Optically- and Thermally-Stimulated Luminescences of Ce-doped SiO₂ Glasses Prepared by Spark Plasma Sintering

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Abstract: Rare-earth doped phosphors have been used in many applications including radiation measurements. In the latter applications, the radiation photons are converted to light so that we can indirectly detect the radiation using a conventional photodetector. In this work, we have prepared and characterized a Ce-doped SiO₂ glass for dosimeter applications. Unlike conventional techniques such as sol-gel synthesis, the sample was prepared by spark plasma sintering. Although the PL emission seems to be only from the Ce³⁺ ions in the structure, due to the X-ray induced luminescence, we have also observed optically-stimulated luminescence (OSL), and thermally- stimulated luminescence (TSL), owing to a pair of silylenes and a set of dioxasilirane and silylene in addition to Ce³⁺. We have measured the detector response vs irradiation dose for both the OSL and TSL. The detector response in both cases is linear over the dose range from at least 1 mGy to 2 Gy. Particularly, the sensitivity of TSL is so high that it should be considered to be a good candidate for practical applications.

Keywords: SiO₂ glass
Cerium
Optically-stimulated luminescence
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1. Introduction

Rare-earth doped phosphors have found practical applications in a number of areas. In radiation measurements, such materials are used in order to convert incident radiation to light so that the radiation is indirectly detected using a conventional photodetector. Examples of applications include computed radiograph imaging plates [1], scintillators [2], and dosimeters [3]. In computed radiography and dosimeter applications, *optically stimulated luminescence* (OSL) [4] and *thermally stimulated luminescence* (TSL) [5] are common phenomena which occur in selected phosphors when they interact with ionizing radiations, and these are applied by means of measuring the radiation dose accumulated in the phosphor. In these processes, a single incident radiation photon ionizes the host material of phosphor, generates an energetic primary electron, which then creates thousands of electron-hole pairs within a volume of several tens nm³. Some of these charges then recombine instantly to emit scintillation light, and others are temporarily trapped by localized shallow centres or stably trapped by deep centres. The charges trapped at shallow centres may be freed back again by phonons until they are either trapped by deep centres or recombine. The charges trapped at deep centres are stable and may not be detrapped unless the phosphor material is heated at elevated temperatures or exposed to light. Eventually, the detrapped charges, as in other cases, recombine at luminescent centers to emit light. Here, the emitted light by optical stimulation is referred to OSL while that emitted by thermal stimulation is referred to TSL. Since the OSL and TSL intensities are in general proportional to the incident radiation dose accumulated, these can be used as a measure of radiation dose. Another class of dosimeters using phosphor materials may be referred to a radiation-induced effect called *radiophotoluminescence* (RPL). In RPL materials, the photoluminescence (PL) emission intensity increases in proportion to the radiation dose delivered. Common RPL materials are an Al₂O₃:Mg,C single crystal [6,7] and Ag-doped phosphate glasses [8,9], which are commercial products of Landauer group and Chiyoda Technol Corp., respectively. Recently, Sm-doped glasses and glass-ceramics have been demonstrated for use as an RPL phosphor in high-resolution and large-dose dosimetry applications [3,10–14].

In this work, we have synthesized Ce-doped SiO₂ glass prepared by a spark plasma sintering (SPS) technique and studied its dosimeter properties. SiO₂ glass is an interesting host material as a dosimeter. Since it consists of relatively light elements and the density is low, the material is equivalent to tissue in terms of the interaction 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 tissue so that no numerical corrections are needed after the measurement. Moreover, in radiation therapy, dosimeter materials are preferred to be as transparent as possible against the incident radiation, particularly when one would like to measure the dose upstream of the patient. Otherwise, the radiation is blocked by the detector and does not make it to the target object. Earlier studies [15] have reported the TSL properties of Ce-doped SiO₂ glasses in detail for the aim to understand the possible defect centres in SiO₂ [16], affecting the scintillation properties. Here, the sample was prepared by sol-gel technology, which is a common synthesis technique to prepare silicate glasses by low temperature reactions. A common melt-quenching technique may not be applicable because of the high melting point of SiO₂ (~1800 °C); for example, common electric furnaces and crucibles are not capable of reaching such high temperatures. In this respect, recently, a new technique to produce a SiO₂ glass using SPS was introduced [17]. SPS is a ceramic processing technique in which high-voltage pulses are passed through the compound to be sintered by the consequent joule heat, while applying a high pressure of several tens to hundreds MPa [18,19]. This technique allows us to raise the sintering temperature very high (above 1000 °C) in a short time (a few minutes), and it also allows lower sintering temperature than usual ceramic sintering processes.

2. Experimental Procedure

We have synthesized a Ce^{3+} -doped SiO_2 glass sample by a spark plasma sintering technique. SiO_2 (99.9 %) glass nano-sized powder (SO-E1, Admatechs) and CeO_2 (99.99 %) powder was homogeneously mixed with the weight ratio of 100:1, respectively. The total mass of the mixture was 0.5 g. The mixture was then loaded in a graphite die and sandwiched and sealed by two graphite punches. The inner diameter of graphite die as well as the outer diameter of punches are approximately 10 mm. This graphite assembly was covered by carbon fabric in order to minimize a possible heat gradient inside the die and ensure that the sample inside was heated homogeneously over the volume. This entire assembly was next loaded to the sintering furnace (La-BOX110, NJS). The sintering temperature was increased from 600 °C to 1300 °C at the rate of 10 °C/min and held for 120 min while applying a pressure of 70 MPa. The sintering was performed under vacuum.

The synthesized sample was further characterized using the following equipment. The PL spectrum was measured using 265-nm excitation light, which was produced with a combination of Xenon lamp (LAX-C100, Asahi Spectra) and an interference band-pass filter (VPF-25C-10-12-26500, OptoSigma). The consequent PL emission light was then collected by an optical fibre (P400-2-UV/VIS, Ocean Optics) and guided to the spectrometer (QW65Pro, Ocean Optics) to measure the spectrum. For X-ray induced luminescence (XL) measurement, the sample was irradiated by X-rays generated by an X-ray tube (XRBOP&N200X4550, Spellman) equipped with a W anode target with a Be window. The consequent emission spectrum was measured in the same manner as the PL described above but using another spectrometer equipped with a Peltier-cooled CCD (DU920P-BU2NC, Andor) and diffraction grating (SR163i-UV, Andor). The details of the setup can be found elsewhere [20]. The OSL emission spectrum was measured using a spectrometer (Quantaaurus-Tau C11367, Hamamatsu) with a stimulation by 630-nm LED, and the OSL excitation spectrum was measured using a spectrofluorometer (FP-8600, JASCO). The TSL glow curve was measured using a reader (TL-2000, NanoGray) [21] with a heating rate of 1 °C/s. For the purposes of characterizing the sample as a dosimeter material, we need to ensure the dose delivered is well defined. The applied tube voltage was fixed to 40 keV while varying the tube current 0.052 – 5.2 mA so that the dose delivery rate is 10 – 1000 mGy/min. The dose rate was calibrated using an ionization chamber (30013, PTW), and the reported dose values are dose in air at the surface of the sample.

3. Results and Discussion

The synthesized sample has a disk shape with a diameter of approximately 10 mm with a thickness of 1 mm. It is colourless, but opaque and semitransparent. Typically, a Ce^{3+} -doped glass does not have any colour since the absorption band is commonly seen in the UV region. We think that the milky appearance arises from the Mie scattering by the inhomogeneity of the glass matrix. On one hand, in more common glass synthesis techniques such as melt-quenching and sol-gel techniques, such inhomogeneity is minimized during the melting or dissolution process. On the other hand, the SPS relies on a solid-state reaction in which the diffusion distance of impurities is much shorter. In order to effectively improve the homogeneity, the sample may be crushed, mixed, and sintered again, and this process may be repeated several times.

Fig. 1 shows the PL spectrum of $\text{SiO}_2\text{:Ce}^{3+}$ prepared by SPS. It has a single band shape with the peak at 400 nm with the full-width at half-maximum (FWHM) of approximately 56 nm. The lifetime of this emission was derived from the PL decay profile depicted in Fig. 2 by fitting the curve to a single exponential decay curve. The extracted decay time constant is 20.8 ns. In many Ce^{3+} -doped glasses, a PL band emission is observed in the UV-blue range, which is due to the transitions from the 5d excited state to the 4f ground state. Unlike intra 4f shell transitions commonly seen in luminescent rare earth ions, emission by Ce^{3+} is from the unshielded 5d excited state; therefore, the emission spectrum is strongly affected by the surrounding crystal field. Moreover, the transition is allowed by the selection rule; thus, the PL lifetime is relatively fast (in the order of ns– μ s) than that of 4f-4f transitions, which is usually in μ s–ms. In our case, since the spectral shape and position as well as the lifetime reasonably agree with the typical PL behaviour of Ce^{3+} emission reported in the literature, the origin of this PL emission is attributed to the 5d $\rightarrow$ 4f emissions of the Ce^{3+} ion.

Fig. 3 illustrates the XL emission spectrum of $\text{SiO}_2\text{:Ce}^{3+}$ glass prepared by SPS. Unlike the PL spectrum, the XL emission spectrum is much broader and has a number of features. In the figure, the spectrum is approximated by a convolution of five Gaussian functions. We think the strongest component at 400 nm due to the Ce^{3+} as seen in the PL spectrum. The origins of the rest of features appeared at longer wavelengths should be due to a pair of silylenes and a set of dioxasilirane and silylene [22–24].

Fig. 4 shows the OSL emission and stimulation spectra. The emission spectrum was measured with a stimulation at 630 nm. The emission spectrum may be approximated by three Gaussian functions. It is clearly seen that the emission spectrum is much broader than that of PL spectrum and rather similar to the XL spectrum. The component with the peak around 400 nm should be due to the emissions by Ce^{3+} ion as observed in the PL measurement, whereas the origins of the rest of components approximated should be related to a pair of silylenes. A set of dioxasilirane and silylene is known to show emission at longer wavelength, which is missing from the OSL emission spectrum. Note that the stimulation spectrum shows the highest value at the shortest wavelength, and it decreases as the stimulation wavelength increases. This shape of the spectrum is much alike the tail shape of the XL spectrum in Fig. 3. This fact implies that a set of dioxasilirane and silylene observed in XL at longer wavelengths may also act as charge trapping centres in which the trapped charges are optically stimutable. The OSL signal depends on the irradiation dose. Fig. 5 illustrates the dose response curve of the OSL from our Ce^{3+} -doped SiO_2 glass. The stimulation wavelength used here is 630 nm. It can be clearly seen that the OSL response is linearly proportional to the irradiation dose over the dose range from 1 mGy to 2 Gy.

Fig. 6 shows the TSL glow curve of Ce^{3+} -doped SiO_2 glass prepared by SPS. The sample was irradiated by X-rays with a dose of 1 Gy prior to the TSL measurement. It was found that the TSL is very strong, and a broad single peak was measured over the temperature range of approximately from 100 °C to 450 °C. Further, glow peak seems to be present above 500 °C, which is beyond the measurement range covered by the instrument. Fig. 7 shows the TSL emission spectrum measured at 250 °C, which is the temperature that the TSL signal is the strongest. As seen in the XL and OSL, it also seems like that the luminescent centres involved in the TSL processes are not only the Ce^{3+} ions but also a pair of silylenes and a set of dioxasilirane and silylene. The glow curve can be approximated by a sum of four Gaussian functions, and this indicates that there are at least four groups of charge trapping centres in which the trapped charges can be stimulated thermally to be freed and to eventually recombine at luminescent centres to emit light. Applying the initial rise method [5] to each of the Gaussians, the derived activation energies are 0.41, 0.71, 1.00, and 2.17 eV, respectively for the peaks from lower to higher temperatures. It should be noted here that latter value is significantly high to be stimulated by heat. A possible reason is that the fitting was done only for the tail portion of the peak; therefore, the estimation for this trapping centre may be

inaccurate. Fig. 8 illustrates the dose response curve of TSL. It is seen that the TSL response signal is linearly proportional to the irradiation dose over the range of measurement, from 1 mGy to 2 Gy. It should be pointed out here that 1 mGy is the lowest possible dose to irradiate in our current experimental setup, and above 2 Gy, the TSL signal was too strong for TSL reader to detect without saturating. We believe that it has a detection sensitivity comparable to that of commercial dosimeters, which allow us to measure as small as μGy . Fig. 9 demonstrates an X-ray image of integrated circuit obtained using the Ce^{3+} -doped SiO_2 sample. The electrode structure inside the package is clearly observed, and this also shows the capability to be used as a radiation imaging plate.

One may be interested in the origin of these radiation-induced luminescence (OSL and TSL). These phenomena are often seen as a result of radiative recombination of radiation-generated charges, which were trapped at localized centres but can be de-trapped by external stimulation (light for OSL and heat for TSL). Such trapping centres can be intrinsic defects, which are included as the sample was synthesized, or extrinsic defects, which were generated by irradiation. Optical transmittance was measured as a function of irradiation dose as shown in Fig. 10 to study any defect centres contributed to the above radiation-induced luminescence. Very strong absorption bands are present in the near-UV region, which are due to typical absorptions by $\text{Ce}^{3+/4+}$ ions. Other than the latter absorption, no particular features are observed. Furthermore, there is no significant difference caused by irradiation. Based on these experimental results, we think that there is no significant generation of defect (extrinsic) centres by irradiation so the OSL and TSL are based on intrinsic trapping centres. Further investigations are needed in order to understand the mechanisms in more detail.

5. Conclusion

We have synthesized a Ce^{3+} -doped SiO_2 glass by a spark plasma sintering technique and characterized the dosimeter properties in terms of OSL and TSL. The prepared sample looks opaque but semitransparent to light indicating that the sample includes a large number of defects causing Mie scattering. The PL characterizations indicated that Ce^{3+} ion is activated and shows a strong band emission in the UV-blue range. On the other hand, the XL emission spectrum suggests the presence of additional luminescent centres in the longer wavelength region, which are attributed to a pair of silylenes and a set of dioxasilirane and silylene. The OSL may be stimulating the charges trapped by a set of dioxasilirane and silylene. The TSL should be thermally stimulating those charges trapped at other centres since all the luminescent centres seen in XL are acting for TSL. Moreover, the OSL and TSL intensities are linearly proportional to the incident radiation dose at least over the range from 1 mGy to 2 Gy. Although the lower side of the dose range tested here was limited by the instrument available, it should easily have detection ability to much lower dose, particularly with TSL.

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List of Figures

Fig. 1 PL spectrum of $\text{SiO}_2\text{:Ce}^{3+}$ glass prepared by SPS. The inset is a 2D contour map of PL excitation vs. emission. The diagonal line is the excitation light measured by the detector.

Fig. 2 PL decay profile of $\text{SiO}_2\text{:Ce}^{3+}$ glass prepared by SPS. The decay curve is fitted by an exponential decay functions, $A \exp(t/\tau)$ where A is the amplitude, τ is the time constant, and t is the time in ns.

Fig. 3 XL spectrum of $\text{SiO}_2\text{:Ce}^{3+}$ glass prepared by SPS. The spectrum was approximated by a convolution of five Gaussian functions.

Fig. 4 Normalized OSL emission and stimulation spectra of $\text{SiO}_2\text{:Ce}^{3+}$ glass prepared by SPS. The emission spectrum was measured by a 630-nm stimulation while the stimulation spectrum was measured by monitoring the OSL signal at 440 nm. The black solid line is the total fit composed of three Gaussians.

Fig. 5 OSL signal as a function of X-ray dose delivered. The stimulation wavelength is 630 nm.

Fig. 6 TSL glow curve of X-irradiated $\text{SiO}_2\text{:Ce}^{3+}$ glass prepared by SPS. Activation energies estimated for each Gaussian deconvolution component are 0.41, 0.71, 1.00, and 2.17 eV. The delivered X-ray dose is approximately 1 Gy. The heating rate is 1 °C/s.

Fig. 7 TSL spectrum recorded at 250 °C. The delivered X-ray dose prior to the measurement is approximately 5 Gy. The spectrum was deconvoluted into four Gaussian functions.

Fig. 8 The integrated TSL as a function of delivered X-ray dose.

Fig. 9 X-ray image of an integrated circuit (IC) demonstrated using TSL of $\text{SiO}_2\text{:Ce}^{3+}$ glass prepared by SPS. The inset shows a photograph of the IC used. The heating temperature is ~250 °C.

Fig. 10 Optical transmittance spectra of $\text{SiO}_2\text{:Ce}^{3+}$ glass as a function of irradiation dose.

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