Sensors and Materials, Vol. 27, No. 3 (2015) 263–268
MYU Tokyo

S & M 1064

Photoluminescence and Scintillation Properties of SiO_2 Glass Activated with Eu^{2+}

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(Received October 10, 2014; accepted January 30, 2015)

Key words: scintillator, glass, photoluminescence, thermoluminescence, Eu^{2+} 5d-4f transition

The basic photoluminescence and scintillation properties of Eu-doped SiO_2 glass are reported. When UV light was excited to the glass, an intense blue emission band was observed owing to the $4f^6 5d\text{-}4f^7$ ($^8S_{7/2}$) transition of Eu^{2+} emission centers. The fluorescence quantum efficiency (QE) and the decay time of Eu^{2+} were calculated to be about 95% and 1230 ns, respectively. The 5d-4f emission band of Eu^{2+} also appeared in the 450 nm wavelength range in the X-ray-excited radioluminescence spectrum. By ^{241}Am α-ray-irradiated pulse height spectra, the relative scintillation light output was found to be about 110% compared with reference lithium silicate glass (GS20) scintillator.

1. Introduction

A scintillator converts the energy of an absorbed ionizing radiation, such as an X-ray or γ-ray radiation or a charged particle, into many low-energy (~eV) photons. The materials combined with photodetectors are used as radiation detectors in various field techniques, such as medical imaging, homeland security, oil-well logging and gas industry, and so on. Glass-based scintillators are generally significantly disadvantageous in terms of their light output compared with that of single-crystal and ceramic materials. The cause is known to be related to the presence of point defects acting as trap levels that limit the transfer efficiency of free electrons and holes from the host matrix to luminescent centers. The only commercial glass scintillator is Ce^{3+}-doped $^6Li_2O$-SiO_2-Al_2O_3-MgO glass for thermal neutron detection developed in 1960–1980s.[1,2] The lithium silicate glass showed high light yield, and it is well known that the production of glass with large size is very difficult and costly. To our knowledge, no new glass scintillators provided a higher performance than the lithium silicate glass since 2000. However, in recent studies, Ce^{3+}- and Pr^{3+}-doped SiO_2 glass samples were found to show

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excellent scintillation performance characteristics, such as high radioluminescence intensity and fast response, due to the 5d-4f transition of Ce^{3+} and Pr^{3+} ions.[3,4]

Thus, in this work, we evaluated the basic photoluminescence and scintillation properties of Eu-doped SiO_2 glass. Eu^{2+} ions are widely used as emission centers for phosphor materials in radiation detection systems because of their high fluorescence quantum efficiency and suitable emission wavelength for photodetectors, such as photomultiplier tubes, owing to the interconfigurational $4f^6 5d$-$4f^7$ ($^8S_{7/2}$) transition of Eu^{2+}.[5–11] From this evaluation, we the report optical transmittance, photoluminescence, fluorescence quantum efficiency, decay time, radioluminescence, scintillation light output, and thermoluminescence properties of the Eu-doped SiO_2 glass, and finally, we discuss the possibility of using such glass as a scintillation material.

2. Experimental Procedures

The 0.7% Eu-doped SiO_2 glass was prepared by a sol-gel method. The processes involved are reported in detail in ref. 4. The X-ray diffraction (XRD) patterns of the Eu-doped glass were recorded using a Rigaku Ultima IV-PXS diffractometer working with Cu-Kα radiation in a continuous scan mode from 3° to 90° of 2θ with a 0.02° sampling interval and a 2° min^{-1} scan rate. The optical transmittance spectrum of the Eu-doped glass was recorded on a JASCO V-670 spectrometer in the wavelength range from 190 to 2700 nm. The excitation-emission matrix at room temperature was demonstrated using a Quantaurus-QY (Hamamatsu) spectrometer based on Hamamatsu's established C9920 systems equipped with a xenon lamp, and a calibrated integrating sphere with a radius of 3.3 inches. The fluorescence photons from the Eu-doped glass were detected by a multichannel spectrometer through the side of the sphere. The fluorescence quantum efficiency (QE) was determined by the difference between the number of photons emitted as photoluminescence from the sample and that absorbed by the sample. The photoluminescence decay time profile was obtained by a Quantaurus-Tau (Hamamatsu) spectrometer at room temperature. In the measurement, a light-emitting diode (LED) wavelength of 365 nm was used as an excitation source. The radioluminescence spectrum measurement of the Eu-doped SiO_2 glass was performed at room temperature under X-ray irradiation. Figure 1 illustrates the measurement setup. The X-ray source was the original X-ray generator (XRB80P Monoblock, Spellman), which was equipped with a tungsten target. The generator was supplied with a voltage of 80 kV and a current of 2.5 mA. The spectra were measured using a DU920P CCD spectrometer (Andor), which was cooled down to 210–230 K by a Peltier module. The scintillation light was sent to the CCD through a 1.5 m optical fiber to prevent the direct X-ray irradiation of the CCD. The thermoluminescence (TL) glow curve of the Eu-doped glass was measured in air atmosphere with a TL-2000 reader manufactured by Nanogray Inc. A linear heating rate of 1 $K \cdot s^{-1}$ was used to record the glow curves, and the TL intensities were recorded in the temperature range of 320–700 K. The scintillation light output of the Eu-doped glass was evaluated using the α-ray-irradiated pulse height spectra. A ^{241}Am sealed source was used as an α-ray source (E_α = 5.5 MeV). The Eu-doped glass was attached to a window of the R7600U (Hamamatsu) photomultiplier tube (PMT) with

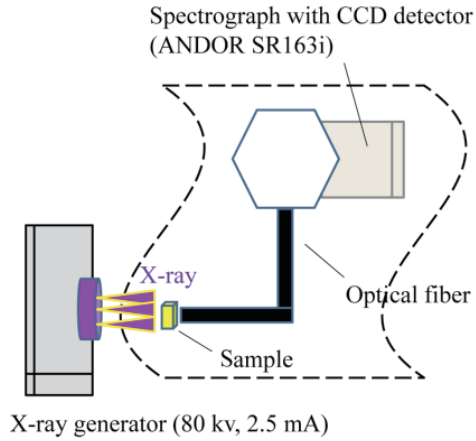


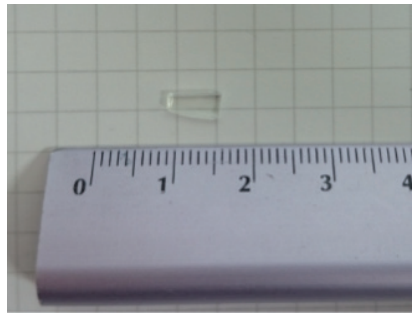
Fig. 1. (Color online) Experimental setup of X-ray-excited radioluminescence spectrum measurement.

optical grease (OKEN 6262A). The scintillation light from the glass was measured by the PMT supplied with a voltage of 600–650 V, the signals were fed into a preamplifier (ORTEC 113) and a shaping amplifier (ORTEC 572), and a histogram was obtained with a multichannel analyzer (Amptec 8000A). The optimum shaping time for the Eu-doped glass was 6 μs according to the results of the photoluminescence decay time profile measurements. The scintillation light output of the Eu-doped glass was compared with that of the Ce^{3+}-doped lithium silicate glass scintillator (GS20, Saint-Gobain K.K.) from the α-ray peak channel number and QE of PMT.

3. Results and Discussion

Figure 2 shows the as-prepared Eu-doped glass. The glass was cut and polished for the measurements. The glass is colorless and transparent under visual observation, which corresponds well to its transmittance spectrum measurement in a later section. The XRD patterns of the Eu-doped glass are illustrated in Fig. 3. The XRD patterns show broad bands without specific diffraction peaks. This clearly indicates the amorphous nature within the resolution limit of the XRD instrument. The ultraviolet-infrared range transmittance spectrum of the Eu-doped glass is displayed in Fig. 4. Considering the band gap energy of the SiO_2 glass (E_g ~9 eV), the red shift of the absorption edge may be caused by the intense absorption bands of Eu ions, such as like Eu^{2+} and Eu^{3+}. In infrared regions, no absorption bands related to OH groups were observed.

Figure 5 shows the excitation-emission matrix of the Eu-doped glass. In the matrix, an intense emission band was observed at 450 nm under excitation at 350–400 nm. The emission band can be ascribed to the allowed $4f^6 5d\text{-}4f^7$ ($^8S_{7/2}$) transition of Eu^{2+}.[12] In addition, other emission peaks, such as that formed by the $4f^6\text{-}4f^6$ ($^5D_0\text{-}^7F_{1,2}$) transition of Eu^{3+}, were absolutely not observed. This clearly indicates that Eu ions exist as Eu^{2+}



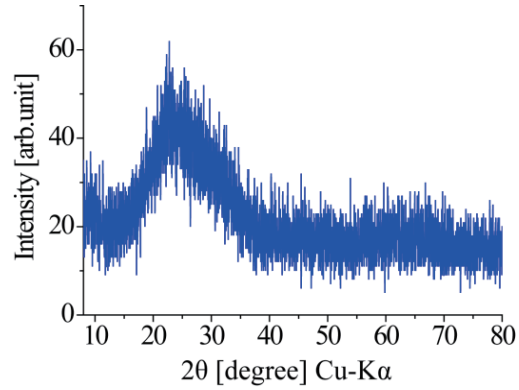
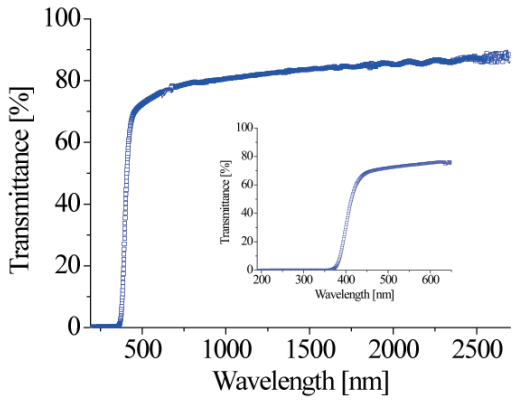


Fig. 2 (left). (Color online) View of polished Eu-doped SiO_2 glass.
Fig. 3 (right). (Color online) XRD patterns of Eu-doped SiO_2 glass.



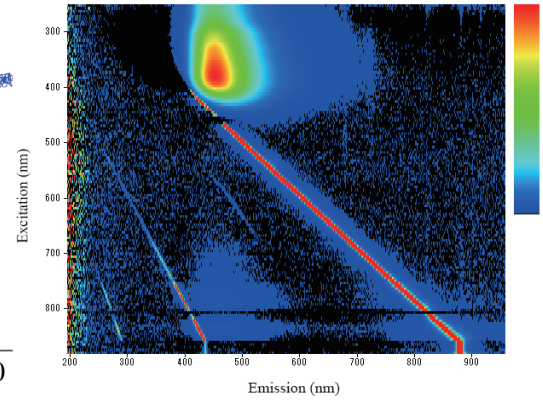


Fig. 4 (left). (Color online) Transmittance spectrum of Eu-doped SiO_2 glass in UV-NIR wavelength region.
Fig. 5 (right). (Color online) Excitation-emission matrix of Eu-doped SiO_2 glass.

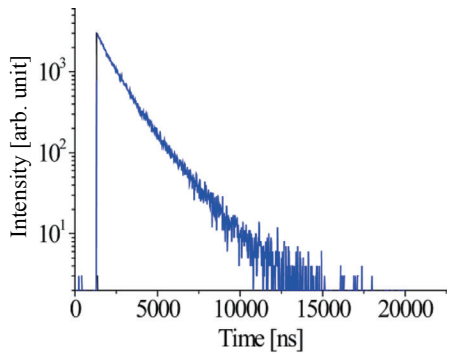
inside the glass matrix. The fluorescence QE of Eu^{2+} was estimated to be approximately 95%. The photoluminescence decay time profile is displayed in Fig. 6. The calculated decay time was obtained as about 1300 ns by single exponential equation fitting through the deconvolution of the instrumental response.

Figure 7 shows the X-ray-excited radioluminescene spectrum of the Eu-doped glass. The spectrum exhibited only the intense blue emission band of Eu^{2+} as photo-excited luminescence. Thus, it is clear that some of the electrons and holes generated by ionizing the glass with X-rays recombine through the Eu^{2+} emission centers. To understand more the transfer process of the electrons and holes, the TL glow curve was also recorded, as shown in Fig. 8. By evaluation, the Eu-doped glass was found to show a broad glow peak with a center at 400 K. This may be due to the presence of the continuous trap-

level distributions of the electrons and holes. The trap levels result in the nonradiative recombination between the trapped holes and electrons and the decrease in the light output of the scintillation material.

The α-ray-irradiated pulse height spectra of the Eu-doped glass are displayed in Fig. 9. In the spectra, an α-ray peak of the Eu-doped glass was successfully detected at 300 ch, while that of the GS20 glass was observed at 270 ch. The QEs of both samples at the respective emission wavelengths are similar (~45%). Thus, the light output of the Eu^{2+}-doped SiO_2 glass was found to be approximately 110% compared with that of the GS20 glass scintillator.

In this study, we obtained a new glass scintillator with higher light output than a GS20 commercial scintillator based on SiO_2 glass. Thus, our study is expected to contribute to the development of next-generation glass scintillators. In future work, we will optimize the synthesis process and the composition of the host glass matrix to reduce the numbers of electron and hole traps related to structural defects and some impurities.



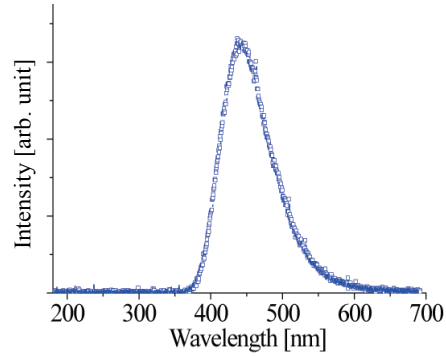
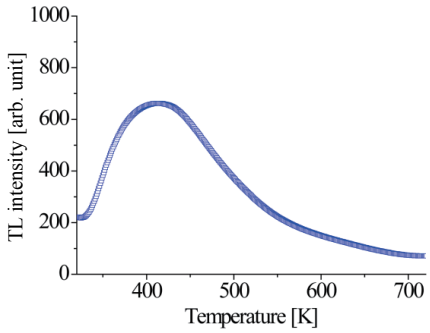


Fig. 6 (left). (Color online) Photoluminescence decay time profile of Eu-doped SiO_2 glass.
Fig. 7 (right). (Color online) X-ray-excited radioluminescence spectrum of Eu-doped SiO_2 glass.



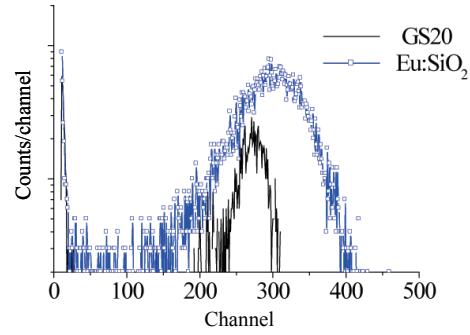


Fig. 8 (left). (Color online) TL glow curve of Eu-doped SiO_2 glass.
Fig. 9 (right). (Color online) α-ray-irradiated pulse height spectra of Eu-doped SiO_2 glass and GS20 glass scintillator.

4. Conclusions

The photoluminescence and scintillation properties of Eu-doped SiO_2 glass were evaluated. The Eu-doped glass showed a high fluorescence QE (~95%) due to the 5d-4f transition of Eu^{2+}, and the decay time was about 1230 ns. In the radioluminescence spectrum under X-ray excitation, the Eu^{2+} 5d-4f emission band at 450 nm was observed as the photoluminescence one. From the ^{241}Am α-ray-irradiated pulse height spectra, the scintillation light output of the Eu-doped glass was higher than that of the GS20 glass commercial scintillator.

Acknowledgements

This work was partially supported by the SPRITS program, Kyoto University, and the Cooperative Research Project of Research Institute of Electronics, Shizuoka University

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