FULL PAPER

Evaluation of radiation-induced luminescence properties in Tl-doped SiO₂ glasses prepared by the spark plasma sintering method

Kosuke HASHIMOTO¹,², Daiki SHIRATORI¹, Daisuke NAKAUCHI¹, Takumi KATO¹, Noriaki KAWAGUCHI¹ and Takayuki YANAGIDA¹

¹Nara Institute of Science and Technology (NAIST), 8916–5 Takayama-cho, Ikoma, Nara 630–0192, Japan

We successfully synthesized Tl-doped SiO₂ glasses by the spark plasma sintering method, and the prepared glasses doped with various concentration of Tl were studied for optical, scintillation, thermally-stimulated luminescence (TSL), and optically-stimulated luminescence (OSL) properties. The Tl-doped samples indicated photoluminescence (PL) due to Tl⁺ ions characterized as an emission peak around 310 nm. The PL decay time constants ascribed to the emission from Tl⁺ were 0.56–0.60 μs. In the scintillation, an emission peak due to Tl⁺ was observed as well as the PL. The highest PL quantum yield and light yield among the present samples were 10.2% and 1100 photons/MeV under ²⁴¹Am α-ray exposure, respectively. Moreover, the Tl-doped samples showed the TSL and OSL emission peak caused by Tl⁺ and the dynamic range in OSL was confirmed from 0.01 to 100 mGy.

Key-words : Glass, SiO₂, Thallium, Spark plasma sintering, Dosimeter

1. Introduction

Luminescent materials have often been used as radiation detectors for medical,¹ security,² personal dose monitoring,³ and environmental monitoring.⁴ The luminescent materials used for the ionizing radiation detectors are mainly sorted to two types, and these materials are called such as a scintillator⁵ and a storage-type luminescent material.⁶ The former one converts energy of ionizing radiations into a large amount of low energy photons such as ultraviolet and visible light immediately. When ionizing radiations interact with scintillators, a lot of secondary electrons are generated and directly transported to emission centers for the recombination, and then scintillators show a luminescence (scintillation). The latter one temporally stores energy of ionizing radiations as a form of electrons and holes captured at localized trapping centers. When ionizing radiations interact with the storage-type luminescent materials, a large number of electrons are generated. Then, some of them are trapped at trapping centers, which are metastable state. The electrons in metastable state can be reactivated by external stimulations (heat or light) and then recombine at emission centers with a luminescence. The luminescence caused by heat and light stimulation is known as thermally stimulated luminescence (TSL)⁷ and optically stimulated luminescence (OSL),⁸ respectively. Moreover, in the case that electrons generated by radiations are trapped and generate new emission centers, photoluminescence (PL) from newly generated emission centers is called radio-photoluminescence (RPL).⁹ TSL, OSL, and RPL are categorized to storage-type luminescence. An intensity of storage-type luminescence depends on the radiation dose accumulated for a certain period of time. Hence, the luminescent materials showing TSL, OSL, or RPL can be utilized as radiation detectors such as personal dosimeters and imaging plates.

In terms of the material forms, single crystals and ceramics have mainly been applied for scintillators and storage-type luminescent materials.¹⁰ On the other hand, also glasses can be applied for scintillators and storage-type luminescent materials because glasses have notable properties such as low production cost, large-volume production possibility and high formability in an arbitrary shape. Today, only a couple of glass materials are used in practice for radiation measurements: Ag-doped phosphate glass as a personal dosimeter and Ce-doped lithium silicate glass as a scintillator for neutron detection.¹⁰ Therefore, there is much room for studying glass materials in radiation measurements.

Up to now, our research group has investigated radiation-induced luminescence properties of SiO₂ glasses doped with Eu and Ce prepared by the spark plasma sintering (SPS) method.¹¹,¹² SiO₂ glass is an interesting host material as a personal dosimeter. Since it consists of relatively light elements and the density is low, the material is equivalent to tissue in terms of the interaction probability with high-energy radiations. In other words, the response...
of such tissue-equivalent dosimeter against the incident radiation energy is similar to that of a human tissue so that no numerical corrections are needed after the measurement ideally. Furthermore, the common melt quenching technique may not be applicable for SiO₂ glass due to the high softening temperature of SiO₂ (~1800 °C). Actually, common electric furnaces and crucibles are not capable of reaching such high temperatures. The SPS method can solve this problem because the SPS method allows us to raise the sintering temperature very high over 1000 °C in a short time within a few minutes and makes materials in lower sintering temperature than usual ceramic sintering processes.¹³ Accordingly, radiation-induced luminescence properties of the SiO₂ glasses prepared by the SPS method have been researched.

In this work, to expand our previous researches, we have focused on Ti⁺ ions as emission centers. Ti⁺ ions can be one of major candidates for the emission center since Ti⁺-doped luminescent materials typified by NaI and CsI show an intense luminescence attributed to 6sp→6s² transitions of Ti⁺ ions.⁴⁻¹⁴ Therefore, we have synthesized Ti⁺-doped SiO₂ glasses prepared by the SPS method and studied its optical, scintillation, and dosimetric properties. Generally, scintillators and dosimeters have been investigated in different communities although they have the same purpose to measure ionizing radiation by luminescent materials. Recently, we have found that scintillation and dosimetric properties have a complementary relationship,¹⁵ and in order to understand radiation-induced luminescence phenomena totally, we have evaluated both of these properties in one material.

2. Experimental

Ti⁺-doped SiO₂ glasses were synthesized by the SPS method. SiO₂ glass nano-sized powder (99.9%, Admatechs) and Ti₂O₃ powder (99.9%, Fujifilm) were homogeneously mixed. The chemical compositions of the prepared samples are xTi₂O₃-(100 - x)SiO₂ (x = 0.0005, 0.0025, 0.005, 0.025). The total mass of the mixture was 0.5 g. Then, the mixture was loaded in a graphite die and sandwiched and sealed with two graphite punches. This assembly was set in the sintering furnace (La-Box110, Sinter Land Inc.). The detailed information on synthesis was written in the previous report.¹¹ After the synthesized samples were polished to thickness of 2.11 ± 0.23 mm, they were evaluated on the optical characteristics and various luminescence characteristics by radiation irradiation.

X-ray diffraction (XRD) patterns were measured to confirm that obtained samples were amorphous by MiniFlex 600 (RIGAKU). Transmittance spectra were measured in a spectral range from 190 to 2700 nm at 1 nm step by using a spectrophotometer (V670, JASCO). PL quantum yields (PLQY) were measured with use of a Quantaurus-QY device (C11347-01, Hamamatsu). In order to calculate PLQY, the numbers of absorbed photons (N_{absorb} 270 nm) and emitted photons (N_{emit} from 290 to 600 nm) were determined by PL intensities with/without the sample, and PLQY was calculated as \( QY = \frac{N_{emit}}{N_{absorb}} \). The PL excitation and emission spectra were measured by a spectrofluorometer (FP-8600, JASCO) which is equipped with a Xe-lamp as an excitation source. The measurements of PL decay curves were done using a Quantaurus-t(C11367, Hamamatsu). Here, the excitation wavelength was 270 nm, and monitoring emission wavelength was 310 nm.

X-ray-induced scintillation spectra were measured with our laboratory-constructed setup, and the instrumental details can be found elsewhere.¹⁶ The irradiation source was a conventional X-ray tube equipped with a tungsten anode target and a beryllium window. The applied tube voltage and current were 80 kV and 1.2 mA, respectively. The scintillation photons were detected by a monochromator equipped with a CCD-based detector (Shamrock 163 monochromator, and DU-420-BU2 CCD, Andor) through an optical fiber, and the scintillation spectra were measured. In the pulse height measurement, we mounted each sample on the photomultiplier tube (PMT, R877-100, Hamamatsu) with a silicon grease (6262A, OKEN), and the sample was covered by several layers of Teflon reflectors to guide scintillation photons to the PMT. Here, the scintillation light is converted to electronic signal by the PMT, which is then processed by the preamplifier (113, ORTEC), shaping-amplifier (572, ORTEG) with 10 µs shaping time and multichannel analyzer (AMPTEK Pocket MCA). The pulse height spectra are eventually stored on a computer.

As dosimetric properties, TSL glow curves were measured using a TSL reader (TL-2000, Nanogray Inc.).¹⁷ During the measurement, the heating rate was 1 °C/s, and the temperature range of the measurement was from 50 to 490 °C. TSL spectra were measured with a CCD-based spectrometer (QE Pro, Ocean Optics) while heated on a ceramic heater system (SGR-SHO-A, Sakaguchi) at 90 °C.¹⁸ The OSL stimulation and emission spectra were measured by the spectrofluorometer (FP-8600, JASCO) and an optical filter (BPF340, Asahi spectra). In measurements of OSL emission spectra and dose response functions, the range of the monitor wavelength was 340 ± 50 nm while the stimulation wavelength was 415 nm. For measurements of TSL and OSL dose responses, the irradiation dose was controlled by the distance from the X-ray source (0–82 cm) and tube current (0.052–5.2 mA). The dose calibration was performed by using an air-filled ionization chamber (Model 30013, PTW). In the measurements, the tested dose range was from 0.01 to 10000 mGy for TSL and 0.01 to 100 mGy for OSL.

3. Results & discussion

Figure 1(a) shows a photograph of the Ti⁺-doped samples under room light. The samples are placed in an ascending order of Ti⁺-concentration (0.001, 0.005, 0.01, and 0.05%) from left to right. All the samples looked transparent in naked eyes. During irradiation of ultraviolet (UV) light (254 nm), all the samples exhibited the white-blue luminescence as shown in Fig. 1(b).

Figure 2 shows the result of XRD measurement for all the samples. The measured XRD pattern showed only the
halo peak at the range of 10–40 degrees, and the glass samples did not include any crystalline phases. Hence, it can be concluded that all the synthesized samples are amorphous state.

In-line transmittance spectra of all the samples are shown in Fig. 3. All the samples showed a transmittance of approximately 70–80% in the range from 300 nm to the near infrared region. In the ultraviolet region, absorption bands were observed at around 220 nm in the 0.001 and 0.005% Tl-doped samples. Another absorption band around 270 nm was also observed in the 0.01 and 0.05% Tl-doped samples. Because it has been well known that the band gap of SiO$_2$ is around 9 eV $\approx$ 140 nm, the absorption bands observed in UV range was caused by the Tl-doping.

Because the absorption bands were detected at 220 and 270 nm, PL emission spectra were measured under excitation at 220 and 270 nm. Figure 4(a) illustrates the emission spectra excited at 220 nm and the excitation spectra monitored at 270 nm. Under the excitation at 220 nm, an emission band was confirmed at around 270 nm in the 0.001 and 0.005% Tl-doped samples, and it was due to defects like oxygen-deficiency centers (ODCs). In the 0.01 and 0.05% Tl-doped samples, another emission peak was mainly detected around 310 nm while the peak intensity at around 270 nm decreased with increase of Tl amount. In addition, a broad emission band was observed around 350–500 nm. Judging from the excitation and emission wavelengths, the emission peak at 310 nm was attributed to Tl$^+$. The emission band at 350–500 nm is due to self-trapped exciton (STE) localized near the Tl$^+$ because the spectral shape and emission wavelength are similar to those in Tl-doped phosphors reported in the past study. Figure 4(b) shows the excitation spectra monitored at 310 nm. Two excitation peaks were observed around 220 and 270–280 nm which are due to Tl$^+$, and these bands coincided with the absorption bands observed in Fig. 3. Since the excitation peak located at 270–280 nm overlapped with the emission peak caused by ODCs, the emission peak intensity at 270 nm decreased with increase of Tl amount.

Figure 5 presents the emission spectra when the excitation wavelength is 250–270 nm, and the excitation spectra...
monitored at 350–390 nm. Under the excitation at 250–270 nm, an emission peak at 310 and 400 nm as well as a broad emission band around 350–500 nm were confirmed. When the excitation wavelength was 270 nm, these samples indicated the maximum emission peak at 310 nm was Tl⁺. The observed emission peak at 400 nm was considered to be due to ODCs according to the previous study. In addition, the emission band at 350–500 nm is due to STE localized near the Tl⁺. Summarizing the above results, the absorption bands were detected around 220 and 270 nm due to ODCs, Tl⁺, and STE localized near the Tl⁺. Moreover, the emission peaks were observed at 270, 310, 400, and 350–500 nm caused by ODCs, Tl⁺, ODCs, and STE localized near the Tl⁺, respectively.

Figure 6 shows the PL decay curves of the Tl-doped samples monitored at 310 nm upon 270 nm excitation. The decay curves were deduced as a sum of some exponential decay functions using the following equation.

\[ f(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) + \cdots + I_k \exp(-t/\tau_k) \]

where \( f(t) \) is the scintillation intensity during the decay, \( I_k \) is the amplitude of \( k \)-th component, \( \tau_k \) is the decay time constant of \( k \)-th component, and \( t \) is the time. The measured decay curves monitored at 310 nm were approximated by a single exponential decay function with a constant background level. The obtained decay time constants were summarized in Table 1, which were 0.56–0.60 μs. These values correspond to the value due to Tl⁺.14)

Figure 7 exhibits X-ray induced scintillation spectra. All the samples showed the broad emission from 350 to 500 nm. Moreover, the 0.001 and 0.005%, and 0.01 and 0.05% Tl-doped samples mainly showed the emission peak at 270 and 310 nm, respectively. In the 0.01% Tl-doped sample, the emission peak at 270 nm appeared as a shoulder since the peak intensity decreased due to the absorption of Tl⁺. The emission at 310 nm is attributed to the 6s⁶ - 6s² transitions of Tl⁺, and the broad emission from 350 to 500 nm is attributed to STE localized near the Tl⁺ as well as PL. In addition, judging from the PL spectra, the emission peak at 270 nm in scintillation spectra also is due to ODCs. As same as the PL, the emission intensity at 270 nm decreased with Tl concentration due to the absorption bands at around 270 nm observed in Fig. 3.

Figure 8 presents the pulse high spectra measured for Tl-doped samples under the 241Am α-ray irradiation. The glass scintillator (GS20) was used as a reference, which had a light yield of about 3400 ph/MeV under α-rays from 241Am. As a result of measurements, the light yields of the 0.001, 0.005, 0.01, and 0.05% Tl-doped samples were deduced to be 73, 170, 360, and 1100 ph/MeV, respectively. The 0.05% Tl-doped sample showed maximum light yield among the present samples, which was higher compared with Eu-doped SiO₂ glasses prepared by the SPS method.12)

Figure 9 shows the TSL glow curves of Tl-doped samples. All the samples were irradiated by X-rays with dose of 1000 mGy prior to the TSL measurement. The 0.005 and 0.01% Tl-doped samples showed a glow peak near 90 °C, and the 0.001% Tl-doped samples showed a glow

| Tl concentration (%) | Decay time constants (μs) |
|----------------------|--------------------------|
| 0.001                | 0.56                     |
| 0.005                | 0.60                     |
| 0.01                 | 0.60                     |
| 0.05                 | 0.59                     |
peak near 130 °C. In the 0.05% Tl-doped samples, three peaks appeared around 90, 180, and 330 °C. The Tl-doped samples showed no correlation between the change of TSL glow curves and Tl concentration. In general, the TSL intensity depends on not only the emission efficiency but also energy transportation efficiency. Thus, one possible interpretation for this is that TSL glow curves is not simply correlated with only Tl concentration (emission efficiency). Moreover, in this case, there is a possibility that the emission efficiency and TSL mechanism are different in each sample because the main emission center is different in the samples with high and low Tl concentrations.

Figure 10 shows the TSL emission spectra of all the samples measured around 90 °C which is the temperature that the TSL intensity was the strongest. The spectra showed the same spectral shape to the scintillation spectra. The emission peak at 310 nm is attributed to the 6sp–6s2 transitions of Tl+2, and the broad emission from 350 to 500 nm is attributed to STE localized near the Tl+2. Moreover, the emission peak at 270 nm is due to ODCs. In the 0.01% Tl-doped sample, the emission peak at 270 nm appeared as a shoulder since the peak intensity decreased due to the absorption of Tl+2.

Figure 11 illustrates the TSL dose response functions. In order to evaluate dose response functions, the TSL intensity of glow curves were integrated in a temperature range from 50 to 490 °C. The 0.005, 0.01, and 0.05% Tl-doped samples showed linear responses from 100 to 10000 mGy. The detection limit of 100 mGy is not sufficient for practical application of personal dosimeter. Thus, we evaluated not only TSL but OSL properties as described below.

Figure 12 shows the OSL emission and stimulation spectra. The stimulation spectra have a broad tail feature and show the highest value at the shortest wavelength, and it decreases as the stimulation wavelength increases. The emission spectra were measured with a stimulation at 415 nm. Analogically with PL and scintillation spectra, the peak around 310 nm is due to Tl+2. Although TL does not show a clear dependence on TI concentration, OSL intensity shows a positive proportionality with Tl concentration. Figure 13 illustrates the dose response functions of the OSL. In this figure, the OSL intensity defined as an integrated value of an OSL decay curve which is the OSL intensity as a function of time during stimulation of con-
stant intensity. It can be clearly seen that the OSL intensity is in proportional to the irradiation dose over the dose range from 0.01 to 100 mGy for the 0.05% Tl-doped samples. This sensitivity is equivalent to the commercial dosimeters.

4. Conclusion

SiO$_2$ glasses were successfully synthesized using the SPS method with Tl concentrations of 0.001, 0.005, 0.01, and 0.05%, and their optical, scintillation, and dosimetric properties were evaluated. We confirmed the transparency and amorphous state for all the samples by in-line transmittance spectra and XRD measurements, respectively. In all the case of PL, scintillation, TSL, and OSL, the highly Tl-doped samples clearly showed the emission peak derived from 6sp–6s$^2$ transitions of Tl$^+$ ions at 310 nm. From the evaluation of TSL and OSL dose response functions, the best detection limit was 0.01 mGy for the 0.05% Tl-doped sample.

Acknowledgements This work was supported by Grant-in-Aid for Scientific Research A (17H01375) and B (18H03468 and 19H03533), and Young Scientists B (17K14911). Cooperative Research Project of Research Center for Biomedical Engineering, Iketani Foundation, Murata Foundation and Nippon Sheet Glass Foundation are also acknowledged.

References

1) Q. Wei, T. Ma, N. Jiang, T. Xu, Z. Lyu, Y. Hu and Y. Liu, Nucl. Instrum. Meth. A, 953, 163242 (2020).
2) J. Glodo, Y. Wang, R. Shawgo, C. Brecher, R. H. Hawrami, J. Tower and K. S. Shah, Phys. Procedia, 90, 285–290 (2017).
3) Y. Miyamoto, H. Nanto, T. Kurobori, Y. Fujimoto, T. Yanagida, J. Ueda, S. Tanabe and T. Yamamoto, Radiat. Meas., 71, 529–532 (2014).
4) S. Moriiuchi, M. Tsutsumi and K. Saito, Jpn. J. Health Phys., 44, 122–133 (2009).
5) T. Yanagida, Proc. Jpn. Acad., Ser. B, 94, 75–97 (2018).
6) T. Yanagida, G. Okada and N. Kawaguchi, J. Lumin., 207, 14–21 (2019).
7) C. Jones, J. Radiol. Prot., (review of the Thermoluminescence dosimetry materials: properties and uses), 16 (1996).
8) L. Bøtter-Jensen, K. J. Thomsen and M. Jain, Radiat. Meas., 45, 253–257 (2010).
9) T. Yamamoto, A. Rosenfeld, T. Kron, F. D’Errico, M. Moscovitch, RPL Dosimetry: Principles and Applications (2011) pp. 217–230.
10) A. D. Bross, Nucl. Instrum. Meth. A, 247, 319–326 (1986).
11) G. Okada, S. Kasap and T. Yanagida, Opt. Mater., 61, 15–20 (2016).
12) Y. Isokawa, H. Kimura, T. Kato, N. Kawaguchi and T. Yanagida, Opt. Mater., 90, 187–193 (2019).
13) T. Yanagida, Adv. Sci. Tech., 98, 44–53 (2016).
14) M. Gascón, S. Lam, S. Wang, S. Curtarolo and R. S. Feigelson, Radiat. Meas., 56, 70–75 (2013).
15) T. Yanagida, J. Lumin., 169, 544–548 (2016).
16) T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi and T. Yanagitani, Opt. Mater., 35, 2480–2485 (2013).
17) T. Yanagida, Y. Fujimoto, N. Kawaguchi and S. Yanagida, J. Ceram. Soc. Jpn., 121, 988–991 (2013).
18) G. Okada, T. Kato, D. Nakauchi, K. Fukuda and T. Yanagida, Sens. Mater., 28, 897–904 (2016).
19) L. Skuja, J. Non-Cryst. Solids, 239, 16–48 (1998).
20) H. Kimura, F. Nakamura, T. Kato, D. Nakauchi, G. Okada, N. Kawaguchi and T. Yanagida, J. Mater. Sci.-Mater. El., 29, 8498–8503 (2018).
21) R. Reisfeld and S. Morag, Appl. Phys. Lett., 21, 57–58 (1972).