

Ionizing Radiation Sensor Utilizing Radiophotoluminescence in Ag⁺-Activated Phosphate Glass and Its Application to Environmental Radiation Monitoring

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Optical properties such as optical absorption spectrum and radiophotoluminescence (RPL) emission and excitation spectra of Ag⁺-activated phosphate glass before and after X-ray irradiation were investigated in this study. It is found that the RPL emission spectrum consists of two emission band peaks at about 460 (blue luminescence) and 560 nm (orange luminescence). The excitation spectrum of RPL consists of two excitation bands at about 315 and 360 nm. It is also found that 560 nm RPL peak intensity gradually increases with time after exposure to X-rays, which strongly suggests that the 560 nm RPL peak is ascribed to Ag²⁺ ions. The 460 nm RPL peak is ascribed to Ag⁰ ions, because a blue luminescence is observed in femtosecond pulsed laser light-irradiated glass, in which Ag⁰ ions are produced by the photoreduction process of Ag⁺ ions in glass. The application of the RPL phenomenon in Ag⁺-activated phosphate glass to the environmental monitoring of ionizing natural radiation is also demonstrated.

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1. Introduction

Ag⁺-activated phosphate glass after exposure to ionizing radiation exhibits an intense luminescence caused by excitation with ultraviolet light. This phenomenon is called radiophotoluminescence (RPL). When the Ag⁺-activated phosphate glass is exposed to ionizing radiation, electron-hole pairs will be produced. The electrons are captured into Ag⁺ ions in the glass structure, and then the Ag⁺ ions change to Ag⁰ ions. On the other hand, the holes are captured by the PO₄ tetrahedron at the beginning of migration and then produce Ag²⁺ ions owing to interaction with Ag⁺ ions over time. It has been reported that both Ag⁰ and Ag²⁺ ions can be the centers of luminescence in phosphate glass.^(1,2) As RPL intensity is proportional to the amount of irradiation, Ag⁺-activated phosphate glass can be applied to individual monitoring of ionizing radiation. Moreover, the centers of luminescence will never disappear unless the glasses are annealed at a high temperature of about 400°C. This allows some excellent features such as repeatable measurement and small dispersions among samples.⁽³⁾ Recently, a dosimeter utilizing the RPL phenomenon in Ag⁺-activated phosphate glass have been widely used as accurate personal dosimeters at many radiation facilities in Japan, France, and Germany.⁽⁴⁾

However, there has been no report on the RPL excitation and emission properties in Ag⁺-activated phosphate glass since Yokota's report⁽¹⁾ in 1969. In this study, we evaluate the emission and excitation properties of RPL in Ag⁺-activated phosphate glass and discuss the mechanism of RPL, which is based on RPL excitation and emission properties. In an application of the RPL phenomenon in Ag⁺-activated phosphate glass, environmental monitoring of natural ionizing radiation is demonstrated.

2. Materials and Methods

Optical absorption spectra of Ag⁺-activated phosphate glass GD-450 (AGC Techno Glass Co., Ltd.), supplied by Chiyoda Technol Corp., were measured using a Hitachi Spectrophotometer (U-2010). The composition of the Ag⁺-activated phosphate glass GD-450 is shown in Table 1. X-ray irradiation of Ag⁺-activated phosphate glass was carried out using an X-ray tube operated at 30 kV and 20 mA. The emission and excitation spectra of RPL of Ag⁺-activated phosphate glass were measured using a Hitachi F-4500 fluorescence spectrometer at room temperature. The RPL spectra were corrected for the diffraction efficiency of the grating and the optical response of the photomultiplier.

Table 1
Composition of Ag⁺-doped phosphate glass GD-450.

Elements	mol%
P	20.69
O	64.95
Al	4.61
Na	9.72
Ag	0.03

The photoinduced reduction⁽⁵⁾ of Ag^+ ions to produce Ag^0 ions was carried out using a titanium-sapphire femtosecond laser (Coherent Co., Ltd.). 20 μm spots were formed at the focal point of the laser beam in Ag^+ -activated phosphate glass after irradiation with a 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 was observed using a conventional microscope after femtosecond pulsed laser beam irradiation was carried out.

3. Results and Discussion

3.1 Optical absorption bands

Typical optical absorption spectra of the X-ray irradiated Ag^+ -activated phosphate glass are shown in Fig. 1. The peak separation of the optical absorption spectrum was carried out using an analysis software “fityk,” which is very common software for the component separation of a Gaussian peak. It was found from the peak separation of the spectrum that the absorption spectrum consists of three absorption bands, which peaked at about 255, 315, and 360 nm in the ultraviolet wavelength region. Each absorption band increased with increasing X-ray irradiation dose, as shown in Fig. 2. It was confirmed that the intensity of each absorption band at about 255, 315, and 360 nm increased with irradiation dose, as shown in Fig. 3. The origin of three absorption bands has not been clarified up to now, although there are some reports on absorption bands of Ag ions and their aggregation centers in the phosphate glass.^(5,6)

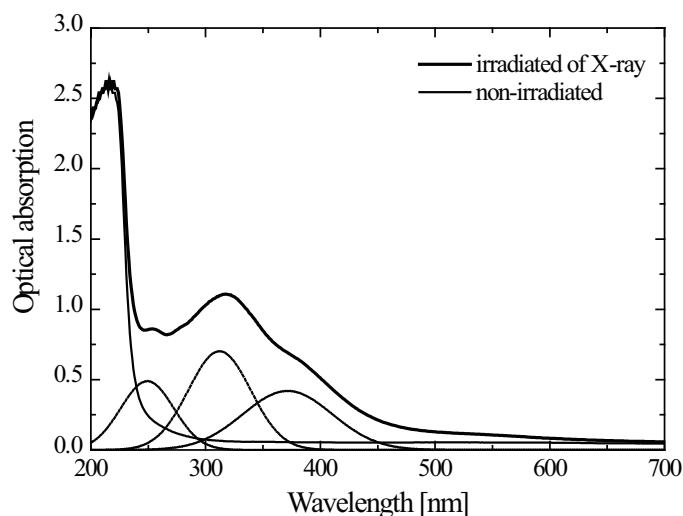


Fig. 1. Typical optical absorption spectrum of Ag^+ -doped phosphate glass before and after X-ray irradiation.

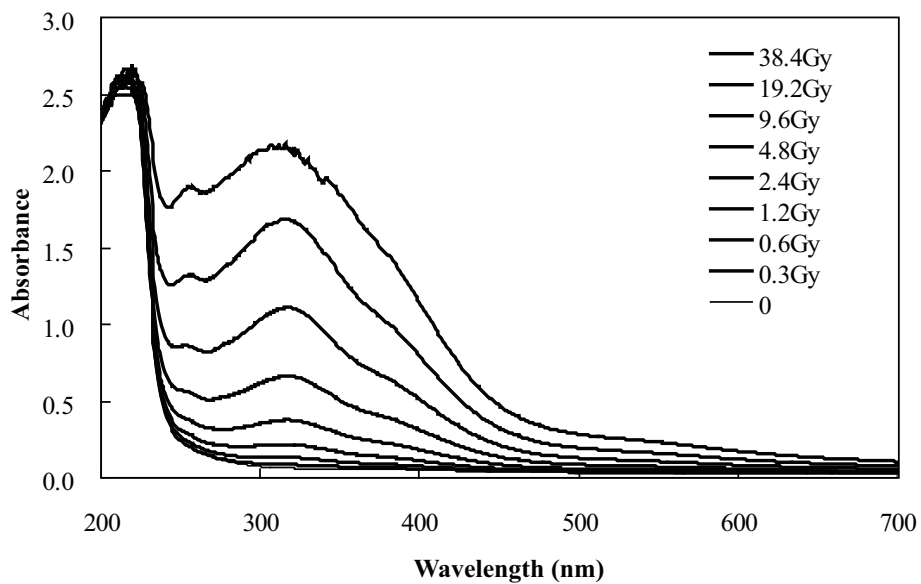


Fig. 2. Change in optical absorption spectrum as a function of X-ray irradiation dose.

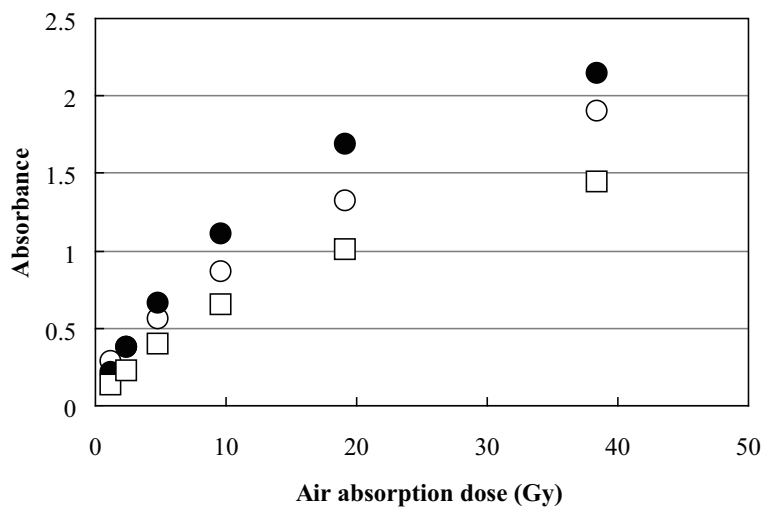


Fig. 3. Peak intensities of optical absorption bands, namely, 255 nm band (○), 315 nm band (●) and 360 nm band (□).

3.2 RPL emission and excitation spectrum

Typical RPL emission and its excitation spectrum of X-ray irradiated Ag^+ -activated phosphate glass are shown in Fig. 4. It can be seen that the excitation bands at 315 and 360 nm correspond to the optical absorption bands in the ultraviolet wavelength region.

On the other hand, the RPL emission spectrum consists of two emission bands at about 460 and 560 nm. The finding that the RPL spectrum consists of two peaks is reported here for the first time. From the viewpoint of individual monitoring of ionizing radiation, it was confirmed that RPL intensity almost linearly increased with X-ray absorption dose up to 5 Gy.

3.3 Change in RPL spectrum after X-ray irradiation

It was previously reported that RPL intensity increases with elapsed time immediately after the glass is excited with X-rays. This phenomenon is the so-called “build-up effect,” pointed out by Yokota.⁽¹⁾

Figure 5 shows the change in RPL spectrum as a function of elapsed time just after X-ray irradiation of the Ag^+ -activated phosphate glass. The X-ray irradiation dose was

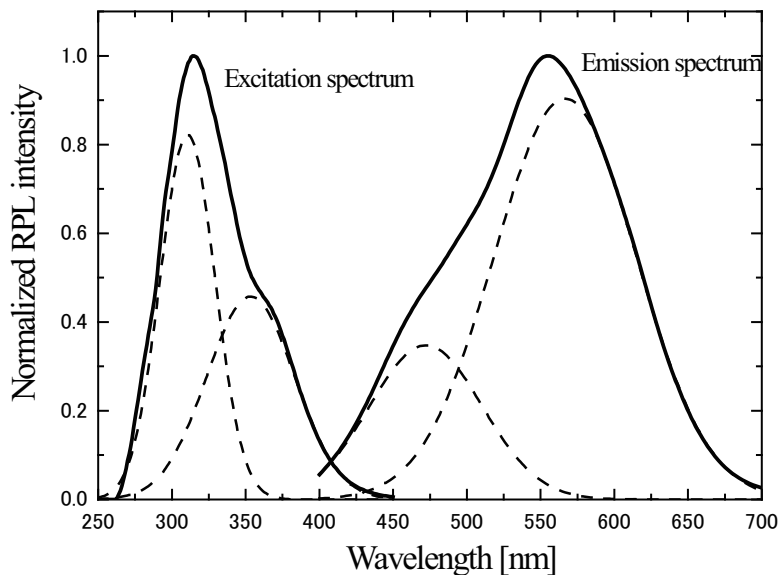


Fig. 4. Typical RPL emission and excitation spectra of Ag^+ -doped phosphate glass after X-ray irradiation. The emission spectrum was observed by exciting with 315 nm light. The excitation spectrum was observed for 560 nm emission.

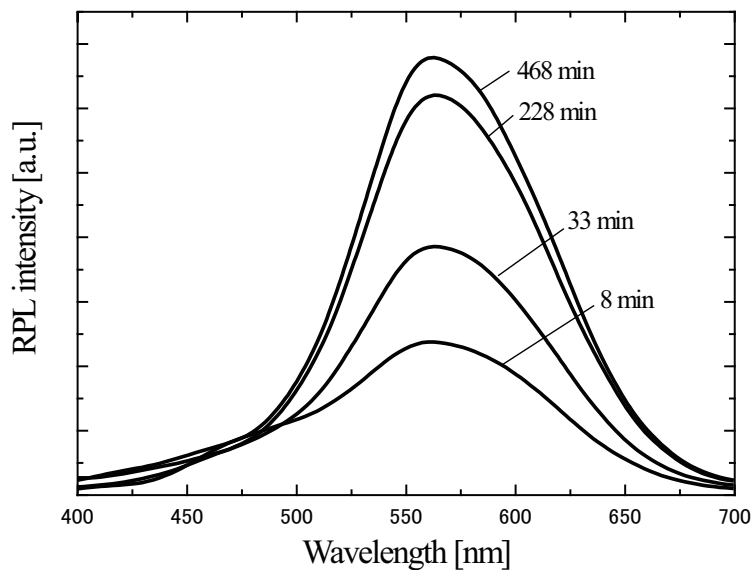


Fig. 5. Change in the RPL spectra as a function of elapsed time after X-ray irradiation in Ag⁺-doped phosphate glass.

about 0.5 Gy. Figure 6 shows the RPL peak intensities of two emission bands, 460 and 560 nm, as a function of elapsed time. It can be seen from Figs. 5 and 6 that the RPL intensity of the 560 nm emission band increased with elapsed time, although the intensity of the 460 nm emission band did not change.

Yokota⁽¹⁾ reported that the build-up process time depends on the content of Ag⁺ ions in the glass. He also pointed out that large amounts of HPO₄ are induced in the glass when the content of Ag⁺ ions in the glass is below 1 wt%, and Ag²⁺ ions are produced with elapsed time after X-ray irradiation, in accordance with the following reaction:



It can, therefore, be pointed out that the RPL emission band at 560 nm is ascribed to the Ag²⁺ ions, which are induced by the capture of holes at Ag⁺ ions, because 560 nm RPL intensity increased with elapsed time.

3.4 Femtosecond pulse laser beam irradiation

Femtosecond pulsed lasers are widely used for material microprocessing. Owing to their ultrasmall pulse width and ultrahigh light intensity, the process is generally

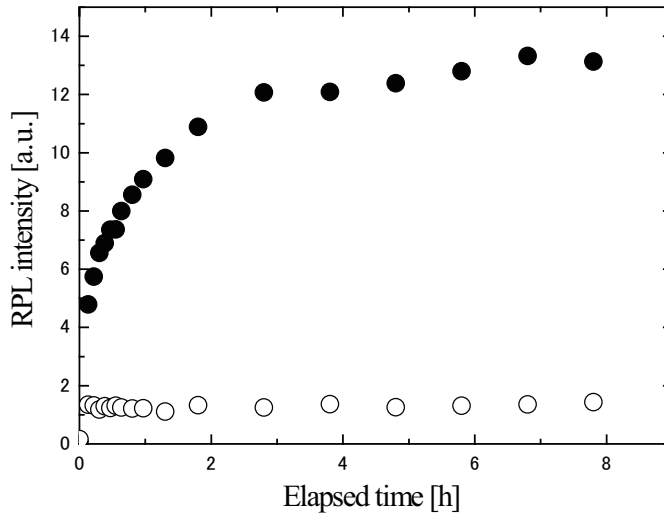


Fig. 6. Peak intensities of RPL emission bands (●: 560 nm peak, ○: 460 nm peak) of the Ag^+ -doped phosphate glass as a function of elapsed time.

characterized by the nonthermal diffusion process.^(7,8) To produce Ag^0 ions, femtosecond pulsed laser beam irradiation was carried out using a titanium-sapphire pulsed laser. Shimotsuma *et al.* have reported that femtosecond pulsed laser beam irradiation reduces Ag^+ ions to produce Ag^0 ions.⁽⁵⁾

Figure 7 shows a microscope image of the Ag^+ -activated phosphate glass after irradiation with the femtosecond pulsed laser beam: (a) coloration due to the valence state change from Ag^+ ions to Ag^0 ions, (b) array of 10×10 spots, and (c) fluorescence from spots. The fluorescence spectrum from the spots is shown in Fig. 8. It can be seen that the dominant emission band of the fluorescence was located at wavelengths in the range of about 400 to 500 nm (blue luminescence). On the basis of the result described above, we would like to point out that the origin of the 460 nm RPL peak can be ascribed to Ag^0 ions, as shown in Fig. 9.

3.5 Application to environmental radiation monitoring with glass dosimeter

Environmental radiation dose measurement at seven points in Ishikawa prefecture shown in Fig. 10 was carried out utilizing the RPL phenomenon in Ag^+ -activated phosphate glass (glass dosimeter). The measured environmental dose per month at each point is shown in Fig. 11. The dose per month is as low as about 0.9 mGy/month (30 $\mu\text{Gy}/\text{day}$), which is the same as that of other electronic dosimeters such as the direct ion storage (DIS) dosimeter and the optically stimulated luminescence (OSL) dosimeter, which

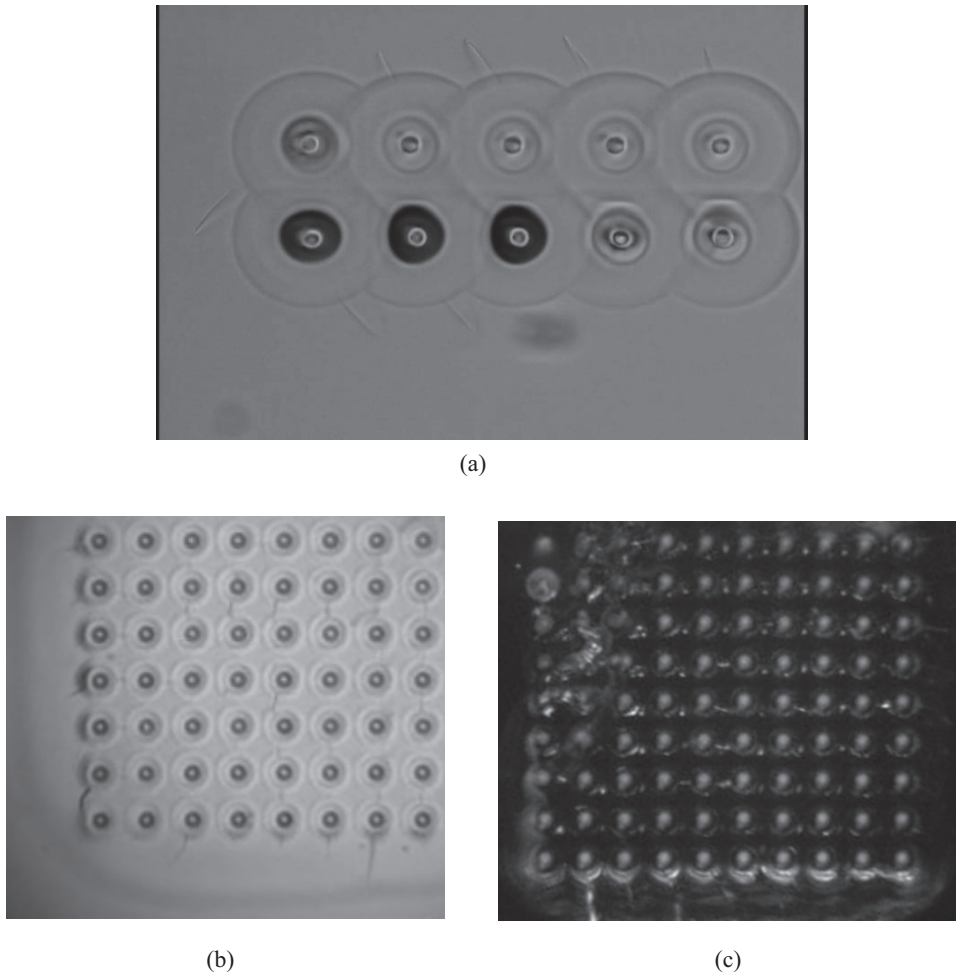


Fig. 7. Optical microscope images of Ag⁺-activated phosphate glass irradiated with femto-second laser: (a) coloration due to the color center formation and valence state change from Ag⁺ to Ag⁰ in the laser-irradiated spots, (b) optical microphotograph of array of 10 × 10 spots, and (c) fluorescence from the spots under excitation with ultraviolet light.

we observed at almost the same points several years ago.⁽⁹⁾ In the winter season, we observed a slightly higher dose, for example, in November and January, as shown in Fig. 11. The reason why the dose change exhibits such a tendency is not clear, although one can point out that a slightly high dose in winter season may be ascribed to thunder storms in this season.⁽¹⁰⁾ The result indicated that the glass dosimeter can be useful as a sensor for environmental radiation monitoring, because the luminescence centers of RPL never disappear at room temperature.

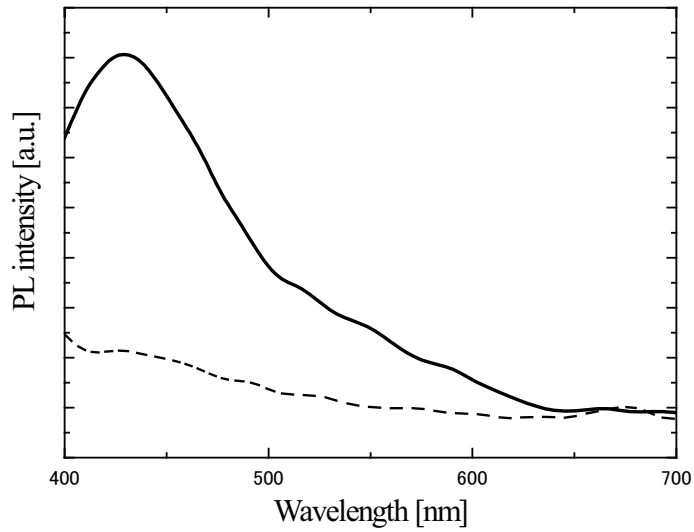


Fig. 8. Fluorescence spectra of the Ag^+ -doped phosphate glass before (broken line) and after (solid line) femtosecond pulse laser irradiation.

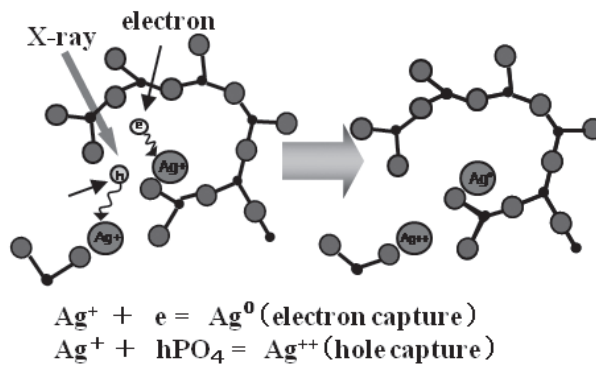


Fig. 9. Formation of fluorescence centers such as Ag^0 and Ag^{2+} .

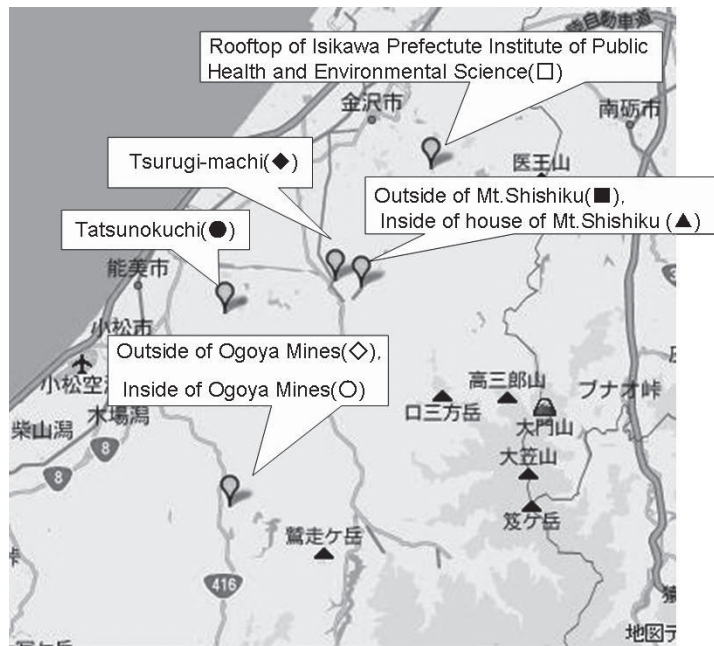


Fig. 10. Map of seven points, namely, Tsurugi-machi (◆), Tatsunokuchi (●), outside of Mt. Shishiku (■), inside of house in Mt. Shishiku (▲), outside of Ogoya Mines (◇), inside of Ogoya Mines (○), and rooftop of Ishikawa Prefecture Institute of Public Health and Environmental Science (□) in Ishikawa prefecture, in which environmental radiation dose was measured using the glass dosimeter .

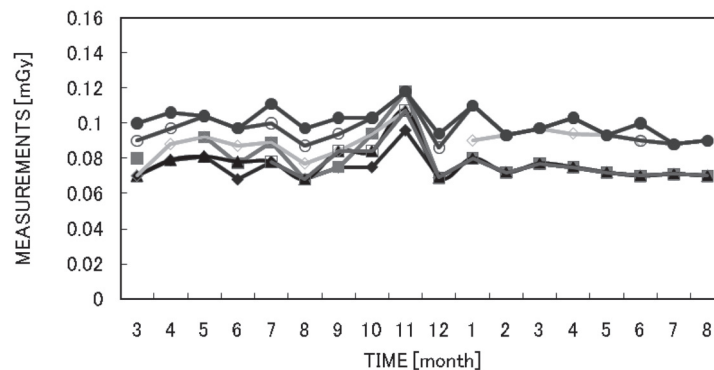


Fig. 11. Environmental radiation doses measured using the glass dosimeter in seven points, namely, Tsurugi-machi (◆), Tatsunokuchi (●), outside of Mt. Shishiku (■), inside of house in Mt. Shishiku (▲), outside of Ogoya Mines (◇), inside of Ogoya Mines (○), and rooftop of Ishikawa Prefecture Institute of Public Health and Environmental Science (□) in Ishikawa prefecture. The measurements of environmental radiation dose were carried out from March in 2008 to August 2009.

4. Summary

The optical properties such as optical absorption spectrum and RPL emission and excitation spectra of the Ag⁺-activated phosphate glass were investigated in this study. The following results were obtained:

- (1) The RPL emission spectrum consists of two emission bands with peaks at about 460 and 560 nm. On the other hand, the excitation spectrum consists of two excitation bands with peaks at about 315 and 360 nm.
- (2) 560 nm RPL peak intensity gradually increased with time after the exposure to X-rays, which strongly suggests that the 560 nm RPL peak is ascribed to Ag²⁺ ions, as indicated in Fig. 6.
- (3) The 460 nm RPL is ascribed to Ag⁰ ions, because the blue luminescence at about 460 nm was observed in femtosecond pulsed laser pulsed beam-irradiated glass, in which Ag⁰ ions are produced by the photoreduction process of Ag⁺ ions in glass.
- (4) The glass dosimeter is useful as a sensor for environmental radiation monitoring.

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