

Local Environment of Strontium Cations Activating NaTaO₃ Photocatalysts

Longjie An,[†] Takuro Sasaki,[‡] Peter G. Weidler,[§] Christof Wöll,[§] Nobuyuki Ichikuni,[‡] and Hiroshi Onishi^{*,†}

[†]Department of Chemistry, Graduate School of Science, Kobe University, Rokko dai, Nada, Kobe, Hyogo 657 8501, Japan

[‡]Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, Yayoi cho, Inage, Chiba 263 8522, Japan

[§]Institute for Functional Interfaces, Karlsruhe Institute of Technology, Campus Nord, 76344 Eggenstein Leopoldshafen, Germany

ABSTRACT: Sodium tantalate, NaTaO₃, is one of the best semiconductors for photocatalytic water splitting and CO₂ reduction. Doping with metal cations is crucial for enhancing the quantum efficiency of the desired reactions. Nevertheless, details related to the doping of the host metal oxide and activation by guest metal cations are not sufficiently known. The most fundamental question concerns the increase in the quantum efficiency via doping with guest cations that are impurities in the host lattice. In this study, the local environment of Sr cations, which are the typically used guest cations in NaTaO₃, was characterized by extended X ray absorption fine structure spectroscopy. The results reveal the presence of two Sr–O shells in the Sr doped NaTaO₃ photocatalysts. The small shell with an unexpectedly short Sr–O bond length of 1.96 Å corresponds to SrO₆ octahedra embedded in the corner shared network of TaO₆ octahedra. The other shell with a Sr–O bond length of 2.60 Å corresponds to SrO₁₂ cuboctahedra with Sr cations at positions previously occupied by Na cations. Rietveld analysis of the X ray diffraction data confirmed the formation of a NaTaO₃–Sr(Sr_{1/3}Ta_{2/3})O₃ solid solution to accommodate the two Sr–O shells in NaTaO₃ with no requirement for creating oxygen anion vacancies. Mechanisms for increasing the quantum efficiency via doping with Sr cations are discussed in the context of the revealed environment.

KEYWORDS: photocatalysis, recombination, doping, X ray absorption, Rietveld analysis, perovskite structure, solid solution, solar hydrogen

1. INTRODUCTION

Sodium tantalate, NaTaO₃ is the semiconductor photocatalyst for highly efficient artificial photosynthesis. Kudo and co workers used this perovskite structured metal oxide for the overall water splitting reaction. A quantum efficiency of greater than 50% has been reported for water splitting using NaTaO₃ doped with lanthanum.^{1,2} Doping with alkaline earth metal cations is effective in enhancing the efficiency as well.^{3,4} The rate of H₂ production was 1.7 mmol h⁻¹ on pristine NaTaO₃ and increased to 19.8, 9.5, 9.3, or 4.9 mmol h⁻¹ via doping with La³⁺, Sr²⁺, Ba²⁺ or Ca²⁺ cations, respectively.⁵ Doping with two metal cations^{6–10} has been subsequently examined for the sensitization of this wide band gap semiconductor to visible light. Currently, studies are being extensively carried out on double doping with one cation and one anion.^{11–18} The photocatalytic reduction of CO₂ using pristine¹⁹ and metal doped NaTaO₃^{20,21} also has been reported.

Doping with metal cations is crucial for the modification of NaTaO₃ photocatalysts, as demonstrated in the above mentioned studies. Nevertheless, details related to the doping and activation of the host metal oxide for increased water

splitting efficiency are not known. Since these cations are impurities in the crystalline host lattice, the increase in the quantum efficiency via doping with metal cations is the most fundamental question that needs to be answered. Recently, An and Onishi²² challenged a received hypothesis that Na⁺ cations in NaTaO₃ are simply doped with alkaline earth metal cations. They proposed the formation of a NaTaO₃–Sr(Sr_{1/3}Ta_{2/3})O₃ solid solution in Sr doped NaTaO₃ photocatalysts, in addition to similar solid solutions in Ca and Ba doped photocatalysts. Regularly separated 10 nm steps spontaneously appeared on the surface of NaTaO₃ particles doped with alkaline earth metal cations,⁴ as was observed on particles doped with lanthanum.¹ The lattice mismatch in a particle consisting of a Sr rich solid solution shell over a Sr poor solid solution core induced the steps at the surface.²² The doping of Ta⁵⁺ cations with alkaline earth metal cations has been further argued to be

crucial to the enhanced quantum efficiency in the solid solution.

In their study,²² the doping of Ta cations was evidenced by the symmetry driven presence or absence of a Raman band. In this study, X ray absorption fine structure (XAFS) spectroscopy and Rietveld analysis of the X ray diffraction (XRD) data were utilized to determine the local environment of the Sr cations in NaTaO₃ photocatalysts. Extended X ray absorption fine structure (EXAFS) should be useful for characterizing the metal cations embedded in NaTaO₃. Only one extended²³ and one near edge²⁴ structure of La doped photocatalysts have been reported to date.

NaTaO₃ exhibits a perovskite structure with a slightly distorted orthorhombic symmetry (*Pbnm*, *a* = 5.48 Å, *b* = 5.52 Å, *c* = 7.79 Å) at room temperature.²⁵ The orthorhombic cell comprises four NaTaO₃ units, and a cube with a side length of 3.89 Å, the volume of which corresponds to one fourth of the orthorhombic cell volume, is assigned to one NaTaO₃ unit on average. In the average cubic unit cell, which is shown in Figure 1, Na cations at the A sites are coordinated to 12 O anions, affording NaO₁₂ cuboctahedra. Tantalum cations at the B sites are at the centers of TaO₆ octahedra.

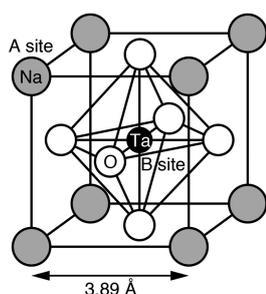


Figure 1. Average cubic unit cell of NaTaO₃ with Na⁺ and Ta⁵⁺ cations at the A and B sites, respectively.

2. EXPERIMENTAL SECTION

2.1. Photocatalyst Preparation. Strontium doped NaTaO₃ photocatalysts were prepared through a solid state reaction. First, mixtures of Na₂CO₃ (99.8%, Kanto), Ta₂O₅ (99.99%, Rare Metallic Co. Ltd.), and SrCO₃ (99.9%, Kanto)

were calcined in alumina crucibles at 1173 K for 1 h and then at 1423 K for 10 h according to methods reported previously.^{1,3,22} The Sr/Ta ratio in the mixtures with a constant Na/Ta molar ratio of 1.05 was adjusted to 0, 2, 8, 20, and 50 mol %. Excess Na remaining in the calcined products was washed with water. Hereafter, the water washed photocatalysts are denoted as NTO, Sr NTO (2 mol %), Sr NTO (8 mol %), Sr NTO (20 mol %), and Sr NTO (50 mol %). The concentrations of Sr in the photocatalysts were quantified as 0, 2.1, 8.3, 20.8, and 49.0 mol % by energy dispersive X ray fluorescence spectrometry (Shimadzu, EDX 720). A single perovskite structured phase for NTO and each Sr NTO was confirmed by XRD (Figure S1 in the Supporting Information) using a SmartLab diffractometer (Rigaku). Sr NTO (50 mol %) was washed with an aqueous HCl solution (1 mol L⁻¹) for 10 min at room temperature and then washed with water until the pH of the washing fluid was maintained at 7. HCl washed Sr NTO (50 mol %) exhibited a decrease in the Sr concentration to 44.2 mol %. A small but finite decrease indicates that Sr containing residue on the surface of Sr NTO (50 mol %) does not show any X ray diffraction.

2.2. X-ray Absorption Measurements. Absorption spectra at the Sr K edge and Ta L₃ edge were recorded with a Si(111) double crystal monochromator at BL 12C of the Photon Factory (Tsukuba, Japan). Measurement details have been added to the Supporting Information. Curve fitting analysis of the extended fine structures was carried out using the IFEFFIT package including Athena and Artemis.²⁶

2.3. XRD and Rietveld Analysis. Diffraction patterns for Rietveld analysis were recorded on a D8 Advance diffractometer with Cu Kα_{1,2} radiation (Bruker AXS) equipped with a position sensitive X ray detector (Lynxeye). A Sr NTO (8 mol %) disc was rotated to record diffraction data in the 2θ range of 5–114° with a step of 0.016° and a total counting time of 840 s per step. TOPAS 5.0 software (Bruker AXS) was used for the Rietveld structure refinement.^{27–29}

3. RESULTS AND DISCUSSION

3.1. EXAFS of HCl-Washed Sr-NTO (50 mol %). Sr NTO (50 mol %), the photocatalyst with the highest Sr concentration, exhibited the Sr K edge spectrum with the best signal to noise ratio. To eliminate the possible contribution from Sr containing residues that are soluble in HCl solution,

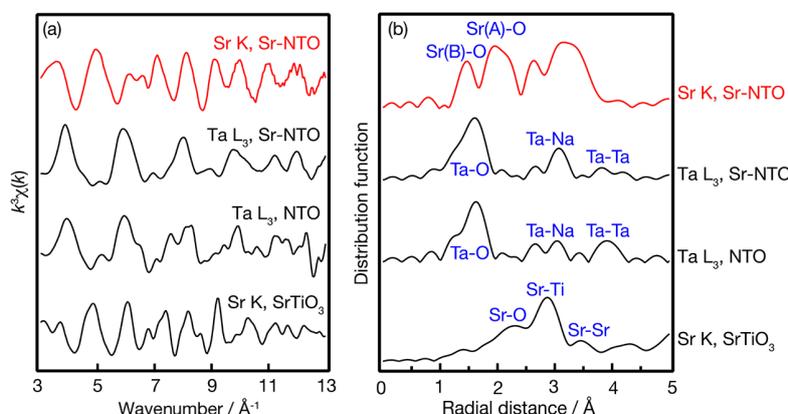


Figure 2. Extended X ray absorption fine structures at the Sr K edge and Ta L₃ edge observed for the HCl washed Sr NTO (50 mol %) photocatalyst. The Ta L₃ edge spectrum of NTO and Sr K edge spectrum of SrTiO₃ are shown for reference. (a) *k*³ weighted absorption spectra. (b) Radial distribution functions normalized to the height of the most intense peak. The *k* range in the Fourier transform was 3–13 Å⁻¹.

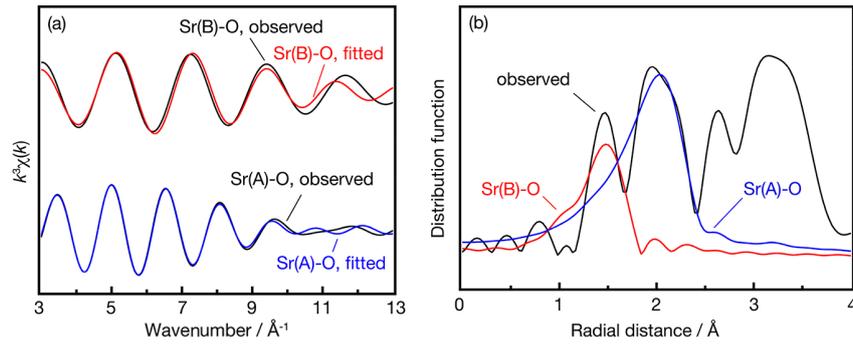


Figure 3. Results of curve fitting of the Sr K edge spectrum of the HCl washed Sr NTO (50 mol %) photocatalyst. (a) Fourier filtered and fitted k^3 weighted absorption spectra. (b) Observed and fitted radial distribution functions.

the HCl washed photocatalyst was examined instead of Sr NTO (50 mol %). Figure 2a shows the Sr K edge EXAFS results for the HCl washed photocatalyst. Fourier transformation of the k^3 weighted absorption spectrum yielded a radial distribution function with peaks at 1.5, 2.0, 2.6, and 3.1 Å (Figure 2b).

The peak at 1.5 Å corresponds to the Sr(B)–O shell with Sr cations at the B sites in NaTaO₃, which is supported by the Ta L₃ edge spectra of the same photocatalyst and of NTO (Figure 2). Radial distribution functions converted from the two Ta L₃ edge spectra peaked at 1.5 Å. Because Ta cations occupy the B sites in NaTaO₃, six O anions of each TaO₆ octahedron are the nearest neighbor atoms to the Ta cation. Hence, the peak of the radial distribution at 1.5 Å provides evidence for the X ray absorption of the M atom at the center of the MO₆ octahedron, which in this case refers to SrO₆, embedded in the host lattice. In the average cubic unit cell shown in Figure 1, the Ta–O distance in the TaO₆ octahedron is 1.95 Å. An apparent Sr(B)–O shell length of 1.5 Å is acceptable considering the phase shifts in the electron scattering by O anions.

The peak of the radial distribution at 2.0 Å is related to the Sr(A)–O shell with Sr cations at the A sites. Pristine NaTaO₃ includes NaO₁₂ cuboctahedra with an average Na–O distance of 2.75 Å. By placing Sr cations at the centers of the cuboctahedra, a Sr–O shell can be observed at 2.0 Å in the radial distribution. The Sr K edge EXAFS result for SrTiO₃ was used as a reference for the occupation of Sr at the A sites in a perovskite structured metal oxide. The cubic cell length of SrTiO₃, 3.90 Å,³⁰ is identical to the average cell length of NaTaO₃. The radial distribution function shown in Figure 2b peaks at 2.2 Å. Similar Sr–O distances, i.e., 2.0 Å in Sr NTO and 2.2 Å in SrTiO₃, indicate that SrO₁₂ cuboctahedra are embedded in the two perovskite structured compounds.

In the preceding paragraphs, we hypothesized that two Sr containing local structures, i.e., a SrO₆ octahedron and a SrO₁₂ cuboctahedron, are simultaneously present in Sr NTO (50 mol %), in accordance with their radial distribution functions. Curve fitting was carried out to test our assumption and to quantify the lengths of the two shells. Oscillations in the absorption spectrum corresponding to the Sr(B)–O shell were isolated and filtered using a window function, followed by inverse Fourier transformation to afford the shell related oscillations. The Fourier filtered oscillations were fitted using one Sr–O shell with four adjustable parameters; shell length, coordination number, threshold energy difference, and squared displacement (Debye–Waller factor). Figure 3a shows the

Fourier filtered and best fit oscillations. The radial distribution function deduced from the best fit oscillations is compared with the original distribution in Figure 3b. Fitting with the Sr(A)–O shell was completed in the same manner using a filtering window tuned for this shell. Table 1 summarizes the refined parameters.

Table 1. Metal–Oxygen Shells in HCl Washed Sr NTO (50 mol %) and SrTiO₃^a

shell	L/Å	CN	dE/eV	$\sigma^2/\text{Å}^2$	R range/Å
Sr(B) O	1.96	1.1	0.4	0.0065	1.12 1.72
Sr(A) O	2.60	6.6	3.8	0.0140	1.68 2.40
Ta O	1.97	5.9	11.3	0.0091	1.12 1.72
Sr O in SrTiO ₃	2.80	15.0	3.2	0.0163	1.40 2.50

^aL is the shell length; CN is the coordination number; dE is the threshold energy difference, σ^2 is the Debye–Waller factor, and R range is the filtering window for inverse Fourier transformation.

The Sr–O shell in SrTiO₃ and the Ta–O shell in Sr NTO (50 mol %) were also fitted for reference. The Sr–O length in SrTiO₃, 2.76 Å,³⁰ and Ta–O length in the average lattice of NaTaO₃, 1.95 Å, were obtained in the refinement with precision better than 0.1 Å. The filtered and fitted oscillations of these reference shells are shown in Figures S2 and S3, respectively.

The most important issue here is the good fit for the two Sr–O shells. The residuals are satisfactorily small in k space (Figure 3a). Hence, the two Sr containing local structures are simultaneously present in Sr NTO (50 mol %). The use of EXAFS to characterize metal cations embedded in NaTaO₃ is thus feasible.

Doping of the B sites with Sr cations, which was concluded here, is possibly key to the enhancement of the quantum efficiency. The electron–hole recombination rate is controlled by the Sr concentration gradient in the Sr NTO photocatalyst particles; a large gradient from the Sr rich surface to the Sr poor core leads to restricted recombination.³¹ The conduction band of NaTaO₃ comprises Ta 5d orbitals.^{32–34} By doping of the B sites with Sr cations, SrO₆ octahedra are embedded in the corner shared network of the TaO₆ octahedra. The embedded octahedra hinder the overlap of the Ta 5d orbitals, which in turn narrows the conduction band with an upward shift of the band minimum. As a result, the light absorption edge for band gap excitation is blue shifted by doping with Sr.²² The concentration gradient of the Sr cations at the B sites induces the energy gradient of the conduction band minimum. Hence, the band gap excited electrons, not holes, are driven by

the energy gradient. Electrons are thereby separated from holes. This hypothesis is a promising mechanism for the enhancement of the quantum efficiency induced by the doping of metals.

The second issue is related to the shell lengths. The Sr(B)–O length is compatible with the Ta–O length in the same photocatalyst, indicating that the embedded SrO₆ octahedra are compressed in the surrounding NaTaO₃ lattice. The compressed SrO₆ octahedra induced marginal distortion in the surrounding lattice. Hence, the energy costs related to the occupation of Sr cations in the B sites can be limited. The SrO₆ octahedra in NaCl structured SrO exhibited a Sr–O bond length of 2.57 Å. The Sr–O bond length in a diatomic SrO molecule is 1.92 Å.³⁵ Theoretical simulations should be conducted in the future to reveal the electronic structures induced by the compressed octahedra in Sr NTO. The Sr(A)–O bond length decreased by 0.15 Å relative to the Na–O bond length in the average lattice of NaTaO₃. The stronger attractive electrostatic force in the Sr²⁺–O²⁻ ion pairs in comparison with that in the Na⁺–O²⁻ pairs decreased the ion pair length.

The coordination numbers are another issue. In pristine NaTaO₃, the A and B site cations are coordinated by 12 and 6 O anions, respectively. If the same number of Na and Ta cations were exchanged with Sr cations, the coordination number of the Sr(A)–O shell would be twice the coordination number of the Sr(B)–O shell. However, this was not observed. The ratio of the coordination numbers was 6 instead of 2 (Table 1). When we assumed that Sr cations alternatively occupy the A or B sites, the coordination number obtained by curve fitting is proportional to the number of Sr cations at each type of site. According to this assumption, the observed ratio predicts a cation number ratio of three Sr cations at A sites per one Sr cation at a B site. This number ratio is in agreement with the composition of NaTaO₃–Sr(Sr_{1/3}Ta_{2/3})O₃ solid solution. Sr(Sr_{1/3}Ta_{2/3})O₃ is a known compound,^{36,37} and its solid solution with NaTaO₃ explains the simultaneous presence of the Sr cations at the A and B sites with no need to create oxygen anion vacancies to balance cationic and anionic charges.

Two more peaks, i.e., one small peak at 2.6 Å and one large peak at 3.1 Å, can be observed in the radial distribution function of Sr NTO (50 mol %) (Figure 2a). In pristine NaTaO₃, each Na cation is coordinated by eight Ta cations with an average Na–Ta distance of 3.37 Å. On the other hand, each Ta cation is coordinated by eight Na cations with the same distance. After simultaneous placement of Sr cations at the A and B sites, Sr(A)–Ta and Sr(B)–Na shells were observed instead of Na–Ta and Ta–Na shells. The two shells with different scattering atoms incidentally produced one peak or one pair of peaks in the radial distribution function. It is difficult to fit the spectrum with a single shell. Hence, fitting by one Sr(A)–Ta shell is possible under the assumption that Ta cations dominate the electron scattering in Sr NTO. Figure S4 and Table S1 show the results obtained from curve fitting on the basis of this assumption.

Nearest Ta–Ta neighbors were examined in the Ta L₃ edge EXAFS of NTO and Sr NTO (50 mol %) to confirm the assignment of the other shells conducted above. The two photocatalysts exhibited Ta–Ta bond lengths of 3.98 and 4.02 Å, which are consistent with the unit cell length of NaTaO₃. Figures S5 and S6 and Tables S2 and S3 show the results obtained from curve fitting.

3.2. EXAFS of Sr-NTO with Low Sr Concentrations.

HCl washed Sr NTO (50 mol %), the photocatalyst with the highest Sr concentration examined herein, contains Sr cations at the A and B sites, as concluded in the preceding subsection. However, the Sr concentrations for the best water splitting efficiency were considerably less than 50 mol %. Iwase et al.⁷ examined the overall water splitting reaction using Sr NTO with Sr concentrations of 0.1–8 mol % and reported an optimum rate for H₂ and O₂ production at 0.5 mol % in the presence of a NiO cocatalyst. An and Onishi²² examined the rate of electron–hole recombination in Sr NTO as a function of the Sr concentration and found a minimum rate at 1.8 mol %. Hence, Sr NTO with lower Sr concentrations (2 and 20 mol %) should be characterized.

Figure 4 shows the Sr K edge EXAFS of Sr NTO (2 mol %), Sr NTO (20 mol %), and HCl washed Sr NTO (50 mol %).

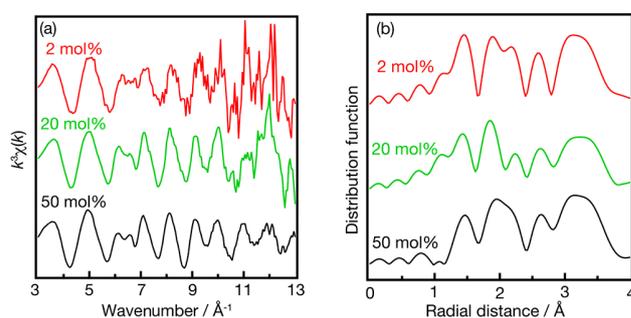


Figure 4. Extended X ray absorption fine structures at the Sr K edge observed for the Sr NTO photocatalysts prepared herein. (a) k^3 weighted absorption spectra. (b) Radial distribution functions normalized to the height of the most intense peak. The k range in the Fourier transform was 3–13 Å⁻¹.

The k^3 weighted absorption spectra of the three Sr NTOs were identical, as shown in panel (a), while the signal to noise ratio accordingly decreased. Hence, the radial distribution functions in panel (b) are not sensitive to the Sr concentration. These results indicate that the local coordination around Sr cations is not sensitive to the Sr concentration. The A and B sites of NaTaO₃ are doubly doped with Sr cations even in the photocatalysts with low Sr concentrations.

3.3. X-ray Absorption Near-Edge Structures of Sr-NTO.

Figure 5 shows the near edge structures at the Sr K edge

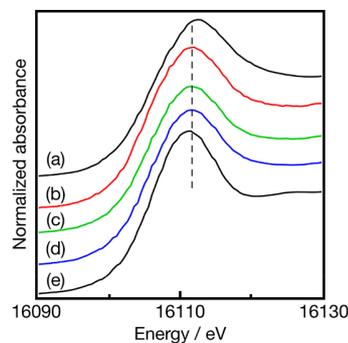


Figure 5. Near edge structures of Sr doped NaTaO₃ photocatalysts and related compounds: (a) SrO, (b) Sr NTO (2 mol %), (c) Sr NTO (8 mol %), (d) Sr NTO (20 mol %), and (e) SrTiO₃. The dashed line represents the peak energy of Sr NTO. The absorbance was normalized to the peak of each spectrum.

observed for the three Sr NTO photocatalysts and two reference compounds, SrO and SrTiO₃. The photocatalysts exhibited a common spectrum with different intensities, with the absorption peak at 16 111 eV. The common spectrum was consistent with the insensitivity of the local Sr coordination to the Sr concentration as indicated by EXAFS. SrO with SrO₆ octahedra produced a peak at an energy greater than 16 111 eV, whereas SrTiO₃ with SrO₁₂ cuboctahedra produced a lower energy peak. With the simultaneous occupation of the Sr cations at the A and B sites in Sr NTO, the absorption peak was naturally observed between the two peaks of SrO and SrTiO₃.

3.4. Rietveld Analysis. The coordination numbers obtained in EXAFS confirmed the formation of the NaTaO₃-Sr(Sr_{1/3}Ta_{2/3})O₃ solid solution in Sr NTO. Rietveld analysis of the XRD data for Sr NTO (8 mol %) was carried out to verify the formation of the solid solution. Refinement started from the orthorhombic structure of pristine NaTaO₃²⁵ with occupation of the Sr cations at the A and B sites. For the refinement of the fractional coordinates, special positions were held constant, and all of the other general positions were refined. The occupancies of Ta and Sr at the 4a sites and of Na and Sr at the 4c sites were constrained to meet the chemical formula Sr_xNa_{1-x}(Sr_{x/3}Ta_{1-x/3})O₃, with the occupancy of Sr at the 4c site as the free fitting parameter. The oxygen occupancy was held to be unity. The introduction of a preferred orientation along [001] was mandatory. In addition, the thermal parameters were refined.

Figure 6 shows the observed and refined patterns. A good fit was obtained, as evidenced by an *R* Bragg value of 1.9 and a

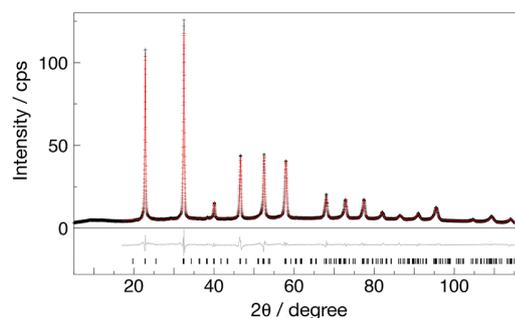


Figure 6. XRD patterns of Sr NTO (8 mol %). Black crosses, observed pattern; red line, calculated pattern; gray line, difference between the two. Vertical bars at the bottom indicate the peak positions.

Table 2. Rietveld Refined Parameters for the Sr NTO (8 mol %) Photocatalyst^a

atom	site	N	occ.	x	y	z	B/Å ²
Ta(B)	4a	4	0.976	0	0	0	0.29
Sr(B)	4a	4	0.024	0	0	0	2.00
Na(A)	4c	4	0.927	0.017	0.473	0.250	0.01
Sr(A)	4c	4	0.073	0.017	0.473	0.250	1.70
O	8d	8	1	0.206	0.253	0.042	0.01
O	4c	4	1	0.005	0.026	0.250	0.01

^aN is the number of equivalent atoms; occ. is the fractional occupation; x, y, and z are the atom coordinates in the unit cell vector length; B is the isotropic displacement parameter.

goodness of fit indicator of 4.2. Table 2 summarizes the refined parameters. The refined unit cell lengths were *a* = 5.5510 (0.0004) Å, *b* = 5.5032 (0.0003) Å, and *c* = 7.7904 (0.0003) Å (the numbers within parentheses represent the estimated errors). The occupation of Sr at the B sites was 0.024, and that at the A sites was 0.073, which led to an overall Sr concentration of 9.7 mol % relative to Ta. This number is in agreement with the composition determined by X ray fluorescence, i.e., 8.3 mol %. Hence, the NaTaO₃-Sr(Sr_{1/3}Ta_{2/3})O₃ solid solution in Sr NTO photocatalysts is supported by Rietveld analysis.

4. CONCLUSIONS

Doping with Sr cations by a solid state reaction leads to simultaneous occupation of the A and B sites of perovskite structured NaTaO₃ by Sr. The EXAFS at the Sr K edge reveals the presence of two Sr-O shells in the photocatalysts doped at 2, 20, and 50 mol %. The Sr-O bond length in each shell in the photocatalyst doped at 50 mol % was quantified by curve fitting. The small shell with a Sr-O bond length of 1.96 Å corresponds to SrO₆ octahedra with Sr cations at the B sites. This length is compatible with the Ta-O bond length in the TaO₆ octahedra, indicating that the surrounding NaTaO₃ lattice compressed the SrO₆ octahedra. The other shell with a Sr-O bond length of 2.60 Å corresponds to SrO₁₂ cuboctahedra with Sr cations at the A sites. The resulting NaTaO₃-Sr(Sr_{1/3}Ta_{2/3})O₃ solid solution accommodates the Sr cations with no requirement for oxygen anion vacancies, as evidenced by the Rietveld refinement of XRD data and the coordination numbers obtained from EXAFS. We therefore propose that SrO₆ octahedra embedded in the corner shared network of the TaO₆ octahedra are crucial to the enhancement of the quantum efficiency via doping of NaTaO₃ photocatalysts with Sr.

AUTHOR INFORMATION

Corresponding Author

*E mail: oni@kobe.u.ac.jp.

Christof Wöll: 0000 0003 1078 3304

Hiroshi Onishi: 0000 0003 1873 9105

Notes

The authors declare no competing financial interest.

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