Radioluminescence and thermally-stimulated luminescence of SiO₂ glasses prepared by spark plasma sintering

Go OKADA,[†] Safa KASAP* and Takayuki YANAGIDA

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

*Electrical and Computer Engineering, University of Saskatchewan, 57 Campus Dr., Saskatoon, SK S7N 5A9, Canada

Bulk SiO₂ glasses have been prepared by spark plasma sintering and characterized towards dosimeter applications. The temperature dependence studies of radioluminescence suggest that there are two possible groups of luminescent centres, which show emissions at 385 and 511 nm. At room temperature, the former emission is predominant while the latter emission significantly increases at low temperatures, especially below 200 K. The origins of these emissions are attributed to a pair of silylene centres and dioxasilirane and silylene, respectively. After irradiating the sample, thermally-stimulated luminescence (TSL) is observed around 160°C and above 300°C, in which the emission is mainly the 385 nm component. The TSL intensity is linearly proportional to the radiation dose delivered, and a linear dynamic range has been demonstrated over 10⁰–10⁴ mGy.

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Key-words : Radioluminescence, Thermally-stimulated luminescence, X-rays, SiO₂, Spark plasma sintering

[Received October 15, 2015; Accepted January 21, 2016]

1. Introduction

Silicon dioxide (SiO₂) is one of the most common chemical compounds in the history of mankind. SiO₂ is, of course, the major constituent of sand and one of the most abundant substances in Earth's crust. In terms of its chemistry, SiO₂ is well-known to be very stable owing to the covalent nature of bonding in this compound. It has a melting temperature that is very high (~2000°C), which means that the production of SiO₂ in glass form is a challenging task as it requires a specialized heating furnace to produce it by a fusion process. Alternatively, SiO₂ glass can be made by synthetic techniques such as gas- and liquid- phase syntheses. An example of the former technique is a chemical vapour deposition (CVD) and latter is a sol-gel process.¹⁾ Recently, a new technique has been developed to make a bulk SiO₂ glass.²⁾ It utilizes a ceramic sintering technique called spark plasma sintering (SPS)^{3,4)} and sinters nano-sized SiO₂ powder under high pressure (~100 MPa) but relatively low temperature.

There is both scientific and technological interest in studying new types of materials for use in dosimetry with the aim of discovering better dosimetric materials or new innovative applications. A dosimeter is a device that measures a radiation dose; very commonly an inorganic phosphor (or called storage phosphor^{5)–11)}) is used as a radiation detector material. When radiation is incident on such a phosphor as a detector, it absorbs the radiation energy and produces many electron-hole pairs. Next, these charges are, in principle, deeply captured by localized centres and are accumulated while exposed to further radiation. These accumulated charges can be released from the trapping centres by optical- or thermal stimulation, and this process is followed by

the recombination of electrons and holes which results in the emission of light. The latter luminescence caused by optical and thermal stimulations are called optically-stimulated luminescence (OSL) and thermally-stimulated luminescence (TSL). Since these luminescence intensities are proportional to the absorbed radiation dose, such storage phosphors are used to measure the radiation dose.

In our earlier work,¹²⁾ we have produced a Ce-doped SiO₂ bulk glass by SPS as a new type of material and studied its properties for dosimetry applications. SiO₂ is a promising dosimeter material since it has a low effective atomic number ($Z_{\text{eff}} = 15.46$) so the energy response is expected to be equivalent to tissue. Tissue equivalent detector can accurately measure the dose that would be absorbed in tissue. Moreover, the Ce-doped SiO₂ was found to give an intense TSL; the sensitivity was found to be comparable with commercial detectors. In order to advance the research and extend our understandings, it is particularly important to study a non-doped SiO₂ glass prepared by the same technique. Therefore, the aim of this work is to characterize SiO₂ glasses prepared by SPS for dosimeter applications.

2. Experimental

Bulk SiO₂ glass samples were prepared by a spark plasma sintering technique based on the work reported by Zhang et al.²⁾ 0.5 g of SiO₂ glass nano-powder (purity 99.9%; SO-E1, Admatechs Co. Ltd.) was loaded in a graphite die with an inner diameter of 10 mm, and the raw powder was kept inside and sealed with two graphite punches. This graphite assembly was then covered by a carbon fabric and loaded into the sintering furnace (La-BOX, NJS). The sintering temperature was controlled as described in the following sequence: the temperature increased to 600°C from the room temperature in about 5 min, kept at 600°C for about another 5 min, increased again up to 1300°C at a constant rate of 10°C/min, and held at 1300°C for 120 min. The entire sintering process was performed in vacuum while applying 70 MPa between the two ends of graphite punches. For comparison purposes, we have also used in this

[†] Corresponding author: G. Okada; E-mail: go-okada@ms.naist.jp

[‡] This article was selected from the presentations at "STAC-9" (The 9th International Conference on the Science and Technology for Advanced Ceramics) held in Tsukuba, Japan (2015), through the regular reviewing procedure.

study alpha-quartz single crystal (CRYSTAL GmbH, Germany) as a crystalline SiO₂ (c-SiO₂) sample. The synthesized sample was polished for further characterizations described below.

X-rays were used for the characterizations in this work. For the measurement of radioluminescence (RL) and its spectrum, the sample was simply irradiated with X-rays. The X-rays were generated by an air-cooled conventional X-ray tube assembly (XRBOP&N200X4550, Spellman), which is equipped with a W anode target and a Be window. The applied tube voltage was fixed to 40 kV (DC) while the current was controlled between 0.052 and 5.2 mA to adjust the dose rate from 0.01 to 1 Gy/min. In order to measure the RL spectrum, the RL emission was collected by an optical fibre during irradiation, and the light was guided to a spectrometer equipped with a Peltier-cooled CCD sensor (DU920P-BU2NC, Andor) and diffraction grating (SR163i-UV, Andor). The details of this setup are described elsewhere.¹³⁾ The RL spectrum was also measured at lower temperatures with a closed-cycle He cryostat system (POFX-101-DS, Pascal Co. Ltd.) in vacuum which enabled the sample temperature to be cooled down to approximately 8 K. The details of the system are explained in a reference.¹⁴⁾

The TSL spectrum was measured with the fibre-coupled spectrometer setup described above while the sample was heated at a specific temperature on a ceramic heater system (SCR-SHQ-A, Sakaguchi). The TSL glow curve was measured using a TSL reader (TL-2000, NanoGray)¹¹⁾ over the temperature range of 50–490°C at a constant heating rate of 1°C/s.

3. Results and discussion

The SiO₂ glass sample used in experiments has a disk shape with a diameter of approximately 10 mm and a thickness of 1 mm. **Figure 1** shows in-line transmittance spectrum of the prepared SiO₂ glass sample in comparison with that of c-SiO₂. It looks glassy and visually transparent, and there is no evidence of significant light scattering in the sample which indicates that the obtained sample is homogeneous on the scale of visible light wavelength. The transmittance is considerably high especially in the UV region while there seems to be a small absorption band around 250 nm, which the crystalline sample does not have, indicating a possible inclusion of some unexpected impurities.

Figure 2 compares the RL spectra of the SiO₂ glass sample of this work and c-SiO₂. The crystalline sample shows an emission with the peak around 450 nm while the glass sample shows a much broader band emission 300–500 nm. A similar emission in

Fig. 1. In-line transmittance spectra of SiO₂ glass prepared by SPS and that of c-SiO₂ as a reference. The inset is the photograph of glass sample.

c-SiO₂ was reported to be due to a self-trapped exciton (STE)¹⁵⁾ whereas the broader emission feature of RL seen in the glass sample suggests that it has supplemental luminescent centres in comparison with the crystalline sample. These centres can be structural defects due to the nature of glass, oxygen vacancies as the sample was synthesized in a strong vacuum environment and/or some contaminations such as carbon from the die and punches used in SPS.

Figure 3 shows the RL spectra of SiO₂ glass sample prepared by SPS at low temperatures. It is clearly seen that the spectral position of the emission shifts towards longer wavelengths as the temperature decreases. The RL intensity also changes with the temperature. It seems like that the RL consists of at least two main components in the UV and blue regions. The latter observation is consistent with earlier studies^{16),17)} which showed that similar fumed transparent SiO₂ glass exhibits photoluminescence emissions in the blue range by dioxasilirane and silylene structures and in the UV range by a pair of silylene centres. The latter emission is effectively pronounced when heated in vacuum as also our synthesis by SPS was performed in a strong vacuum environment. These temperature dependence is further studied in detail below.

Figure 4 (top) shows the RL spectrum of the SiO₂ glass sample prepared by the SPS, measured at 150 K as an example. As

Fig. 2. RL spectra of SiO₂ glass prepared by SPS and c-SiO₂ as a reference.

Fig. 3. RL spectra of SiO₂ glass prepared by SPS at low temperatures. The RL was induced by X-rays (40 kV).

Fig. 4. RL of SiO₂ glass sample at low temperatures. The RL spectrum can be approximated by two Gaussians (top). The RL intensities of two Gaussian components vary depending on the temperature (bottom). The broken lines are guide to eye.

illustrated in the figure, the emission spectrum can be approximated by a sum of two Gaussians with the peak wavelengths at 385 and 511 nm, which are derived by a least-square fitting procedure. Further, in Fig. 4 (bottom), the relative intensities of those two Gaussian peaks are depicted as a function of temperature. Here, the peak positions of Gaussians are fixed over the temperature range. As can be seen, as the temperature decreases, there is a relative increase in the 511 nm emission with respect to the 385 nm emission, which explains red-shift with decreasing temperature in Fig. 3. The Gaussian component at 511 nm increases as the sample is cooled, and the rate of increase is particularly drastic below 200 K. On the other hand, very interestingly, the Gaussian component at 385 nm does not simply monotonically decrease with decreasing temperature. Rather, it actually increases up to 150 K, followed by a sharp decrease until the lowest temperature of measurement range.

Based on these observations above, we suggest a possible interpretation of the temperature dependence as follows. Here, we consider two emission centres (as illustrated in Fig. 5) responsible for the UV (denoted as 1) and blue (denoted as 2) emissions as suggested by the two RL components in Fig. 4 as discussed above, and we assume that the lifetime of e^1 excited state is much longer than that of e^2 . Once X-rays are incident on the sample, electrons and holes are generated in the host matrix and the kinetic energies are transferred to the luminescent centres to excite. At low temperatures, since the e^1 state has long lifetime, the radiative transition ($e^1 \rightarrow g^1$) is less probable and the energy is transferred to the e^2 state via the e^1 state followed by the $e^2 \rightarrow g^2$ radiative transition to occur to emit at 511 nm. In addition, the faster lifetime of e^2 state means that $e^2 \rightarrow g^2$ radiative transition is more probable. As the temperature increases, the energy at the excited state e^1 exceeds the barrier ΔE_2 and the

Fig. 5. Suggested energy transfer mechanisms involved at different temperatures.

Fig. 6. RL decay profile of a SiO₂ glass sample prepared by SPS. The decay can be represented by two exponentials. The derived lifetimes are 1.2 and 11.3 ms.

energy is transferred to e^1 , which is followed by a radiative transition from the e^1 excited state to the g^1 to give the 385 nm light emission. As the temperature increases further, the lattice vibrational energy becomes comparable with the activation energy ΔE_1 for non-radiative transitions to occur via possibly the valence band of SiO₂ or some defect bands, which is observed as the quenching of the radiative transitions observed above 150 K. It is worth mentioning here that, to some extent, the $e^2 \rightarrow g^2$ radiative transition is still observed at room temperature although it is the transition from the lowest excited energy state. This fact can be explained by assigning a fast lifetime to the excited e^2 state.

We are aware that these arguments mentioned above can be only valid if our assumptions of having two excited states with different lifetimes and having a faster lifetime for the low lying energy state (e^2) are true. These assumptions are, in fact, supported by the lifetime measurement shown in Fig. 6. In this measurement, all the emission wavelengths of RL are integrated. The measured decay curve can be approximated by a double-exponential decay function, which indicates that there are two emission components with different lifetimes. The derived lifetimes are 1.2 and 11.3 ms.

Figure 7 shows the TSL glow curves of SiO₂ glass sample prepared by SPS and that of c-SiO₂. Our SiO₂ glass sample shows a relatively intense signal approximately at 160°C and above 300°C. In contrast, the crystalline sample shows a very

Fig. 7. TSL glow curves of SiO₂ glass and crystal. Fig. 8. TSL emission spectrum of SiO₂ glass prepared by spark plasma sintering.

small signal with the peak around 90°C. The results indicate that the glass sample accumulates much more amount of charges and stores at deeper trapping centres in comparison with the c-SiO₂. **Figure 8** shows the TSL emission spectrum of the SiO₂ glass measured at 160°C. With the use of our model above, the predominant emission seems to be due to the $e^1 \rightarrow g^1$ transitions, but a small portion of the $e^2 \rightarrow g^2$ emission is also observed. The presence of latter emission can be interpreted by the same explanation applied for the $e^2 \rightarrow g^2$ emission of RL at higher temperatures as mentioned above. One may wonder here why these transitions are still probable at high temperatures instead of non-radiative relaxation at high temperatures to go over the barrier ΔE_1 . The only explanation we have at this point is that these temperatures are unlikely to be sufficiently high for all the radiative transitions to be quenched. Further studies are required to understand the RL emission mechanism.

In **Fig. 9**, the TSL response of a SiO₂ glass sample against the delivered X-ray dose (air kerma) is demonstrated. Here, the TSL response is defined as an integrated glow peak signal at 160°C measured in our experimental setup. The heating rate used in this measurement is also 1°C/s. A linear response and wide dynamic range are clearly confirmed over the dose range 10⁰–10⁴ mGy. Despite the fact that 1 mGy is the lowest dose we could evaluate the sample, as our X-ray generator is not calibrated for lower dose, the sensitivity is reasonably high for personal dose moni-

Fig. 9. Dose response curve of SiO₂ glass prepared by spark plasma sintering.

toring applications (requiring μ Gy sensitivity) with some instrumentation work to optimize the reader for this particular detector. For applications that require a sensitivity at higher dose such as radiation therapy, the dynamic range should be sufficient as is. For these reasons, we strongly believe that our new type of SiO₂ bulk glass, synthesized by SPS, has excellent potential to be used as a TSL dosimeter.

4. Summary and conclusions

SiO₂ bulk glasses were synthesized by a newly developed process using SPS, and these were characterized for dosimeter applications. Although the samples does not include any intentional luminescent centres, they show mainly two separate emissions around 385 and 511 nm induced by X-rays. The former emission is due to a pair of silylene centres generated when sintered in vacuum and observed especially at room temperature. On the other hand, the latter emission is due to the presence of dioxasilirane and silylene which are typically present when heat-treated in air. In our sample, however, the latter emission is strongly pronounced at low temperatures below 200 K. Despite the presence of two luminescent centres, the near-UV emission occurs predominantly at elevated temperatures as a TSL after the glass sample is irradiated by X-rays. The TSL glow peak observed at 160°C increases linearly with increasing X-ray dose delivered, and the linearity has been confirmed over, at least 4 orders of magnitude, from 10⁰ to 10⁴ mGy.

Acknowledgement The authors gratefully acknowledge Admatechs Co. Ltd. for providing us SiO₂ glass nano-powders used in this research. This research was co-supported by a Grant-in-Aid for Scientific Research (A) (26249147), Grant-in-Aid for Research Activity start-up (15H06409), and Green Photonics Research from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese government (MEXT). It is also partially supported by the Adaptable and Seamless Technology transfer Program (A-STEP) by the Japan Science and Technology (JST) Agency, the Murata Science Foundation, and a cooperative research project of the Research Institute of Electronics, Shizuoka University.

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