

Relationship between anion and cation nonstoichiometries and valence state of titanium in perovskite-type oxynitrides $\text{LaTiO}_{2-x}\text{N}_x$

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Three series of $(\text{La},\text{Sr})\text{TiO}_{2-x}\text{N}_x$ compounds, with either anion nonstoichiometry $\text{LaTiO}_{2+x}\text{N}_{1-x}$, cation nonstoichiometry $\text{La}_{1-x}\text{Ti}_{1+x}\text{O}_2\text{N}$ or an $\text{La}_{1-x}\text{Sr}_x\text{TiO}_2\text{N}$ series, have been prepared in order to clarify, by XPS spectroscopy, the influence of composition on the valence state of titanium. Though the substitution of lanthanum by strontium was effective in the enhancement of reflectivity in the longer wavelength region above the absorption edge, the valence state of titanium did not change in either the $\text{La}_{1-x}\text{Ti}_{1+x}\text{O}_2\text{N}$ or the $\text{La}_{1-x}\text{Sr}_x\text{TiO}_2\text{N}$ series. However, it was found that the increase of oxygen content in the $\text{LaTiO}_{2+x}\text{N}_{1-x}$ series causes oxidation of the titanium.

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Key-words : Perovskite-type oxynitrides, Nonstoichiometry, Bandgap, Reflectivity, XPS, Surface composition, Valence state of titanium

[Received August 29, 2008; Accepted November 20, 2008]

1. Introduction

Chemical bonds in metal nitrides are rich in their variety. Alkali and alkaline earth metals form ionic bonds to nitrogen in compounds such as Li_3N and Ca_3N_2 . Covalent bonds play an important role in main group nitrides such as AlN and Si_3N_4 . Early transition metal nitrides such as TiN and NbN show metallic behavior. These observations are in contrast to the bonding in the corresponding metal oxides which usually show ionic bond character.¹⁾ Nitrogen is less electronegative than oxygen and introduction of nitrogen into metal oxides enhances covalent bond character, so that the excitation and/or emission wavelengths due to the absorption edge would be red-shifted. For example, substitutional doping of nitrogen in TiO_2 photocatalysts effectively contributes to narrowing of the bandgap because the $\text{N}2p$ state mixes with the $\text{O}2p$ state, lowering the potential energy to form the valence band of $\text{TiO}_{2-x}\text{N}_x$.²⁾ This explanation would support the fact that bandgap tuning can be realized in some oxynitrides through proper adjustment of the O/N ratio.

We have shown that the colors of perovskite-type $\text{LaTiO}_{2+x}\text{N}_{1-x}$ can be tuned from reddish orange to very pale blue or very light gray by simple composition adjustment in the anions.³⁾ The parent compound LaTiO_2N has been highlighted as a promising candidate in visible-light-driven photocatalysis.^{4),5)} Furthermore, a series of perovskite-type LaTiO_2N materials with compositions slightly deviating from the stoichiometric metal composition was prepared, to establish that the cation nonstoichiometry in the oxynitride affected reflectivity in the longer wavelength region of the absorption edge.⁶⁾ The higher ratio of titanium to lanthanum

resulted in lower reflectivity. When the Ti/La ratio increases, the excess titanium must be reduced to a lower valence state such as Ti^{3+} approximating $\text{La}^{3+}_{1-x}\text{Ti}^{3+}_x\text{Ti}^{4+}\text{O}_2\text{N}$, based on the assumption that the oxynitride should keep its oxygen and nitrogen ratio despite the compositional deviations. The reduction of reflectivity was thought to be ascribed to the presence of the lower-valence titanium.⁶⁾⁻⁸⁾ The presence of this lower-valence titanium might also affect the color variation of $\text{LaTiO}_{2+x}\text{N}_{1-x}$ if O^{2-} and N^{3-} were assumed in the oxynitrides. Equimolar substitution of La^{3+} by Sr^{2+} to compensate the excess titanium will be effective to prevent the formation of the lower-valence titanium, as expressed in the formula of $\text{La}^{3+}_{1-x}\text{Ti}^{3+}_x\text{Ti}^{4+}\text{O}_2\text{N}$. Such substitutions have been reported by Chevire et al.⁷⁾ and Logvinovich et al.,⁸⁾ in the system $\text{LaTiO}_2\text{N}-\text{ATiO}_3$ ($A = \text{Ca}, \text{Sr}$ and Ba). The charge compensation due to the substitution of N^{3-} by O^{2-} was made by the substitution of these divalent alkaline earth metals for La^{3+} . A similar strategy allows bandgap tuning by control of the O/N ratio⁹⁾ using the substitution of lanthanum, without reducing the valence state of titanium, in $\text{La}^{3+}_{1-x}\text{Sr}^{2+}_x\text{Ti}^{4+}\text{O}_{2-x}\text{N}^{3-}_{1-x}$ for $A = \text{Sr}$. However, it has not been confirmed as yet that the cross-substitution of La^{3+} by Sr^{2+} and N^{3-} by O^{2-} would actually prevent reduction of titanium. Also, no one has examined the phenomena that the excess titanium in $\text{La}_{1-x}\text{Ti}_{1+x}\text{O}_2\text{N}$ may produce lower-valence titanium and that the equimolar substitution may prevent the formation of the lower-valence titanium.⁶⁾

In this paper, we prepared three series of $(\text{La},\text{Sr})\text{TiO}_2\text{N}$ compounds with nonstoichiometries in both cations and anions. The first series have compositions of $\text{LaTiO}_{2+x}\text{N}_{1-x}$ with anion nonstoichiometry. The second series can be expressed as $\text{La}_{1-x}\text{Ti}_{1+x}\text{O}_2\text{N}$ which have cation nonstoichiometry. The last series was prepared from solid-solutions of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_2\text{N}$ by means of substitution of lanthanum by strontium. The influences of these

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nonstoichiometries on the valence state of titanium in perovskite-type oxynitride (La,Sr)TiO₂N were examined by XPS spectroscopy. Relationships between the nonstoichiometries, the valence of titanium and the body color were discussed.

2. Experimental procedure

LaTiO₂N was prepared by heating the oxide precursor under a NH₃ gas flow. The metal-oxide precursor was prepared by the polymerized complex method.^{4),11)} In the case of the preparation for the stoichiometric LaTiO₂N as the standard composition, 2.8422 g (= 0.01 mol) of Ti[OCH(CH₃)₂]₄ (titanium tetraisopropoxide) and 4.3300 g of La(NO₃)₃·6H₂O were dissolved in 49.4 g of ethylene glycol at room temperature. Then, 38.2 g of anhydrous citric acid and 40.0 g of distilled water were added to the solution, and the mixture was stirred at 180°C until a transparent gel was formed. The transparent gel was next heated at 200°C for 30 minutes in mantle heater. The polymer was carbonized at 350°C for 4 h and calcined in air at 500–600°C for 4 h to remove carbon components. Throughout these case of experiments, the amount of La(NO₃)₃·6H₂O was fixed and that of Ti[OCH(CH₃)₂]₄ was varied to get the desired cationic molar ratios. The solvent and additives remained unchanged for the nonstoichiometric oxynitrides. 1.0 g of the powder precursor was set in an alumina boat placed in an alumina tube of a horizontal Siliconit tube furnace. After evacuating the system, argon gas was introduced. The furnace temperature was raised to the nitriding temperature of 950°C over an hour, then the gas was switched to ammonia flowing at a flow rate of 1 dm³/min. The duration of nitridation was 5 h. Some samples were then progressively annealed under ammonia gas at the same temperature for 3 h, with flow rates reduced to 50, 30 and 10 cm³/min respectively to complete the corresponding O/N ratios. Both the argon and ammonium gases used were dried by passing through a soda lime cylinder and a coiled coolant trap (below minus 30°C). After the nitridation was complete, the product was cooled down to room temperature in the furnace.

In the case of preparation for the nonstoichiometric (La, Sr)Ti(O,N)₃, La(NO₃)₃·6H₂O and Sr(NO₃)₂ were mixed at desired ratio (Sr/La) and were also kept to a total (La + Sr) = 0.01 mol. The desired ratio of Ti[OCH(CH₃)₂]₄ was then added so that the ratios of (La + Sr) to Ti should be 0.01 mol to 0.0085, 0.009, 0.0095, 0.01, and 0.011 mol, respectively. Throughout these experiments, the amount of La(NO₃)₃·6H₂O and Sr(NO₃)₂ was fixed and that of Ti[OCH(CH₃)₂]₄ was varied adjustably to get the desired cationic molar ratios. These three starting materials were dissolved in 49.4 g (0.822 mol) of ethylene glycol at room temperature. 38.2 g of anhydrous citric acid and 40.0 g of diluting water were added to the solution, and the mixture was stirred at 180°C until a transparent gel was formed. The procedures thereafter were the same as those for the standard composition LaTiO₂N mentioned above.

The cation ratio of the oxynitrides was determined roughly by fluorescent X-ray analysis (Shimadzu Co., Rayny-800) and precisely by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (Seiko Instruments Inc., SPS1500VR). The oxynitrides for the ICP measurement were dissolved in nitric acid, and prepared or diluted in order to obtain the appropriate concentration for the measurement. Phase identifications and lattice constant determination were performed by powder X-ray diffractometry (Rigaku Co., RINT-2500VHF+) using monochromatized Cu K α radiation with a source power of 40 kV and 150 mA. LaTiO₂N has been reported to have the triclinic unit cell with dimensions of $a = 0.56097(1)$ nm, $b = 0.78719(2)$ nm, $c =$

$0.55752(1)$ nm, $\alpha = 90.199(2)^\circ$, $\beta = 90.154(3)^\circ$, and $\gamma = 89.988(8)^\circ$.¹⁰⁾ However, as the peaks were not sharp enough to analyze as the triclinic cell, these oxynitrides were indexed as a pseudo tetragonal cell with dimensions of $a \approx 0.55$ nm, $c \approx 0.78$ nm. In fact, LaTiO₂N was treated as the tetragonal crystal in the JCPDS card No.48-1230. All the samples used in the characterizations described hereafter were confirmed to be composed of a single phase of perovskite-type LaTiO₂N. Optical diffuse reflectance spectra were measured with a double beam spectrometer (JASCO V-550DS). A PTFE (poly-tetrafluoroethylene) compact was used as a reference. The bandgap of the oxynitrides was estimated based on the onset of diffuse reflectance. Diffuse reflectance spectra of bulk samples were analogous to transmission spectra of thin-film samples.¹²⁾

The valence state of each element in the oxynitrides was evaluated by X-ray Photoelectron Spectroscopy (XPS). The XPS analyses were carried out in a KRATOS AXIS ULTRA instrument, equipped with an ultrahigh vacuum (UHV) analytical chamber of base pressure $\sim 2 \times 10^{-9}$ Torr ($\sim 3 \times 10^{-7}$ Pa), a monochromatized Al K α X-ray source, a non monochromatized dual-anode X-ray source (Mg/Al), a hemispherical electron energy analyzer with multi-channel detector, an Ar⁺ sputter gun and a charge-compensating low-energy electron system. For XPS analysis, samples were lightly ground using a mortar and pestle, pressed into thin pellets, then mounted on stainless-steel stubs using double-sided adhesive tape. The grinding was gentle to avoid damages to the samples, but was sufficient to overcome the effects of surface segregation and modification, especially surface oxidation of the samples during storage. All spectra presented here were excited using monochromatized Al K α radiation ($h\nu = 1486.6$ eV), and with the hemispherical electron energy analyzer operated in the fixed analyzer transmission (FAT) mode. The take-off angle with respect to the surface normal was 0°. The charge-compensating low-energy electron system was used to minimize specimen charging during X-ray irradiation. The binding energy scale was calibrated using adventitious hydrocarbon referencing (C 1s = 285.0 eV).

Survey spectra, used in the quantitative analysis of the various elements present in each sample, were collected over the binding energy range 1200–0 eV (0.5 eV increments) at an analyzer pass energy of 80 eV. Elements identified in the samples were Sr, La, Ti, O, N and C. The relative concentration of each element in the near-surface region of samples was calculated using peak areas of the core-level Sr 3d, La 3d_{5/2}, Ti 2p, O 1s, N 1s and C 1s signals, respectively. Relative sensitivity factors, based on instrument-modified Schofield cross-sections, were used in the quantification procedure (5.05, 28.12, 7.81, 2.93, 1.80 and 1.00, respectively).¹³⁾ Estimated uncertainty in the atomic concentration reported for each element is 1–2%. The chemical state of Sr, La, Ti, O, N and C in the near-surface region of each sample was determined from high-resolution narrow-scan spectra taken at pass energy 20 eV over the Sr 3d, La 3d, Ti 2p, O 1s, N 1s and C 1s regions (0.05 eV increments), respectively. To improve the signal-to-noise ratio, 30 spectra were accumulated and added to produce a spectrum.

3. Results and discussion

As mentioned in the introduction, the increase of O/N ratio in the oxynitrides LaTiO_{2+x}N_{1-x} resulted in the enhancement of the optical bandgap to change the body colors from orange, yellow, green, grayish pale blue to white.³⁾ When the oxynitrides contained more titanium than the stoichiometric composition of LaTiO₂N, expressed as La_{1-x}Ti_{1+x}O₂N, the reduction in the reflec-

tivity in the longer wavelength region after the absorption edge, makes the body colors darker.⁶⁾

Figure 1 shows the reflectance spectra of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_2\text{N}$ as a function of x , the amount of substitution of lanthanum by strontium. As seen in the figure, the reflectivity after the absorption edge was enhanced with increasing substitution. **Figure 2** shows the reflectance spectra of nonstoichiometric $(\text{La,Sr})\text{TiO}_2\text{N}$ prepared so that molar ratio of lanthanum to strontium was fixed to be 0.8:0.2 and that of titanium to the sum of the lanthanum and strontium amounts, $\text{Ti}/(\text{La} + \text{Sr})$, increased from 0.95, 1.07 to 1.23, as confirmed by ICP spectroscopy. Obviously, strontium-free oxynitrides showed the lower reflectivity after the absorption edge for all the samples with various $\text{Ti}/(\text{La} + \text{Sr})$ ratios. The bandgap for all the oxynitrides remained unchanged even after varying the $\text{Ti}/(\text{La} + \text{Sr})$ ratios and/or the substituting La^{3+} by Sr^{2+} . It follows that these oxynitrides should have the same O/N ratio because only the O/N ratio affects the width of the bandgap. When we assume that these oxynitrides keep their oxygen and nitrogen composition, the substitution of La^{3+} by Sr^{2+} may require the oxidation of titanium based on the formal charge balance. This consideration is supported by the report that the reduction of reflectivity is ascribed to the presence of the lower-valence titanium.^{6),7)} At least, substitution of La^{3+} by Sr^{2+} seemed

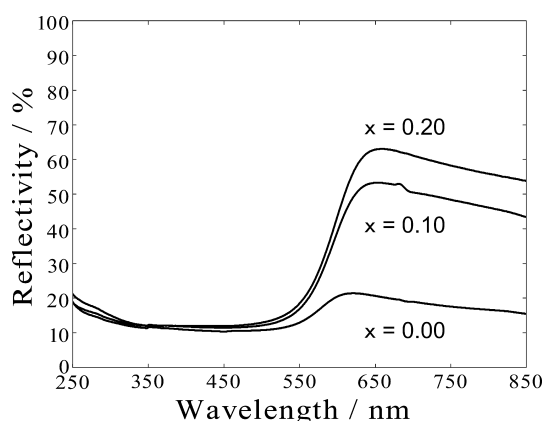


Fig. 1. Reflectance spectra of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_2\text{N}$ as a function of x , the amount of substitution of lanthanum by strontium.

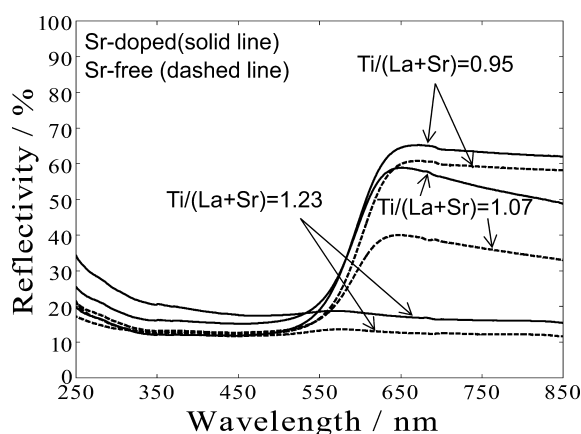


Fig. 2. Reflectance spectra of cation-nonstoichiometric $(\text{La,Sr})\text{TiO}_2\text{N}$ prepared so that molar ratio of lanthanum to strontium was fixed to be 0.8:0.2 and that of titanium to the sum of lanthanum and strontium amounts, $\text{Ti}/(\text{La} + \text{Sr})$ increased from 0.95, 1.07 to 1.23. Those for Sr-free LaTiO_2N with various Ti/La ratios are shown for references.

to be effective in preventing the reduction of reflectivity in the longer wavelength region after the absorption edge.

According to the results shown in Fig. 2, Sr-substitution may reduce the formation of lower-valence titanium such as Ti^{3+} . However, we have not confirmed the valence state of titanium as yet. **Figure 3** shows the schematic diagram of the composition of the samples on which XPS measurements were conducted. In order to interpret the XPS measurements, we present in this diagram the three parameters which strongly affect the valence state of titanium and affect the optical properties. As the origin of three dimensional plots, the stoichiometric composition LaTiO_2N was chosen. The vertical (z) axis represents variation of the O/N ratio, and thus anion nonstoichiometry - the higher the number of the sample, the larger the O/N ratio. The horizontal (y) axis represents variations of the Ti/La ratio, and thus cation nonstoichiometry. The Ti/La ratio increased in the order of Samples #5, #6 and #7. The x axis represents variations of the Sr/La ratio, again with cation nonstoichiometry. The doped-Sr increased in the order Sample #1, #8, #9 and #10. The reflectance spectra of Samples #1, #9 and #10 are presented in Fig. 1. Some narrow scan XPS spectra for the oxynitrides $(\text{La,Sr})\text{Ti}(\text{O,N})_3$ are shown in Figs. 4(a)–(f) and the results of calculated composition ratios in the oxynitrides $(\text{La,Sr})\text{Ti}(\text{O,N})_3$ based on the XPS spectra are listed in Table 1. The ratio $\text{O}/\text{N} = 6.87$ calculated from XPS results should have been normalized so as to be $\text{O}/\text{N} = 2$ for Sample #1, LaTiO_2N , however it is still possible to discuss the trends within the samples on the respective axes.

Figures 4(a)–(c) show the $\text{Ti}2p$, $\text{O}1s$ and $\text{N}1s$ narrow scan XPS spectra for LaTiO_2N with anion nonstoichiometry. The peak assigned to $\text{Ti}2p_{3/2}$ at around 458 eV seemed to comprise of two peaks. The strongest peak at 458.3 eV could be assigned to Ti^{4+} and the shoulder with the lower binding energy was attributed to the existence of a lower valence of titanium, likely Ti^{3+} .¹⁴⁾ The shoulder gradually disappeared and the peak width became narrower with an increase of the O/N ratio, and finally Sample #4, with the largest O/N ratio, seemed to have a single peak corresponding to Ti^{4+} . The $\text{O}1s$ peak at 529.8 eV could be assigned to lattice oxygens in the metal oxide and a broad shoulder with higher binding energy would be ascribed to oxygens in carbonates and/or hydroxides.¹⁴⁾ The $\text{O}1s$ peak position of the lattice oxygens remained unchanged, but the relative intensity of the

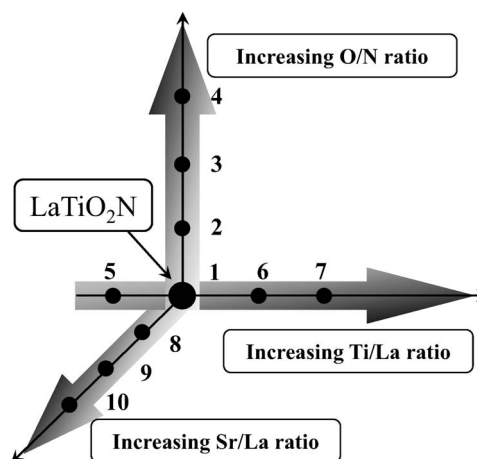


Fig. 3. Schematic diagram of the samples for XPS, in which the three axes represent the parameters which strongly affect the valence state of titanium and affect the optical properties.

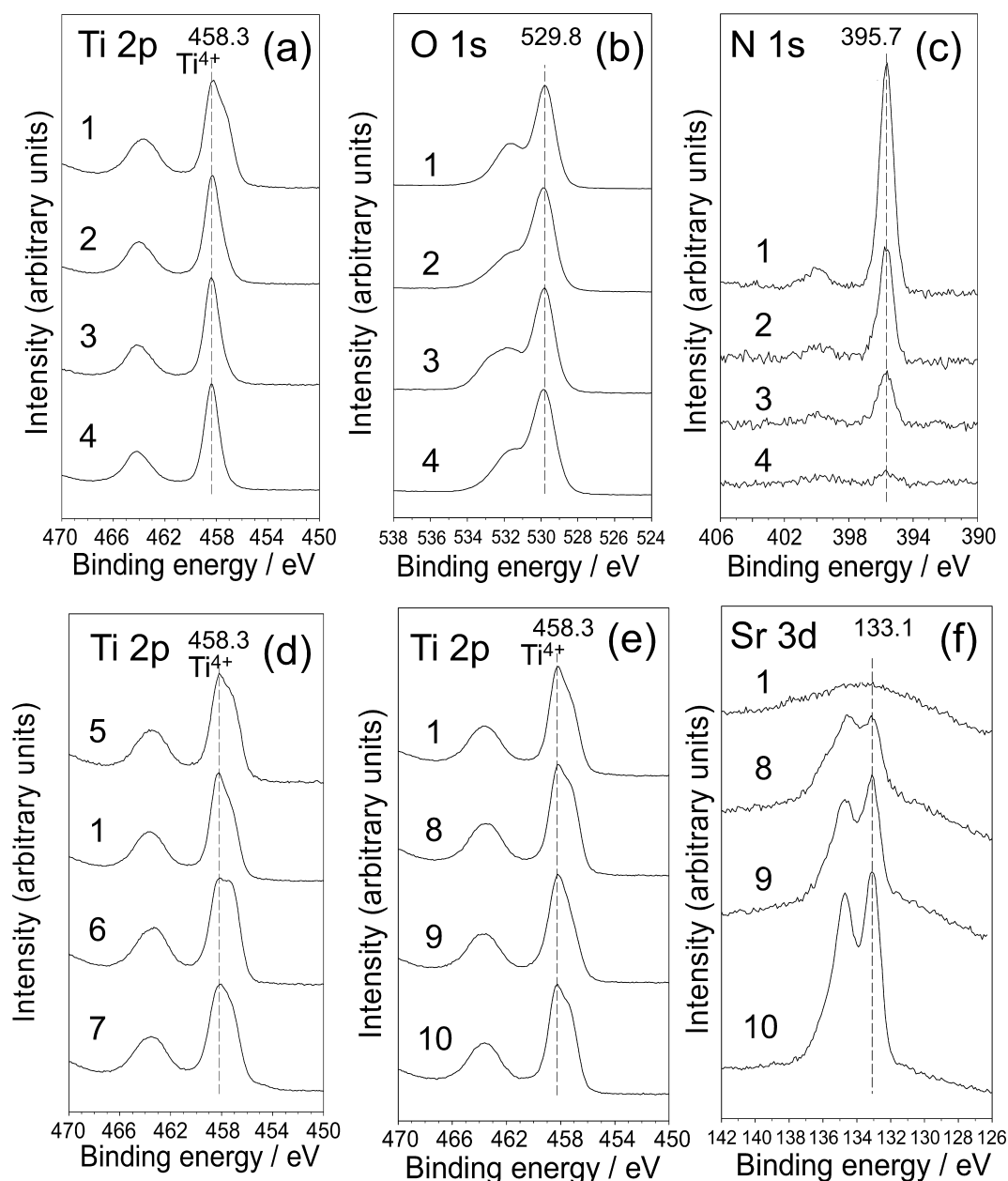


Fig. 4. (a)–(c) Ti2p, O1s and N1s narrow scan XPS spectra for LaTiO_2N with anion nonstoichiometry, (d) Ti2p spectra for LaTiO_2N with various Ti/La ratios and (e) and (f) Ti2p and Sr3d spectra for $(\text{La}, \text{Sr})\text{TiO}_2\text{N}$ with various Sr/La ratios. The sample notations are the same as Fig. 3.

Table 1. Results of Quantitative Analysis of the Constituent Atoms in $(\text{La}, \text{Sr})\text{TiO}_2\text{N}$ by XPS. The Sample Notations are the Same as Fig. 3

Sample Number	1	2	3	4	5	6	7	8	9	10
O/N	6.87	18.88	52.40	187.8	7.20	7.55	6.95	8.20	9.40	10.52
Ti/(La + Sr)	0.78	0.84	0.82	0.78	0.66	0.78	0.88	0.62	0.66	0.55
Sr/La								0.20	0.29	0.48

shoulder to the main peak did not vary significantly. The strong N1s peak was observed at 395.7 eV for Sample #1 along with a very weak peak at around 400 eV. The first peak could be assigned to lattice nitrogens in metal nitrides. The peaks at around 396 eV and 400 eV in the $\text{TiO}_{2-x}\text{N}_x$ films were assigned to atomic $\beta\text{-N}$ of TiN and molecularly chemisorbed $\gamma\text{-N}_2$.²⁾ The peak intensity of the major peak decreased with an increase of

the O/N ratio, which could be confirmed by quantitative analysis of the constituent atoms as shown in Table 1.

When nitrogens are substituted by oxygens and the O/N ratio increases, titanium should be reduced as far as the formal oxidation numbers are concerned, if formal oxidation states of O^{2-} and N^{3-} are assumed. However, the Ti2p XPS spectra indicated that titanium is oxidized when the O/N ratio increases. This phenom-

enon is attributed to the difference in electronegativity between oxygen and nitrogen. The substitution of nitrogen by oxygen, a more electronegative element, involves an increase in ionicity of the bonding.¹⁵⁾ Oxygens attract more electrons from cations than nitrogen so that the cations appear more oxidized and thus appear at higher binding energy as the O/N ratio increases. When we assumed that the titanium takes tetravalent state, the composition of perovskite materials where almost all anions are oxygens should be $\text{LaTiO}_{3.5}$ or $\text{La}_2\text{Ti}_2\text{O}_7$. However, X-ray diffraction showed that all samples maintained a single phase of a perovskite-type structure. Generally, the perovskite-type structure has a large tolerance to anion deficiency or excess, as well as cation nonstoichiometry such as LaNiO_{3-x} ,¹⁶⁾ LaMnO_{3+x} ¹⁷⁾ and $\text{La}_{1-x}\text{Ti}_{1+x}\text{O}_2\text{N}$,⁶⁾ respectively. Oxygen-excess perovskite-type LaTiO_{3+x} would be expected to be stable to some extent. The Ti/La ratios stayed unchanged among these samples, despite the varying O/N ratios.

Among the samples with varying Ti/La ratios, the O/N ratios remained unchanged, as indicated by XPS analysis. The Ti/La ratios increased in the order Sample #5, #1, #6 and #7. The constant O/N ratio agrees with the experimental results that the O/N ratio seemed to be independent of the Ti/La ratio, so that the optical bandgap remained unchanged in spite of the increasing Ti/La ratio. Regarding line shapes for titanium shown in Fig. 4(d), neither significant change nor a systematic trend could be detected among the samples with varying Ti/La ratios. This suggests the Ti/La ratio does not affect the valence state of titanium. We had mentioned that the formation of a low valence state of titanium such as Ti^{3+} would result in the deterioration of reflectivity after the absorption edge.

The narrow scan XPS spectra of Ti2p and Sr3d for the final series of samples #1, #8, #9, #10, in which Sr^{2+} substitution for La^{3+} by made, are shown in Figs. 4(e) and 4(f), respectively. The spectra as a function of Sr/La ratio showed that the ratio did not affect the valence state of titanium. Of course, the intensity of Sr3d peak increased with increasing Sr/La ratio. The Sr3d doublet could be assigned to the spin-orbit split $3d_{3/2}$ (higher binding energy) and $3d_{5/2}$, respectively. However, there are interesting trends on varying the O/N ratios and Ti/(La + Sr). In this series, only the Sr/La ratios were changed. However, it seemed the O/N ratios gradually increased and Ti/(La + Sr) gradually decreased as shown in Table 1, though the Ti/(La + Sr) ratios were supposed to be fixed when the starting materials were weighed. The unexpected decrease in the Ti/(La + Sr) ratios would lead to the improvement in reflectivity after the absorption edge. However simultaneously, the O/N ratios unexpectedly increased. The magnitude of the increment in the O/N ratios in samples #1, #8, #9 and #10 was as small as 1.5 times at most, whereas that seen in the samples #1, #2, #3 and #4 was more than 25 times. Therefore, the blue-shift due to the increase of O/N ratios would be negligible in the samples #1, #8, #9 and #10. Note that the bulk O/N ratio of the samples, determined by an inert gas fusion method,^{3),7),8)} increased from $\text{LaTi}(\text{O}_{0.68}\text{N}_{0.32})_{2.9}$ in Sample #1 to $\text{LaTi}(\text{O}_{0.98}\text{N}_{0.02})_{2.9}$ in Sample #4³⁾ as well as the surface composition of the samples increased, though no significant increase or decrease in the bulk O/N ratio could be detected in the series with either Ti/La or Sr/La variation.

Table 2 shows the comparison of bulk compositions of the oxynitrides numbered as #1, #9 and #10 determined by ICP analysis with those by XPS analysis. The Sr/La ratio of sample number #10 by ICP analysis nearly doubled compared with that of #9. The same trend could be seen in the Sr/La ratio detected by XPS analysis. With regards to the Ti/(La + Sr) ratios deter-

Table 2. Comparison of Bulk Compositions of the Oxynitrides Numbered as #1, #9 and #10 (see Fig. 3) Determined by ICP Analysis with those by XPS Analysis

Sample Number	ICP-AES		XPS	
	Sr/La	Ti/(La + Sr)	Sr/La	Ti/(La + Sr)
1		1.01		0.78
9	0.087	1.07	0.29	0.66
10	0.176	1.08	0.48	0.55

mined by ICP analysis, the ratios stayed unchanged or increased very slightly with increasing Sr/La ratio. This trend seemed reasonable, because the starting materials were weighed so that Ti/(La + Sr) ratios were fixed to be 1. However, the Ti/(La + Sr) ratios determined by XPS analysis, as shown in Table 1, decreased with increasing Sr/La ratio. The reason why the Ti/(La + Sr) ratio determined by XPS analysis should decrease with an increase of Sr/La ratio is not clear yet, but this phenomenon might be attributable to the difference in compositions between the bulk and surface of the oxynitrides. The bulk composition analysis such as ICP spectroscopy gives an average composition of a sample tested. On the other hand, the XPS spectroscopy is very sensitive to the surface.

When the Sr/La ratio increased in stoichiometric $(\text{La,Sr})\text{TiO}_2\text{N}$ or cation-nonstoichiometric $(\text{La,Sr})_{1-x}\text{Ti}_{1+x}\text{O}_2\text{N}$, the strontium component was enriched on the surface of the oxynitrides. The Sr/La ratio determined by XPS was larger than that by ICP-AES for both samples #9 and #10, comparing Table 1 with Table 2. The Ti/(La + Sr) ratio in the vicinity of the surface decreased unexpectedly, and then the reflectivity after the absorption edge would be enhanced, as seen in Figs. 1 and 2. The color of pigments strongly depends on the light reflection from their surface and materials far inside the surface would hardly contribute to the color. Therefore, it may be very natural that the brightness of the oxynitride sample would be governed by the Ti/La ratio in the vicinity of the surface. Strategies to clarify the mechanism to increase/decrease the reflectivity in the oxynitrides, for example, control of particle sizes to vary the surface-to-volume ratio, are currently being explored.

4. Conclusions

Our XPS results showed that the anion nonstoichiometry, but not cation nonstoichiometry, such as an excess titanium to lanthanum ratio and substitution of lanthanum by strontium, affected the valence state of titanium in perovskite-type oxynitrides $(\text{La,Sr})\text{TiO}_2\text{N}$. Though several papers have pointed out that the excess titanium in $\text{La}_{1-x}\text{Ti}_{1+x}\text{O}_2\text{N}$ may produce lower-valence states of titanium,⁶⁾⁻⁸⁾ our results obtained by XPS analysis counter this view. The deterioration or enhancement in reflectivity after the absorption edge is thought to be strongly tied to the high or low Ti/La or Ti/(La + Sr) ratio in the vicinity of the surface.

Acknowledgments This work was partly supported by a Grant-in-Aid (Approved No.19018020) for Scientific Research on Priority Area entitled "Panoscopic Assembling and Highly Ordered Functions for Rare Earth Materials" from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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