Radiophotoluminescence and thermally-stimulated luminescence of Ag-doped $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glass

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Abstract

Recently, we found that Ag-doped $30\text{Li}_3\text{PO}_4\text{-}70\text{Al}(\text{PO}_3)_3$ glass shows radiophotoluminescence (RPL) and thermally-stimulated luminescence (TSL) properties. In this study, we investigated Ag concentration dependence of RPL and TSL in this new glass system. 0 - 1.0% Ag-doped $30\text{Li}_3\text{PO}_4\text{-}70\text{Al}(\text{PO}_3)_3$ glasses were prepared by the melt quenching technique. The as-prepared samples show photoluminescence (PL) emission at 425 nm under 340 nm excitation. After X-ray irradiation, an additional PL emission can be observed around 630 nm with the same excitation wavelength, and this emission is considered to be due to RPL. Among the samples tested, 0.5 and 1.0% Ag-doped samples are the most sensitive and show a linear RPL response over the dose range 0.1 – 20 Gy. For TSL, the Ag-doped samples showed a glow peak around 350 °C. In contrast, non-doped sample showed glow peaks at 370 °C and above 490 °C. The dose responses of all the samples exhibit a linear response in the dose range of 0.1 – 20 Gy.

1. Introduction

Luminescent materials play important roles in various applications including ionizing radiation measurements [1]. One of the notable examples is a scintillator. Scintillators convert high energy ionizing radiation to hundreds of visible photons by quantum cutting via energy transportation from host matrix to the center of luminescence. Scintillators are used in many technical field such as medicine, oil-logging, security and high energy physics. In contrast to scintillator, a dosimeter is also one of the most successful applications. While a scintillator emits light immediately, dosimeter temporarily stores the incident radiation energy, and then the stored energy can be read out in a form of luminescence by external optical or thermal stimulation. The luminescence stimulated optically is called optically stimulated luminescence (OSL) [2] whereas the one by thermal stimulation is called thermally-stimulated luminescence (TSL) [3]. While OSL and TSL are conventional and traditional dosimetry technique, another class of dosimeter called radiophotoluminescence (RPL) stores the dose information as a photoluminescence (PL) intensity signal which varies depending on the incident radiation [4]. The RPL response signal is very stable and stored permanently, unless intentionally erased. Some examples of well-known RPL materials are Ag-doped $\text{NaPO}_3\text{-AlPO}_4$ glass [5], $\text{Al}_2\text{O}_3\text{:Mg,C}$ [6] and Sm-doped materials in a variety of forms such as ceramics, glasses and glass-ceramics [7-9]. The mechanism of RPL may vary by the material, but Ag-doped $\text{NaPO}_3\text{-AlPO}_4$ glass has not been fully clarified, yet. The current understandings are interpreted together with earlier work on radiation induced color centers in Ag^+ -doped phosphate glasses [10]. In the glass matrix, electrons and holes are generated by interacting with ionizing radiation. On one hand, the generated electron is captured by Ag^+ and becomes Ag^0 . On the other hand, the hole migrates towards Ag^+ ion via the PO_4 network and then trapped to become Ag^{2+} [11]. As a result, blue and orange luminescence appear after irradiation by Ag^0 and Ag^{2+} ions, respectively. These luminescent centers are very stable under room temperature and ambient light [12], so it has great advantages such as low signal fading (hence high measurement accuracy) and capability for repetitive measurement. As an alternative to the

conventional Ag-doped sodium aluminophosphate glass system, a substitution of Na by Li is of our particular interest. Since the atomic number of lithium is smaller than sodium, the effective atomic number becomes more equivalent to tissue. In addition, the cross section of ${}^6\text{Li}$ ions is large against thermal neutrons due to the nuclear reaction (${}^6\text{Li} + {}^1_0\text{n} \rightarrow {}^3_1\text{H} + {}^4_2\text{He}$ 4.78 MeV), hence high Q-value; therefore, they are potentially applicable for neutron detectors. Very recently, we successfully developed and demonstrated RPL in the Ag-doped aluminophosphate glass system [13]. The aim of the present work is to study Ag concentration dependence of $\text{Li}_3\text{PO}_4\text{-Al(PO}_3)_3$ glasses on optical, scintillation and dosimeter properties.

2. Experiment

Lithium-aluminophosphate ($\text{Li}_3\text{PO}_4\text{-Al(PO}_3)_3$) glass samples doped with different concentrations of Ag were prepared by the conventional melt-quenching technique. The glass composition is $30\text{Li}_3\text{PO}_4\text{-}70\text{Al(PO}_3)_3\text{-}x\text{Ag}_2\text{O}$ ($x = 0, 0.05, 0.25$ and 0.5 mol.%). The starting materials of high purity grade (99.99 %) were mixed, and the mixture was melted in an alumina crucible inside an electric furnace at the temperature of 1300°C for 30 min in air atmosphere. The melt was then quenched on a pre-heated stainless plate at 200°C . The obtained glass samples were characterized by the following experiments.

The X-ray source used to evaluate the RPL and TSL responses in this study was Spellman X-ray generator (XRBOP&N200X4550) which is equipped with a conventional X-ray tube with a W anode and Be window. The X-ray dose was calibrated using an ionization chamber (PTW TN30013). The X-ray induced scintillation spectrum was measured using our laboratory-made set-up, which was previously described in detail elsewhere [14]. The scintillation decay curve was measured by using our original lab-constructed set-up in order to characterize the scintillation lifetime as well as afterglow [15]. The system is equipped with a pulsed X-ray tube, in which the applied tube voltage is 30 kV and the time resolution is ~ 1 ns. The scintillation decay time profiles were approximated by two or three exponential functions.

The PL spectra of the samples were measured using a CCD-based spectrometer (Ocean Optics QEPro) while exciting the sample at 340 nm. The excitation light was produced by inserting a band pass filter (Asahi Spectra XRR0340) in a white light beam from a Xe lamp (Asahi Spectra LAX-C100). The PL lifetime of Ag-doped samples was measured using Hamamatsu Quantarous- τ (C11367). The excitation source was LED and the wavelength was same as RPL spectrum (340 nm).

The TSL glow curves of all the samples were measured by using a TSL reader (TL-2000, Nanogray Inc) after an irradiation by X-rays at several different doses in order to study the dosimeter properties [16]. The measurement temperature range is from 50 to 490°C , and the heating rate is 1°C/s . The dose response curve, which is the TSL intensity vs irradiation dose, was obtained over the range from 1 Gy to 10 Gy.

3. Results and discussion

Fig. 1 illustrates the 1.0 % Ag-doped $\text{Li}_3\text{PO}_4\text{-Al(PO}_3)_3$ glass prepared in our research as an example. All the synthesized samples look colorless, transparent in the visible range and homogeneous.

Fig. 1 1.0 % Ag-doped $\text{Li}_3\text{PO}_4\text{-Al(PO}_3)_3$ under room light.

Fig. 2 shows the scintillation spectra of 0 – 1.0 % Ag-doped samples under X-ray irradiation. The spectral emission shape was broad, and an intense emission peak appeared at 300 nm except for the non-doped sample. The origin of the emission seen in the Ag-doped samples was attributed to the $4d^95s^1 \rightarrow 4d^{10}$ transitions of Ag^+ . The scintillation intensity increased with increasing the concentration of Ag. In the non-doped sample, no significant signal was observed.

Fig. 2 Scintillation spectra of Ag-doped samples with different dopant concentrations.

The scintillation lifetime constants are summarized in Fig. 3. The lifetimes of the non-doped glass sample were deduced by the approximation of the double-exponential decay function, and the derived lifetimes of faster and slower components were 8.0 ns and 83.9 ns, respectively. On the other hand, the lifetime profiles of Ag-doped glass samples were approximated by third-order exponential approximation. The faster two components were 6.3 - 9.3 ns and 69.6 ns - 1.2 μ s, and we think that these components were due to the host emission since the non-doped sample showed similar decay time components. In addition, the slowest component was 2.1 – 8.1 μ s. The origin of the latter emission is due to Ag^+ because this component was observed in only Ag-doped samples and the lifetime of Ag^+ is similar to the previously reported value which is approximately 8.0 μ s in PL [11]. Furthermore, the slowest lifetime component increased slightly as the concentration increases from 0.1 to 1.0 %. We think this phenomenon is ascribed to a self-absorption of emission as observed in other material systems (e.g., [17]).

Fig. 3 The scintillation lifetimes of host and $4d^9 5s^1 \rightarrow 4d^{10}$ transition of Ag^+ against the Ag concentration. The inset shows the scintillation decay curve of 1.0% Ag-doped glass sample as an example.

Fig. 4 demonstrates RPL in 0.5% Ag-doped $Li_3PO_4-Al(PO_3)_3$ glass. In this figure, two samples are shown under 302 nm UV light. The left sample is as-prepared and the right one is irradiated by X-rays. It is clearly illustrated that the irradiated sample shows strong orange emission while the as-prepared sample does not. This orange emission is ascribed to a result of RPL.

We evaluated the relationship between the irradiated dose and PL emission spectra of glass samples with different concentrations of Ag to investigate the RPL response. The results are shown in Fig. 5. The excitation wavelength was 340 nm. RPL phenomenon was observed from all the samples except for the nondoped sample, and the emission peak around 630 nm was newly created after X-ray irradiation. The origin of latter emission is due to Ag^{2+} ion, which is generated by a valance change of $Ag^+ + h \rightarrow Ag^{2+}$, assuming an analogy with the conventional Ag-doped $NaPO_3-AlPO_4$ system [10]. Regarding the sensitivity of RPL response, the samples doped with 0.5 % and 1.0 % Ag exhibited the RPL phenomenon for X-ray dose as small as 0.1 Gy; however, the sensitivity of 0.1 % Ag doped samples was much lower and required approximately 1 Gy to exhibit RPL. It should be noted here that small band emissions appeared around 450 and 800 nm are also observed in the non-doped sample; thus, these two emissions were attributed to the host emission including some kinds of defects. Further, a change of the two emission shapes was observed by the silver doping and the doping would affect the glass network or coordination environment.

Fig. 4 The reference (left) and the X-ray irradiated (right) samples of 0.5 % Ag doped $Li_3PO_4-Al(PO_3)_3$ glasses under 302 nm UV irradiation.

Fig. 5 PL emission spectra of (a) 0.1, (b) 0.5 and (c) 1.0 % Ag-doped samples as a function of the X-ray irradiation dose from 0 to 5 Gy. (d) compares PL spectra of non-doped sample measured before and after X-ray irradiation of 10 Gy. The excitation wavelength is 340 nm.

Fig. 6 shows the relationship between the irradiated dose and RPL response of Ag-doped glass samples, namely dose response function. The dose response curves were evaluated in the dose range from 0.1 to 20.0 Gy. Here, the RPL response was defined as a difference of integrated PL intensity with respect to that of as-prepared glass sample. The more the sample was irradiated by X-rays, the more valence change was to occur; and the RPL intensity became stronger. It is clearly seen that the RPL signal intensity of all the samples linearly increases as a function of X-ray dose. It is a strong advantage for a dosimetric detector to have a linear response, which makes us easily calibrate the dose from the signal with high accuracy. However, only 0.1 % Ag-doped sample had a low sensitivity and showed linear response over 1 Gy. Therefore, 0.5 % and 1.0 % Ag-doped samples can be good candidates of new RPL dosimeter.

Fig. 6 RPL dose response curves of Ag-doped glass samples with different dopant concentrations.

The PL decay time constants of the emission by RPL are summarized in Table 1. In order to induce the RPL response signal, all the samples were irradiated by X-rays of 5 Gy. The PL decay time profile was measured by monitoring the 630 nm emission under the PL excitation at 340 nm. The measured decay profiles were numerically approximated by the double-exponential function. The extracted time constants can be separated by two groups: fast and slow emission components. The fast component is on the order of several microseconds while the slow component is in the sub-millisecond range. Since the previously reported value for the Ag^{2+} emission in sodium phosphate glass is 2.2 μs [14,18-22] and the value is close to the fast component values, the fast emission is ascribed to emission by Ag^{2+} . On the other hand, the slower decay times measured in our present samples are not consistent with the results of earlier works, in which the reported values were much faster rather than slow [19-22]. It is reasonable if we interpret the origin of the slower emission as the 5s-4d transitions of Ag^{2+} because this electronic transitions are parity forbidden. In addition, both decay time components became faster in proportion to Ag concentrations and this phenomenon was typical in luminescence center activated phosphors.

Table 1
RPL decay times of Ag differently doped glass samples.

Ag concentration	PL decay time of RPL	
	Faster [μs]	Slower [ms]
0.1	10.3	1.0
0.5	9.0	0.5
1.0	7.6	0.4

Fig. 7 shows the TSL glow curves of the non-doped and Ag-doped glass samples with different dopant concentrations. Prior to the measurements, the samples were irradiated by X-rays with the dose of 1 Gy. For the Ag-doped samples, intense and broad glow peak appeared around 350 °C while the non-doped samples showed glow peaks at two different temperature ranges, 370 °C and above 490 °C. The present observation indicates that the glow peak of 490 °C decreased due to an introduction of Ag^+ ions into the host.

The dose response curves are illustrated in Fig. 8. The TSL intensity was defined as a TSL peak of 350 °C. In these evaluations, we have confirmed that 0, 0.1, 0.5 and 1.0 % Ag-doped samples were found to exhibit a good linear response against the irradiation dose over 1 – 10 Gy. We think that the sensitivity needs to be improved for use in low dose measurement applications such as personnel dose monitoring, but the sensitivity should be enough as is for larger dose measurements such as radiation therapies [23].

Fig. 7 TSL glow curves of the non-doped and Ag-doped glass samples with different dopant concentrations after 1 Gy X-ray irradiation.

Fig. 8 TSL dose response curves of non-doped and Ag-doped glass samples with different dopant concentrations.

4. Conclusion

With an aim to develop a new dosimeter material with better tissue equivalency and capability for neutron detection, we have studied RPL and TSL properties of $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glasses doped with varying concentrations of Ag. The scintillation emission peak of all samples was observed around 300 nm with the decay times of 6.3 - 9.3 ns, 69.6 ns - 1.2 μs and 2.1 - 8.1 μs . The faster two components were due to the host including some kinds of defects, and the slowest component was attributed to Ag^+ . On the other hand, as the dosimeter properties, Ag-doped samples show an RPL phenomenon and the new PL emission peak was created around 630 nm due to Ag^{2+} after X-ray irradiation. In addition, the dose response of RPL showed a good linearity over 0.1 - 20 Gy. For the TSL properties, Ag-doped samples showed a glow peak around 350 °C while the non-doped sample showed glow peaks at 370 °C and above 490 °C, and dose response functions were linear from 1 Gy to 20 Gy. Throughout the present work, it is confirmed that the prepared glass samples are applicable for dosimeter applications especially in high dose environment. The suitable concentration of Ag is 0.5-1.0 % from the view point of both RPL and TSL properties.

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