from spectroscopic investigations like Raman spectroscopy, the nature of these intermediates is still mostly unknown. Their characterisation would be a challenging task for future investigations.

Many of the investigated oxynitride perovskites exhibit a considerable photocatalytic activity in different reactions. The decomposition of organic molecules is catalysed under irradiation both in aqueous solution and in the gas phase. Also the water splitting reaction was found to be photocatalysed by oxynitrides. Several studies reveal that partly nitridated compounds are in fact more reactive than stoichiometric ones. The obtained results clearly encourage new studies in this field. Especially the surface area of the samples could further be increased and different co-catalysts may be tested.

In conclusion it can be stated that the partial substitution of nitrogen for oxygen in the perovskite framework leads to surprising new physical and chemical properties and new degrees of structural freedom, making oxynitride perovskites a highly fascinating class of compounds.

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