Photo-induced phenomena in SrTiO$_3$

Fumito FUJISHIRO, Shosuke MOCHIZUKI

Department of Physics, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan

E-mail: fumito@phys.chs.nihon-u.ac.jp

Abstract. When different SrTiO$_3$ single crystals are irradiated at room temperature with a continuous wave 325 nm laser light in an evacuated specimen chamber, their luminescence increase in intensity, creating a broad visible luminescence band centred at about 2.4 eV. Then, introducing oxygen gas into the specimen chamber, the photoluminescence spectra return reversibly to the original weak luminescence with the same laser light irradiation. After removing the laser light irradiation, each photoluminescent state is stored for a long time at room temperature under room light, regardless of any changes of atmosphere. Such photo-induced spectral change has been also observed at different temperatures from 6 K to room temperature. The observed phenomenon is explained by the photo-induced oxygen defect at the surfaces of SrTiO$_3$ crystal. The observed photo-induced optical phenomena are discussed in the light of both the crystal defect chemistry of SrTiO$_3$ and the exciton theory.

1. Introduction

In recent years, considerable attention has been devoted to the search for new photo-induced phenomena to be used as erasable photomemory materials [1]. We have observed the reversible photo-induced spectral transitions in the photoluminescence of Eu$_2$O$_3$ [2], Sm$_2$O$_3$ [3], anatase TiO$_2$ [4], vitreous SiO$_2$ [5] and other materials [6]. When these materials are irradiated at room temperature with a continuous wave (CW) 325 nm laser light in an evacuated specimen chamber, their luminescence change in intensity, creating a broad visible luminescence band. Then, introducing oxygen gas into the specimen chamber, the photoluminescence (PL) spectra return reversibly to the original luminescence with the same laser light irradiation. After removing the laser light irradiation, each PL state is stored for a long time at room temperature under room light, regardless of any changes of atmosphere. Such photo-induced spectral change has been also observed at different temperatures from 6 K to room temperature. Such reversible phenomena may well yield materials for erasable optical storage and white-light-emitting devices. Very recently, we have also observed quite similar photo-induced PL spectral change in strontium titanate SrTiO$_3$ single crystal. Grabner [7] measured the PL properties of doped and undoped SrTiO$_3$ crystals, and observed a near-infrared luminescence band around about 1.6 eV and a visible luminescence band around 2.4 eV. In addition to these PL bands, we have found a near-band-edge emission at 3.2 eV, accompanied by a broad PL band around 2.9 eV [8, 9]. In particular, the 2.4 eV luminescence shows clear spectral change.

In the present paper, we summarize our recent studies on the photo-induced PL spectral change observed for different SrTiO$_3$ crystals and discuss them in the light of both the crystal defect chemistry of SrTiO$_3$ and the exciton theory.
2. Experimental
The SrTiO<sub>3</sub> crystal was grown by the Verneuil method and the as-grown crystal is dark blue. The as-grown crystal became perfectly colourless and transparent by annealing in reducing Ar-H<sub>2</sub> mixture gas atmosphere at high temperature. We have measured the optical density (OD), PL, PL excitation and time-resolved PL spectra for the as-grown and annealed crystals at different temperature between 6 K to room temperature. The details of experimental procedure are described in our previous papers [8, 9]. The reversible photo-induced PL spectral changes were measured by means of a CW He–Cd laser (wavelength= 325 nm) as the excitation source and an optical multichannel analyzer. The specimens were set in a chamber connected with an oil-free vacuum system, which is able to exchange the atmosphere around the specimens at room temperature. The experimental setup is shown in figure 1.

![Figure 1. The experimental setup.](image)

![Figure 2. Optical density spectra of the as-grown and fully-annealed SrTiO<sub>3</sub> crystals at 294 K.](image)

3. Results and discussion
Figure 2 shows the OD spectra of the as-grown and fully-annealed SrTiO<sub>3</sub> crystals at room temperature. As seen in this figure, the as-grown crystal shows an intense background absorption which increases gradually toward IR region. We name tentatively this background NIR absorption. As superposing on the NIR absorption, there appear several absorption peaks around 2.4, 2.15, 2.08 and 0.82 eV and un-resolved absorptions in the energy ranges between 3.1 and 2.6 eV, and between 1.9 and 1.2 eV. The OD spectra increased steeply at photon energies larger than 3.1 eV is ascribed to the fundamental electronic absorption onset (3.2 eV) of cubic SrTiO<sub>3</sub> [8]. With progressing annealing, the absorption around 0.82 eV disappears rapidly and the absorptions around 2.15 and 2.08 eV merge into the broad absorption band around 1.65 eV, decreasing the NIR absorption in intensity. As seen above, many absorptions appear at energies lower than the bandgap energy (3.2 eV), which indicates that there are many crystal-defect-induced levels in the energy gap. The midgap absorptions below 3.1 eV may arise not from homogeneously crystal defects (oxygen vacancies) but from non-Perovskite phases with the Ruddlesden-Popper phases [(SrO)<sub>n</sub>(SrTiO<sub>3</sub>)<sub>n</sub>] [10] and (Ti<sup>3+</sup>-oxygen vacancy-Ti<sup>3+</sup>) complex [11,12].

During a CW 325 nm laser light irradiation in vacuum (or in oxygen) at room temperature, we have measured the PL spectral change of the as-grown and fully-annealed crystals as a function of the irradiation time. The result for the as-grown crystal at room temperature in vacuum is shown in figure 3(a). The irradiation time is shown by each curve. As seen in figure 3 (a), the initial PL spectrum is very broad, and it has an intensity peak at about 2.8 eV and two faint kinks at about 2.4 and 2.15 eV. With increasing irradiation time, the intensity increases, growing the PL component below 2.8 eV and the speed of the spectral change becomes deduced. A difference spectrum between the spectrum obtained at 60 min and rescaled spectrum obtained at 0 min is calculated, which is shown in figure 3.
This figure shows clearly that a broad PL band has grown at 2.4 eV under CW 325nm laser light irradiation in vacuum.

Figure 3. Photo-induced PL spectral change of the as-grown SrTiO₃ crystal at 295 K. (a) Spectral change in vacuum. (b) Extraction of photo-induced component.

Figure 4. Photo-induced PL spectral change of the fully-annealed SrTiO₃ crystal at 295 K. (a) Spectral change in vacuum. (b) Extraction of photo-induced component.

The PL spectra of the as-grown and different annealed SrTiO₃ crystals were measured at different temperatures between 295 and 6 K under a CW 325 nm and a pulsed 355 nm laser light of different laser fluences. With decreasing temperature, the 2.4 eV band merged in the broad band at room temperature becomes prominent and then the PL spectra of these crystals below 30 K are characterized by the 2.4 eV band for weak excitation. As typical results, the PL spectra of the as-grown and fully annealed crystals are shown in figure 5. It has also found that the photo-induced PL spectral change has been more clearly observed at 13 K. The result for the fully-annealed SrTiO₃, single crystal is shown in figure 6 (a), as a typical result. The irradiation time is given by each curve. The peak intensity of the 2.4 eV luminescence is plotted against irradiation time in figure 6 (b). The PL increases in intensity and then tends to saturate at 90 min without any change of the spectral shape. It
has been found that the magnitude of the spectral change at 2.4 eV for 60 min is nearly independent of temperature.

4. Mechanism of the photo-induced photoluminescence spectral change in SrTiO₃

Through our many optical experiments [8, 9, 13] on the as-grown SrTiO₃ crystal and the SrTiO₃ crystals recovered from different annealing stages, it has found that the PL of real SrTiO₃ crystals is considerably affected by crystal defects. All of the results on the reversible photo-induced PL spectral change of the as-grown and different annealed SrTiO₃ single crystals may be summarized as follows.

(1) The reversible photo-induced PL spectral change can be observed at different temperatures, from 6 K to room temperature. The spectral change takes time and the speed of change is nearly independent of temperature, but it increases with increasing light intensity.

(2) The spectral change tends to saturate at long light irradiation time (more than 90 min).

(3) The spectral change is induced by changing the specimen atmosphere between oxygen gas and vacuum only under a CW 325 nm laser light.

(4) After removing the light irradiation, each PL property persists for a long time even at room temperature under room light, regardless of any changes of atmosphere.

The result (1) indicates that the observed spectral changes are not phonon-assisted phenomena but purely electronic ones and that the PL band at 2.4 eV is an extrinsic luminescence due to the luminescence centres introduced by a CW 325 nm laser light. Since the 325 nm (= 3.81 eV) laser light never dissociates directly free O₂ molecule, the result (3) indicates that the phenomena arise from the photo-induced associative detachment and the photo-induced dissociative adsorption of O₂ molecules near the SrTiO₃ surface. In this case, photo-excited SrTiO₃ crystal acts as a photocatalyst for decomposing O₂ molecule and also as an oxygen reservoir. The results also summarize how spectral change arises naturally from the photo-activated oxidation and reduction. The reduction of SrTiO₃,
surface under a CW 325 nm laser light in vacuum may be accompanied by creation of electron-captured oxygen vacancy $V''_O$. Using a local spin density approximation plane-wave pseudo potential method, Astala and Bristowe [14] have shown that the doubly positively charged state is most stable. It is well in agreement with the experimental result that oxygen deficiency in SrTiO$_3$ enhances the electrical conductivity even at low temperatures [15]. This means that most of the electrons around oxygen vacancies are released and, therefore, such oxygen vacancy sites are relatively positively charged. Therefore, the oxygen vacancies tend to trap photo-generated electrons. Several authors [11, 12, 16] proposed another type of defect, ($\text{Ti}^{3+}$-$V''_O$-$\text{Ti}^{3+}$) complex, at SrTiO$_3$ surface. Taking account of this complex, the photo-induced oxygen desorption can be explained as follows.

$$\text{SrTiO}_3 \text{ in lattice} \xleftarrow{\text{CW 325 nm laser photon}} (\text{Ti}^{3+} - V''_O - \text{Ti}^{3+}) \text{ complex} + \frac{1}{2} O_2 \quad (1)$$

In the complex, the Ti$^{3+}$ ions act as hole traps ($S_h$), while the vacancy $V''_O$ do as electron traps ($S_e$). In SrTiO$_3$ crystal, it has been known that electrons determine well the transport properties, for example, electrical conductivity and photoconduction, while any phenomena related to holes have been not observed. This indicates that holes are almost trapped around crystal defects. Toyozawa [17] proposed three types of symmetry-breaking instabilities of excitons in the phonon field and when the electron and the hole have deformation potentials of opposite sign, the decomposition into a pair of self-trapped particles occurs. This instability of an exciton leads to lattice decomposition into an electron centre (an anion vacancy) $S_e$ and a hole centre (an anion interstitial) $S_h$, if exciton is formed in the bulk. On surfaces, the hole center is emitted out of the surface, thus leaving only the electron center. Therefore, such exciton instability may result in oxygen desorption at SrTiO$_3$ surface in vacuum and thus the oxygen vacancies produced give rise to the 2.4 eV luminescence. It is noted that the CW 325 nm laser light is indispensable for the spectral change due to the photo-induced oxidation and -reduction in SrTiO$_3$. The CW 325 nm laser fluence in our experiments was at most 0.8 Wcm$^{-2}$, and therefore any bond breaking mechanism based on the instability under high-density excitation may be rejected from the present discussion. Unlike alkali halides, a single interband excitation never induces the desorption of surface atom in semiconductors, since the binding energy of atoms is larger than the energy gap. In the case of photo-excitation of such semiconductor, only atom around crystal defect at the surfaces can be released [18, 19, 20, 21]. Astala and Bristowe[14]calculated the oxygen vacancy formation energy of about 7 eV, which are approximately twice of the bulk energy gap and are slightly smaller than twice of the CW 325 nm laser photon energy, at the TiO$_2$-terminated (100) surface of SrTiO$_3$. Both the oxygen defects (for example, $\text{Ti}^{3+}$-$O''_v$-$\text{Ti}^{3+}$ and $O''_v$) inherent to SrTiO$_3$ surfaces and the infinite continuity of the laser light may enable the 325 nm laser photon to release O$_2$ molecule from the surface. Incidentally, the pulsed 355 nm laser light (the pulse width = 4–5 ns), though the photon energy is close to the CW 325 nm laser light, never induced the spectral change even at 14 mJcm$^{-2}$ [8]. The oxygen desorption via such excited state may occur immediately after a laser pulse incidence. However, it is found that relatively long time is taken to complete the spectral change in SrTiO$_3$ as the result (2). This indicates that the photo-induced oxygen desorption probability is very low at SrTiO$_3$ surface. The observed saturation tendency with further increasing irradiation time suggests that the photo-induced oxygen defect increases the potential energy of the surface irradiated by light. In such case, equilibrium may be realized in a system composed of a matter (SrTiO$_3$ crystal) and a radiation field (325 nm laser photon field). It can be assumed that the intensity, coherency and continuity of laser light determine the degree of fluctuation in the system and the dynamics of the photo-induced PL spectral change.

Recently, there are several reports on the photo-induced change of dielectric and transport properties of SrTiO$_3$ crystal under ultraviolet irradiation and the change is frequently explained as the intrinsic property of SrTiO$_3$ crystal. However, if some of photo-generated carriers are trapped at the oxygen defects, large enhancement of the dielectric constant may be observed as an extrinsic effect. In the past, Uwe [22] pointed out the importance of the ferroelectric microregion [23] in the photo-
excited SrTiO$_3$ crystal, as follows. Photo-generated electrons create Ti$^{3+}$ ions and then these ions produce electric dipoles with oxygen defects. The dipoles may produce ferroelectric microregions which give large enhancement of the dielectric constant.

Finally, since some chemical heterogeneity on the surface has been pointed out for the surfaces of SrTiO$_3$ crystal reduced and oxidized at high temperatures [10] and small amount of OH$^-$ ions are introduced inevitably during crystal growth by the Verneuil method, these effects must be considered for more detailed discussion.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Culture and Technology, Japan. This work was also supported by an Interdisciplinary General Joint Research Grant for Nihon University.

References

[1] Nagaosa N, Ogawa T 1989 Theory of photoinduced structure change Phys. Rev. B 39 4472–4483.
[2] Mochizuki S, Nakanishi T, Suzuki Y and Ishi K 2001 Reversible photoinduced spectral change in Eu$_2$O$_3$ at room temperature Appl. Phys. Lett. 79 3785–3787
[3] Mochizuki S 2003 Intense white luminescence of Sm$_2$O$_3$ irradiated with ultraviolet laser light under vacuum Physica B 340–342 944–948
[4] Mochizuki S, Shimizu T and Fujishiro F 2003 Photoluminescence study on defects in pristine anatase and anatase-based composites Physica B 340–342 956–959
[5] Mochizuki S and Araki H 2003 UV-laser-light-produced defects and reversible blue–white photoluminescence change in silica Physica B 340–342 969–973
[6] Mochizuki S and Fujishiro F 2003 Structural, electrical and optical studies on AgI–anatase composites J. Phys.: Condens. Matter 15 5057–5072
[7] Grabner L 1969 Photoluminescence in SrTiO$_3$, Phys. Rev. 177 1315–1323
[8] Mochizuki S, Fujishiro F and Minami S 2005 Photoluminescence and reversible photo-induced spectral change of SrTiO$_3$, J. Phys.: Condens. Matter 17 923–948
[9] Mochizuki S, Minami S and Fujishiro F 2005 The reversible UV-laser-light-induced spectral change and origin of the 2.4 eV luminescence band in SrTiO$_3$, J. Lumin. 112 267–270
[10] Szot K and Speier W 1999 Surfaces of reduced and oxidized SrTiO$_3$ from atomic force microscopy Phys. Rev. B 60 5909–5926
[11] Henrich V E, Dresselhaus G and Zeiger H J 1978 Surface defects and the electronic structure of SrTiO$_3$ surfaces Phys. Rev. B 17 4908–4921
[12] Kimura S, Yamauchi J, Tsukada M and Watanabe S 1995 First-principles study on electronic structure of the (001) surface of SrTiO$_3$, Phys. Rev. B 51 11049–11054
[13] Fujishiro F and Mochizuki S 2005 Optical spectra change of Verneuil-grown SrTiO$_3$, single crystal during decolorization process submitted.
[14] Astala R and Bristowe P D 2001 Ab initio study of the oxygen vacancy in SrTiO$_3$, Modelling Simul. Mater. Sci. Eng. 9 415–422
[15] Jourdan M and Adrian H 2003 Possibility of unconventional superconductivity of SrTiO$_{1.8}$ Physica C 388/389 509–510
[16] Cord B and Courths R 1985 Electronic study of SrTiO$_3$(001) surfaces by photoemission Surf. Sci. 162 34–38
[17] Toyozawa Y 1983 Symmetry breaking excitonic instabilities in deformable lattice Physica B+C 117–118 23–29
[18] Puchin V E, Shluger A L and Itoh N 1993 Theoretical studies of atomic emission and defect formation by electronic excitation at the (100) surface of NaCl Phys. Rev. B 47 10760–10768
[19] Itoh N, Kansaki J, Okano A and Nakai Y 1995 Laser-Beam Interaction with Defects on Semiconductor Surfaces: An Approach to Generation of Defect-Free Surfaces Annu. Rev.
Mater. Sci. 25 97–127

[20] Itoh N and Stonham A M 2000 Material Modification by Electronic Excitation (Cambridge: Cambridge University Press)

[21] Song K S and Williams R T 1993 Self-Trapped Excitons (Berlin: Springer)

[22] Uwe H 2003 Impurity effect in quantum paraelectrics Meeting Abstract of the Physical Society of Japan 58 640

[23] Abe H, Harada K, Matsuo R J, Uwe H and Ohshima K 2002 X-ray diffuse scattering associated with ferroelectric microregions in KT\textsubscript{a1-x}Nb\textsubscript{x}O\textsubscript{3} J. Phys.: Condens. Matter 13 3257