Radiophotoluminescence Properties of Ag-Doped Phosphate Glasses Containing Different Alkali Metal Cations

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(Received January 4, 2016; accepted May 18, 2016)

Keywords: radiophotoluminescence, dosimetry, phosphate glass

For many years, the radiophotoluminescence (RPL) of Ag-doped phosphate glass has been exploited in personal dosimetry. In this study, we investigated the optical properties of Ag-doped phosphate glasses of various compositions containing alkali metals as cations. We found that the peak wavelengths of the RPL bands depend on alkali metal species. Corresponding excitation bands also appeared in the excitation spectra after irradiation. In addition, we observed differences in the stability of the RPL fluorescent centers after heat treatment. These results indicate that RPL fluorescent center formation and initialization processes depend on the alkali metal species in the host phosphate glasses.

1. Introduction

Radiophotoluminescence (RPL) has been investigated for a long time in Ag-doped phosphate glasses (PGs) applied to passive dosimeters. In previous studies, the formation of fluorescent centers in Ag-doped phosphate glasses was investigated by Schulman and Compton,(1) Yokota,(2,3) and Miyamoto and co-workers(4,5) by optical spectroscopy or electron spin resonance (ESR) measurements. The results indicate that the valence state of Ag+ ions in the glasses changes upon exposure to X-ray, gamma ray, or intense laser irradiation. However, fluorescent center formation has not yet been conclusively elucidated. In addition to the fluorescent centers based on Ag, Okada et al. observed RPL in Sm-doped PGs after high-dose X-ray irradiation and ascribed the RPL to the valence change of Sm ions, i.e., Sm3+ to Sm2+.(6) Consequently, these glasses are applicable to medical and environmental dosimetry.

Although RPL is used in practical applications, some phenomena remain unexplained. For example, the ‘build up’ process, i.e., the gradual increase in fluorescence intensity over several tens of hours after irradiation, has not been thoroughly analyzed. Another example is the initialization of RPL by heating. Therefore, we began a detailed investigation on the factors affecting the RPL properties.

In this study, we focused on the composition of Ag-doped PGs. It has been reported that PGs containing over 40 mol% NaPO3 exhibit RPL, and that the NaPO3 content affects the RPL

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fluorescence properties. 

In our previous research, we found that the presence of alkali metals in PG is necessary to achieve RPL, and the alkali metal content affects the RPL properties. In this study, we further investigated the effect of alkali metals in the host on the RPL properties. We investigated the photoluminescence (PL) and RPL properties of Ag-doped PGs, where the hosts are composed of alkali metal phosphates, i.e., LiPO$_3$, NaPO$_3$, (KPO$_3$)$_n$, RbH$_2$PO$_4$, and CsH$_2$PO$_4$. We investigated the correlation between the species of alkali metals and the RPL properties.

2. Experiments

All reagents were purchased from Kojundo Chemical Laboratory Co., Ltd. The glass samples were prepared by a conventional melt-quenching method in air. The raw materials, AgCl (99.99%) and LiPO$_3$ (99%) (the prepared glass is called Li/Ag hereafter), were mixed, loaded into an alumina crucible, and melted at 800–950 °C for 30 min in an electric furnace. Finally, the glass melt was quenched on a stainless-steel plate heated to 573 K, a temperature below the glass-transition temperature of the PG. The same procedure was carried out with NaPO$_3$ (99%) (Na/Ag), (KPO$_3$)$_n$ (99%) (K/Ag), RbH$_2$PO$_4$ (99%) (Rb/Ag), and CsH$_2$PO$_4$ (99%) (Cs/Ag) in place of LiPO$_3$. The Ag concentration was 0.1 mol% for all PGs. The samples were irradiated at room temperature with X-rays using an X-ray tube operating at 40 mA and 40 kV. To ensure that the Ag fluorescent centers in the glass were stable after the irradiation, PL measurements were performed 24 h after irradiation. Furthermore, the PL spectra were measured after heat treatment to investigate the initialization process. The PL and RPL properties were analyzed using PL and RPL spectra and the temporal luminescence profiles. PL and RPL spectra were collected using an F-7000 (Hitachi) fluorescence spectrometer. The temporal profiles were recorded using DeltaFlex 3000U-TMK2 (Horiba). Absorption spectra were measured using a Hitachi U-3500 spectrophotometer.

3. Results and Discussion

3.1 PL and PL excitation spectra before and after X-ray irradiation

The PL spectra of the Ag-doped PGs before the irradiation are shown in Fig. 1. The excitation wavelength was 210 nm. All the samples have emission bands at around 300 nm. These bands are
attributed to Ag\(^+\).\(^{(9)}\) Figure 2 shows the excitation spectra of the Ag-doped PGs emitted before the irradiation. The emission wavelength was set at 300 nm. All the samples have excitation bands at around 220 nm. The peak wavelengths and energies of the PL and excitation bands before the irradiation are summarized in Table 1. The emission band shifts toward longer wavelength, increasing the atomic number of the alkali metal in the host. On the other hand, no such correlation was found for the excitation band. The PL spectra of the Ag-doped PGs before and after the X-ray irradiation are shown in Fig. 3. The excitation wavelengths were set at the maxima of the excitation band, in the wavelength region of 280–320 nm. Figure 4 shows the excitation spectra of the RPL band of Ag-doped PGs of different glass compositions. None of the nonirradiated samples have emission bands between 400 and 750 nm. All the irradiated samples exhibited new emission bands, i.e., RPL bands. The changes in the fluorescence spectra of all the samples after the X-ray irradiation can be explained by the changes in the valence state of Ag. It is known that RPL in commercial glass is based on the change of Ag\(^+\) ions into Ag\(^0\) and Ag\(^{2+}\) after irradiation.\(^{(4)}\) This result suggests that a similar change occurs in the valence state of Ag in all the samples. These new emission bands are located at longer wavelengths with increasing atomic number of the alkali metal in the host. Two fluorescence bands appear to be located at 540 and 650 nm. K/Ag is likely to have both peaks. These new excitation bands are located at longer wavelengths with increasing atomic number of the alkali metals. The peak wavelengths and energies of the RPL and the excitation bands are listed in Table 2.

![Fig. 2. (Color online) Excitation spectra of Ag-doped phosphate glasses of different glass compositions with emission at about 300 nm.](image)

**Table 1**

Peak wavelengths and energies of PL and excitation bands before irradiation.

|        | Li/Ag | Na/Ag | K/Ag | Rb/Ag | Cs/Ag |
|--------|-------|-------|------|-------|-------|
| PL (nm)| 304   | 323   | 318  | 327   | 338   |
| PL (eV)| 4.08  | 3.84  | 3.90 | 3.79  | 3.67  |
| Excitation (nm)| 223 | 215 | 213 | 214 | 220 |
| Excitation (eV)| 5.56 | 5.77 | 5.82 | 5.79 | 5.64 |
Fig. 3. (Color online) Fluorescence spectra of phosphate glasses of different glass compositions before and after the X-ray irradiation. The compositions are (a) LiPO$_3$, (b) NaPO$_3$, (c) (KPO$_3$)$_n$, (d) RbH$_2$PO$_4$, and (e) CsH$_2$PO$_4$. 

Fig. 4. (Color online) Excitation spectra of Ag-doped phosphate glasses of different glass compositions for RPL.
Table 2
Peak wavelengths and energies of PL and excitation bands after irradiation.

|        | Li/Ag | Na/Ag | K/Ag | Rb/Ag | Cs/Ag |
|--------|-------|-------|------|-------|-------|
| PL (nm)| 640   | 660   | 538  | 527   | 543   |
| PL (eV)| 1.94  | 1.88  | 2.30 | 2.35  | 2.28  |
| Excitation (nm)| 313 | 315 | 314 | 287 | 289 |
| Excitation (eV)| 3.96 | 3.94 | 3.95 | 4.32 | 4.29 |

3.2 Effects of heat treatment

Figure 5 shows the PL spectra of the X-ray irradiated Ag-doped PGs before and after heat treatments with excitation at 310 nm. The heat treatment was carried out for 30 min at each temperature. As shown in Fig. 3, RPL bands were observed at 650 nm for Li/Ag and Na/Ag. We observed the decrease in the RPL intensity with temperature and the disappearance of the RPL after heat treatment at 523 K for 30 min for both Li/Ag and Na/Ag samples. On the other hand, the RPL intensity of the Na/Ag samples increased after heat treatment at 373 K for 30 min. At higher temperature, the intensity decreased. For the K/Ag sample, a peculiar feature was observed. After heat treatment at 373 K for 30 min, the K/Ag sample exhibited an emission band at 740 nm, whereas it exhibited an emission band at 530 nm before the heat treatment. This result indicates that the emission band at 740 nm arises from changes in the sample caused by the heat treatment at 373 K. This new band disappeared after heat treatment at 523 K for 30 min. For Rb/Ag and Cs/Ag samples, RPL intensity increased after heat treatment at 373 K for 30 min. At higher temperature, the intensity decreased, and the RPL disappeared after heat treatment at 523 and 473 K for 30 min for Rb/Ag and Cs/Ag samples, respectively.

All the samples were initialized by heat treatment, and this result is in line with those for commercial products. These results indicate that the formation and initialization processes of the fluorescent centers depend on the species of the alkali metals in the host.

3.3 Absorption spectra before and after X-ray irradiation

Figure 6 shows the absorption spectra of the Ag-doped PGs before and after the X-ray irradiation. We observed absorption bands at 250–300 nm in all the samples. Moreover, we observed new absorption bands at 300–450 nm after the X-ray irradiation, except in the Cs/Ag sample. A deconvolution with Gaussian bands leads to absorption bands at 270–350 nm. The peak wavelengths of these absorption bands are consistent with those of the excitation bands shown in Fig. 4. Therefore, these new absorption bands are correlated with the appearance of the RPL. On the other hand, we observed little change for the Cs/Ag sample. This result is consistent with the excitation spectrum in Fig. 4, which has no excitation band around 300–400 nm at room temperature.

3.4 Decay characteristics of RPL fluorescence

Figure 7 shows the fluorescence decay curves of Ag-doped PGs of Li/Ag with excitation at 325 nm. The measurements were also performed for the other samples. The monitored wavelengths were 640, 660, 540, 530, and 540 nm for Li/Ag, Na/Ag, K/Ag, Rb/Ag, and Cs/Ag, respectively.
Fig. 5. (Color online) Fluorescence spectra (left) and excitation spectra (right) of Ag-doped phosphate glasses of different glass compositions for RPL. The compositions are (a) Li/Ag, (b) Na/Ag, (c) K/Ag, (d) Rb/Ag, and (e) Cs/Ag.
Fig. 6. (Color online) Absorption spectra of Ag-doped phosphate glasses of different glass compositions before and after X-ray irradiation.

Fig. 7. Fluorescence decay curve of Li/Ag with excitation at 325 nm. The detection wavelength was 640 nm.
The decay curves were satisfactorily fitted with a sum of two exponential decay functions. Table 3 shows the list of the decay time constants. These decay time constants became shorter with increasing atomic number of the alkali metals.

### 4. Conclusions

We investigated the PL and RPL properties of Ag-doped phosphate glasses of various compositions in a host. We focused on the alkali metal species as cations in the host. The RPL properties, such as the peak wavelengths of the RPL bands and the thermal stability of the new fluorescent centers, strongly depend on the alkali metal species in the host. These results indicate that RPL fluorescent center formation and initialization processes depend on the alkali metal species in the host phosphate glasses.

### Acknowledgements

The authors wish to thank Mr. S. Kayamori for his assistance in carrying out experiments. This work was partly supported by the Technical Division, Graduate School of Engineering, Tohoku University and the Cooperative Research Project of the Research Institute of Electronics, Shizuoka University.

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