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Luminescence mechanism of (Pr, Al)-doped $SrTiO_3$ fine particles investigated by x-ray absorption spectroscopy

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The Ti K x-ray absorption spectra of fine particles of the practical luminescence material (Pr, Al)-doped $SrTiO_3$ were measured under UV irradiation. Significant changes were induced by the UV irradiation both in the pre-edge region and in the $1s$-$4p$ main absorption edge. Surprisingly, similar changes were observed for a $SrTiO_3$ single crystal in a quantum paraelectric state, which also emits a faint greenish light under strong UV irradiation. High-resolution x-ray diffraction measurements reveal that the electron charge-density distributions in the two samples are identical, which indicates that the photoabsorption mechanism of Ti^{4+} ions in the oxygen octahedra is the same.

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$SrTiO_3$ (STO) is one of the most widely used simple-cubic perovskite oxides and has a quantum paraelectric (QPE) phase below $T \sim 105$ K,[1,2] which results from the competition between quantum fluctuation and cooperative dipole-dipole interactions.[2] In this phase, the dielectric constant slightly increases to the order of 1×10^4 at low temperatures.[3,4] Recently, the photoinduced phase transition of STO has reawakened great interest among many researchers: under ultraviolet (UV) photoirradiation, QPE-STO undergoes phase transition from a paraelectric state to a ferroelectric state, accompanied by a faint greenish luminescence.[5] A gigantic enhancement of the dielectric constant of the order of 1×10^6 upon UV irradiation under a weak dc electric field has been reported.[3] These new findings help elucidate the basic nature of QPE-STO and lead to new ideas for highly efficient electronic devices since the photoinduced phase transition enables more rapid phase switching than the thermal transition.

Very recently, visible luminescence from several STO-based single crystals has been reported: electron-carrier-doped STO single crystals emit blue light under UV irradiation at room temperature. Electron doping into the Ti $3d$ subband is done in several ways: by substituting (i) Sr^{2+} for La^{3+} or (ii) Ti^{4+} for Nb^{5+}, or by (iii) Ar^+-irradiation to introduce oxygen defects.[6] Blue luminescence intensity increases with carrier concentration. Thus, the doped carriers play a crucial role in the light-emission process. Kan *et al.* claimed that the doped electrons recombine with holes in an in-gap state, as a result of which blue light is emitted.

In this Brief Report, we report a spectroscopic study of yet another STO-based light-emitting sample, (Pr, Al)-doped $SrTiO_3$ (Pr-STO) fine particles, a luminescence material for practical applications such as vacuum fluorescence displays and field-emission displays. Under UV irradiation with a photon energy higher than the band gap of ~ 3.2 eV, a red brilliant light is emitted at room temperature. The central wavelength of 616 nm corresponds to intra-$4f$ emission from the excited-state $^1D_2$ to the ground-state $^3H_4$ of Pr^{3+} ions.[7]

In all the above samples, an electron in oxygen $2p$ valence bands is photoexcited to a Ti $3d$ conduction band by the UV light and then creates a self-trapped exciton and/or transfers to a defect level to emit visible light. At the initial stage of UV absorption, the local environment of the Ti^{4+} ion is quite important for understanding the subsequent light-emission process. In the last decade, it has come to be recognized that the pre-edge structures in K-edge x-ray absorption spectra (XAS) of $3d$ transition metals include much information about the local environment of the atoms as well as details concerning electronic structure. In the case of perovskite titanates, Ti K pre-edge XAS is very sensitive to the off centering of a Ti atom in the oxygen octahedron.[8] Thus, we conducted an XAS study on Pr-STO fine particles to determine the changes in the local environment of a Ti atom induced by UV irradiation. The spectra resembled that of a STO single crystal,[9] which prompted us to investigate the light-emitting process.

Pr-STO is a white phosphor powder with an average particle size of $1-3$ μm. The sample was synthesized by the solid-phase method, which is the most common manufacturing method for powder phosphors.[7] First, a mixture of $SrCO_3$, TiO_2, $PrCl_4$, and $Al(OH)_3$ was fired with nominal Pr and Al concentrations of 0.2 mol % and 15 mol %, respectively. Powder diffraction experiments were performed at room temperature using a large Debye-Scherrer camera with an imaging plate installed at BL02B2 of the SPring-8 facility.[10] Diffraction intensity data of pure STO and Pr-STO with a d spacing of 0.52 Å were accumulated with wavelengths of 0.356 84(4) Å ($\sim$35 keV) and 0.497 35(8) Å ($\sim$25 keV), and were employed in the maximum entropy method (MEM)/Rietveld analysis.[11] Ti K-edge XAS experiments were performed on the BL-7C of the Photon Factory at the Institute of Materials Structure Science (KEK-PF). The x-ray energy was varied using a Si(111) double-crystal monochromator and higher-order harmonics were removed with a higher-order harmonic-rejection mirror. All spectra were measured using the transmission mode at room tem-

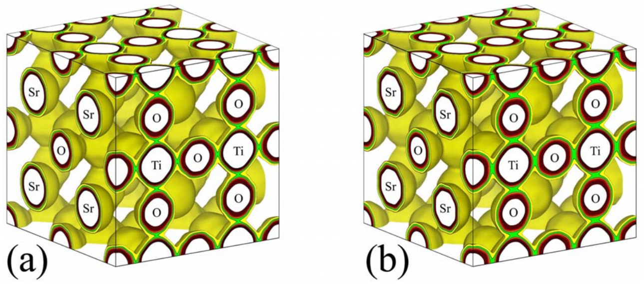

FIG. 1. (Color online) Electron-density distributions at room temperature of (a) (Pr, Al)-doped $SrTiO_3$ and (b) pure $SrTiO_3$. The contour lines are drawn from 0.45 [yellow (light gray)] to 2.05 e Å^{-3} with 0.2 e Å^{-3} intervals.

perature. The UV light was guided by an optical fiber onto the sample. A Hg-Xe lamp of 50 mW/cm^2 (Hamamatsu Photonics K.K., Lightningcure LC5) was used as a UV light source. The powder sample was spread thinly over an adhesive tape in order to accommodate the effective penetration depth of UV light and x ray.

Figure 1 shows the electron-density distributions $\rho(\mathbf{r})$ of (a) Pr-STO and (b) pure STO. The level of the equidensity surface drawn in yellow is 0.45 e Å^{-3} and the contour lines are drawn up to 2.05 e Å^{-3}. The best fit to data was obtained for Al substitution for Ti with 6.1%. The main impurity was $SrAl_{12}O_{19}$ of the order of 0.1%. The Pr concentration could not be determined. No clear difference could be found between the two figures, which suggests that the bonding of Ti^{4+} ions in oxygen octahedra is quite stable even in the case of Pr-doped STO. This stability provides an important background for the light-emitting process in perovskite titanates, which will be discussed below.

Figure 2(a) shows Ti K-edge XAS of Pr-STO with [red (gray) thin solid] and without (black dashed) UV irradiation. The spectra are normalized to unity at the peak maximum (4993 eV). In both spectra, three characteristic peaks (A_1, A_2, and A_3) followed by main edge jumps caused by $1s \rightarrow 4p$ dipole transition are observed. These features are well attributable to transition to $3d$ unoccupied states. The inset shows details around the pre-edge region. According to the results of the azimuthal-angle-dependent Ti K-XAS experiment of a STO single crystal,[9] both A_1 and A_2 peaks are presumably of an almost pure quadrupole ($1s \rightarrow 3d$) origin, whereas the A_3 peak is essentially of dipole origin. Moreover, the A_1 and A_2 peaks are assigned to t_{2g} and e_g components, respectively. Indeed, the energy separation between two peaks corresponds to the crystal-field splitting energy reported for an oxygen $1s$ XAS measurement in STO.[12]

Also shown in the figure by a blue (dark gray) thick solid line is the difference spectrum between UV off and on. This line reveals the effect of irradiation. Two marked peaks appear in the pre-edge region (B_1) and at the main edge (B_2). Among the three peaks in the pre-edge XAS, only the A_2 peak is responsible for the appearance of the B_1 peak. This is also quite clear from the XAS shown in the inset. The red line increases in intensity only at the A_2 peak, clearly indicating the enhancement of the e_g component by UV irradiation. It should be noted that the intensities of the A_1 and A_3 peaks are unchanged.

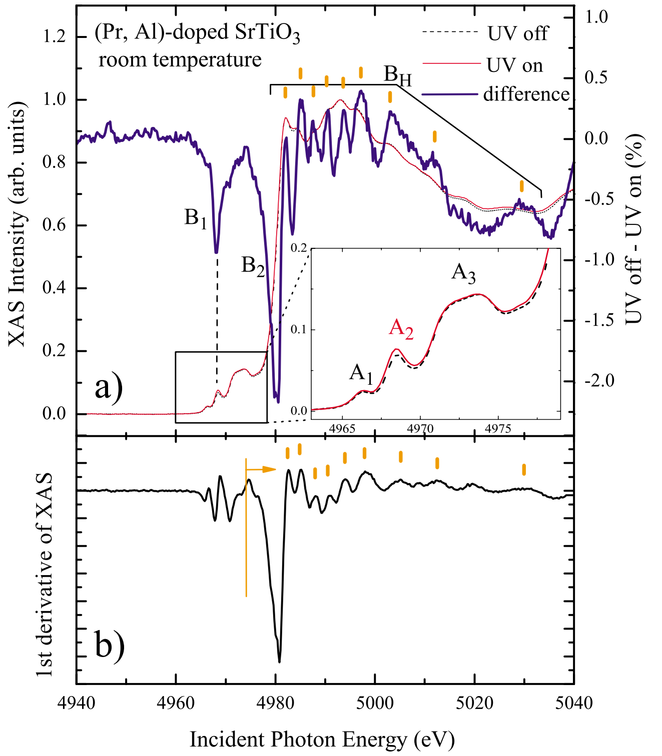

FIG. 2. (Color online) (a) Normalized Ti K-edge x-ray absorption spectra of (Pr, Al)-doped $SrTiO_3$ fine particles with [red (thin solid)] and without [black (dashed)] UV irradiation. The difference spectrum (with the ordinate on the right axis) is indicated by a blue (thick) solid line. The inset shows the details around the pre-edge region; it can be seen that the A_2 peak increases slightly under UV irradiation. (b) The first derivative of the absorption spectrum.

The B_2 peak has a different origin from the B_1 peak. Compared with the first derivative XAS shown in Fig. 2(b), the B_2 peak, together with the other features in the higher-energy region (B_H), is almost identical in the two cases, as indicated by the tick marks. This is in contrast to the difference in the pre-edge region. This is direct evidence of a chemical shift of the Ti K main edge toward a lower photon energy upon UV irradiation.

Figure 3 shows the Ti K-edge XAS obtained for a $SrTiO_3$ single crystal in a quantum paraelectric state. The spectra correspond to those in Fig. 2(a). It is quite normal for the absorption spectra of the Pr-STO powder and STO single crystal to resemble each other closely; however, it is very surprising that the difference spectra are also similar not only at characteristic peaks, but also in the details of the oscillating part. The difference spectrum of the nonfluorescent STO in a normal paraelectric state diminishes. The resemblance of difference spectra suggests a common UV light absorption mechanism for the two fluorescent materials. The doped Al has little influence on the Ti K-XAS itself because the x-ray absorption fine structure in the vicinity of the edge only reflects the local environment around the photoabsorbing atom, in this study, Ti. Around this Ti atom, one of the nearest or next-nearest Ti atoms is statistically substituted for an Al atom; besides, each Ti or Al atom is surrounded by an oxygen octahedron, therefore the Al doping effect on Ti K-XAS

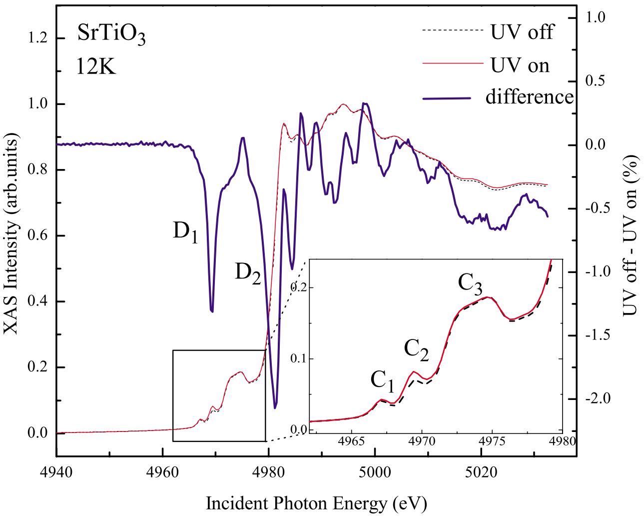

FIG. 3. (Color online) Normalized Ti *K*-edge x-ray absorption spectra of a SrTiO$_3$ single crystal in quantum paraelectric state with [red (thin solid)] and without [black (dashed)] UV irradiation. The difference spectrum (with the ordinate on the right axis) is shown by a blue (thick) solid line. The details around the pre-edge region are shown in the inset.

is obscured. We note, however, the difference in the lifetime of fluorescence. In the case of Pr-STO, the red fluorescence diminishes in intensity soon after the UV light is turned off, whereas the green fluorescence of STO in the QPE phase survives a bit longer. In the following, we will discuss the pre-edge region and the main absorption edge followed by a higher-energy region.

As was already mentioned in the case of Pr-STO, the C_2 peak is essentially of quadrupole origin $[1s \rightarrow 3d(e_g)]$ and is uniquely responsible for the D_1 difference peak. On the other hand, both the C_1 and C_2 peaks increase in intensity with increasing temperature in contrast to their behavior under UV irradiation. According to Ref. 9, the temperature dependence of the C_1 and C_2 peaks can be attributed to the isotropic thermal-random vibration, while UV irradiation induces uniaxial vibration of a Ti atom in the direction of a Ti-O bond. This strongly suggests that the same uniaxial vibration of the Ti atom is provoked in Pr-STO under UV irradiation.

Next, we focus on the main absorption edge. The chemical shift can be linked to two possible causes: a thermal lattice expansion and/or the relatively longer lifetime of valence holes. Thermal effects in the spectrum appear both at the C_1 and C_2 pre-edge peaks; however; UV irradiation only affects the C_2 (and A_2) peak. Thus, it may be tentatively concluded that the chemical shift toward lower photon energies caused by UV irradiation is due to the influence of holes created in the oxygen $2p$ bands. The similar UV-induced energy shift was reported for light-induced spin-transition compounds.[13] The compounds undergo spin transition from low-spin to high-spin states under UV irradiation showing the shift of the spectra to the lower energy side. As for STO and Pr-STO, the energy of UV light is absorbed by the lattice causing electron transition from oxygen $2p$ occupied bands to Ti $3d$ unoccupied bands, which in turn gives rise to uniaxial vibration of the Ti atom along the Ti-O bond. The excited electrons recombine with valence holes to couple in a self-trapped exciton state[6] (STO) and/or transferred to the Pr $4f$ states via $5d$ states (Pr-STO). In the case of fluorescent titanates, valence holes created by UV irradiation survive slightly longer and pull down the unoccupied bands, shifting the spectrum toward lower photon energies.

Photoabsorption by the uniaxial vibration of Ti atoms in oxygen octahedra plays an essential part in the light-emitting process. From another viewpoint, the uniaxial vibration of Ti atoms serves as an energy absorber of UV light. However, the energy-transfer process from the host STO matrix to Pr (as a color center) remains unclear. Among the large family of perovskite titanates, STO has relatively stable oxygen octahedra with O_h symmetry and provides a suitable stage for photoluminescence phenomena even in the case of doped STO. Thus, higher luminous efficiency could be achieved in nanoparticles.

In summary, we have measured the Ti *K*-edge XAS of red phosphor (Pr, Al)-doped SrTiO$_3$ fine particles under UV irradiation. Changes that are characteristic of a QPE-phase STO single crystal were observed both in the pre-edge region and the main absorption edge. High-resolution x-ray diffraction measurements revealed relatively stable oxygen octahedra in Pr-STO. Hence, the change in the pre-edge region can be linked to the uniaxial vibration of Ti atoms in oxygen octahedra induced by UV irradiation. The energy of UV light thus absorbed is converted into a brilliant red emission.

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