Dosimetric properties in Cu-doped silica glasses synthesized by the spark plasma sintering method

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We synthesized SiO2 glasses doped with various concentrations of Cu (0.001, 0.005, 0.01, and 0.05 mol %) by the spark plasma sintering (SPS) method, and investigated optical, scintillation, and dosimetric properties. The Cu-doped samples indicated photoluminescence (PL) due to the 3d10–3d4s1 transition of Cu+ at around 500 nm under an excitation at 270 nm. The 0.005 % Cu-doped sample showed the highest PL quantum yield (QY) among the present samples, and the QY was 34 %. The decay time constants ascribed to the PL from Cu+ were 47–52 and 121–124 µs. The scintillation and thermally-stimulated luminescence (TSL) peaks were observed to be due to Cu+ as well as PL. The TSL glow curves of all the samples showed two glow peaks around 130 and 300 °C. In TSL dose response functions, the 0.005 and 0.01 % Cu-doped samples showed detection limit of 0.1 mGy.

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

1. Introduction

Ionizing radiation detectors using luminescent materials have been utilized in industrial and scientific fields such as medical, security, personal dose monitoring, and environmental monitoring. Such materials are mainly sorted to two types of scintillators and dosimetric materials. Scintillators convert energy of ionizing radiations into a large amount of low energy photons immediately. When ionizing radiations interact with scintillators, a lot of secondary electrons are generated and directly transported to emission centers, and then scintillators show a luminescence via a recombination at luminescence center. In contrast, dosimetric materials temporally store a part of radiation energy as a form of electrons and holes captured at trapping centers. The electrons or holes are released by a stimulation of heat [thermally stimulated luminescence (TSL)] or light [optically stimulated luminescence (OSL)]. and then recombine at emission centers with a luminescence. The emission intensity depends on the radiation dose accumulated for a certain period of time. Hence, the luminescent materials that exhibit TSL or OSL can be used as radiation detectors such as personal dosimeters and imaging plates.11)

SiO2 glass is attractive material for dosimetric applications. Because of its relatively light elements and low density, it is comparable to human tissue in terms of the interaction probability with high-energy radiations. Ideally, dosimetric material does not require numerical corrections after the measurements of TSL or OSL because the response to incident radiation energy is similar to that of human tissues. However, the general melt quenching method may not be applicable to SiO2 glass due to the very high softening temperature of SiO2 (1700 °C).12) Actually, such a high temperature cannot be reached by general crucibles and electric furnaces. The spark plasma sintering (SPS) method solves this problem because the sintering temperature can be increased to high temperatures (> 1000 °C) in a short time and the materials can be synthesized at lower sintering temperature.

Up to now, our research group has examined radiation-induced luminescence properties of SiO2 glasses doped with Eu and Ce prepared by the SPS method, and they showed preferable properties for radiation detectors.13),14) In particular, the Eu-doped SiO2 glasses showed a high sensitivity of 0.01 mGy which was higher than that of commercial dosimeters. However, the stable supply of rare-earth elements has become a major issue. Thus, we have also focused on the emission center elements other than rare-earth elements and reported the dosimetric properties of SiO2 glasses doped with ns2 ions such as Tl and Sn.15),16)

In this work, Cu-doped SiO2 glasses were prepared by the SPS method, and their dosimetric properties were evaluated. In general, transition metal ions exhibit efficient luminescence mainly due to 3d–3d transitions. Among them, the 3d10–4s3d6 transition of Cu+ exhibits luminescence in the blue to green regions. The luminescence wavelength of Cu+ is suitable for the wavelength sensitivity of conventional photomultiplier tubes, which is...
a desirable property for radiation detectors. Therefore, we have focused on Cu\(^+\) ions as a dopant for the luminescence materials.

2. Experimental

SiO\(_2\) glasses doped with different concentrations of Cu ions (0.001, 0.005, 0.01, and 0.05 mol %) were synthesized by the SPS method using the sintering furnace (Sinter Land LabX-100). The detailed condition on sintering was explained in our past research.\(^{14}\) SiO\(_2\) nano-sized powder (99.9\%, Admatechs) and Cu\(_2\)O powder (99\%, Kojundo Chemical Laboratory co.) were used as raw powder materials. After sintering, the glass samples were optically polished, and these thicknesses were adjusted to 1.7 mm.

X-ray diffraction (XRD) patterns were measured to confirm that obtained samples were amorphous by MiniFlex 600 (RIGAKU). As optical properties, in-line transmittance spectra in the spectral range from 200 to 700 nm were obtained using a spectrophotometer (V670, JASCO). Photoluminescence (PL) excitation/emission contour maps and PL quantum yields (QYs) were measured using a Quantaurus-QY (C11347, Hamamatsu Photonics). Measurements of PL decay curves were performed by a Quantaurus-\(\theta\) (C11367, Hamamatsu Photonics). The X-ray-induced scintillation spectra were measured by using our laboratory-made setup, and the detail information was described in a previous report.\(^{20}\)

As TSL properties, the measurements of TSL glow curves were done using a TSL reader (TL-2000, Nanogray Inc.) with the heating rate of 1 °C/s.\(^{21}\) We measured TSL spectra using a CCD-based spectrometer (QE Pro, Ocean Optics) and a ceramic heater system (SGR-SHO-A, Sakaguchi).\(^{22}\) After the samples were irradiated by X-rays, the TSL spectra and glow curves were measured. In order to confirm TSL dose responses, the irradiation dose was changed by the tube current (0.052–5.2 mA), the irradiation time (6–60 s), and the distance from the X-ray source (0–82 cm). The tested dose range was from 0.01 to 100 mGy, which was confirmed by an air-filled ionization chamber (Model 30013, PTW), and the values of dose refer to dose in air at the entrance of the sample.

3. Results & discussion

Figures 1(a) and 1(b) shows photographs of the glass samples under room light and UV lamp, respectively. All the samples had a diameter of 10 mm, and thickness of 1.7 mm after polishing as described above. The samples are arranged from left to right in an ascending order of the Cu-concentration (0.001, 0.005, 0.01, and 0.05 mol %). With increasing the Cu-concentration, the color of the samples gradually changed from colorless to reddish purple. Under UV lamp at 254 nm, all the samples exhibited luminescence of the blue-green color.

Figure 2 shows the XRD patterns of the glass samples. The measured XRD patterns of all the samples included only the halo peak at the range of 10–40 degrees and no crystalline phases. Hence, it could be concluded that all the samples were amorphous state although these were synthesized below the melting point of SiO\(_2\).

In-line transmittance spectra of the glass samples are represented in Fig. 3. The 0.001 and 0.005 % Cu-doped samples showed a transmittance of approximately 80 % in the range from 300 to 700 nm. With increasing the Cu-concentration, the overall transmittance became remarkably lower, and it was consistent with the appearance of the samples. According to the previous study, SiO\(_2\) glasses prepared by the SPS method include some amorphous microparticles.\(^{16}\) Thus, this low transmittance is possibly due to the increase of some scattering center such as grain boundaries among amorphous particles. As the overall transmittance decreased with increasing Cu-concentration, scattering may make the TSL inside the sample undetectable and reduce the intensity of the TSL. The transmittance spectra indicated an absorption bands at around 270 nm. We attribute this absorption band to the 3d\(^{10}\)–3d\(^{9}\)4s\(^1\) transition of Cu\(^+\) ions since the similar features were previously reported.\(^{23}\)–\(^{25}\) Moreover, the 0.01 and 0.05 % Cu-doped samples showed another absorption band near...
590 nm, and this absorption band is considered to be due to $2E_g \rightarrow 2T_g$ transition of Cu$^{2+}$.\(^{26,28}\)

**Figure 4** illustrates the PL excitation/emission contour map of the 0.005 % Cu-doped sample. The sample showed an intense emission at around 500 nm under an excitation at 270 nm. The excitation wavelength agreed well with the absorption wavelength in in-line transmission spectra, and these spectral features are typical for the $3d^{10} \rightarrow 3d^{9}4s^1$ transition of Cu$^{+}$.\(^{23,24}\) Thus, it is reasonable to consider that this emission is due to $3d^{9}4s^1 \rightarrow 3d^{10}$ transition of Cu$^{+}$.\(^{29}\)

**Figure 5** shows the PL decay curves of the glass samples monitored at 500 nm upon the 260 nm excitation. Dotted line represents a fitting function.

**Table 1. PL decay time constants**

| Cu-concentration | 1st (µs) | 2nd (µs) |
|------------------|----------|----------|
| 0.001 %          | 47       | 121      |
| 0.005 %          | 52       | 124      |
| 0.01 %           | 48       | 122      |
| 0.05 %           | 48       | 122      |

**Figure 6** shows X-ray-induced scintillation spectra. The irradiation dose is 0.6 Gy.

**Figure 7** illustrates the TSL glow curves of the glass samples measured after X-ray irradiation of 1 Gy. Two levels ($T_{2g}$ and $T_{1g}$) because the Cu forms the distorted tetrahedral sites. The first and second components of the PL decay time constants are considered to be assigned to the emission transitions from the triplet states $T_{2g}$ and $T_{1g}$ to the $1A_{1g}$ ground state.\(^{29}\)

**Figure 6** shows X-ray-induced scintillation spectra. The irradiation dose is 0.6 Gy. A broad scintillation peak appeared at around 500 nm in all the samples. The 0.005 % Cu-doped sample exhibited the highest scintillation intensity among the samples. In the samples doped with Cu more than 0.01 %, the scintillation intensity decreased, and the trend is same to that of PL $Q_Y$s. The scintillation peak seemed to be due to the $3d^{9}4s^1 \rightarrow 3d^{10}$ transition of Cu$^{+}$ since its emission wavelength was the same as that of PL.

**Figure 7** illustrates the TSL glow curves of the glass samples after irradiation of 1 Gy. All the samples showed two glow peaks around 130 and 300 °C regardless of Cu-concentration. The shape of the glow curve was similar to that of the non-doped SiO$_2$ glass prepared by the SPS method.\(^{30}\) Moreover, the change in TSL intensity with regards to the Cu-concentration was consistent with that in the $Q_Y$s. Thus, it was suggested that no new trapping centers generated in SiO$_2$ by Cu-doping. On the other
hand, the TSL intensity of the 0.01% Cu-doped sample was higher than that of the 0.001% Cu-doped sample although the QY of the 0.01% Cu-doped sample was lower than that of the 0.001% Cu-doped sample. In general, the TSL intensity depends on not only the emission efficiency (QY) but also energy transportation efficiency. Hence, one possible interpretation for this is that the energy transportation efficiency from the host to emission center increased by increasing Cu-concentration. In addition, as the overall transmittance decreased with increasing Cu-concentration, scattering may make the TSL inside the sample undetectable and reduce the intensity of the TSL.

Figure 8 presents the TSL spectra of the glass samples stimulated at around 130 °C which is the temperature with the strongest TSL intensity after X-ray irradiation of 5 Gy. A broad peak appeared at around 500 nm in all the samples. The spectra were identical to the shape of the PL and scintillation spectra, this luminescence would be due to Cu2+. Figure 9 exhibits the TSL dose response functions. Here, the vertical axis shows the integrated TSL intensity of glow curves in a temperature range from 50 to 490 °C. Among the present samples, the 0.005 and 0.01% Cu-doped samples showed the highest sensitivity with the dynamic range from 0.1 to 1000 mGy. Although this sensitivity is inferior to those of SiO2 glasses doped with Eu, Tl, and Sn, this is equivalent to that of commercial dosimeter products.31) It should be noted that the emission longer than 520 nm was not detected in the TSL glow curve measurements (Fig. 7) due to the thermal-radiation cut filter equipped in the instrument. Although the present investigations were done using a common commercial TSL reader, the sensitivity would be improved by using an optimized reader setup in order to detect luminescence in overall wavelength.

4. Conclusion

We investigated the optical, scintillation, and dosimetric properties of SiO2 glasses doped with different concentrations of Cu ions synthesized by the SPS method. XRD patterns confirmed that all the samples were the amorphous state without the crystalline phase. In all the case of PL, scintillation, and TSL, the Cu-doped samples showed the emission peak derived from the 3d10→3d4s1 transition of Cu2+ at around 500 nm. In addition, all the samples showed two TSL glow peaks around 130 and 300 °C. In the TSL dose response functions, 0.005 and 0.01% Cu-doped samples showed linearly response from 0.1 to 1000 mGy which comparable some commercial products.

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