

Influence of the Hydride Content on the Local Structure of a Perovskite Oxyhydride $\text{BaTiO}_{3-x}\text{H}_x$

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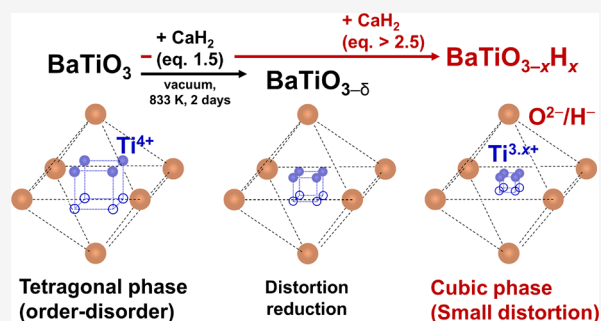
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ABSTRACT: The local structure of BaTiO_3 perovskite has been investigated for studying phase transitions by several groups. While it has been shown that H^- doping into BaTiO_3 changes its long-range average crystal symmetry from tetragonal to cubic, factors contributing to the structural change have not been fully understood. In this work, we investigated the dependence of the local structure of $\text{BaTiO}_{3-x}\text{H}_x$ on the doped H^- amount by means of Raman and X-ray absorption fine-structure (XAFS) spectroscopy measurements. The x value of $\text{BaTiO}_{3-x}\text{H}_x$ could vary in the range of 0–0.5 by changing the amount of the CaH_2 precursor in the topochemical synthesis of $\text{BaTiO}_{3-x}\text{H}_x$. Raman spectroscopy indicated that the cubic phase is induced in the initial tetragonal phase when the doped H^- amount was relatively large ($x \geq 0.2$). On the other hand, XAFS measurements revealed that the symmetry of the TiO_6 octahedral in $\text{BaTiO}_{3-x}\text{H}_x$ is strongly affected by the doped H^- amount. The local distortion of the Ti [111] displacement is relaxed with an increase of H^- , causing the tetragonal-to-cubic structural change.



INTRODUCTION

Mixed-anion compounds in which at least two anionic species exist in a single phase can provide unique physical and chemical properties.^{1,2} Oxyhydrides have attracted attention as a new class of materials, which can be applied to all-solid-state cells,³ host materials for rare-earth-activated phosphors,^{4,5} and other optical applications.^{6,7} A perovskite oxyhydride, $\text{BaTiO}_{3-x}\text{H}_x$, is probably one of the most studied oxyhydrides as it exhibits electronic and H^- conduction^{8,9} and catalytic activities for ammonia synthesis,¹⁰ CO_2 methanation,¹¹ and liquid-phase hydrogenation.¹²

For these applications, understanding the electronic state and structure of $\text{BaTiO}_{3-x}\text{H}_x$ is important. $\text{BaTiO}_{3-x}\text{H}_x$ ($x \approx 0.5$) can be obtained by a topochemical reaction of BaTiO_3 with CaH_2 at ~ 853 K in vacuo followed by washing with NH_4Cl –methanol solution.⁸ The hydride content, x , is controllable by changing the preparation parameters such as the CaH_2 amount to be mixed with BaTiO_3 and the duration of heating. The value of the hydride content has a great effect on the catalytic performance and hydride conductivity for $\text{BaTiO}_{3-x}\text{H}_x$. Hence, an observation of structural and/or electronic state changes in $\text{BaTiO}_{3-x}\text{H}_x$ caused by the x degree would be of importance for these applications. The substitution of H^- for O^{2-} causes not only an expansion of the unit cell but also a phase transformation from tetragonal to cubic, which are observed by X-ray and neutron diffraction measurements.^{1,13} This suggests that the local structure of the

TiO_6 octahedral in BaTiO_3 would be influenced by H^- substitution.

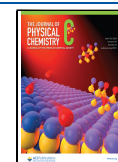
While the long-range-order structure in $\text{BaTiO}_{3-x}\text{H}_x$ has been investigated, the local structure analysis has not been conducted enough. In order to improve the unique catalytic performance of $\text{BaTiO}_{3-x}\text{H}_x$ and discuss the detailed reaction mechanism, an investigation on the local structure of the TiO_6 octahedral is essential. In addition, the mechanism of the structural change from tetragonal BaTiO_3 to cubic $\text{BaTiO}_{3-x}\text{H}_x$ has not been fully clarified in terms of the local structure of the materials. Because $\text{BaTiO}_{3-x}\text{H}_x$ has several factors affecting the structural change (e.g., increased electron density and distortion caused by H^- doping), analysis of its fine-structure change with respect to the H^- concentration is important to understand the structural change behavior and will contribute to the basic understanding of its fascinating properties.

In this work, we investigated the relationship between the Ti local structure and H^- doped amount into the lattice of BaTiO_3 . The x value of $\text{BaTiO}_{3-x}\text{H}_x$ varied in the range of 0–0.5 by controlling the preparation conditions. The crystal

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symmetry and the local structure around the Ti ion were observed by means of Raman for long-range-order structures and XAFS spectroscopy for local structures, revealing that a high concentration of H^- reduces the [111] off-centering of Ti^{4+} in TiO_6 octahedra.

EXPERIMENTAL SECTION

Preparation of $\text{BaTiO}_{3-x}\text{H}_x$. $\text{BaTiO}_{3-x}\text{H}_x$ was synthesized by CaH_2 reduction of BaTiO_3 as reported previously.⁸ An amount of 1.4 g of BaTiO_3 (BT-01, SAKAI Chemical Industry) and an appropriate amount of CaH_2 (Sigma-Aldrich, >97%, 0.126–0.755 g) were mixed in a N_2 -filled glovebox and pelletized with 0.5 g of mixture powder. The pellet was subsequently heated at 833 K for two days in an evacuated Pyrex tube. The resulting blue-black solid was washed in NH_4Cl (Kanto Chemical, >98.5%) containing methanol solution (0.1 M, 300 mL) for 2 h.

Preparation of Oxygen-Deficient $\text{BaTiO}_{3-\delta}$. Ba and Ti sources were prepared by the polymerized complex method reported previously.¹⁴ Briefly, $\text{Ti}(\text{O}-i\text{Pr})_4$ (Kanto Chemical, >97.0%), BaCO_3 (Kanto Chemical, >99.0%), ethylene glycol (Kanto Chemical, >99.5%), and anhydrous citric acid (FUJIFILM Wako Pure Chemical, >98.0%) were dissolved in a methanol (Kanto Chemical, $\geq 99.8\%$) solution at a molar ratio of 1:1:40:10. The solution was heated at 573 K on a hot plate and calcined at 673 K in a mantle heater. The resultant black powder was subsequently calcined on an Al_2O_3 plate at 823 K for 5 h in air. The obtained Ba and Ti precursors were heated at 1173 K under a H_2 gas flow (20 mL min^{-1}) for 2 h.

General Characterization. X-ray diffraction (XRD) patterns were collected with a Rigaku MiniFlex 600 diffractometer. Scanning electron microscopy (SEM) observations combined with energy dispersive X-ray spectroscopy (EDS) measurements were conducted with a JEOL JSM-IT100LA electron microscope. UV–visible diffuse reflectance spectroscopy (UV–vis DRS) was studied by a JASCO V-770. Thermogravimetric (TG) curves were collected by a Shimadzu DTG-60. Raman spectra were obtained with a JASCO NRS-4500.

X-ray Absorption Fine-Structure (XAFS) Measurement. The Ti K-edge XAFS measurements were conducted on the BL12C beamline of Photon factory (proposal no. 2020G597). XAFS spectra were acquired in the transmission mode at room temperature using a Si(111) double-crystal monochromator. The samples were diluted with boron nitride and compressed into pellets. Data of X-ray absorption near-edge structure (XANES) spectra and expanded X-ray absorption fine structure (EXAFS) were analyzed using the Athena software package.¹⁵

RESULTS AND DISCUSSION

Figure 1A shows XRD patterns of $\text{BaTiO}_{3-x}\text{H}_x$ prepared with different amounts of CaH_2 . Lattice constants were calculated from the XRD patterns using a cubic perovskite model^{1,13} and are listed in Table 1. The lattice constants increased with increasing the CaH_2 amount, indicating lattice expansion by O^{2-}/H^- exchange. The hydride anion (H^- , 1.40 Å) is larger than the oxide anion (O^{2-} , 1.35 Å) in a 12-coordination environment, and reduced Ti^{4+} species that were generated as a result of O^{2-}/H^- exchange are larger than Ti^{4+} in a six-coordination environment.^{16,17} Therefore, the lattice expansion caused by an increase in the H^- concentration in the host

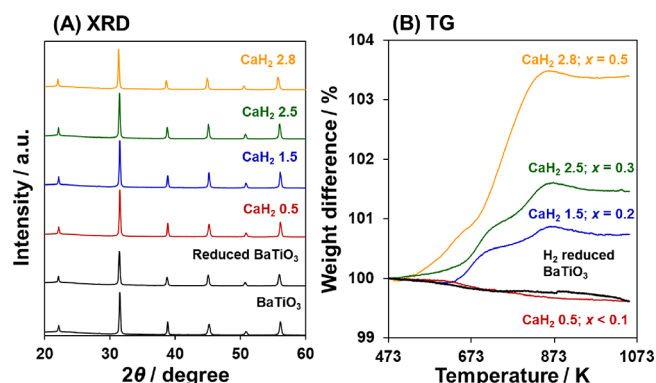


Figure 1. (A) XRD patterns of $\text{BaTiO}_{3-x}\text{H}_x$ prepared with different amounts of CaH_2 along with BaTiO_3 and reduced- BaTiO_3 . (B) TG curves of $\text{BaTiO}_{3-x}\text{H}_x$ prepared with different amounts of CaH_2 along with reduced BaTiO_3 under an air flow (80 mL min^{-1}) with a ramp rate of 5 K min^{-1} . Note that the number next to CaH_2 means the molar ratio of CaH_2 to BaTiO_3 in the synthesis. For example, “ CaH_2 2.8” indicates that the mole amount of CaH_2 was 2.8 times larger than that of BaTiO_3 .

Table 1. Elemental Analysis and Lattice Constants of $\text{BaTiO}_{3-x}\text{H}_x$ with EDS and XRD Analysis

sample	elements ^a (%)			lattice constant ^b (Å)
	Ba	Ti	Ca	
BaTiO_3	50.1 ± 0.5	49.7 ± 0.8	0.2 ± 0.1	
$x < 0.1$	49.8 ± 0.1	49.9 ± 0.3	0.4 ± 0.1	4.0087
$x = 0.2$	48.9 ± 0.1	50.4 ± 0.1	0.8 ± 0.2	4.0101
$x = 0.3$	49.4 ± 0.1	49.7 ± 0.2	0.8 ± 0.1	4.0167
$x = 0.5$	46.1 ± 0.1	53.1 ± 0.2	0.9 ± 0.1	4.0326

^aAverage value of five views at $\times 10,000$ magnification with standard deviations. ^bCalculated on the basis of a cubic perovskite model.

BaTiO_3 is reasonable. In the previous studies, TiH_2 is included as an impurity due to the decomposition of $\text{BaTiO}_{3-x}\text{H}_x$ at higher H^- concentrations,^{8,18} but no diffraction peaks of TiH_2 were observed in this study. The amount of H^- , x , was calculated by a TG-DTA measurement (Figure 1B). The weight gains indicate the substitution of O^{2-} for H^- in $\text{BaTiO}_{3-x}\text{H}_x$ as shown in the DTA curves (Figure S1), which has been confirmed by the previous Rietveld analysis for X-ray and neutron diffraction.⁸ The H^- concentration indeed increased with an increase in CaH_2 . H_2 -reduced BaTiO_3 and $x < 0.1$ samples exhibited a small weight loss (0.4 wt %) during the heating. The origin of the weight loss would come from a gradual release of adsorbed water in the surface.¹³ The names of the prepared $\text{BaTiO}_{3-x}\text{H}_x$ samples are referred to as x values hereafter.

The morphology and element distribution of $\text{BaTiO}_{3-x}\text{H}_x$ were studied by SEM observation. Figure 2 shows the SEM images of BaTiO_3 and $x = 0.5$ samples. The morphological

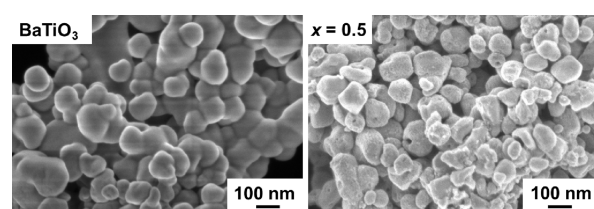


Figure 2. SEM images of BaTiO_3 and $\text{BaTiO}_{3-x}\text{H}_x$ ($x = 0.5$).

character of BaTiO_3 remained even after BaTiO_3 was heated with CaH_2 at 833 K to form $\text{BaTiO}_{2.5}\text{H}_{0.5}$. This is an indication that $\text{BaTiO}_{2.5}\text{H}_{0.5}$ was produced by a topochemical reaction, as discussed previously.⁸

Elemental analysis was conducted with an EDS apparatus in SEM equipment. EDS mapping showed that not only Ba, Ti, and O but also Ca was present in the same particles (Figure S2), indicating that the washing process could not remove the Ca species completely. The Ca doping into the A site of BaTiO_3 is unlikely because the temperature for the synthesis is too low to allow for the diffusion of A-site cations into the perovskite lattice.¹⁹ The element ratios are listed in Table 1. The ratio of Ti was larger than that of Ba with increasing x values, suggesting that a part of Ba species was lost during the H^- doping process of $\text{BaTiO}_{3-x}\text{H}_x$ due to TiH_2 formation, although it was not observed in XRD measurements.

The optical property was studied by UV–vis DRS measurements (Figure 3). While the pristine BaTiO_3 has no

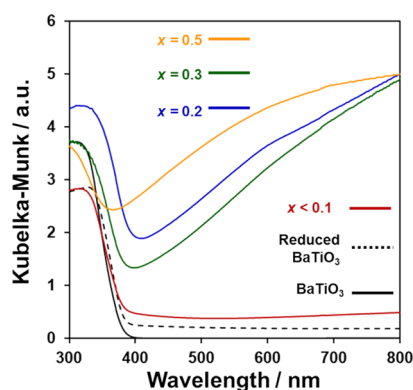


Figure 3. UV–vis DR spectra of $\text{BaTiO}_{3-x}\text{H}_x$ along with BaTiO_3 and reduced BaTiO_3 .

absorption in the visible region ($\lambda > 400$ nm), the reduced BaTiO_3 and $\text{BaTiO}_{3-x}\text{H}_x$ exhibit absorption at longer wavelengths than the band gap excitation at around 380 nm. The absorption of the Ti^{4+} -based perovskite oxides (e.g., SrTiO_3) appearing in the visible–IR region reflects an increased electron density.²⁰ The visible light absorption was dramatically pronounced in the samples with $x \geq 0.2$, suggesting that the electronic property of the $x < 0.1$ sample is similar to that of reduced BaTiO_3 . The spectra also suggest that the electron densities of $\text{BaTiO}_{3-x}\text{H}_x$ with $x \geq 0.2$ are not dramatically enhanced by the x value.

The local structure of $\text{BaTiO}_{3-x}\text{H}_x$ was studied by Raman spectroscopy measurements. Figure 4A displays the Raman spectra of $\text{BaTiO}_{3-x}\text{H}_x$, BaTiO_3 , and reduced BaTiO_3 at room temperature. A tetragonal BaTiO_3 shows Raman scattering as broad peaks at around 250, 520 and 720 cm^{-1} and as a sharp peak at around 306 cm^{-1} , as reported previously.^{21,22} These active modes were observed at 303, 516, 715, and approximately 250 cm^{-1} in the BaTiO_3 spectrum measured in this study. While these peaks were weakened in the $x < 0.1$ sample and the reduced BaTiO_3 , significant peak broadening was observed in the samples having x values larger than 0.2. Because these vibration modes are not active in cubic BaTiO_3 ,²³ the reduction of the peaks indicates the increasing O_h symmetry in the TiO_6 octahedron. It is noted that the phase of $\text{BaTiO}_{3-x}\text{H}_x$ is not completely cubic, judging from the observable Raman peaks in the samples. Moreover, the

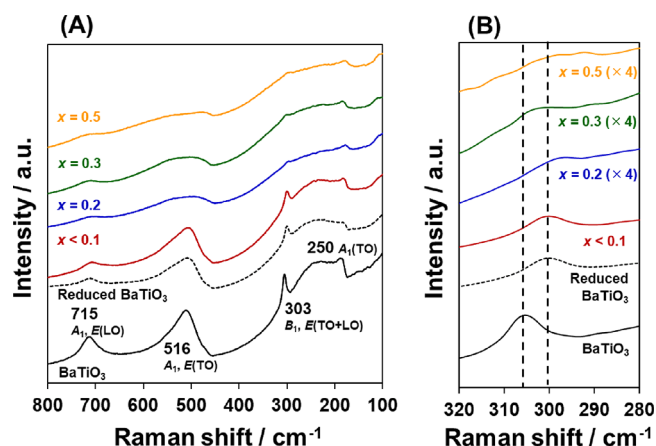


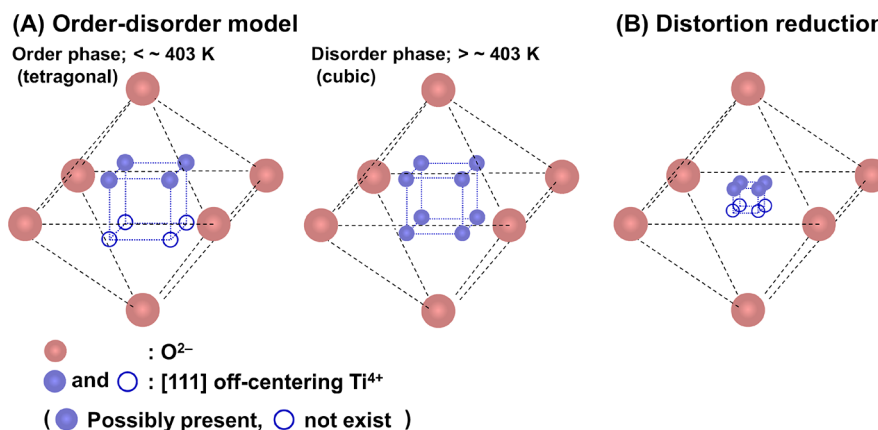
Figure 4. Raman spectra of $\text{BaTiO}_{3-x}\text{H}_x$, BaTiO_3 , and reduced BaTiO_3 : (A) entire spectra and (B) an enlarged view for the B_1 mode. The wavelength of the operating laser was 532 nm.

position of 303 cm^{-1} in BaTiO_3 is shifted to lower energies with H_2 reduction or a small amount of H^- doping (Figure 4B). Because the B_1 vibration is based on the opposite movement of oxygen at [001] and [110] sites in TiO_6 , the redshift indicates that the Coulombic force between O^{2-} anions varied because of the generation of oxygen vacancies upon the O^{2-}/H^- exchange.²⁴ As it has been reported that oxygen vacancy generation causes a mixed phase of tetragonal and cubic structures,²⁵ $\text{BaTiO}_{3-x}\text{H}_x$ and reduced BaTiO_3 might have a local cubic phase during the long-range tetragonal structure.

The mechanism of the tetragonal-to-cubic phase transition of BaTiO_3 could be explained by an order–disorder model, as shown in Scheme 1A.^{25–27} On the other hand, the tetragonal-to-cubic phase transition is also achieved when Ti atoms are shifted to the center of the TiO_6 octahedra (i.e., reduction of distortion along the [111] direction). For example, it has been reported that the A-site cation substitution in ABO_3 perovskites induces Ti off-centering due to differences in the ionic size.²⁷ Furthermore, doping of H^- causes a large amount of electron doping at the same time. As a result, the TiO_6 distortion due to a second-order Jahn–Teller effect will be reduced.²⁷ Thus, doping of foreign elements into BaTiO_3 would reduce Ti off-centering, leading to a cubic phase, as shown in Scheme 1B. Because H^- doping would affect not only soft phonon modes but also the substitution of anions with different sizes, further investigation of the BaTiO_3 local structure was needed to reveal the mechanism of the structural change.

To further investigate the local structural change around the Ti atom, XAFS analysis was performed as it is sensitive to the coordination structure of a target element.^{28,29} The normalized Ti K-edge XANES spectra of $\text{BaTiO}_{3-x}\text{H}_x$ with different x values are shown in Figure 5A. The Ti K-edge XANES spectra were clearly changed both in the pre-edge (shown as a_{1-3}) and the main K-edge (shown as b) regions when the value of x is larger than 0.2 (Figure 5B). Especially, the intensity of a_2 is decreased with increasing the H^- amount. The a_2 peak consists of two components: the $\text{Ti } 1s \rightarrow 3d_{eg}$ quadrupole transition and the $\text{Ti } 1s \rightarrow 4p$ dipole transition.³⁰ When the Ti atom is displaced from the central symmetry point in TiO_6 , the component of the quadrupole transition increases due to the reinforced Ti 3d–4p hybridization. As a result, the a_2 peak

Scheme 1. (A) Order–Disorder Phase Transition Model of BaTiO_3^a and (B) Reduction of Distortion along the $[111]$ Direction



^aRed and blue spheres designate the O^{2-} and Ti^{4+} ions, respectively.

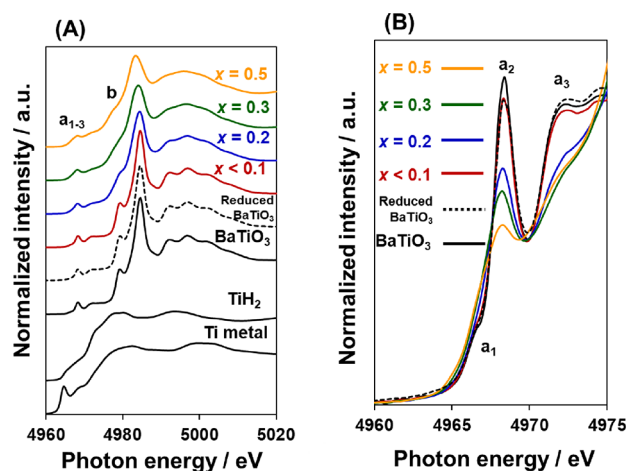


Figure 5. Ti K-edge XANES spectra of $\text{BaTiO}_{3-x}\text{H}_x$. (A) Ti K-edge absorption region and (B) pre-edge region. The pre-edge region was normalized at the bottom between a_2 and a_3 .

intensity is enhanced.³¹ Therefore, the opposite behavior, that is, the decrease of the a_2 peak in Figure 5B, is attributable to the decrease of the $[111]$ off-center of the Ti atom and the weakening of the Ti 3d–4p orbital hybridization. In the Ti-based perovskite oxide PbTiO_3 , the a_2 peak intensity decreases with an increasing temperature because, in the ferroelectric phase at room temperature, the Ti atoms are displaced from the central symmetry point, but in the polarized phase at a high temperature, the Ti atoms are located at the central symmetry point.³² In the case of $\text{BaTiO}_{3-x}\text{H}_x$, doping of H^- causes a high level of electron doping (as discussed above with Figure 3), which leads to weakened distortion of the $\text{TiO}_{6-x}\text{H}_x$ octahedra in $\text{BaTiO}_{3-x}\text{H}_x$ due to a second-order Jahn–Teller effect.

Therefore, it is reasonable to conclude that heavy H^- doping relaxes the distortion of the octahedral $\text{TiO}_{6-x}\text{H}_x$ units in $\text{BaTiO}_{3-x}\text{H}_x$; in other words, a high concentration of H^- reduces the $[111]$ off-centering of Ti^{4+} in $\text{TiO}_{6-x}\text{H}_x$ octahedra. Although the reduction of the pre-edge absorption intensity was observed in not only $\text{BaTiO}_{3-x}\text{H}_x$ but also H_2 -reduced BaTiO_3 , the impact of H^- doping is clearly larger than that of simple H_2 reduction.

The local structural difference was supported by EXAFS oscillation for the Ti K-edge. The Fourier transform (FT) of

k^3 -weighted Ti K-edge EXAFS for the samples is shown in Figure 6. The radial distance of the shell configuration, which

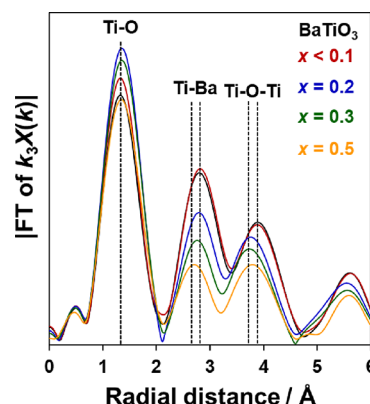


Figure 6. Ti K-edge FT-EXAFS oscillation of $\text{BaTiO}_{3-x}\text{H}_x$. The used k -space region was $3\text{--}7.8 \text{ \AA}^{-1}$ due to an overlap of the Ba L_{III} edge.

is assignable to bonds of Ti–Ba and Ti–O–Ti, was decreased with increasing the x value up to 0.2, indicating the reduction of average Ti–Ba and Ti–O–Ti lengths due to the structural change from tetragonal to cubic. With increasing the x value, the bond length of Ti–O–Ti becomes larger, causing a lattice expansion, as displayed in the XRD results (Figure 1). Attenuation of the EXAFS oscillation with increasing the doped H^- amount suggests the reduction of the long-range structural order due to random H^- substitution, as reported previously.^{6,33}

Considering the results of XANES and EXAFS, it can be concluded that increasing the H^- concentration in $\text{BaTiO}_{3-x}\text{H}_x$ alters the local structure around the Ti center. The H^- substitution relaxes the local distortion of the TiO_6 octahedron existing in the host BaTiO_3 , leading to the structural change from tetragonal to cubic. The Ti K-edge XANES measurements were also conducted for the pristine BaTiO_3 powder under heating conditions. The Curie temperature of the cubic/tetragonal transition in BaTiO_3 has been reported to be $393\text{--}403 \text{ K}$.¹⁹ As shown in Figure S3, both Ti K-edge and pre-edge region spectra showed no change in the Curie temperature region. This result strongly suggests that the order–disorder phase transition effect on Ti K-edge XANES is

difficult to observe in the case of the powder BaTiO₃ sample because the stretching direction for the *c* axis is uneven in the powder form. Therefore, it is most likely that the difference in Ti K-edge XANES spectra among the BaTiO_{3-x}H_x samples with different *x* values arises not from the order–disorder transition but from reduction of the local disorder of the TiO₆ octahedron that is induced by O²⁻/H⁻ exchange.

CONCLUSIONS

The dependence of the Ti local structure in BaTiO_{3-x}H_x on the doped H⁻ amount was investigated by Raman and XAFS spectroscopy measurements. Raman spectroscopy showed that the tetragonal BaTiO₃ transformed to a cubic-like phase locally upon heavy doping of H⁻ (*x* ≥ 0.2) and also suggested that the local structural change is caused not only by the different anion sizes of O²⁻ and H⁻ but also by an increase in the electron density accompanied with H⁻ doping. While it was difficult to distinguish between the order–disorder transition and off-center disappearance by means of Raman spectroscopy, XANES and EXAFS analyses of the Ti K-edge in BaTiO_{3-x}H_x revealed that the H⁻ doping improved the symmetry of the TiO₆ octahedron in the material thereby leading to the tetragonal-to-cubic local structural change. This study highlights that the XAFS measurement is a useful tool in visualizing the change in the local structure around the metal center in oxyhydrides with respect to the H⁻ concentration. It is also expected that the reaction mechanism and H⁻ behavior during catalytic reactions over oxyhydrides can be monitored by an *in situ* XAFS technique. This possibility is under consideration in our group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c00915>.

Additional characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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