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# Radiation-induced luminescence and photoluminescence from sol-gel silica glasses and phosphosilicate glasses by 1 MeV H<sup>+</sup> irradiations

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#### Abstract

Radiation-induced luminescence (RIL), photoluminescence (PL) and PL excitation (PLE) spectra have been applied to the study of photon emission from sol–gel silica glasses and phosphosilicate glasses. The photoemissions from oxygen excess-related defects are observed at about 1.98 eV by PL and RIL. The irradiation of 1 MeV H<sup>+</sup> is investigated with the excitation bands at 2.11 and 2.13 eV by PLE. The effects of ion irradiation on the glass samples show that the defects were increased in the silica glass and decreased in the phosphosilicate glass.  $\bigcirc$  2004 Elsevier B.V. All rights reserved.

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## 1. Introduction

For fuel cell applications, the membranes with high proton conductivity and high chemical and thermal durability are requested as the electrolyte separators of the fuel cell. Therefore, a series of perfluorosulfonic polymers such as Nafion are accepted as third-generation electrolyte separator materials. However, these polymers exhibit chemical and thermal degradation at a temperature higher than  $100^{\circ}$ C; the recent activity focuses on the fourth-generation materials of higher photon conductivity, higher chemical and thermal durability [1].

Fast proton-conducting glass, synthesized by the sol–gel method (phosphosilicate glasses,  $(P_2O_5)_x(SiO_2)_{1-x}$ ), have a great advantage in a high ionic conductivity in the medium temperature range (<500°C): they are lightweight, heat-resistant and have a non-CO toxification. These glasses are candidate materials of the fourth-generation electrolyte, and their fundamental properties have

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been examined [1]. Nogami et al. proposed proton conductivity, D of the glass is presented as  $\log D = \log[H^+][OH^-]$ , where  $[H^+]$  and  $[OH^-]$ are the density of proton and water in the glass, respectively [2]. This result indicates that an improvement in proton conductivity can be achieved by proton doping in the glass. Therefore, the authors have studied the proton ion-doping effect on proton conductivity of the glass by tandem-type accelerators. In this study, the doped proton ion is expected to recombine with  $(P_2O_5)_x(SiO_2)_{1-x}$  bonding and creates a new conductivity mechanism with defects in the glass during the doping process.

In the study for the phosphosilicate glass and its proton conductivity [3], the sol-gel method has the advantage of preparation of glass with random structure organization. Many studies have been carried out to investigate the structure of phosphosilicate glass [4–6].

However, dynamic structure changes and their effects on the ion conductivity mechanism (induced by proton doping) are not clear. There are difficulties in the in situ observation of the microstructure change (due to the peculiar porous structure of the glass [7]) and the irradiation hazard during ion doping.

Several researches have been performed to measure the radiation-induced luminescence (RIL) spectra from silica glasses after irradiations. The red band (1.9 eV), blue band (2.7 eV) and UV band (4.3 eV) induced by the electron irradiation (cathode luminescence (CL)) [8] and the blue band (3.1 eV) by the gamma and X-ray irradiations [9] have been found. Though there are few reports about in situ RIL observation, it is expected to show the recombination and damage process of the glass during irradiation. There are also few reports about in situ RIL observations to investigate the dynamic effects of structural change by implanting of an ion on the proton conduction mechanism in phosphosilicate glass. RIL spectroscopy is a promising technique that would help to clarify the complicated change in the glass structure and the influence on the proton conductivity mechanism.

In the present paper, the  $1 \text{ MeV H}^+$  ion beam was irradiated on the silica glasses (SiO<sub>2</sub>) and the

phosphosilicate glasses synthesized by the sol-gel method. The changes in the optical properties (absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra) were measured (before/after ion irradiations and in situ RIL) to investigate the correlation between the dynamic structural and optical property changes of the glass samples.

#### 2. Experimental method

#### 2.1. Materials

Silica glass, SiO<sub>2</sub> and phosphosilicate glasses,  $(P_2O_5)_x(SiO_2)_{1-x}$  were used in the present study and the latter materials were synthesized in the following procedures.

Tetraethylorthosilicate, TEOS (99.9%. Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, Colcate, Japan), was partially hydrolyzed at room temperature with a solution of H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH, and HCl in molar ratios of 1:1:0.01 per mol of TEOS. After the solution was stirred for 30 min, trimethyl phosphate (>98%, PO(OCH<sub>3</sub>)<sub>3</sub>, Nacalai Tesque, Japan) was added, followed by stirring at room temperature for 1 h. The resulting solution was hydrolyzed by adding the mixed solution of 4H<sub>2</sub>O, 1C<sub>2</sub>H<sub>5</sub>OH, and 0.04HCl per mol of the total amount of alkoxides for 1 h. After hydrolyzing, the amount of HCONH<sub>2</sub> added in the solution was changed to 1-3 ml for 5 g of oxide glass, followed by stirring for 1 h. The obtained solution was left for 3-4 weeks to form a stiff gel 0.1-0.5 mm thick. The gel was heated in air at 50°C/h to 600°C or 700°C and held at that temperature for 2h. The porous SiO<sub>2</sub> glass was prepared by the hydrolysis of 1 mol of TEOS with 4 mol H<sub>2</sub>O and 1 ml HCONH<sub>2</sub> per 5 g of oxide glass. 5P<sub>2</sub>O<sub>5</sub>95SiO<sub>2</sub> glass was also prepared from H<sub>3</sub>PO<sub>4</sub> instead of PO(OCH<sub>3</sub>)<sub>3</sub>.

# 2.2. Irradiation conditions and spectroscopy measurements

The ion irradiation experiments were performed using the 3 MV tandem accelerator in Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) at JAERI Takasaki. The H<sup>+</sup> ion irradiations were performed using fluencies of  $5 \times 10^{15}$  ions/cm<sup>2</sup>, at 1 MeV at room temperature, with a beam current density of  $0.2 \,\mu\text{A/cm}^2$ . The ion beam direction was almost normal to the target surface.

For the optical absorption spectroscopy, the spectra were observed by a double monochromator (Shimadzu UV-2100) with a high-performance blazed holographic grating in the aberration-corrected Czerny-Turner mounting, with a resolution of 0.1 nm ( $\sim$  30 meV).

For the PL and PLE spectroscopy, the spectra were recorded under 150 W Xe lamp illuminations and detected by a monochromator (Shimadzu RF-5300PC) with a concave, blazed holographic grating, F/2.5, 1300 grooves/mm. The accuracy of the wavelength is within 1.5 nm.

For the RIL spectroscopy, the light emitted from the target was focused into an optical fiber input that was located  $60^{\circ}$  and 30 cm from the target. The interface between the vacuum chamber and air is a view port, which is made from fused silica with no surface coating, that the transmittance at the ultraviolet (UV) range above 5 eV is very low. The spectrometer (Hamamatsu PMA-11) consists of the thermoelectric-cooling type Back-thinned (BT) charge-coupled device (CCD) image sensors operated, which has a compact Czerny-Turner type spectrograph with F number 4, optical fiber probe and control circuit. The wavelength resolution is less than 2 nm.

#### 3. Experimental results

Fig. 1 shows the UV and visible absorption spectra of the silica glass, SiO<sub>2</sub> and phosphosilicate glass, 5P<sub>2</sub>O<sub>5</sub>95SiO<sub>2</sub> samples obtained by the PL method. The solid lines and broken lines represent absorption spectra of the samples before and after 1 MeV H<sup>+</sup> ion irradiation, respectively. After irradiation, the absorption of SiO<sub>2</sub> sample increases in all measured regions, whereas a decrease was found in 5P2O595SiO2 sample over 5 eV. It proves the absence of the characteristic atomic or ionic absorbance in this range. In each spectrum, there are no conspicuous peaks since there are not any specific absorption peaks in this region. The absorbance of the  $SiO_2$  sample is lower than that of the  $5P_2O_595SiO_2$  sample, since the doped phosphor-produced porous structure contributed to the optical absorbance. The absorbances after irradiation are higher in each pair of the spectra, since defects were produced by the irradiations. This effect is so called "color center". The reason for the fluctuations in the region at about  $\sim 6.2 \, \text{eV}$ is the low transmittance of the light, which causes sensitive changes in the absorbance.

Fig. 2 shows the PL spectra excited at 2.14 eV (580 nm) from the SiO<sub>2</sub> sample (a,b) and the 5P<sub>2</sub>O<sub>5</sub>95SiO<sub>2</sub> sample (c,d) after and before ion irradiation, respectively. They are plotted in the same scale to compare the quantities. The red bands at 1.97 eV (630 nm) appeared in each



Fig. 1. Optical absorption spectra of the silica glass (upper lines) and the phosphosilicate glass (lower lines). The solid lines and broken lines represent for as-prepared (before irradiation) and 1 MeV  $H^+$  ion irradiation (after irradiation), respectively.



Fig. 2. PL spectra excited at 2.14 eV (580 nm) from the silica glass (a,b) and the phosphosilicate glass (c,d).



Fig. 3. PLE spectra detected at 1.97 eV (630 nm) from the silica glass (a,b) and the phosphosilicate glass (c,d).

spectrum. The center of the bands is located at the same position for the SiO<sub>2</sub> sample (Fig. 2(a), (b)), although the intensities are increased by the irradiation. This is because there are porous structures that were formed during the sol-gel process in the as-prepared samples [2]. The intensities of the peaks are decreased by the irradiation as the color center effects for the  $5P_2O_595SiO_2$  sample (Fig. 2(c),(d)).

Fig. 3 shows the PLE spectra detected at 1.97 eV from the SiO<sub>2</sub> sample (a,b) and the  $5P_2O_595SiO_2$  sample (c,d), after and before ion irradiation, respectively. The green bands with twin peaks

centered at 2.11 and 2.13 eV appeared in each spectrum. For the SiO<sub>2</sub> sample, the intensities of peaks are very low before irradiation (Fig. 3(b)), although they increased after irradiation (Fig. 3(a)). For the  $5P_2O_595SiO_2$  sample, the irradiation decreased the intensities of the peaks, especially for the lower energy peak (2.11 eV).

Fig. 4 shows the RIL spectra of the SiO<sub>2</sub> sample (a,b) and the  $5P_2O_595SiO_2$  sample (c,d), as observed at 0 and 420 s after the start of the irradiations, respectively. The measurement photon energy region is 1.31-6.2 eV (200-950 nm), the resolution is below 30 meV (2 nm)



Fig. 4. RIL spectra of the silica glass (a,b) and the phosphosilicate glass (c,d) at irradiation time 0 and 420 s. The dashed lines are fitting lines calculated by deconvolution of two Lorentzian curves with centers of 1.92 and 1.98 eV. The peaks at 1.76 eV are experimental humps that could not be removed. In the spectra of phosphosilicate glass at 420 s (d), there are no peaks.



Fig. 5. Time dependencies of intensity of the band at 1.98 eV with  $1 \text{ MeV H}^+$  irradiation time for the silica glass (upper line) and the phosphosilicate glass (lower line).

(FWHM) and the exposure time is 5 s. The peaks at 1.76 eV are experimental humps that could not be removed. As deconvolution of the spectra, there are two peaks in the red band in each spectrum. The dashed lines and solid lines are representative of the calculated deconvolution and these aggregates, respectively. The peaks in Fig. 4(a)–(c) are 1.92 and 1.98 eV with the widths 0.16 and 0.05 eV, respectively. The small peak at 1.79 eV is originated from a luminescence of Chrome ( $Cr^{3+}$  694 nm) that was mingled during the sol-gel process. For the spectra of the  $5P_2O_595SiO_2$  sample at t = 420 s (Fig. 4(d)), the peak intensity is not high enough to be deconvoluted.

Fig. 5 shows the time dependencies of the Red band (1.98 eV) of the 1 MeV H<sup>+</sup> RIL for the SiO<sub>2</sub> sample and the  $5P_2O_595SiO_2$  sample. For the SiO<sub>2</sub> sample, the intensity increased rapidly in the early stage of the irradiation, then turned to a slow decease with the lifetime of 100 s and followed a

very slow increase. For the  $5P_2O_595SiO_2$  sample, the rapid increase and following decay with the lifetime of 10 s were observed.

# 4. Discussion

The SiO<sub>2</sub> sample shows a variety of PL phenomena due to defects in the sol-gel silica glass network; oxygen deficiency-related defects  $(\equiv Si^*,$  $\equiv$ Si-Si $\equiv$ , oxygen vacancies,..) and excess-related defects  $(\equiv Si-O^*)$ oxygen O = O,... [7]. The mechanism of RIL is explained on the analogy of PL phenomena. Several bands are observed in the experiment; the band centered at 2.11 and 2.13 eV in the PLE (Fig. 3), 1.92 eV in the RIL (Fig. 4) and 1.98 eV in the both PL (Fig. 2) and RIL (Fig. 4). The mechanism of PLE is comparatively simple [7]. The PLE spectra have a single band that consists of a non-bridging oxygen hole center (NBOHC)  $\equiv$  Si–O<sup>\*</sup> and a Proxy radical (POR)  $\equiv$  Si–O–O<sup>\*</sup>. For the as-prepared silica sample, the activities of the oxygen excessrelated defects that produce the red band are low. However, the activities were elevated by the ion irradiation (Fig. 3(a) and (b)). For the  $5P_2O_595SiO_2$  sample, the activities had been elevated in the as-prepared state, and then the effects by the irradiation were little. The red bands of the PLE spectra are anti-symmetrical and deconvoluted into two peaks, R<sub>1</sub> (2.11 eV, FWHM 0.04 eV) and  $R_2$  (2.13 eV, FWHM 0.02 eV) by Lorentzian curve fitting. The relative intensity  $R_1: R_2$  ratios of those peaks before and after irradiation are 1:1 (Fig. 3(a)) and 10:2 (Fig. 3(b)) at the SiO<sub>2</sub> sample and 4:4 (Fig. 3(c)) and 2:3(Fig. 3(d)) at the  $5P_2O_595SiO_2$  sample, respectively. The assignments of excitation levels are not performed [10], though the existences of siteselective excitations are confirmed. In the case of the SiO<sub>2</sub> sample (Fig. 3(a) and (b)), the intensities of peaks increased by the irradiations, since the defects of the sol-gel silica glass networks had been activated. In the  $5P_2O_595SiO_2$  sample (Fig. 3(c) and (d)), the results are contrary, since the existence of phosphor prevents the generations of the defects from forming phosphorus centers (O=P, P-O-S, P-O-P,..).

In the RIL spectra, the band with the peak of 1.98 eV appeared only in the SiO<sub>2</sub> sample (Fig. 4). The peak positions are nearly the same at 1.97 eV in the PL spectra, though the shape is asymmetrically tailed as a skirt on lower energy side (Fig. 2). It is derived from the difference of the excitation process. In the PL spectra, the excitation occurs by absorptions of a photon with energy 2.14 eV, therefore the energy loss is about 0.2 eV as thermal activation energy. In the RIL spectra, the irradiation is the collision between the target glass and a H<sup>+</sup> ion with kinematics energy of 1 MeV, therefore the excitation is produced by the inelastic collision accompanied by electronic excitations. The red band (1.97 eV) in the RIL spectra of the 5P2O595SiO2 sample has disappeared. It is considered that the production of the NBOHC ( $\equiv$ Si-O<sup>\*</sup>) is not proceeded dominantly, since some relaxation processes occur. The phosphosilicate glass is currently believed to consist of silicon-oxygen, SiO<sub>4</sub>, and phosphorus-oxygen,  $O = PO_3$ , tetrahedral bonded randomly in a three-dimensional network where each silicon atom is bonded with four silicon or phosphorus atoms by oxygen linkages. Furthermore, each phosphorus atom has only three such bridging bonds [6]. Therefore, the NBOHC ( $\equiv$ Si–O<sup>\*</sup>) are not effectively produced by the  $H^+$  ion irradiation.

#### 5. Summary

The results of the present work consist of absorption, PL, PLE and RIL spectroscopy of the silica glass,  $SiO_2$  and the phosphosilicate glass,  $(P_2O_5)_x(SiO_2)_{1-x}$  prepared by the sol–gel methods. In the PL and PLE spectra, the irradiations produced activity on the silica glass and disrupted it on the phosphosilicate glass. In the RIL by 1 MeV H<sup>+</sup> ion beam irradiation, a green band (2.0 eV) and the variation of the intensities were observed in the silica glass and the phosphosilicate glass.

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