#### **OPEN ACCESS**

# A UV-induced one-dimensional motion of titanium ions in perovskite titanates

To cite this article: Nobuo Nakajima et al 2009 J. Phys.: Conf. Ser. 190 012083

View the article online for updates and enhancements.

### You may also like

- <u>Towards a high performing UV-A sensor</u> <u>based on Silicon Carbide and</u> <u>hydrogenated Silicon Nitride absorbing</u> <u>layers</u> M. Mazzillo, A. Sciuto, G. Mannino et al.
- <u>ORFEUS II and IUE Spectroscopy of EX</u>

Hydrae Christopher W. Mauche

- <u>Ultraviolet CMOS Image-Sensor Via</u> <u>Energy Down Shift Mechanism of Blue-Light Emitting Quantum-Dots for</u> <u>Environment Analysis</u> Uihyeon Jung, Jun-seong Park, Tae-Hun Shim et al.





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 18.223.172.224 on 04/05/2024 at 13:01

Journal of Physics: Conference Series 190 (2009) 012083

## A UV-induced one-dimensional motion of titanium ions in perovskite titanates

#### Nobuo Nakajima<sup>1</sup>, Masataka Deguchi<sup>1</sup>, Naoki Ishimatsu<sup>1</sup>, Hiroshi Maruyama<sup>1</sup>, Kotaro Ishiji<sup>2</sup>, Toshiaki Iwazumi<sup>3</sup>

<sup>1</sup>Grad. Sch. of Sci., Hiroshima Univ., 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan
<sup>2</sup>SAGA Light Source., 8-7 Yayoigaoka, Tosu, Saga 841-0005, Japan
<sup>3</sup>Grad. Sch. of Engnr., Osaka Prefecture Univ., 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

E-mail: nobuo@hiroshima-u.ac.jp

Abstract. The UV irradiation effect in the practical luminescence material (Pr, Al)-doped SrTiO<sub>3</sub> was investigated by x-ray absorption spectroscopy at the Ti K-edge. Two characteristic peaks observed in difference spectra between UV off- and on-spectra show different UV energy dependence; above the common onset UV energy of  $\sim 3.3$  eV, which is nearly equal to the band-gap energy, a difference peak at the main absorption edge changes its intensity in accordance with the photoluminescence excitation spectrum, while another difference peak in the pre-edge region does not. Through the consideration of the energy scheme, the Ti 3d conduction-band bottom is responsible for the pre-edge features and is rather insensitive to UV energy, whereas the main edge together with other features in the higher-energy region is attributable to the upper-lying 4p states that are strongly influenced by UV light via valence holes. These results enable us to propose a mechanism of UV absorption followed by visible light emission.

#### 1. Introduction

A photoinduced effect in perovskite titanates is one of the key issues in the field of dielectric materials; SrTiO<sub>3</sub> (STO) in a quantum paraelectric phase undergoes transition to a ferroelectric one under UV irradiation [1, 2], which gives insight into the nature of ferroelectricity in the oxides. The defect-doped STO also shows a promising property as a candidate for a surfaceemitting device [3, 4]. Recently we have reported a x-ray absorption spectroscopic (XAS) study on the UV-induced visible-light-emitting phenomena which is common in STO-based materials [5]. (Pr, Al)-doped SrTiO<sub>3</sub> (Pr-STO) fine particles, a luminescence material in practical use for vacuum fluorescence displays, emit red brilliant light under UV irradiation as well as a pure-STO in a quantum paraelectric phase emits faint greenish light [6]. In the previous report, we have concluded that UV-induced one-dimensional motion of titanium ions along the Ti-O direction serves as UV energy absorbers. However, the energy transfer process from titanium ions to color centers was unclear. Indeed, UV light transfer electrons from the oxygen 2p valence band to the titanium 3d conduction one, which should be followed by some light-emitting processes, such as the formation of self-trapped excitions or the intra-4f transition in the doped rare-earth ions. One of the remaining problems is then how the long persistent emission is established in STO, not in other perovskite titanates. The UV-energy dependence of luminescence intensity, i.e., a photoluminescence excitation (PLE) spectrum, would give some information about the electronic band structure around the band gap.

14th International Conference on X-Ray Absorption Fine Structure (2	XAFS14)	IOP Publishing
Journal of Physics: Conference Series 190 (2009) 012083	doi:10.1088/174	42-6596/190/1/012083

In the present study, another Ti K-edge XAS study using monochromatic UV light was performed for Pr-STO. As is the case with the non-monochromatized ('white') UV irradiation spectra, slight but distinct changes were observed both at the pre-edge and at the main edge. These two features, however, show different UV energy dependence. Especially, the amount of the spectral shift at the main edge is directly proportional to the PLE spectrum. This result prompts us to discuss the visible light-emitting process based on the electronic band structure.

#### 2. Experimental

A small amount of Pr-STO powder with the same lot number in the previous study was used in this study. The sample was synthesized by a solid-phase method from a mixture or SrCO<sub>3</sub>, TiO<sub>2</sub>, PrCl<sub>4</sub> and Al(OH)<sub>3</sub> and was ground to obtain powder with an average particle size of 1-3  $\mu$ m. The Al substitution for Ti was confirmed as 6.1% by high-resolution x-ray diffraction (XRD) measurement. The starting concentration of Pr was 0.2 mol%, but was below the detection limit of XRD.

Ti K-edge XAS measurements were performed on the BL-7C and 9A of the Photon Factory at the Institute of Materials Structure Science (KEK-PF). On both beamlines, the x-ray energy were varied using Si(111) double-crystal monochromators and higher-order harmonics were removed using higher-order harmonic-rejection mirrors. All spectra presented in this paper were measured using the transmission mode at room temperature. A Hg-Xe lamp (Hamamatsu Photonics K.K., Lightningcure LC5) with a heat-ray-cutting filter was used as a UV source. The UV light was guided by an optical fiber onto the sample. Between the fiber and the sample, five band-path filters with central wavelengths of 313, 320, 365, 370 and 380 nm ( $\pm 5$  nm) were placed in turn. The light intensity on the sample was fixed to be 80 mW/cm<sup>2</sup>. The powder sample was spread thinly over an adhesive tape in order to accommodate the effective penetration depth of UV light and x ray.

PLE spectra were measured using a standard fluorescence spectrophotometer (Hitachi F-4500) monitoring at a wavelength of 615 nm which corresponds to intra-4f emission from the excited-state  ${}^{1}D_{2}$  to the ground-state  ${}^{3}H_{4}$  of  $\mathrm{Pr}^{3+}$  ions [7, 8].

#### 3. Results and Discussion

The Ti K-edge XAS spectrum of Pr-STO is shown in the figure 1a with a thin solid line. The spectrum is normalized to unity at the peak maximum (4993 eV). The UV irradiation effect on the spectrum is so small that cannot be clearly seen on this scale. Three pre-edge peaks(A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub>) followed by main edge jump caused by  $1s \rightarrow 4p$  dipole transition are observed. The pre-edge peaks are assigned to transition to 3d unoccupied states. Among them, both the A<sub>1</sub> and A<sub>2</sub> peaks are of quadrupole origin and are attributable to  $1s \rightarrow 3d$ - $t_{2g}$  and  $1s \rightarrow 3d$ - $e_g$  transitions, respectively. Also shown in the figure by a thick solid line is the difference spectrum between UV off and on, which clearly demonstrates the UV effect on the XAS spectrum. In this result, the UV excitation wavelength ( $\lambda_{\rm UV}$ ) is set to 313 nm ( $\sim$ 4 eV) which is larger than the band-gap energy of 3.2 eV, so that the difference spectrum is essentially the same as that of non-monochromatized (white) UV irradiation [5]. Two major peaks are observed in the pre-edge region (B<sub>1</sub>) and at the main edge (B<sub>2</sub>). The origins of these two peaks are different. The B<sub>2</sub> peak is rather simple.

The  $B_2$  peak, together with other features in the higher-energy region, is caused by a chemical shift of the XAS spectrum toward lower energy upon UV irradiation, which is confirmed by comparison with the first derivative XAS shown in Fig. 1b. The physical meaning of the shift is comprehended by the existence of oxygen 2p valence holes created by UV light. This is also confirmed by the fact that the more the UV intensity is increased, i.e., the more valence holes are created, the larger the  $B_2$  peak becomes.



Figure 1. a) Normalized Ti K-edge x-ray absorption spectra of (Pr, Al)doped SrTiO<sub>3</sub> fine particle under room temperature (thin solid line). The difference spectrum between UV (313 nm) on and off is drawn by a thick solid line with its ordinate on the right axis. b) The first derivative of the absorption spectrum. The sign of the ordinate is reversed so that the B<sub>2</sub> peak has the same sign.

On the contrary, the height of the  $B_1$  peak is rather insensitive to UV intensity and the peak profile itself is not a differential form. The peak energy is identical to that of the  $A_2$  peak, therefore the enhancement of only the  $A_2$  peak by UV light results in the appearance of the  $B_1$ peak. From another viewpoint, the 3d- $e_g$  component is strengthened by UV irradiation because of the lack of inversion symmetry at the Ti<sup>4+</sup> site. In our previous reports [5, 9], we concluded that UV irradiation induces the electron transition from oxygen 2p occupied bands to Ti 3dunoccupied ones, which in turn induces the one-dimensional vibration of Ti<sup>4+</sup> ion along Ti-O bond direction.

In this paper, further results showing other experimental proof of the above mechanism are presented. Figure 2 shows the difference spectra for various  $\lambda_{UV}$ . The top spectrum is the same as shown in Fig. 1. The bottom one is for  $\lambda_{UV}=380$  nm (3.26 eV) which is slightly above the band-gap energy of 3.2 eV. Both the B<sub>1</sub> and B<sub>2</sub> peaks appear below  $\lambda_{UV}=370$  nm (3.35 eV). Here again, the two peaks have different dependence on  $\lambda_{UV}$  as well as their origins are different. Above the common onset energy of ~3.3 eV, the intensity of the B<sub>2</sub> peak changes gradually, however, that of the B<sub>1</sub> peak keeps a constant value. This result can be understood satisfactorily with the aid of the PLE spectrum. In Fig. 3, the PLE spectrum is shown by a thick solid line, which is scaled to a plot of  $\lambda_{UV}$  versus the B<sub>2</sub> peak intensity (right ordinate) with filled circles. Also drawn by a thin solid line is the same PLE spectrum rescaled to another plot for the B<sub>1</sub> peak. The error bars were determined from signal-to-noise ratios of the corresponding spectra. Because red fluorescence with the wavelength of 615 nm was used to monitor the emission intensity,  $\lambda_{UM}=307.5$  nm necessarily becomes the second harmonic of the monochromator that results in creation of an artifactitious, sharp spike peak in the PLE spectrum at this UV wavelength.

Firstly, the plots for the B<sub>2</sub> peaks synchronize the PLE spectrum which reflects the joint density of states (JDOS) between the valence-band top and the conduction band bottom. The  $\lambda_{\rm UV}$  dependence of the B<sub>2</sub> peak can then be viewed as quantum efficiency of the  ${\rm Pr}^{3+1}D_2 \rightarrow {}^{3}H_4$  decay channel; the more UV light is absorbed by the electron transition from oxygen 2p bands to Ti 3d ones, the stronger red brilliant light is emitted. On the other hands, the plots for

14th International Conference on X-Ray Absorption Fine Structure (	(XAFS14)	IOP Publishing
Journal of Physics: Conference Series 190 (2009) 012083	doi:10.1088/174	42-6596/190/1/012083

the  $B_1$  peaks do *not* synchronize the PLE spectrum, even though taking into account error bars. The above difference in the UV wavelength dependence originates from their different physical origins; Ti 3*d* bands for the  $B_1$  peak and 4p bands for the  $B_2$  peak.

The enhancement of the  $A_2$  peaks in XAS spectra, i.e. the appearance of the  $B_1$  peaks in difference spectra, should be an evidence of the lack of inversion symmetry around Ti<sup>4+</sup> ions, however, Pr-STO as well as a pure SrTiO<sub>3</sub> is basically a paraelectric material, hence anharmonic oscillation of Ti<sup>4+</sup> ions along Ti-O bonds can only explain the  $B_1$  peak. Then, given that this anharmonic oscillation is provoked by UV irradiation, there still exists uncertainty on the amplitude of vibration. We tentatively assume that the amplitude of vibration, i. e. a degree of a Ti<sup>4+</sup> off-centering from a body-center, does not depend  $\lambda_{UV}$ . If this is not the case, the hybridization between the Ti 3d and oxygen 2p states may be strongly influenced at the resonance  $\lambda_{UV}$ , probably the PLE maximum around 345 nm. The profile of the B<sub>2</sub> peak can then no longer be in a simple differential form, which is different from our result. We therefore come to the conclusion that a degree of a Ti<sup>4+</sup> off-centering is independent of  $\lambda_{UV}$ . This results in the fact that the B<sub>1</sub> peak intensity is rather insensitive to  $\lambda_{UV}$  above the onset UV energy of ~3.3 eV (~375 nm).

The behavior of the  $B_2$  peak is simple. As mentioned above, the PLE spectrum can be viewed as JDOS, which in turn can be interpreted as oscillator strength of interband transition. Therefore the intensity of the PLE spectrum is proportional to the number of valence holes created by UV light. In the case of Pr-STO, the main decay channel is not the direct recombination of excited electrons and holes but the dipole-forbidden 4f-4f transitions of  $Pr^{3+}$  ions, which is confirmed by the photoluminescence (PL) spectra (not shown here). The valence holes created by UV light survive considerably longer and pull down the unoccupied Ti 4p bands toward the Fermi level. Thus, the intensity of the  $B_2$  peak, i.e. the shift of the 4p bands, reflects the number of valence holes.

The visible light-emitting process of Pr-STO discussed above can be summarized as follow;



Figure 2. Difference spectra for UV excitation wavelength ( $\lambda_{\rm UV}$ ) of 313, 320, 365, 370 and 380 nm. Each spectrum is vertically shifted by 1% for clarity.



Figure 3. Comparison of photoluminescence excitation spectra (solid lines)to the plots of UV wavelength ( $\lambda_{\rm UV}$ ) versus B<sub>1</sub> (•) and B<sub>2</sub> (□) peak intensity (right ordinate). A thick (thin) solid line is scaled to B<sub>2</sub> (B<sub>1</sub>) peak intensity. A sharp spike peak at  $\lambda_{\rm UV}$ =307.5 nm is an influence of the second harmonic.

14th International Conference on X-Ray Absorption Fine Structure (2	XAFS14)	IOP Publishing
Journal of Physics: Conference Series 190 (2009) 012083	doi:10.1088	3/1742-6596/190/1/012083

once the UV light is absorbed by the  $Ti^{4+}$  oscillating absorbers at the onset UV excitation wavelength of 375 nm, the excess energy of excited electrons is transferred to the color centers,  $Pr^{3+}$  ions. The energy transfer to the Pr 4f states located within the band gap is mediated by the Ti 4p unoccupied bands that are shifted downward by valence holes. As for the fluorescence properties, the long-persistent one-dimensional anharmonic vibration of UV absorbing ions and the suitable energy levels of doped ions located just below the conduction band minimum are two essential factors. Recently, we have performed x-ray diffraction measurement under UV irradiation and have succeeded in visualizing the one-dimensional motion of  $Ti^{4+}$  ions, which will be written elsewhere.

#### 4. Conclusion

We have measured the Ti K-edge XAS of red phosphor (Pr, Al)-doped SrTiO<sub>3</sub> fine particles under irradiation of monochromatized UV light. Two characteristic peaks observed in the difference spectra between UV off and on have different UV wavelength dependence. The difference peak at the white-line changes its intensity in accordance with the PLE spectrum which reflects the oscillator strength of interband transition. Another difference peak at the pre-edge shows little dependence on UV wavelength, which can be interpreted that the Ti<sup>4+</sup> ions start to vibrate along the Ti-O direction above the given UV energy and serve as energy absorbers. Finally, valence holes with longer lifetime would be a key to establish an overlap between the conduction band bottom and impurity (color center) levels.

#### Acknowledgments

We thank Prof. Y. Harima of Hiroshima Univ. for giving us an opportunity to measure PLE spectra. The staff of Photon Factory are acknowledged for their machine operation. This work was performed under the approval of the Photon Factory Program Advisory Committee (PF-PAC) (Contracts No. 2006G361, 2008G626).

#### References

- [1] Takesada M, Yagi T, Itoh M and Koshihara S 2003 J. Phys. Soc. Jpn. 72 37
- [2] Hasegawa T, Mouri S, Yamada Y and Tanaka K 2003 J. Phys. Soc. Jpn. 72 42
- [3] Kan D, Terashima T, Kanda R, Masuno A, Tanaka K, Chu S, Kan H, Ishizumi A, Kanemitsu Y, Shimakawa Y and Takano M 2005 *Nat. Mater.* **4** 816
- [4] Kan D, Kanda R, Kanemitsu Y, Shimakawa Y, Takano M, Terashima T and Ishizumi A 2006 Appl. Phys. Lett. 88 191916
- [5] Deguchi M, Nakajima N, Kawakami K, Ishimatsu N, Maruyama H, Moriyoshi C, Kuroiwa Y, Nozawa S, Ishiji K and Iwazumi T 2008 *Phys. Rev.* B **78** 073103
- [6] Mochizuki S, Fujishiro F and Minami S 2005 J. Phys.: Condens. Matter 17 923
- [7] Yamamoto H and Okamoto S 2000 Displays **21** 93
- [8] Okamoto S and Yamamoto H 2001 Appl. Phys. Lett. 78 655
- [9] Nozawa S, Iwazumi T and Osawa H 2005 Phys. Rev. B 72 121101(R)