

Ultrafast structural modulation in the photoexcited BiVO₄ observed by transient XAFS spectroscopy

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Developing photocatalysts and photoelectrodes to promote the decomposition of water using sunlight is one of the most important issues to build a sustainable society. BiVO₄ is a promising candidate for a photocatalyst in practical use to produce hydrogen from water with sunlight since its bandgap is enough low to excite electrons in the valence band to the conduction band (2.4 eV – 2.6 eV) by sunlight. Although there have been studies accomplished to understand its photoelectrons and photoholes in excited state, its catalytic reaction mechanism remains unknown. In this study, we observed the photoexcited states of BiVO₄ by a transient x-ray absorption fine structure (XAFS) spectroscopy. XAFS can provide the local pictures of the electronic states and the structure of BiVO₄. The transient XAFS method has become a powerful tool to study photoexcited states of materials.^[1] A structural distortion following coherent oscillation was observed in our experiments.

The BiVO₄ sample was prepared according to the procedure of ref. 2. Transient XAFS experiments were conducted in SPring-8 Angstrom Compact LASer (SACLA), and Photon Factory Advanced Ring (PF-AR). SACLA is an x-ray free electron laser (XFEL), which provides ultrashort (< 10 fs) and intense x-ray pulses (> 10⁹ photons/pulse). PF-AR is a synchrotron facility, where just one electron bunch orbits and which provides a 100-ps x-rays pulse every 1.26 μs. A 400-nm femtosecond laser was employed as an excitation laser in SACLA whereas a 343-nm pulse laser was employed in PF-AR. Transient XAFS of the delay times shorter than 300 ps were mainly measured in SACLA. The XAFS spectra of the delay times longer than 150 ps were measured in PF-AR.

The difference spectra between transient XAFS spectrum measured in SACLA of each delay time (-10 ps, 2 ps, 6 ps, 40 ps or 306 ps) and that of the ground state are displayed in Fig. 1 (a). Distinct changes are seen around 13430 eV, 13445 eV and 13460 eV for the delay time of 306 ps. The changes were also seen for the 40-ps delay. However, there are no changes around 13430 eV and 13460 eV in the difference spectrum of 2 ps. These results imply that the photoexcited state at 2 ps has different electronic states or local structures from

the excited state at 153 ps. The time evolution of x-ray absorption at 13430 eV, 13445 eV and 13460 eV are shown in Fig. 1 (b). The change of x-ray absorption at 13445 eV was also observed around the time 0 and the change of the x-ray absorption was reproduced by the convolution of a step function and a gaussian function whose FWHM was 500 fs which was the time resolution of our experimental setup. This result indicates that the change of the XAFS spectrum at 2 ps was caused simultaneously with the photoexcitation. Any absorption changes were not found around 13430 eV and 13460 eV. The results also support that there are two different processes after photoexcitation of BiVO₄. The kinetic traces of the x-ray absorption at 13430 eV, 13445 eV and 13460 eV seem to be consistent to each other. These traces were fitted with an exponential function ($y = A \cdot \exp(-t/\tau)$) and the lifetime τ were estimated as 13 ± 5 ps for 13430 eV, 14 ± 2 ps for 13445 eV and 13 ± 8 ps for 13460 eV, respectively. Transient XAFS spectra of the longer delay time were observed in PF-AR. The XAFS spectrum at 150 ps was consistent to the XAFS spectrum of 306 ps in Fig. 1 (a). The metastable state decayed gradually in 100 ns. The lifetime was estimated as 40 ns from the kinetic trace of the x-ray absorption at 13445 eV.

The feature of the difference spectrum at the delay time of 1 ps is not identical to the difference spectrum between the XAFS spectrum of the ground state ($\mu t(\text{gs})$) and the that positively shifted by 1 eV. This implies that the difference spectrum at 2 ps is not caused by the change of the valence of Bi ($\text{Bi}^{3+} \rightarrow \text{Bi}^{4+}$). The difference between $\mu t(\text{gs})$ and the $\mu t(\text{gs})$ modulated by a debye-waller factor ($\sigma(T)$) reproduce the feature of the difference spectrum at 2 ps. $\sigma(T)$ reduces the amplitude of XAFS oscillation according to structural disorders. This result indicate that structural disorders modulate the XAFS spectrum at 2 ps. Several groups reported that coherent oscillations are provoked by the photoexcitation of BiVO₄ and the oscillations are dumped within 2 ps. It is expected that the coherent oscillations become incoherent oscillations at the delay time of 2 ps, which leads in the disorder of the Bi atoms. The excited state of BiVO₄ will be discussed further in this presentation.

References:

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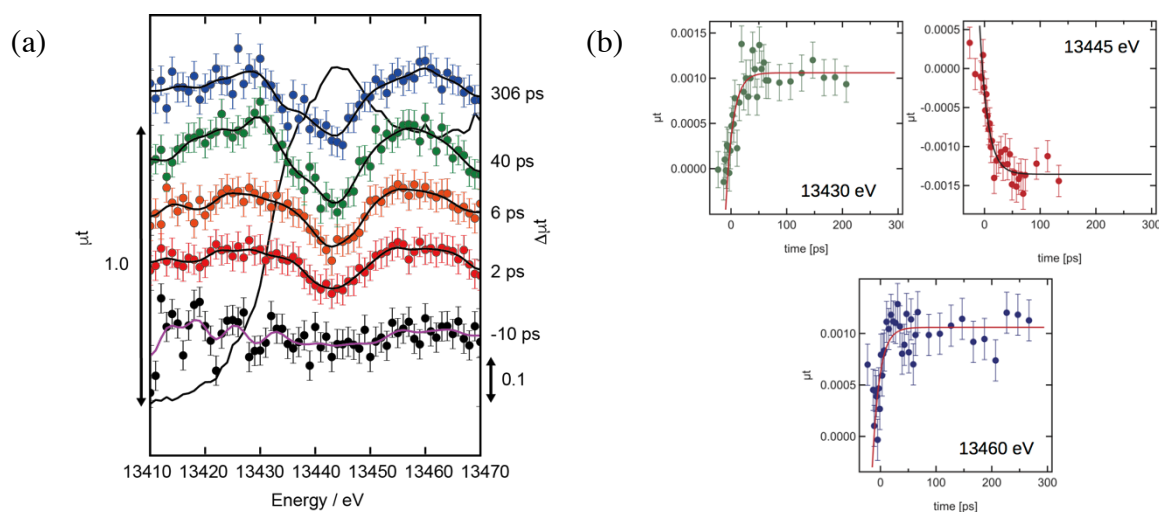


Fig. 1 (a) Transient Bi L_{III} edge XAFS spectra of BiVO₄ (b) Time evolution of the x-ray absorption of 13430 eV, 13445 eV and 13460 eV.