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Radiophotoluminescence from silver-doped phosphate glass

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A B S T R A C T

Glass dosimeter utilizing radiophotoluminescence (RPL) is one of accumulation type solid state dosimeters, which is based on luminescence phenomenon of silver (Ag^+ ions)-doped phosphate glass exposed to ionizing radiation. In this study, to clarify the emission mechanism of yellow and blue RPL peaks, optical properties of Ag^+-doped glass, such as optical absorption spectrum, RPL excitation spectrum before and after X-ray irradiation as well as the lifetime of both RPL peaks are measured. From the results, we discuss the emission mechanism of yellow (peaked at 2.21 eV) and blue (peaked at 2.70 eV) RPL using a proposed energy band diagram for RPL emission and excitation in Ag^+-doped phosphate glass. It is found that the radiative lifetime of blue RPL is three orders of magnitude faster than that of yellow RPL.

1. Introduction

Ag^+-doped phosphate glass after exposure to ionizing radiation exhibits an intense luminescence caused by excitation with ultraviolet(UV) light. This phenomenon is called radiophotoluminescence (RPL). As RPL intensity is proportional to the amount of irradiation, glass dosimeter utilizing RPL phenomenon can be applied to individual monitoring of ionizing radiation as well as monitoring of environmental natural radiation. Moreover, the luminescence centers such as Ag^0 and Ag^{++} ions will never disappear unless the glass dosimeter is annealed at about 400 °C. This allows some excellent features such as repeatable measurements and small dispersions among samples (Ikegami, 1991; Nomura et al., 2002; Piesch and Burgkhardt, 1994). So, the glass dosimeter has been widely used as one of the accumulation type dosimeter among other types such as thermoluminescent dosimeter (TLD) and optically stimulated luminescence dosimeter (OSLD) at many radiation facilities in Japan, France and Germany (Ranogajek-Komor, 2007). However, there remain the problems to solve, such as the clarification of RPL emission mechanism and build up process of yellow RPL peak.

In this study, we discuss the emission mechanism of yellow and blue RPL peaks using proposed energy band diagram for the valence change of Ag ions in Ag^+-doped phosphate glass. The feature of yellow and blue RPL peaks is also discussed based on the lifetime data of both RPL peaks.

2. Experimental

The Ag^+-doped phosphate glass as the glass dosimeter (GD-450) (AGC TECHNO GLASS Co., Ltd.), which is transparent in the wavelength region from 300 to 800 nm was used for the experiment. The weight composition of the glass was 31.55% P, 51.16% O, 6.12% Al, 11.00% Na and 0.17% Ag.

The measurements of optical absorption spectra, RPL excitation and emission spectra before and after X-ray irradiation in the Ag^+-doped phosphate glass were carried out using a Hitachi Spectrophotometer (U-2010) and a Hitachi F-4500 fluorescence spectrometer, respectively, at room temperature. Radiative lifetime measurements were carried out using a time-resolved spectrofluorometer

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(Horiba Ltd, NAES-1100), which operated based on the time-correlated multi-photon counting technique (Kurobori et al., 2010). The RPL spectra were corrected for the diffraction efficiency of the grating and the optical response of the photomultiplier.

X-ray irradiation was carried out using an X-ray tube, operated at 30 kV and 20 mA. The photo induced reduction (Shimotsuma et al., 2005) of Ag^+ ions to produce Ag^0 ions was carried out using the Titanium-Sapphire femtosecond laser (Coherent Co. Ltd). A 20 μm spots were formed at the focal point of the laser beam in Ag^+-doped phosphate glass after irradiation by 120 fs laser pulse operating at a wavelength of 800 nm (repetition rate: 250 kHz, pulse power: 750 mW). The morphology of laser beam spots were observed using a conventional microscope, after femtosecond laser irradiation was carried out.

3. Results and discussion

3.1. RPL emission image for X-ray absorption dose

The RPL emission images as a function of X-ray absorbed dose when the X-ray irradiated Ag^+-doped phosphate glass is excited using UV light, are shown in Fig. 1, where it is seen that the intensity of orange (yellow + blue) color emission in human eye increases with the absorbed dose. This result coincides with that of previous report (Perry, 1987; Shih-Ming et al., 2007), in which RPL intensity was almost linearly increased with X-ray absorption dose up to 10 Gy.

3.2. RPL emission and excitation spectrum

Typical RPL emission and its excitation spectra of X-ray irradiated Ag^+-doped phosphate glass are shown in Fig. 2. It can be seen that the RPL emission spectrum consists of two emission bands peaked at about 2.70 eV (460 nm) and 2.21 eV (560 nm). On the other hand, the RPL excitation spectrum consists of two excitation bands peaked at about 3.93 eV (315 nm) and 3.32 eV (373 nm). The fact that RPL emission spectrum consists of two emission bands such as yellow color emission and blue color emission has been reported in previous paper (Miyamoto et al., 2010). The radiative lifetime of yellow and blue RPL peaks are estimated. The lifetime is 2 ∼ 4 μs for yellow RPL and 2 ∼ 10 ns for blue RPL, respectively, which was dependent on the irradiation dose (Kurobori et al., 2010), which indicates that the lifetime of blue RPL peak is about three orders of magnitude faster than that of yellow RPL peak.

3.3. Optical absorption spectrum

It is confirmed that the X-ray irradiated phosphate glass was colored in dark brown as shown in inset of Fig. 3.To investigate the relationship between RPL excitation bands and optical absorption bands of Ag^+-doped phosphate glass, the optical absorption spectrum before and after X-ray irradiation was carried out. Typical

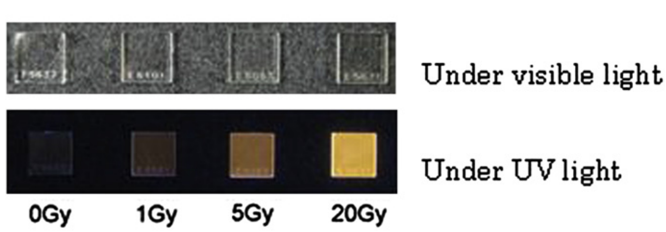

Fig. 1. RPL emission images of Ag^+-doped phosphate glass as a function of X-ray absorbed dose: (a) Ag^+-doped phosphate glass under visible light, (b) Ag^+-doped phosphate glass under UV light.

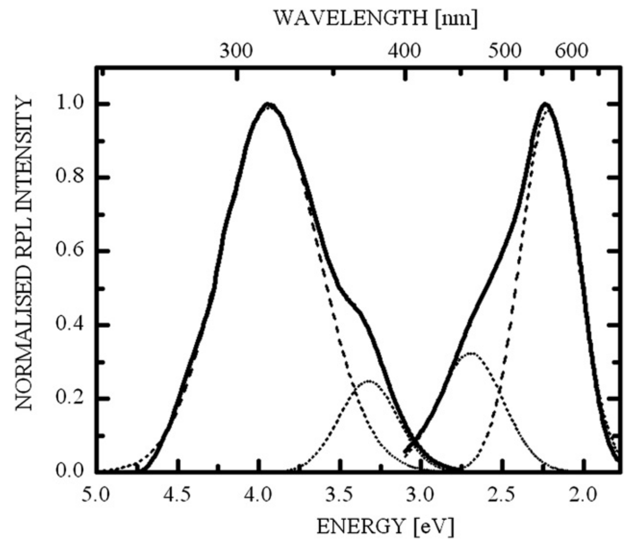

Fig. 2. Typical RPL emission and excitation spectra of Ag^+-doped phosphate glass after X-ray irradiation. The peak separation of the excitation and emission spectra of RPL indicated using dashed lines was carried out using the component separation of Gaussian bands (dashed lines).

optical absorption spectrum of the X-ray irradiated Ag^+-doped phosphate glass are shown in Fig. 3. In addition, the absorption spectra were decomposed into separate Gaussian bands (dashed lines).It was found from the peak separation of the spectrum that the absorption spectrum consists of seven absorption bands. They peaked at about 5.96 eV (208 nm), 5.51 eV (225 nm), 4.92 eV (252 nm), 4.59 eV (270 nm), 4.03 eV (308 nm), 3.50 eV (354 nm) and 2.92 eV (424 nm) in the wavelength region from 200 nm to 500 nm, which coincides with the result reported by Kurobori et al. (Kurobori et al., 2010). In their report, it was pointed out that optical absorption band at about 3.50 eV (354 nm) is attributed to Ag^0 ions ($Ag^+ + e^- \rightarrow Ag^0$) and that at 4.03 eV (308 nm) is attributed to Ag^{++} ions ($Ag^+ + h^+ \rightarrow Ag^{++}$). Kurobori et al. also pointed out that absorption band at 4.59 eV (270 nm) is due to Ag^{++} ions ($Ag^0 + Ag^+ \rightarrow Ag^{++}$). From comparison of RPL excitation spectrum

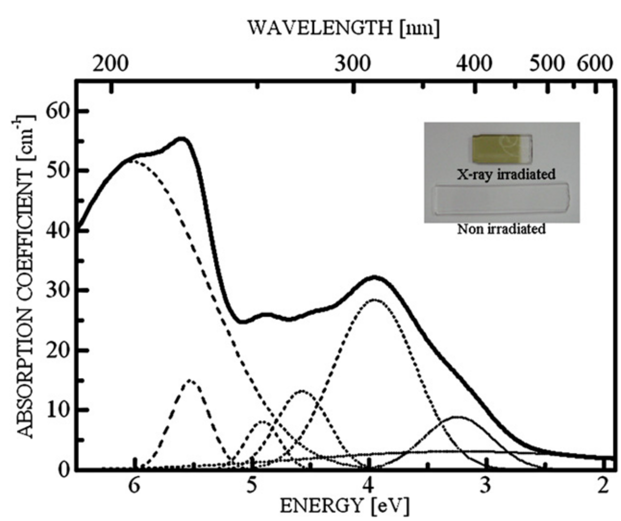

Fig. 3. Optical absorption spectrum of Ag^+-doped phosphate glass after X-ray irradiation. The glass after X-ray irradiation was colored in dark brown as shown in the inset. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)