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Perovskite-type $SrTi_{1-x}Nb_x(O,N)_3$ compounds: Synthesis, crystal structure and optical properties

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ABSTRACT

The synthesis, crystal structure, thermal stability and absorbance spectra of perovskite-type oxynitrides with the general formula $SrTi_{1-x}Nb_x(O,N)_3$ (x=0.05, 0.10, 0.20, 0.50, 0.80, 0.90, 0.95) have been investigated. Oxide samples were prepared by a polymerized complex synthesis route and post-treated under ammonia at 850 °C for 24 h to substitute nitrogen for oxygen. Synchrotron X-ray powder diffraction (XRD) evidenced that the mixed oxide phases were all transformed into oxynitrides with perovskite-type structure during a thermal ammonolysis. $SrTi_{1-x}Nb_x(O,N)_3$ with compositions $x \le 0.80$ crystallized in a cubic and samples with $x \ge 0.90$ in a tetragonal structure. The Rietveld refinement indicated a continuous enlargement of the lattice parameters towards higher niobium content of the samples. Thermogravimetric analysis (TGA) and hotgas extraction revealed the dependence of the nitrogen incorporation upon the degree of niobium content. Furthermore, TGA disclosed stability for all oxynitrides at $T \le 400$ °C. Diffuse reflectance spectroscopy indicated a continuous decrease of the band gap's width from 3.24 eV ($SrTi_{0.95}Nb_{0.05}$ ($O,N)_3$) to 1.82 eV ($SrTi_{0.05}Nb_{0.95}(O,N)_3$) caused by the increasing amount of nitrogen towards the latter composition.

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1. Introduction

Perovskites tolerate substitutions with a wide range of elements because of their flexible crystal structure. Cationic substitutions in ABX₃ perovskite-type compounds are well explored and provide a large class of functional materials used for diverse applications depending on their specific composition [1–3]. Anionic substitution in perovskites is comparatively less investigated. Oxygen is most likely replaced by nitrogen and fluorine, leading to oxynitrides and oxyfluorides [4] and the synthesis of oxynitrides has been successfully accomplished in the past [5–10]. The resulting increase of negative charge (N^{3–}) compared to the parent oxide can be balanced by substituting with a higher valence A- or B-site cation (e.g. BaTiO₃ \rightarrow LaTiO₂N [10]), by changing the oxidation state of the transition metal (e.g. SrMoO₄ \rightarrow SrMoO_{2.5}N_{0.5} [11]), by reducing the

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number of anions (e.g. $BaTaO_{3.5} \rightarrow BaTaON_2$ [12]) and by forming oxygen vacancies ($SrTiO_3 \rightarrow SrTiO_{3-\delta}N_x$ [13]).

In a perovskite-type d⁰ transition-metal oxide (with d⁰ such as Ti⁴⁺, Ta⁵⁺ and Nb⁵⁺), the top of the valence band is mainly formed by oxygen 2p (O 2p) interactions, whereas the bottom of the conduction band consists of interactions between the transitionmetal dt_{2g} and O 2p orbitals [14]. The purpose of nitrogen insertion into the oxide lattice is to modify the electronic structure of the pristine oxide primarily at the valence band [15]. Since nitrogen $(\chi(N)=3.04)$ is less electronegative than oxygen $(\chi(O)=3.44)$, the nitrogen 2p (N 2p) levels are energetically located above the O 2p levels and mixing of N 2p and O 2p levels therefore leads to a narrower band gap. Hence, oxynitrides may absorb visible light and are consequently often coloured [16,17]. Chévire et al. [10] reported a progressive colour and band-gap change in the system LaTiO₂ N-ATiO₃ (A=Sr, Ba) depending on the nitrogen content. Furthermore, it has recently been shown that nitrogen substitution can diminish the band gap by \sim 1.6 eV from 3.3 eV for LaNbO₄ down to 1.7 eV for LaNbON₂ [8]. Nevertheless, besides modelling the band gap with nitrogen, structural distortions and the electronegativity χ of the B-site cation can also change the electronic configuration near the Fermi level [14,16,17].

Because of their variable colours, oxynitrides have a potential as non-toxic pigments whereby they could replace the currently used pigments that contain dangerous elements (Cd, Pb, Cr, Hg,

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etc.) [16,18]. It was demonstrated that depending on the cationic composition, $Ca_{1-x}La_xTaO_{(2-x)}N_{(1+x)}$ obtain colours from red to yellow. Therefore it could substitute cadmium sulphoselenide pigments, which are widely used nowadays [17]. Furthermore, the possibility to tailor the band gap promotes oxynitrides as interesting candidates in the photocatalytical and photoelectrochemical water-splitting reaction [5,6,19]. A shortcoming of most oxide semiconductors used as photocatalysts is their wide band gap which prohibits them from absorbing solar radiation $\sim \lambda > 400$ nm [20]. Because the photon flux is highest in the range of the visible light (400 nm $< \lambda <$ 700 nm). oxynitrides may provide an efficient solar energy to hydrogen conversion-rate. Another requirement for a material used in the photocatalytic approach is that it should be defect-free (e.g. no anionic vacancies) in order to prevent electron-hole recombination [20]. Nitridation of SrTiO₃ has been shown to evoke undesired oxygen vacancies but a diminishment of these was achieved by co-substituting La^{3+} and N^{3-} in SrTiO₃ [21]. Recently, the effect of co-"doping" SrTiO₃ with Nb⁵⁺ and N³⁻ has been studied and a change of the band gap and the photocatalytic activity with the amount of the niobium "dopant" was observed [22]. The cross substitution of SrTiO₃ with nitrogen and niobium leads to the system $SrTi_{1-x}Nb_x(O,N)_3$ and the reaction can be generalized as

$$SrTiO_3 + xNb^{5+} + xN^{3-} \rightarrow SrTi_{1-x}Nb_xO_{3-x}N_x + xTi^{4+} + xO^{2-}$$
 (1)

The two end compounds of the system, $SrTiO_3$ and $SrNbO_2N$ crystallize in the cubic space group Pm-3m [23] and in a distorted perovskite structure, respectively. A tetragonal structure with space group I4/mcm has been suggested for $SrNbO_2N$ [9,24]. A recent work that combined neutron with electron diffraction postulated that besides the rotation about the *c*-axis also an anionic ordering might be present in $SrNbO_2N$, thus lowering the symmetry to the monoclinic space group I112/m [25].

In the present work, the structural changes between the cubic $SrTiO_3$ and the distorted $SrNbO_2N$ were investigated. Additionally, the influence of these structural modifications on the band gap was analyzed. Furthermore, a progressive change of the nitrogen amount in the anionic lattice was expected, which in turn would influence the evolution of the band gap and colour throughout the solid solution.

2. Experimental

2.1. Oxide precursors

A series of seven oxide precursor with the general composition $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_{3+0.5x}$ (*x*=0.05, 0.10, 0.20, 0.50, 0.80, 0.90, 0.95) was prepared by a Pechini-type polymerized complex route with citric acid (CA) as chelating and ethylene glycol (EG) as polymerizing agents. The molar ratio of the cations (strontium, titanium and niobium), EG and CA was according to Sr/Ti/Nb/EG/CA=1/1-x/x/40/10 where *x* stands for the desired substitution level for a specific composition [26].

Titanium isopropoxide (Ti(O-*i*Pr)₄, Sigma-Aldrich, 99.999%) was added to EG (Merck, \geq 99.5%), therein CA (Alfa Aesar, \geq 99%) was appended. Strontium nitrate (Sr(NO₃)₂, Merck, \geq 99%) was dissolved in deionized water and niobium pentachloride (NbCl₅, Sigma-Aldrich, \geq 99%) in EtOH (Merck, \geq 99.5%). Both solutions were poured into the mixture of EG, CA and Ti(O-*i*Pr)₄. In the following, this mix was stirred for 4 h under reflux at 70 °C to promote the complete dissolution of CA and the formation of metal–citrate complexes. Thereafter, the viscous solution was heated at 120 °C for 4 h in order to continue the polymer formation by an esterification between CA and EG. Afterwards, the gel was slowly heated up to 300 °C to decompose the organic matrix. Finally, the obtained

black residues were ground with an agate pestle and heated in an alumina crucible at 1000 °C for 6 h with a heating ramp of 10 °C min⁻¹ resulting in white oxide powders.

2.2. Thermal ammonolysis

The as-synthesized oxide precursors were transformed into oxynitrides via thermal ammonolysis, a reaction between an oxide precursor and ammonia (NH₃) at elevated temperatures [6,7,12]. Batches of 1.5 g oxide powder were mixed with potassium chloride (KCl) in the molar ratio oxide/KCl = 1/3. KCl acted as flux to enhance the phase formation and crystallinity of the oxynitride. The reaction was carried out in an alumina cavity-reactor. The air inside the cavity-reactor was evacuated twice before filling it to atmospheric pressure with argon (Ar) (Messer, \geq 99.998%). Afterwards, the samples were heated with 10 °C min⁻¹ under Ar up to 750 °C. At this temperature, Ar was replaced by NH₃ (Messer, \geq 99.98%) and further heated until reaching the reaction temperature of 850 °C. The reaction was completed after 24 h and the oxynitride samples were cooled down under Ar. The flow rate during the synthesis was 200 mL min⁻¹ for NH₃ and Ar. Thereafter, the powders were washed with deionized water to eliminate all traces of KCl. The complete removal of the flux was confirmed by testing the supernatant water with an aqueous solution of AgNO₃. Finally, all powders were dried at 130 °C for approximately 3 h.

2.3. Characterisation

Lab source X-ray diffraction (XRD) measurements were performed for all oxides, oxynitrides and reoxidized oxynitrides. The instrument was a PANanalytical X'Pert PRO system with XCelerator detector operating in Bragg–Brentano geometry $(\theta/2\theta)$ using Cu $K\alpha_1$ (45 kV and 40 mA) and a Ge (1 1 1) incident monochromator.

Synchrotron XRD experiments were performed for all oxides and oxynitrides at the MS Powder beamline at the Swiss Light Source. The incident X-rays were monochromatized to the wavelength of 0.44 Å. Quartz capillaries (Hilgenberg GmbH) with a nominal diameter of 0.33 mm were filled with the powders and sealed with capillary wax. The diffraction patterns were scanned from 0.1° to 116° with a step size of 0.004° in 2 θ . XRD patterns of the oxynitrides were analysed by Rietveld refinement using the software *FullProf* [27]. Thompson–Cox–Hastings pseudo-Voigt [28] was chosen as a profile function and the refined range was from 10° to 50° in 2 θ .

Thermogravimetric analysis (TGA) was used to study the thermal reoxidation and stability in air as well as the nitrogen content of the oxynitrides. The experiments were performed with a NETZSCH STA 409 CD thermobalance coupled to a NETZSCH QMS 403 C Aeolos mass spectrometer. Around 50 mg of each oxynitride was heated in an alumina crucible with 10 °C min⁻¹ up to 1500 °C in synthetic air with a flow of 50 mL min⁻¹. Additionally, to check the gas species absorbed and released at each temperature, coupled mass spectrometry (MS) was used for certain specific measurements with an Ar/O₂ atmosphere (volume ratio of 80/20). The other experimental parameters were the same as those of the TGA measurements. The nitrogen stoichiometry (*y*) was evaluated from the weight gain Δm measured during the experiment according to Ref. [6]:

$$y = \frac{2\Delta m}{[(3/2)M(O_2) - M(N_2)]} \times \frac{M(ABO_{x+3y/2})}{m(ABO_{x+3y/2})}$$
(2)

where $M(O_2)$ is the molar mass of molecular oxygen, $M(N_2)$ is the molar mass of molecular nitrogen, $M(ABO_{x+3y/2})$ is the molar

mass of the formed oxide and $m(ABO_{x+3y/2})$ is the mass of the formed oxide.

Hotgas extraction using a LECO TC500 analyzer provided the O/N content of the samples x=0.20, 0.50, 0.80 for SrTi_{1-x} Nb_x(O,N)₃ oxynitrides. Nitrogen was measured as N₂ by thermal conductivity and oxygen as CO₂ by infrared radiation.

UV-visible diffuse reflectance spectra were collected with a UV-3600 Shimadzu UV-vis–NIR spectrophotometer with an integrating sphere over a spectral range of 300–1500 nm (4.13–0.83 eV), measuring in reflectance mode. The powders were pressed into pellets of about 200 mg each. Only for the relatively dark oxynitride sample x=0.20, BaSO₄ powder was added in the ratio 1/9=sample /BaSO₄. The diffuse reflectance was transformed into absorbance according to Ref. [29]

$$A = R_{\max} - R_{cd} \tag{3}$$

where *A* is the absorbance, R_{max} is the maximum value of the diffuse reflectance and R_{cd} is the diffuse reflectance measured over a certain wavelength interval.

Shapiro's method [30] was chosen to approximate the optical band gap E_g . The minimal absorbance A calculated with Eq. (3) is set to zero and the band gap wavelength is determined by extrapolating the long-wavelength edge (the onset) of the absorbance to this zero line.

3. Results and discussion

3.1. X-ray diffraction and Rietveld refinement

The diffraction pattern of the oxides revealed mixed crystal phases for the different niobium substitution levels. Samples x=0.05-0.50 crystallized in space group Pm-3m, sample x=0.80 crystallized in space group R3m and samples x=0.90 and 0.95 possessed a layered-perovskite structure (Pna21) as shown in Fig. 1. After nitrogen substitution, the diffraction pattern indicated perovskite-type structure for all seven compositions, thus offering a $SrTi_{1-x}Nb_x(O,N)_3$ solid solution (Fig. 2). Oxynitride samples with x=0.20 and 0.50 had a minor impurity phase.

The results of the Rietveld analysis done for the oxynitrides, i.e. crystallographic data as well as agreement factors are given in Table 1. The cubic space group *Pm*-3*m* was chosen as model for samples x = 0.05 - 0.80, according to the end member SrTiO₃. For samples x=0.90 and 0.95, the tetragonal space group *I*4/*mcm* [9.24] was used as a first approach because peak splitting in x=0.90 and 0.95 in the higher order reflections was observed (Fig. 3). In a second approach, these two samples were refined in the monoclinic space group *I*112/*m* [25] which allows the possibility of anionic ordering. The refinement with the monoclinic structure did not show an improvement of the agreement factor. Yet, with our X-ray data we could neither exclude nor postulate an anionic ordering. The tetragonal *I*4/*mcm* evolves from the cubic *Pm-3m* by an octahedral rotation about the cubic [0 0 1] axis with out-of-phase rotations of successive planes (a⁰a⁰c⁻ in Glazer notation [31]). The structural effect of octahedral tilting is to double some or all of the cubic unit cell axes, which gives rise to the splitting of reflections and appearance of superlattice reflections in the XRD pattern [32]. The reflection splitting for x = 0.95 is apparent, whereas it is less pronounced in x=0.90 (Fig. 3). Thus it is expected that the octahedral tilting in sample x=0.90 is smaller than in sample x=0.95. This is plausible since Goldschmidt's tolerance factor t [32] deviates slightly but increasingly from unity moving towards the niobium-rich side of the system. The enlargement of the unit cell parameters with increasing niobium



Fig. 1. Synchrotron XRD pattern of oxide samples x=0.05 (*Pm*-3*m*), x=0.80 (*R*3*m*) and x=0.95 (*Pna*21); $\lambda=0.44$ Å.



Fig. 2. Synchrotron XRD pattern of oxynitride samples x=0.05-0.95 with perovskite-type structure, 'o' assigns impurity phase; $\lambda=0.44$ Å.

Table 1

Summary of Rietveld refinement of oxynitride samples x = 0.05 - 0.95.

Nb content <i>x</i>	0.05	0.10	0.20	0.50	0.80	0.90	0.95
Space group a (Å)	Pm-3m 3.8983(0)	Pm-3m 3.9046(9)	<i>Pm-3m</i> 3.9149(8)	Pm-3m 3.9636(6)	Pm-3m 3.9989(0)	14/mcm 5.6720(6)	I4/mcm 5.6794(7)
b (A) c (Å) Volume (Å ³)	59.241	59.542	60.005	62.271	63.947	8.0473(9) 258.902	8.0609(0) 260.014
Sr x y z site occ ^a U $(\hat{\Delta}^2)$	0 0 1a 1 0.55582	0 0 1a 1 0.47607	0 0 1a 1 0.47194	0 0 1a 1.06445	0 0 1a 1 0.99909	0 ½ ¼ 4b 1 0.84100	0 ½ ¼ 4b 1 0.82022
Ti/Nb x y z site occ $U_{iso} (Å^2)^{b}$	¹ / ₂ 1/ ₂ 1b 0.95/0.05 0.36354	¹ / ₂ 1/ ₂ 1b 0.90/0.10 0.33362	¹ / ₂ 1/ ₂ 1b 0.80/0.20 0.33272	¹ / ₂ 1/ ₂ 1/ ₂ 1/ ₂ 0.50/0.50 0.31537	¹ / ₂ 1/ ₂ 1b 0.20/0.80 0.49357	0 0 ½ 4c 0.10/0.90 0.63103	0 0 ½ 4c 0.05/0.95 0.48134
$O/N(1)$ x y z site occ U_{iso} (Å ²)	0 ½ ½ 3c 2.94/0.06 0.71559	0 ½ ½ 3c 2.92/0.08 0.66620	0 ½ ½ 3c 2.79/0.21 0.69350	0 ½ ½ 3c 2.55/0.45 1.70249	0 ½ ½ 3c 2.40/0.60 2.33547	0 0 14 4a 0.71/0.29 1.48502	0 0 ¼ 4a 0.70/0.30 1.36128
$O/N(2)$ x y z site occ $U_{iso}(Å^2)$						0.7701(7) 0.2701(7) 0 8h 1.41/0.59 1.68651	0.7723(2) 0.2723(2) 0 8h 1.41/0.59 1.24993
< B-X-B > (deg.) x^2 R_{wp} R_p	(3x) 180 1.29 4.23 3.44	(3x) 180 2.28 4.80 3.86	(3x) 180 3.94 6.71 5.47	(3x) 180 4.14 6.87 5.25	(3x) 180 3.10 4.84 3.88	(2x) 170.8 (1x) 180 1.84 5.23 3.85	(2x) 169.8 (1x) 180 1.52 4.76 3.86

For samples x = 0.05 - 0.80 the space group Pm-3m was used. The samples x = 0.90 and 0.95 were refined in the tetragonal space group I4/mcm.

^a Cationic occupancy according to the chosen substitution level; anionic substitution level calculated from TGA and hotgas extraction.

^b Constraints B(Ti) = B(Nb).



Fig. 3. Synchrotron XRD pattern of oxynitride in samples x=0.90 and 0.95 showing splitting of higher order reflections. The split tetragonal (*I*4/*mcm*) 116, 332 and 420 reflections correspond to the cubic (*Pm*-3*m*) 310 reflection; λ =0.44 Å.

content (ionic radii $r(\text{Ti}^{4+})=0.61$ Å and $r(\text{Nb}^{5+})=0.64$ Å) is detectable as a shift of the reflections towards lower 2θ angles (Fig. 2) and this observation could be confirmed by Rietveld

refinement (Table 1). Similar to our results, Sulaeman et al. [22] reported on an enlargement of the unit cell parameters with increasing amount of niobium. In short, the crystal structure between $SrTiO_3$ and $SrNbO_2N$ evolves with a linear enlargement of the unit cell towards the niobium-rich side of the solid solution (Fig. 4). An octahedral rotation (with possible anion order) is initiated between samples 0.80 < x < 0.90, changing the symmetry from cubic to tetragonal (monoclinic). As an example, the refinement plot of samples x=0.05 and 0.95 are presented in Fig. 5.

3.2. Thermal stability, reoxidation behaviour and nitrogen content

All oxynitrides in our system showed thermal stability in air up to $T \sim 400$ °C. Above this temperature, the release of nitrogen and uptake of oxygen lead to reoxidation of the compound. The seven samples can be divided into three groups according to their characteristic reoxidation behaviour.

Group I (x=0.90 and 0.95) formed a reoxidation intermediate assigned as B in Fig. 6(a). Characteristic for this intermediate (B) is the mass gain which is higher than the transformation of an oxynitride into its corresponding oxide would suggest. Similar behaviour was also observed previously [8,12,16] and it was



Fig. 4. Enlargement of the unit cell parameter a_p in the oxynitride samples crystallizing in the cubic perovskite-type structure (x=0.05–0.80). The plot illustrates the existence of a solid solution.



Fig. 5. Rietveld refinement of samples (a) x=0.05 (Pm-3m) and (b) x=0.95 I4/mcm.

postulated that the intermediate (B) is a partially oxidized phase that retains dinitrogen weakly bonded in the oxide matrix [33]. Above 1100 °C, the sharp mass decrease originates from the



Fig. 6. (a) TGA plots of group I (x=0.90 and 0.95) with A: oxynitride, B: intermediate, C: oxide (b) MS data of x=0.90.

release of the bonded nitrogen, finally leading to a fully oxidized phase.

To determine the nature of the evolved gases, the MS-signals of x=0.90 were tracked (Fig. 6(b)). In the range of 500 °C < T < 600 °C, there is a positive peak in the MS-signal of N₂ (m/z=28) and a negative peak in the MS-signal of O₂ (m/z=32). It illustrates the release of N₂ and uptake of O₂, mirroring the sharp mass increase in the TGA plot (between stage A and B). The mass drop between stage B and C ($T\sim1100$ °C) is again accompanied by a small peak in the MS-signal of N₂ (m/z=28), which is caused by the complete release of the remaining N₂. XRD patterns of the reoxidized products revealed layered perovskite-structures similar to their oxide precursors.

Group II (x=0.20, 0.50 and 0.80) samples have in common that they do not form a stable oxide phase upon heating (Fig. 7(a)). Samples x=0.20 and 0.80 possess also an intermediate stage (B) but by further temperature increase, the samples' weight slowly continue to decrease (C'). Sample x=0.50 differs most from all the others because it did not form an intermediate phase and uninterruptedly lost weight after reaching its maximum.

The MS-signals of sample x=0.20 were investigated (Fig. 7(b)) and revealed at $T\sim 600$ °C a peak for N₂ (m/z=28). Similar to Group I, N₂ is released while forming the intermediate stage. Various smaller signals follow in the range 900 °C < T < 1300 °C suggesting that nitrogen further evolves without reaching a stability plateau. XRD indicated that only sample x=0.20 transformed into a cubic structure with space group *Pm*-3*m*, the other two compounds consisted of various oxide phases.

Group III (x=0.05 and 0.10) exhibited the smallest mass change of all samples but they also consisted of the three distinct stages (Fig. 8(a)). However, the mass difference Δm between stage B and C was only small.



Fig. 7. (a) TGA plots of group II (x=0.20, 0.50 and 0.80) with A: oxynitride, B: intermediate, C': unstable phase (b) MS data of x=0.20.



Fig. 8. (a) TGA plots of group III (x=0.05 and 0.10) with A: oxynitride, B: intermediate, C: oxide (b) MS data of x=0.10.



Fig. 9. Dependence of nitrogen content upon niobium substitution. The circles represent the experimentally determined nitrogen content *y*. The dotted line indicates the expected nitrogen values *y* according to the co-substitution of Nb⁵⁺ and N³⁻ (Eq. (1)).

In sample x=0.10 (Fig. 8(b)), no release of N₂ could be monitored, but the signal of NO (m/z=30) was observed that is correlated to the nitrogen release between A and B. All reoxidized compounds had a cubic structure with space group *Pm-3m*.

The small weight loss at low temperatures (T < 500 °C) in some of the samples (stage A in Fig. 7(a) and Fig. 8(a)) could be attributed to the release of H₂O and NH₃, which was monitored by the MS-signals of the mentioned molecules m/z=18 and m/z=17, respectively. Such behaviour has been previously reported elsewhere [16].

TGA was additionally used to determine the nitrogen stoichiometry (*y*) using Eq. (2). Hotgas extraction was considered for group II samples. It was not possible to apply Eq. (2) for group II samples because stable oxide phases were not formed and they decomposed into various phases. Fig. 9 indicates the dependence of nitrogen content upon niobium substitution. The dotted line represents the theoretically expected nitrogen stoichiometry *y*. For most of the samples (except x=0.05 and 0.20) the experimentally determined nitrogen is slightly below the theoretically expected value (according to Eq. (1)). A possible explanation is that some of the cations are in a reduced state (as Ti³⁺ and Nb^{3+/} ⁴⁺) and/or that the anionic lattice is oxygen deficient.

3.3. Colour, absorbance spectra and optical band gap

After the ammonia treatment, the oxynitrides underwent a gradual colour change from bluish/greenish (x=0.05) to reddish/ brownish (x=0.95). The absorbance of visible light giving the individual hue to the samples illustrates that their electronic structure has been changed compared to the white, insulating pristine oxides (Table 2).

The absorbance in the oxynitrides is illustrated in Fig. 10. Samples x=0.05, 0.10 and 0.20 feature a shoulder at around 375–450 nm. Liu et al. [13,34] reported that this shoulder can be attributed to isolated N 2p levels, which are energetically located above the O 2p levels within the band gap of the material. With increasing nitrogen content, the shoulders disappear because of complete mixing between N 2p and O 2p levels. The band gap E_g is approximated by the absorption minima that originate from valence- to conduction-band electron-transitions (interband transitions). The band gap E_g progressively decreases from 3.24 eV (x=0.05) to 1.82 eV (x=0.95). These values are in good agreement with other reported values for the band gap in SrTiO₃ ($E_g=$ 3.2–3.3 eV) [35–37] and in SrNbO₂N ($E_g=$ 1.8 eV) [38]. Yet, our

Table 2Oxynitride samples x = 0.05 - 0.95 with selected bond angles and electronegativities γ .

Oxynitride sample <i>x</i>	Sample colour	B–X–B bond angles	B-site cation average χ^a
0.05	and the	180°	1.543
0.10	Contraction of the	180°	1.546
0.20		180°	1.552
0.50	to the	180°	1.570
0.80	E. C. St.	180°	1.588
0.90	Service States	170.8°	1.594
0.95	and the second	169.8°	1.597

 $^{\rm a}$ The electronegativity χ for the B-site cation was averaged by its Ti/Nb ratio.



Fig. 10. Absorbance spectra of oxynitride samples (a) x=0.05-0.20 and (b) x=0.50-0.95. The spectra were obtained from UV-vis diffuse reflectance measurements.

results differ slightly from the ones obtained by Sulaeman et al. [22]. As they reported, the nitrogen content did not change much with increasing niobium "doping" and as a consequence the band gap E_g did not continously decrease. The differences in the synthesis route (microwave assisted solvothermal synthesis by Sulaeman et al. [22]) might lead to the observed discrepancies.



Fig. 11. Band gap energy E_g vs. nitrogen content (y).

Each sample features an absorbance after the band gap E_g towards longer wavelengths as shown in Fig. 10. Likewise to our samples, an absorption of wavelengths longer than E_g was reported by Liu et al. [34], who attributed it to the presence of oxygen vacancies in nitrogen doped SrTiO₃. Also Kim et al. [9] and Siritanaratkul et al. [38] detected a similar absorption in SrNbO₂N, BaNbO₂N and CaNbO₂N. They correlated it with the introduction of charge carriers into the conduction band, which in turn reflects a partial reduction of Nb⁵⁺. Also for absorption spectra of TiO₂ an increasing background absorbance towards longer wavelengths was reported and it was attributed to free carriers injected by reduced titanium ions [39]. The reason for the absorbance in our samples cannot be identified unambiguously because oxygen vacancies as well as partial reduction of the B-site cations are conceivable.

Fig. 11 demonstrates that the nearly linear trend of the mixed N 2p and O 2p levels is interrupted by the compounds x=0.50 and 0.80, which possess a comparatively small band gap. This observation can be explained if besides nitrogen content, the electronegativity γ of the B-site cation and the crystal symmetry are taken into account (Table 2). Throughout the solid solution, the titanium cation $(\chi = 1.54)$ is increasingly replaced by the more electronegative niobium cation ($\chi = 1.6$). A more electronegative transition metal cation has its t_{2g} orbitals closer to the anionic p orbitals leading to more covalent bonds and a narrower band gap [14,16]. Therefore, with progressive niobium content, the band gap E_g is not only diminished by the larger nitrogen abundance but additionally by the increasing electronegativity χ of the B-site cation. This effect is observable in samples x = 0.50 and 0.80. Yet, there is no continuation of this trend for x=0.90 and 0.95 as it would be suggested by the even more increasing electronegativity γ . Crystal structure investigations revealed that the solid solution transforms from Pm-3m to I4/mcm between x=0.80 and 0.90. B-X-B bond angles of 180° provide the best orbital overlap and therefore strongest covalence for bonds between N/O p orbitals and metal d orbitals. Distortions to bond angles $(180^{\circ} - \phi)$ reduce the overlap and covalent character, thus making the band gap E_g wider [14,16]. Rietveld refinement provided B–X–B bond angles of 170.8° and 169.8° for x=0.90 and 0.95, respectively. Consequently, in those samples, the decreasing crystal symmetry (increase of E_g) is countervailing the increasing electronegativity χ (decrease of E_g), thus providing a dependence of the band gap E_g predominantly on nitrogen content.

4. Conclusions

Perovskite-type structures with seven different compositions of $SrTi_{1-x}Nb_x(O,N)_3$ were successfully prepared via thermal

ammonolysis of oxide precursors. The crystal structure/symmetry of the oxynitride series changed from cubic Pm-3m to tetragonal I4/mcm by initiation of an octahedral tilting between x=0.80 and 0.90. The tilting increased from x=0.90 towards x=0.95 and the refined cell parameters showed a continuous enlargement towards higher niobium and nitrogen content.

The amount of nitrogen insertion could be adjusted by appropriate co-substitution with niobium. TGA and hotgas extraction revealed that rising niobium content favoured nitrogen incorporation.

Nitrogen insertion could lower the energy gap E_g between valence and conduction band into the range of visible light as shown by the change from white oxides into coloured oxynitride powders. The width of E_g was correlated with the nitrogen amount and it diminished from 3.24 eV down to 1.82 eV with increasing nitrogen (and niobium) content. Other factors besides the nitrogen presence, e.g. the electronegativity χ and symmetry changes also influenced the band gap E_g and explained some of the non-linear variations.

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