

# Unravelling structural properties of NaTaO<sub>3</sub>-LaCrO<sub>3</sub> solid solution photocatalysts

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**Abstract:** Solid solutions NaTaO<sub>3</sub>-LaCrO<sub>3</sub> have been prepared through a two-step solid-state method. Characterizations of solid solutions suggest substitution of La for Na and Cr for Ta. XANES and XPS confirm the valence states of La and Cr to be +3 and +6, respectively. Herein, local structure around La in the solid solutions is also investigated by EXAFS.

**Keywords:** Photocatalysis, Perovskite structure, Solid solution.

## 1. Introduction

Perovskite-structured oxides receive increasing attention because of their potential applications for efficient water splitting. Among perovskite oxides, sodium tantalate (NaTaO<sub>3</sub>) has been a focus of research due to its ultrahigh efficiency. A quantum efficiency of 56% on La-doped NaTaO<sub>3</sub> under UV light is reported.<sup>1</sup> This is the world-record efficiency for photocatalytic water splitting. Doping alkaline earth metals (Ca, Sr or Ba) enhanced water-splitting efficiency up to similar extents.<sup>2</sup> Unfortunately, their practical applications are limited since they are inactive under visible light. Therefore, sensitizing NaTaO<sub>3</sub> to visible light is crucial to deal with this issue.

Doping half-filled transition metal (B) together with another metal (A) to balance the charge without need for oxygen vacancy is a promising way of visible light sensitization through the formation of a solid solution of NaTaO<sub>3</sub>-ABO<sub>3</sub>. Recently, solid solutions of NaTaO<sub>3</sub>-ABO<sub>3</sub> involving La-Cr,<sup>3</sup> La-Co,<sup>4</sup> La-Fe,<sup>5</sup> and La-Ir<sup>6</sup> are reported to show promising photocatalytic performances. Nevertheless, their structural properties have not yet been fully understood. Therefore, this study aims to elucidate the structural properties of a solid solution, namely NaTaO<sub>3</sub>-LaCrO<sub>3</sub>, for visible light photocatalysis.

## 2. Experimental

**2.1. Photocatalyst preparation.** Solid solution photocatalysts were prepared through a two-step solid-state method. First, Na<sub>2</sub>CO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, La<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> were mixed in an agate mortar for 30 min and transferred to an alumina crucible for calcination at 1173 K for 1 h and then at 1423 K for 10 h with intermittent grinding for 30 min. The dopants/Ta molar ratio was varied. Meanwhile, the Na/Ta molar ratio and the La/Cr molar ratio in the mixtures were adjusted to 1.05 and 1, respectively. The calcined products are washed with water, and denoted as x%LaCr-NTO, in which *x* represents the molar ratio of dopants over Ta.

**2.2. Photocatalyst characterization.** The photocatalyst products were subsequently characterized by an energy-dispersed X-ray fluorescence (EDX) spectrometer (Shimadzu, EDX-720), an X-ray diffractometer (XRD) (Rigaku, SmartLab), a scanning electron microscope (SEM) (Hitachi High-Technologies, S-4800), a diffuse reflectance spectrometer (DRS) (Jasco, V-570), an X-ray photoelectron spectrometer (XPS) (Ulvac-Phi, PHI X-tool) with an Al K $\alpha$  excitation source, a Raman spectrometer equipped with a He-Cd laser light source (Kimmon, IK4401R-D), grating spectrometer (Horiba Jobin Yvon, iHR320), and charge-coupled device detector (Andor, DU440BU). IR absorption spectra were obtained by using a Fourier transform spectrometer (Jasco, FT/IR610). The photocatalyst-covered CaF<sub>2</sub> plate was put in a vacuum of 10 Pa. Absorbance spectra with and without UV light irradiation were then recorded. A Hg-Xe lamp (San-ei Electric, UVS-204S) was used as a UV light source.

**2.3. X-ray absorption measurements.** Absorption spectra at the La  $L_3$ -edge were recorded with a Si(111) double-crystal monochromator at the BL-12C of Photon Factory (Tsukuba, Japan). La  $K$ -edge spectra of  $\text{La}_2\text{O}_3$ ,  $\text{LaCrO}_3$ , 20%LaCr-NTO, and 8%LaCr-NTO were determined in the transmission mode at the BL-NW10A of Photon Factory. Meanwhile, those of 4%LaCr-NTO, 2%LaCr-NTO, and 1%LaCr-NTO were determined in the fluorescence mode using a 19-element solid-state detector. Curve-fitting analysis of the extended fine structures was done with the IFEFFIT package including Athena and Artemis.

### 3. Results and discussion

Single phase of perovskite-structured NTO is always obtained for all the doped samples. The dopant concentration on the surface is higher than that in bulk, indicating dopant segregation on the surface. One-to-one ratio of La and Cr doping is observed, which then supports the substitution scheme of La for Na and Cr for Ta. With the same dopant concentration of 2 mol%, La-NTO gives a higher intensity of  $860\text{ cm}^{-1}$  Raman band, an indication of Ta-site occupation, as compared to Cr-NTO. Simultaneous doping with La and Cr produces a more intense  $860\text{ cm}^{-1}$  Raman band. The intensity of the  $860\text{ cm}^{-1}$  Raman band linearly increases with the increase in the concentration of dopants. Unfortunately, Raman technique is unable to confirm whether La contributes to the  $860\text{ cm}^{-1}$  Raman band in the doubly doped system of LaCr-NTO.

Furthermore, it is revealed from the SEM images that increasing the dopant concentration decreases the particle size. Surface reconstruction into terraces and steps is absent here. With increasing dopant concentration, the absorption edge extends monotonically to the visible region, indicating band gap narrowing. The visible light absorption from 430 to 750 nm due to the transition of electrons within the  $d$  orbitals of  $\text{Cr}^{3+}$  becomes increasingly apparent as well. According to the UV-induced IR absorption measurement, the steady-state population of excited electrons increases by introducing La, while the presence of Cr is detrimental to the generation of excited electrons.

Herein, XAS study is focused on La as its occupation preference in the doubly doped system of LaCr-NTO is not fully understood. XANES investigation then reveals that the feature of the La  $L_3$ -edge is similar among the samples. The position of white line remains relatively unaltered upon Cr doping. Upon closer inspection, the white line position is found to be almost the same, located at about 5488.1 eV. By considering the white line position of the standard compound ( $\text{La}_2\text{O}_3$ ), the valence state of La is identified to be +3. Moreover, the  $k^3$ -weighted EXAFS oscillations are observed to be relatively similar among the samples, and the radial distribution functions are also quite sensitive to the dopant concentration. With the increase in the dopant concentration, the S/N ratio of the EXAFS oscillations increases. The first, second, and third shells of the radial distribution functions of the LaCr-NTO samples are identified to be the La-O, La-Ta, and La-La coordination, respectively. The detailed local structure around La is revealed and then discussed after interpreting the fitted parameters.

### 4. Conclusions

La and Cr are well received by  $\text{NaTaO}_3$  in one-to-one ration forming a solid solution of  $\text{NaTaO}_3$ - $\text{LaCrO}_3$ . The prepared solid solutions show absorption of the visible light. Raman spectra hints occupation of Ta-site, while EXAFS indicates lattice shrinkage upon incorporation of  $\text{LaCrO}_3$ . Since the visible light harvesting can be tuned by varying the concentration of  $\text{LaCrO}_3$ , the prepared solid solutions are expected to work for visible light photocatalysis.

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