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Thermal oxidation of oxynitride perovskites in different atmospheres

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ABSTRACT

Oxynitride perovskites with bright and variable colour have the potential to be employed as non-toxic pigments, and to substitute colourants that contain harmful heavy metals. For this application it is extremely important to have a precise knowledge about the materials stability. The thermal stability of oxynitride perovskites in different atmospheres was measured by thermogravimetry in combination with mass spectroscopy (MS). The studied compounds, namely $LaTiO_2N$, $SrNbO_2N$ and $SrTaO_2N$, were heated up to 1200 °C in argon–oxygen mixtures with varying oxygen contents. It was found that the thermal behaviour of the studied oxynitrides changes drastically with the oxygen concentration. When heated up in pure argon the oxynitrides transform to oxides containing transition metals of lower oxidation state and/or binary nitrides. For oxygen contents between 0.5% and 20% the samples were completely oxidised. The oxidation rate increases with oxygen content. MS analysis of the gaseous products (including N_2, NO and NO_2) reveals a complex reaction mechanism, which is strongly modified by the composition of the atmosphere.

1. Introduction

Many oxynitride perovskites with transition metals in d^0 electronic configuration show bright colours and can be used as non-toxic pigments substituting dyes that contain problematic heavy metals (e.g. cadmium, chromium, mercury, arsenic, etc.) which are harmful for the human health and the environment [2]. Most of the d^0-oxynitride perovskites are stable in air, water and even in concentrated acids. Their stability at high temperature, on the other hand, varies a lot depending on the A and B cation in the general formula ABO_2N. For the pigment application it is important to study the thermal stability of oxynitrides, since pigments are usually submitted to heat treatments when they are incorporated into the desired commodities, such as polymers, rubbers, glasses, enamels and ceramics [3].

Marchand et al. [4,5] have first reported on the unconventional oxidation behaviour of some oxynitride compounds when heated in air. In a temperature range between 540 and 920 °C these oxynitrides exhibit a much larger weight increase than expected for the substitution of 1 N^{3-} by 1.5 O^{2-} according to Eq. (I). At higher temperatures the weight rapidly decreases and reaches the expected value. This unusual behaviour stems from the retention of nitrogen molecules within the structure during the oxidation process and the resulting formation of an intermediate phase, which contains the full final oxygen content and di-nitrogen molecules bonded to the cations. The nitrogen is finally detached from the samples at higher temperatures (Eq. (II)).

$$ABO_2N + \tfrac{3}{4}O_2 \rightarrow ABO_{3.5} + \tfrac{1}{2}N_2 \qquad \text{(I)}$$

$$ABO_2N + \tfrac{3}{4}O_2 \rightarrow ABO_{3.5}(N_2)_x + (\tfrac{1}{2} - x)N_2 \rightarrow ABO_{3.5} + xN_2 \qquad \text{(II)}$$

To the best of our knowledge, all previous oxidation studies on perovskite oxynitrides were done in air while no systematic investigation about the influence of the oxygen content on the reaction mechanism was performed so far. Recently, we reported the thermal decomposition of $LaTiO_2N$ in He [6] and the oxidation of $SrNbO_2N$ under 20% and 1% of O_2 [7]. While the reaction in 20% oxygen showed the above-described oxidation behaviour (see Fig. 3), a completely different behaviour was observed in an atmosphere of 1% O_2. The intermediate reaction product was not observed, but the weight increased progressively up to ca. 920 °C where a small sudden weight loss was found. Finally, the reaction finished with the expected mass corresponding to $SrNbO_{3.5}$. This significantly different behaviour motivated us to study systematically the thermal oxidation of oxynitride perovskites when submitted to heat treatment under atmospheres with different oxygen concentrations, namely between 0% and 20% O_2.

2. Experimental

The oxynitrides studied in this work ($SrNbO_2N$, $SrTaO_2N$, and $LaTiO_2N$) were prepared from the corresponding oxides of the general composition $ABO_{3.5}$. $SrNbO_{3.5}$ and $SrTaO_{3.5}$ were prepared

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by conventional solid-state synthesis. Stoichiometric quantities of $SrCO_3$ (99.9%, Aldrich), Ta_2O_5 (99%, Aldrich) and Nb_2O_5 (99.9%, Aldrich) were well ground under iso-propanol in an agate mortar. The mixtures were reacted at 1100 °C for 48 h in air in a box furnace. $LaTiO_{3.5}$ was obtained by a soft chemistry approach, using $La(NO_3)_3{\cdot}6H_2O$ (p.a., Fluka), titanium(IV) isopropoxide $C_{12}H_{28}O_4Ti$ (97%, Aldrich) and citric acid (99%, Fluka) as chelating agent. The molar ratio of citric acid:metal ions was 2:1. In a first step titanium citrate was formed by dissolving titanium(IV) isopropoxide in an aqueous solution of citric acid under constant stirring at approximately 70 °C. To this solution the stoichiometric quantity of $La(NO_3)_3{\cdot}6H_2O$ was slowly added. The solution was dried on a hot plate at 120 °C. The organic matrix was burned out at 650 °C, yielding an X-ray amorphous oxide powder.

Approximately 1 g of each oxide were reacted with ammonia to yield the respective oxynitrides. The ammonolysis of all three compounds was done in a tube furnace with an ammonia flow of 25 ml/min. $SrNbO_2N$, $SrTaO_2N$ and $LaTiO_2N$ were obtained at 950 °C (54 h), 1000 °C (36 h) and 950 °C (36 h), respectively.

The samples were characterised by X-ray diffraction using a Seifert θ/θ 3000, diffractometer operating with Cu Kα radiation. Scans were performed in the angular range of $2\theta = 10–60°$ with an increment of 0.02° and a counting time of 4 s per data point. The quantitative phase analysis was done by Rietveld refinements using the FullProf software [8].

The thermal reoxidation studies were performed on a NETZSCH STA 409C thermobalance connected to a Balzers QMG quadrupole mass spectrometer by a skimmer coupling system. The oxidation reactions of the oxynitrides were carried out in the range of 25–1200 °C with a heating rate of 10 °C/min in Ar/O_2 mixtures with O_2 contents varying between 0% and 20% (both gases from Linde with 99.99% purity). The experiment was done in dynamic atmosphere of 40 ml/min. To allow the detection of N_2 ($m/e = 28$) evolving during the reaction, mixtures of oxygen/argon instead of oxygen/nitrogen were used.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the studied oxynitride compounds. All three compounds were found to be single phase. $SrNbO_2N$ and $SrTaO_2N$ possess tetragonal distorted perovskite structures while $LaTiO_2N$ is triclinic [9–11].

Mass spectrometry (MS) analyses were done for the following molar masses: 15, 16, 17, 18, 28, 29, 30, 44 and 46. For the sake of clearness only the masses related to nitrogen elimination, i.e. 28 (N_2) and 30 (NO) are shown in Figs. 3, 5 and 8. The other masses were monitored to cross check if the obtained results were exclusively related to nitrogen-containing gases. As an example, $m/e = 28$ could be attributed either to N_2 or to CO evolving during the reaction. The same m/e signal could also be due to CO_2 fragmenting in the mass spectrometer to CO + O. In the latter case the $m/e = 28$ signal would be accompanied by a far more intense signal for $m/e = 44$. Thus, if specific peaks appear at MS 28 and at MS 44, it means that it is not N_2 but CO_2 detaching from the sample. CO and N_2, on the other hand, can be distinguished by their isotope patterns, i.e. the intensity ratio $m/e = 28/29/30$. In the CO case, small intensities at MS 16 and MS 29 are detected, which eliminate the suspicion if the MS 28 signal in fact corresponds to N_2. In a similar manner, CO_2 and NO_2 (both $m/e = 46$) can be separated since CO_2 has its main peak at MS 44. These examples illustrate the necessity to compare the signals of different masses to confirm which molecules are evolving during the reaction.

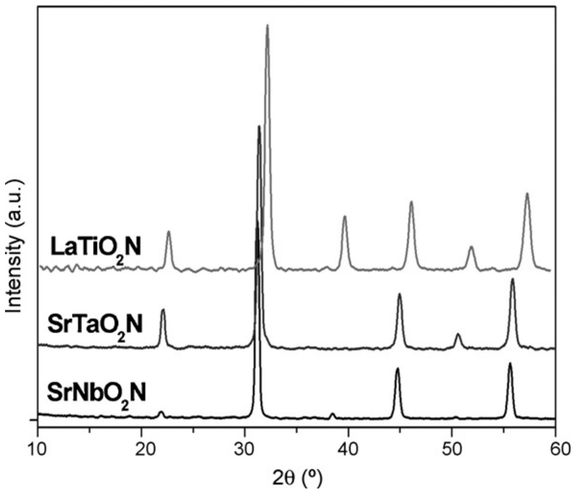

Fig. 1. XRD patterns of the studied oxynitride perovskites $LaTiO_2N$, $SrNbO_2N$ and $SrTaO_2N$.

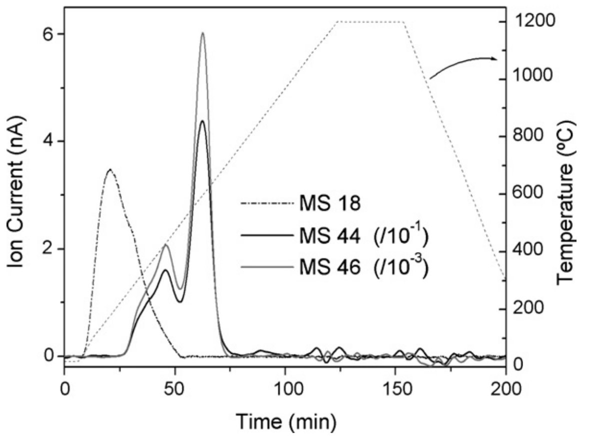

Fig. 2. MS 18 (H_2O), 44 and 46 (CO_2) signals of $SrNbO_2N$ reacted in an atmosphere of 5% O_2 in argon.

Species with MS 17 and 15 were measured to verify if NH_3 was released during the reactions, but none of the samples showed peaks at these masses (except for signals corresponding to MS 18, which indicates H_2O). It can therefore be concluded that nitrogen is not eliminated as ammonia during the heat treatment in any of the studied atmospheres. Although the compounds were stored at 120 °C prior to the measurements, all samples show small signals in the MS 18 channel between 200 and 300 °C and MS 44/46 between 150 and 750 °C, corresponding to the elimination of water and CO_2, respectively, chemically bonded to the sample. An example is plotted in Fig. 2 for $SrNbO_2N$ heated in 5% of oxygen in argon. The water peak appears at ca. 220 °C, while the CO_2 signal has a broad first signal between 220 and 480 °C followed by a more intense peak, which disappears at 670 °C. The presence of chemically bonded water and carbonate was attributed to traces of H_2O and CO_2 in the ammonia gas. It can be minimised by not cooling the samples in ammonia but changing the atmosphere to high-purity nitrogen at high temperatures [12].

Results of the thermogravimetric analyses of $SrNbO_2N$ in varying oxygen contents are plotted in Fig. 3. The top panel gives the weight change during reaction while the lower two panels show the ion currents for two selected m/e values, namely 28 and 30. It is apparent that for oxygen concentrations between 3% and 20% the behaviour of the TG curves is quite similar: at a temperature of roughly 440 °C the weight starts to increase. After passing through a maximum the weight slowly decreases and then in a relatively sharp temperature interval of 915–960 °C drops to a value of 102.5% of the initial mass. $SrNbO_{3.5}$ was identified as final reaction prod-

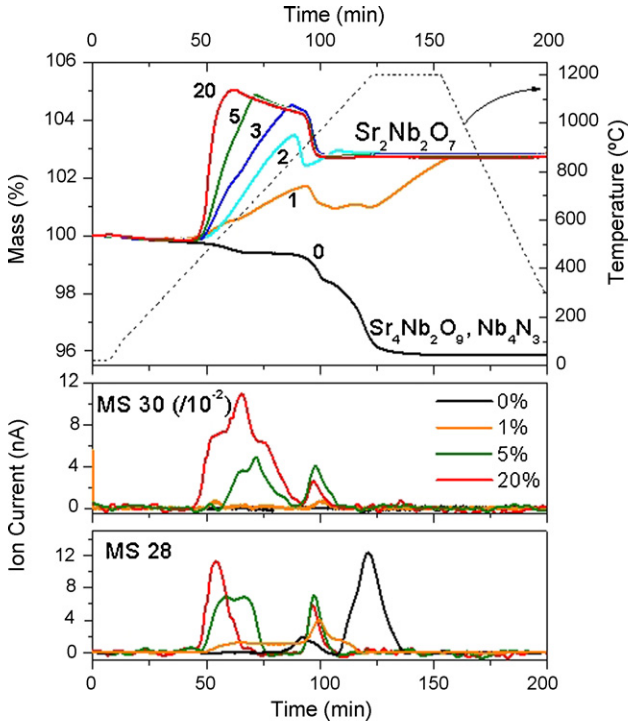

Fig. 3. Thermogravimetric and mass spectroscopy curves for $SrNbO_2N$ in atmospheres with different oxygen concentrations (the analysis under 0.5% O_2 is discussed in the text but not shown because it took 2 h to complete the reaction).

uct by XRD (Fig. 4). The observed weight gain does not match the expected value of 4.41% because the sample loses water and carbon dioxide during the heating treatment as shown in Fig. 2. This effect partially compensates the weight gain by oxidation. The intermediate weight maximum is found because during a certain temperature regime the fully oxidised compound retains parts of the nitrogen. The retained nitrogen is bonded as N_2-molecule in the structure ($SrNbO_{3.5}(N_2)_x$) as found by Le Gendre et al. using thermogravimetry, Raman spectroscopy and O/N analysis [4,5]. It is important to note that already at the beginning of the oxidation, $SrNbO_2N$ starts to lose molecular nitrogen as evidenced by the pronounced $m/e = 28$ signal found in the MS spectra at 480 °C. This indicates that only part of the nitrogen remains bonded in the oxide structure. After the weight reaches its maximum the N_2 evolution rate decreases strongly, leading to a slight weight change and a reduction of the MS 28 signal. Finally, at approximately 950 °C the remaining N_2 molecules are abruptly detached and the weight reaches the final value. The simultaneous oxygen assimilation and N_2 loss (between 440 and 960 °C) explains the differences in weight gain observed for different oxygen contents. The lower the O_2 concentration, the higher is the required temperature for the sample to become completely oxidised while at the same time N_2 is successively released. As a consequence the maximum achieved weight becomes smaller with lower O_2 content and is reached at higher temperatures.

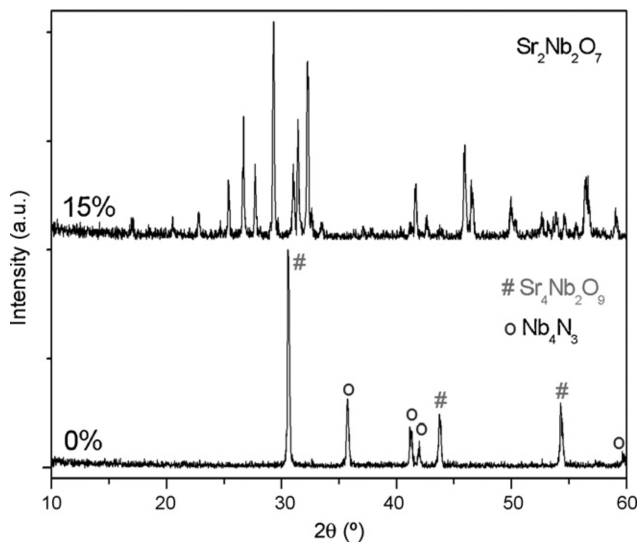

Fig. 4. X-ray diffraction patterns for $SrNbO_2N$ after the TG/MS experiments under 0% and 15% O_2.

It is furthermore interesting to note that although the largest part of the nitrogen is released as N_2, small amounts of NO were also detected (middle panel of Fig. 3). When heated in 20% O_2, the onset of the oxidation is accompanied by the formation of small quantities of NO ($m/e = 30$). At the weight maximum an additional peak for NO was found. During the plateau the NO evolution rate decreases to yield a final smaller maximum at 950 °C when the residual fraction of N_2 is released as well. The formation of NO is probably due to the presence of nitrogen species that are bonded in the perovskite structure, which react with O_2 and form NO instead of recombining to N_2. The temperatures at which NO is formed are too low for the reaction of N_2 with O_2. The NO molecules must therefore be built by reactions of more reactive nitrogen species during the reoxidation. Although the sensitivity of the mass spectrometer is not completely identical for the various masses, a comparison of the ion currents (10^{-9} and 10^{-11} for $m/e = 28$ and 30, respectively) clearly indicates that the largest part of nitride ions form N_2 while the formation of nitrogen monoxide is only a side reaction. The occurrence of NO is a quite interesting finding since until now the studies of the thermal oxidation behaviour of oxynitride perovskites have only reported the evolution of N_2. In contrast to the NO signal, the MS 44 peaks (NO_2) always showed the same behaviour as the ones of MS 46, indicating that no NO_2 is formed, independently of the oxygen percentage. Upon decreasing the oxygen content to 5%, the first NO peaks become significantly smaller. Obviously the lower O_2 concentration only allows a reaction at higher temperatures.

For 0.5% and 1% O_2 the TGA curves reveal different reaction behaviour than the one described above. Because the O_2 concentration becomes too low for the samples to be completely oxidised below 950 °C, the N_2 detaches earlier than the total oxidation occurs. In that case, the reaction apparently happens in three different stages:

(1) Formation of $SrNbO_x(N_2)_y$ ($2 < x < 3.5$, $y \leq ½$): some oxygen reacts with the oxynitride sample (weight increase) within a broad temperature range and simultaneously a constant small amount of N_2 is detached, leading to the plateau observed in the MS 28 signal between 470 and 870 °C.
(2) Formation of $SrNbO_x$ ($2 < x < 3.5$): N_2 is detached from the sample, the weight goes abruptly down and a sharp peak appears in the MS 28 signal at the same temperature as for the other measurements (ca. 950 °C). A very small quantity of NO also evolves from the sample at this temperature.
(3) Oxidation to $SrNbO_{3.5}$: the oxygen uptake continues and the final product is obtained after 30 min at 1200 °C.

For $SrNbO_2N$ reacted in 0.5% O_2, the 30 min at 1200 °C was not sufficient to complete the oxidation. It was necessary to heat the sample almost 2 h at 1200 °C to get the same weight increase as for the other runs. Nevertheless, the weight increase started at roughly the same temperature as for the higher oxygen concentrations and the weight drop at 950 °C was also found. It can therefore be concluded that the temperature at which the oxynitrides start to oxidise (around 440 °C) and the one at which the retained N_2 is completely detached (950 °C) are independent of the oxygen content in the atmosphere.

For 0% O_2 (pure argon atmosphere) $SrNbO_2N$ showed a completely different thermal behaviour. The sample only loses weight, reaching a final value of 95.5% of the initial mass. This finding is not surprising, since there is no oxygen to react with the sample. A small N_2 peak and accompanied by a step in the TG signal appears at the characteristic temperature of 950 °C. It is worth mentioning, that in oxygen-free atmosphere the evolution of N_2 already starts at a slightly lower temperature of 870 °C. The most intense N_2 signal occurs between 1060 and 1200 °C, thus at a much higher temperature than for the reactions in oxygen containing atmospheres. This peak corresponds to the TG signal revealing a weight loss of 2.6% in this temperature region. No NO peaks were observed, which is understandable since there is no oxygen to form nitrogen monoxide. As final reaction products, the two phases $Sr_4Nb_2O_9$ and Nb_4N_3 were detected by XRD as shown in Fig. 4. Evidently, in an oxygen-free atmosphere, nitrogen is not completely released as N_2 but a part of it remains, forming the reduced binary nitride Nb_4N_3. On the other hand, not the entire niobium becomes reduced but parts of it remain as Nb^{5+} in $Sr_4Nb_2O_9$. A quantitative phase analysis by Rietveld refinement yielded a molar mixture of 70% $Sr_4Nb_2O_9$ and 30% Nb_4N_3. This composition is very close to the expected ratio of 67% to 33%. The corresponding theoretical weight loss of 2.4% is not in so good agreement with the experimentally found value of 3.6%, probably because there is still some CO_2 evolution from the sample together with N_2. The weight loss corresponding to the phase decomposition was measured only after the plateau at approximately 820 °C, because the first step at the thermogravimetric curve corresponds to water and carbon dioxide evolution as discussed for Fig. 2.

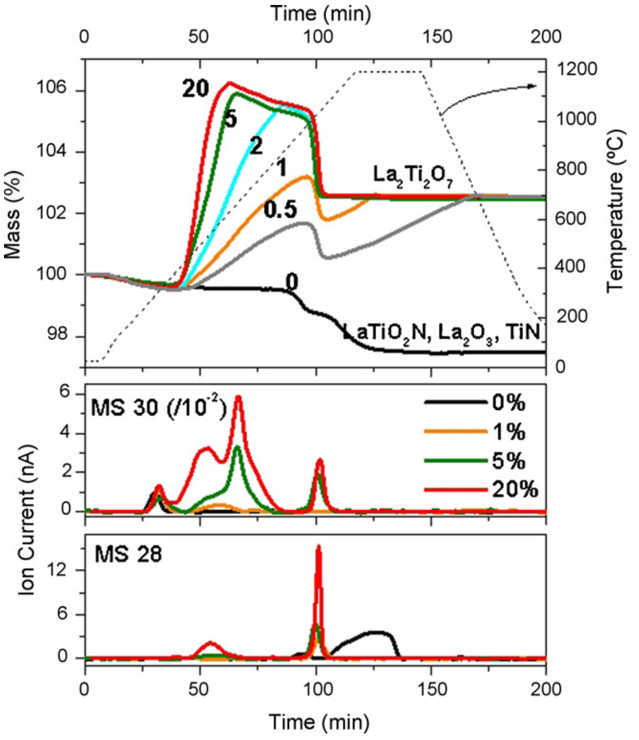

Fig. 5. Thermogravimetric and mass spectroscopy curves for $LaTiO_2N$ in atmospheres with different oxygen concentrations.

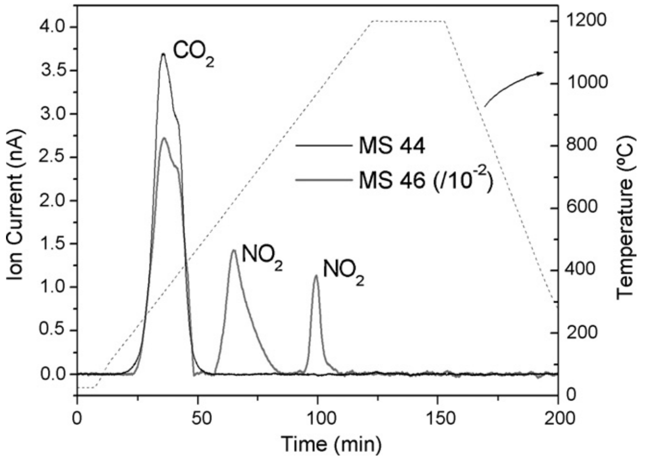

Fig. 6. Plots of MS 44 and MS 46 for $LaTiO_2N$ reacted under 20% O_2.

The thermogravimetric and mass spectroscopic analyses of $LaTiO_2N$ are depicted in Fig. 5. $LaTiO_2N$ shows a quite similar behaviour to $SrNbO_2N$. For the samples reacted under oxygen concentrations higher than 1%, the weight starts to increase at ca. 380 °C, and at 960 °C goes rapidly down to the final value. Nitrogen ($m/e = 28$) is released at ca. 400 °C, where a small peak appears and at 960 °C the biggest peak occurs for all the atmospheres. Small NO peaks ($m/e = 30$) were found at 270 °C for all reaction gases as shown in the middle panel of Fig. 5. The reactions in 2–20% O_2 also lead to the elimination of NO between 470 and 820 °C and at 970 °C. The intensities of these signals increase with the O_2 concentration. Furthermore, the evolution of CO_2 (MS 44 and 46) has been detected between 60 and 420 °C for all the samples. Only the TGA run in 20% O_2 shows a different behaviour. It yields two additional comparatively intense peaks at 650 and 960 °C, as shown in Fig. 6. Because no related signals were found for MS 44, these two peaks correspond to the formation of NO_2. It is possible that for this high-oxygen concentration nitrogen is not only oxidised to NO but also to NO_2. It is interesting to note that in contrast to $SrNbO_2N$, a NO_2 evolution is observed for $LaTiO_2N$. Under 0.5% and 1% O_2, $LaTiO_2N$ shows generally the same behaviour as $SrNbO_2N$. Both compounds start to oxidise between 380 and 440 °C, but they keep some N_2 in

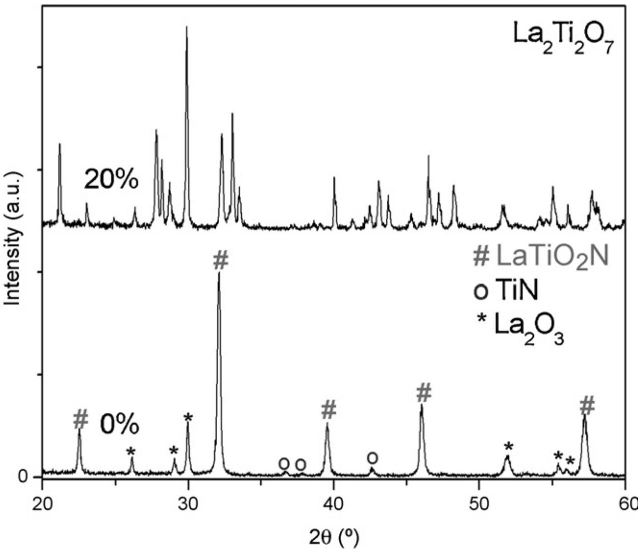

Fig. 7. X-ray diffraction patterns for $LaTiO_2N$ samples after been reacted at TG/MS under 0% and 20% O_2.

the structure. The remaining N_2 is released at 960 °C, and the oxidation continues until 1200 °C. All TGA experiments in atmospheres containing at least small amounts of oxygen lead to the same weight gain and resulted in $La_2Ti_2O_7$ as reaction product, as showed in the XRD pattern in Fig. 7. The total weight gain of 2.6% does not match with the expected value of 4.3%. As explained above, this is because the sample also loses water and CO_2, which partly compensates the weight gain during oxidation. The evolution of these two gases can already be detected by a small loss between room temperature and 400 °C.

The sample heated in pure argon (0% O_2) only shows weight decrease, leading to 97.5% of the original mass. The first step in the TGA curve corresponds to water and carbon dioxide evolution, and the second step corresponds to the decomposition of the oxynitride perovskite as confirmed by the MS 28 results. N_2 starts to detach at 970 °C and is completely eliminated only at 1200 °C. A very small NO evolution is also observed at 270 °C, most likely at this low temperature only NO molecules that were simply superficially bonded to the sample can be eliminated. The final product was composed of 76% $LaTiO_2N$, 14% La_2O_3 and 10% TiN as determined by Rietveld refinement of the respective XRD. The calculated weight loss of 1.7% is in good agreement with the measured value of 1.4%. It is interesting to note that in contrast to $SrNbO_2N$, which is completely decomposed under the same reaction condition, for $LaTiO_2N$ 76% of the oxynitride is still stable after 30 min at 1200 °C. Also the reaction products are different. In addition to one binary nitride containing the transition metal in a reduced oxidation state, the binary oxide La_2O_3 is formed while for $SrNbO_2N$ a complex oxide ($Sr_4Nb_2O_9$) was found. In an earlier report Logvinoch et al. [6] studied the thermal stability of $LaTiO_2N$ under oxygen-free He atmosphere. Also in this gas the oxynitride decomposed in La_2O_3 and TiN but together with a perovskite-type phase of unknown composition.

The thermogravimetric analysis of $SrTaO_2N$ showed a quite different behaviour from $SrNbO_2N$ and $LaTiO_2N$. Depending on the oxygen concentration in the gas phase, the reactions result in different final weight changes as depicted in Fig. 8. The XRD pattern shown in Fig. 9 proves a different chemical composition of the reaction products. The samples reacted under 10–20% O_2 start to oxidise at 480 °C, as detected by the weight increase in TGA. As for the other two compounds, the weight reaches a maximum and starts to decrease slowly. At 1050 °C the weight goes sharply down to the final value. N_2 and a minor amount of NO evolve from the sample at approximately the same temperatures, firstly between 540 and 720 °C and secondly at 1070 °C. The obtained oxidised phase is pure $Sr_2Ta_2O_7$ as was verified by XRD. The total weight gain value of 1.7% is significantly lower than the expected 3.2%. As already discussed this discrepancy is due to the release of water and CO_2. All thermogravimetric investigations of $SrTaO_2N$ showed a peak in MS 18 between 60 and 370 °C corresponding to H_2O evolution and a broad peak between 270 and 870 °C in the MS channels 44 and 46, due to the releasing of CO_2.

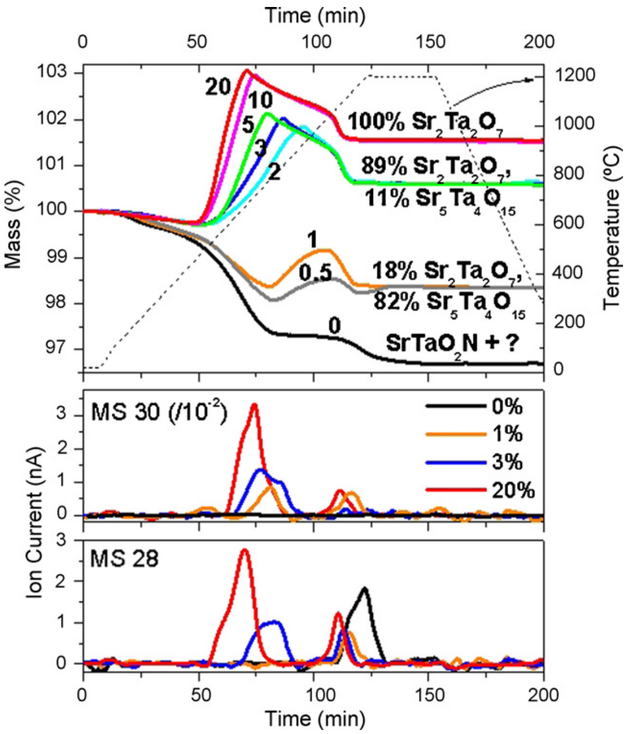

Fig. 8. Thermogravimetric and mass spectroscopy curves for $SrTaO_2N$ in atmospheres with different oxygen concentrations.

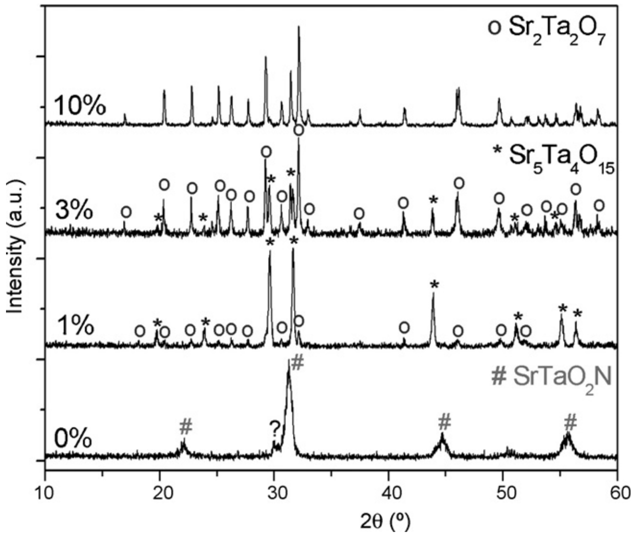

Fig. 9. X-ray diffraction patterns for $SrTaO_2N$ samples after been reacted at TG/MS with 0%, 1%, 3% and 10% O_2.

For 2–5% O_2 the first steps of the reaction are similar to the above-described behaviour, only the maximum weight value is smaller than for higher oxygen percentages. The N_2 and NO evolutions occur simultaneously, but at slightly higher temperatures than for the aliquots reacted under 10–20% O_2. A broad peak appears between 670 and 840 °C and the next at 1100 °C. The final weight was 100.7% of the initial mass. The Rietveld analysis showed that the obtained phases were 89% $Sr_2Ta_2O_7$ and 11% $Sr_5Ta_4O_{15}$.

For 0.5% and 1% O_2 the samples start to lose weight at 60 °C, corresponding to H_2O and CO_2 elimination as discussed above (Fig. 2). At ca. 790 °C the weight starts to slightly re-increase and at 1050 °C it decreases to reach a final value of 98.4%. A small amount of NO is eliminated between 740 and 820 °C and at 1120 °C, while the N_2 peak appears only at 1120 °C. The obtained products were the same as found for 2–5% oxygen, only the ratio varied: 18% $Sr_2Ta_2O_7$ and 82% $Sr_5Ta_4O_{15}$.

For 0% O_2 the reaction is characterised by two steps in the TG. The first weight loss corresponds to water and carbon dioxide elimination while the second is due to N_2 evolution as evidenced by the N_2 peak between 1120 and 1200 °C observed for $m/e = 28$. A formation of nitrogen monoxide was not observed. The results of MS analysis for the three oxynitride samples are summarised in Table 1. The obtained final weight was 96.5% of the initial mass. The resulted compounds were $SrTaO_2N$ and a second phase, which could not be identified. As shown in the XRD pattern in Fig. 9, the main peak of this phase appears at $2\theta = 30.2°$. The colour of the

Table 1
Summary of the results from the mass spectroscopy analysis listing the temperature ranges in which the specific gases were released and the *m*/*e* values used to identify them

% O_2	MS	Temperature (°C)		
		$SrNbO_2N$	$LaTiO_2N$	$SrTaO_2N$
All atmospheres	18 (H_2O)	90–490	240–460	60–370
	44 + 46 (CO_2)	220–480, 670	60–420	270–870
0	28 (N_2)	870–950, 1060–1200	970–1200	1120–1200
	30 (NO)	–	270	–
1	28 (N_2)	470–1150	400, 960	1120
	30 (NO)	950	270	740–820, 1120
5	28 (N_2)	450–710, 950	400, 960	670–840, 1100
	30 (NO)	540–890, 950	270, 470–820, 970	670–840, 1100
20	28 (N_2)	440–680, 950	400, 960	540–720, 1070
	30 (NO)	440–900, 950	270, 400–820, 970	540–720, 1070
	Only 46 (NO_2)	–	650, 960	–

reacted powder was dark orange with black particles. This indicates that the second phase besides $SrTaO_2N$ contains Ta in a reduced oxidation state. It is worth mentioning that $SrTaO_2N$ remains relatively stable in oxygen-free atmosphere, even after being submitted to 1200 °C for 30 min. For both the obtained oxide phases ($Sr_2Ta_2O_7$ and $Sr_5Ta_4O_{15}$) tantalum remains in its highest oxidation state, i.e. as Ta^{5+}. It could be expected that for smaller oxygen amounts the final products would contain some reduced tantalum but this is apparently not the case. In contrast to $Sr_2Ta_2O_7$, which possesses a layered perovskite structure, $Sr_5Ta_4O_{15}$ is a hexagonal perovskite with cationic vacancies and can be written as $Sr_5Ta_4\square O_{15}$ [13]. Its oxygen/cation ratio is 1.67 while for $Sr_2Ta_2O_7$ it is 1.75. Thus, it can be one explanation for the formation of $Sr_5Ta_4O_{15}$ under atmospheres with low oxygen content.

4. Conclusion

The thermal oxidation of three different oxynitride perovskites in O_2/Ar atmosphere with varying O_2 contents has been studied by a combination of thermogravimetry and MS. In pure argon remarkable differences in the thermal behaviour of the three compounds were found. $SrNbO_2N$ completely decomposes into $Sr_4Nb_2O_9$ and Nb_4N_3 while for $LaTiO_2N$ ca. 76% of the original oxynitride remained stable even after 30 min at 1200 °C. For the rest of the material a partial decomposition to La_2O_3 and TiN was found. $SrTaO_2N$ was considerably stable and only a small quantity of a second phase, which could not be identified but apparently contains tantalum in a reduced oxidation state was detected. When oxygen was present in the atmosphere $SrNbO_2N$ and $LaTiO_2N$ were completely oxidised to the respective oxides $A_2B_2O_7$ relatively fast (less than 1 h) even for O_2 concentrations as low as 0.5%. The higher the oxygen concentration in the atmosphere, the faster the oxidation proceeded. $SrTaO_2N$ showed a different behaviour. At low O_2 concentrations (0.5–5%) two different phases $Sr_5Ta_4O_{15}$ and $Sr_2Ta_2O_7$, were formed, while for $c(O_2) > 10\%$ the single reaction product was $Sr_2Ta_2O_7$. For all investigated oxynitrides the evolution of N_2 and NO showed a similar behaviour. N_2 is released at higher temperatures for lower O_2 concentrations. The first peak appears at ca. 440, 380 and 480 °C (for $SrNbO_2N$, $LaTiO_2N$ and $SrTaO_2N$, respectively), where the samples weight starts to increase (oxygen uptake) then the rate decreases to almost zero and finally the remaining N_2 is released in a small temperature interval at ca. 950, 960 and 1050 °C (for $SrNbO_2N$, $LaTiO_2N$ and $SrTaO_2N$, respectively). For 0% O_2 the N_2 peaks appeared only at ca. 1200 °C. The NO is mostly eliminated at the onset of the samples oxidation at approximately 400 °C. The intensity of the peaks increases with higher O_2 concentration, because it is easier to oxidise the nitrogen in oxygen-rich atmospheres. The contribution of the NO release during the oxidation is two orders of magnitude smaller than the N_2. Only $LaTiO_2N$ reacted in 20% O_2 showed small NO_2 peaks together with NO, all the other samples did not release nitrogen in the form of NO_2. To the best of our knowledge the thermal investigations performed so far only detected N_2 as gaseous product during the thermal treatment of oxynitrides. Here, we for the first time identified NO and NO_2 as additional reaction products however in a much lower concentration than N_2. This report has shown that the studied oxynitrides are thermally stable to roughly 400 °C even in air. Therefore, they can be used as pigments in all applications where lower temperatures occur. When protected from air, they can be even used at much higher temperatures for example as glazes for ceramics. Upon high temperatures (during fire or waste combustion) in oxidising atmospheres, the oxynitrides react to harmless products like indissoluble oxides and N_2. The amount of NO_x released from the samples is very small (app. 1% of the total N-content) so these materials can be considered as non-toxic not only during use, but also in their disposal.

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