

# Optical Properties in the Visible Luminescence of $\text{SiO}_2\text{:B}_2\text{O}_3\text{:CaO:GdF}_3$ Glass Scintillators Containing $\text{CeF}_3$

J. M. PARK

*Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup 56212, Korea*

H. J. KIM\* and Sujita KARKI

*Department of Physics, Kyungpook National University, Daegu 41566, Korea*

J. KAEWKHAO and B. DAMDEE

*Center of Excellence in Glass Technology and Materials Science (CEGM),  
Nakhon Pathom Rajabhat University, Nakhon pathom 73000, Thailand and  
Physics Program, Faculty of Science and Technology,  
Nakhon Pathom Rajabhat University, Nakhon pathom 73000, Thailand*

S. KOTHAN and S. KAEWJAENG

*Department of Radiologic Technology, Faculty of Associated Medical Sciences,  
Chiang Mai University, Chiang Mai 50200, Thailand*

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$\text{CeF}_3$ -doped silicaborate-calcium-gadolinium glass scintillators, with the formula  $10\text{SiO}_2\text{:}(55-x)\text{B}_2\text{O}_3\text{:}10\text{CaO:}25\text{GdF}_3\text{:}x\text{CeF}_3$ , were fabricated by the melt-quenching technique. The doping concentration of the  $\text{CeF}_3$  was from 0.00 mol% to 0.20 mol%. The optical properties of the  $\text{CeF}_3$  doped glass scintillators were studied by using various radiation sources. The transition state of the  $\text{CeF}_3$ -doped glass scintillators studied by using the absorption and photo-luminescence spectrum results. The X-ray, photo, proton and laser-induced luminescence spectra were also studied to understand the luminescence mechanism under various conditions. To understand the temperature dependence, the laser-induced luminescence and the decay component of the  $\text{CeF}_3$ -doped glass scintillator were studied while the temperature was varied from 300 K to 10 K. The emission wavelength spectrum showed from 350 nm to 55 nm under various radiation sources. Also the  $\text{CeF}_3$ -doped glass scintillator have one decay component as 34 ns at room temperature.

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## I. INTRODUCTION

$\text{CeF}_3$ -doped glass and glass ceramic scintillators of various shapes and large volumes can be easily fabricated at a low cost [1].  $\text{Ce}^{3+}$  is a rare-earth material with a  $4f\text{-}5d$  transition. Thus, the  $\text{CeF}_3$ -doped glass scintillator has a broad emission wavelength from 300 nm to 600 nm, and a fast decay time of a few nanoseconds [2, 3]. The  $\text{CeF}_3$ -doped glass scintillator also has high resistance to harsh environmental conditions such as a high radioactivity dose, moisture, and impact [4]. Thus, the  $\text{CeF}_3$ -doped glass and glass ceramic scintillators have the potential to replace single-crystal scintillators in nuclear

and high-energy physics, medical imaging, and homeland security applications [4,5].

The energy transfer from  $\text{Gd}^{3+}$  ions to  $\text{Ce}^{3+}$  ions has already been reported in many previous papers [6, 7]. The  $\text{Gd}^{3+}$  ion has many sharp band gaps that are placed between the  $^8\text{S}_{7/2}$  and  $^6\text{I}_J$  multiplet states [8,9]. The excitation energy from the radiation source is captured by the  $\text{Gd}^{3+}$  ions, and then the many sharp band gaps of the  $\text{Gd}^{3+}$  ions efficiently transfer the energy to the  $\text{Ce}^{3+}$  ion. Finally,  $\text{Ce}^{3+}$  emits the scintillation light. We have already fabricated and studied the luminescence properties of the glass scintillators with the composition of  $25\text{Gd}_2\text{O}_3\text{:}10\text{CaO:}10\text{SiO}_2\text{:}(55-x)\text{B}_2\text{O}_3\text{:}x\text{CeF}_3$  [1]. Since the oxide ( $\text{Gd}_2\text{O}_3$ ) has a higher bond length than the fluoride ( $\text{GdF}_3$ ), the luminescence properties of the fluoride could be better than the oxide in many cases

\*E-mail: hongjoo@knu.ac.kr; Fax: +82-53-939-1259

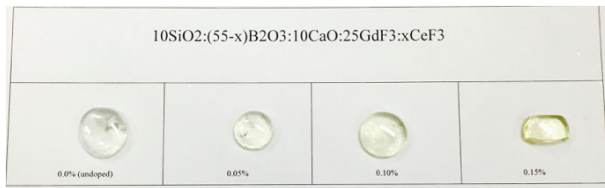


Fig. 1. (Color online)  $\text{CeF}_3$ -doped SBCG glasses.

[10, 11]. Thus, we have fabricated the  $\text{CeF}_3$ -doped silicaborate-calcium-gadolinium glass (SBCG:Ce glass) to replace  $\text{Gd}_2\text{O}_3$  with  $\text{GdF}_3$  and studied the luminescence properties. The SBCG:Ce glasses have luminescence properties in the visible range and a very fast decay times of 34 ns. We studied the optical properties in the visible luminescence of the SBCG:Ce glasses by using UV laser, X-rays, and proton sources. We also studied the luminescence properties at low temperatures.

## II. EXPERIMENTS

### 1. Preparation Of the Glass Scintillators

SBCG:Ce glasses were fabricated by using the melt-quenching technique. We doped the high-purity cerium fluoride ( $\text{CeF}_3$ ) in the base material of high-purity silicon oxide ( $\text{SiO}_2$ ), boric acid ( $\text{H}_3\text{BO}_3$ ), calcium oxide ( $\text{CaO}$ ), and gadolinium fluoride ( $\text{GdF}_3$ ). These chemical materials were melted at  $1400^\circ\text{C}$  in a high-purity alumina crucible, and then they were quenched at room temperature. After that, the glasses were annealed at  $500^\circ\text{C}$  for 3 hours to reduce the thermal strain [1]. The glass composition ratio was  $10\text{SiO}_2:(55-x)\text{B}_2\text{O}_3:10\text{CaO}:25\text{GdF}_3:x\text{CeF}_3$ , where  $x$  is 0.0, 0.05, 0.10, and 0.15 mol%. Figure 1 showed the SBCG:Ce glasses.

### 2. Measurement Systems

In order to study the luminescence properties, the SBCG:Ce glasses were irradiated with photons, laser, X-ray and 100 MeV proton beams. The absorption spectra were measured by using a V-650 spectrometer (JASCO Co.) at room temperature.

The photo-induced excitation and emission spectra were measured by using a xenon lamp (HORIBA Jobin Yvon Inc. Fluolog-3 Model FL3-21). The xenon source was placed at  $90^\circ$  from a photo multiplier tube (Jobin Yvon Inc., R928P), and the SBCG:Ce glass was located at  $45^\circ$  from the xenon source [12].

The laser-induced emission spectra were measured by using a pulsed laser source (CNI, 266 nm UV solid-state laser, MPL-F-266) with an excitation wavelength

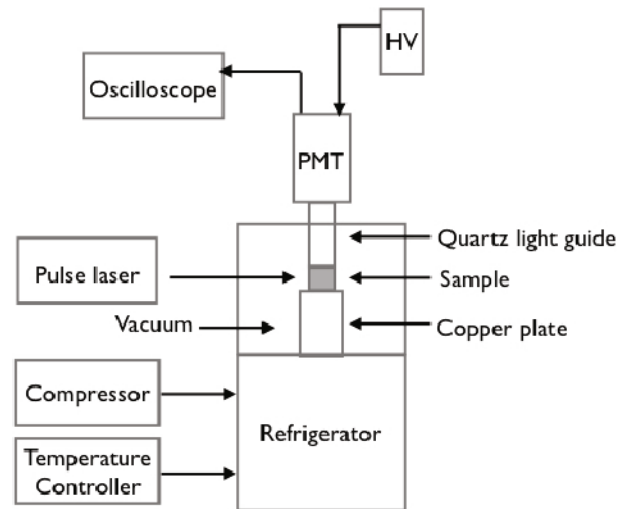


Fig. 2. Photograph of the experimental setup for the measurement of the decay component while temperature was changed.

of 266 nm, pulse width of 10 ns, and repetition rate of 6.06 kHz. To understand the temperature dependence of scintillation properties, the laser-induced emission spectrum was measured while the temperature was varied. The 0.15 mol%  $\text{CeF}_3$  doped SBCG glass was attached to a copper plate with thermal grease. The top face of the SBCG:Ce glass was attached to a quartz light guide, and the end of the quartz light guide was connected to an optical fiber. The signal was transmitted to a QE65000 spectrometer (Ocean Optics Co.). The temperature range was from 300 K to 10 K.

The decay component was also measured as the temperature was changed by using the same low-temperature setup used for the laser-induced emission spectrum. The scintillation signal was read by a photo multiplier tube (Hamamatsu, H6610), and the result was recorded by an oscilloscope (Lecroy, 610Zi). Figure 2 shows the experimental setup for the measurement of the decay component while temperature was changed.

X-ray induced emission spectra were measured by using an X-ray generator (DRGEM Co.), the QE65000 spectrometer, and an optical fiber.

The proton-induced emission spectra were measured at the KOMAC (Korea Multi-purpose Accelerator Complex) accelerator facility [13]. The 100 MeV proton beam irradiated to the SBCG:Ce glass for 10 s. The distance between the SBCG:Ce glass and beam window was 85 cm. The SBCG:Ce glass was connected to the optical fiber, and the optical fiber was linked to a USB4000 spectrometer (Ocean Optics Co.). Figure 3 shows the experimental set-up for the measurement of the proton-induced emission spectrum.

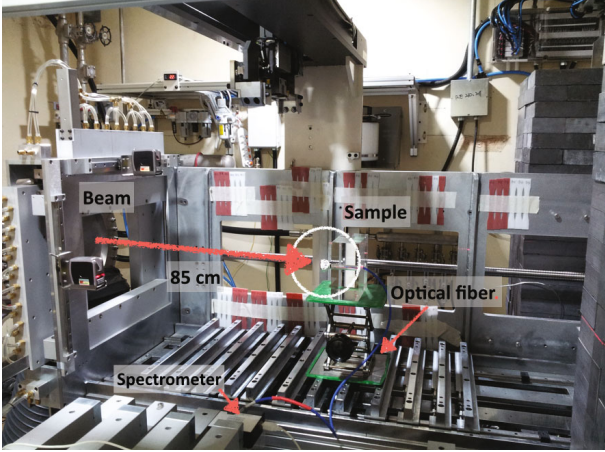


Fig. 3. (Color online) Photograph of the proton beam line with a glass scintillator.

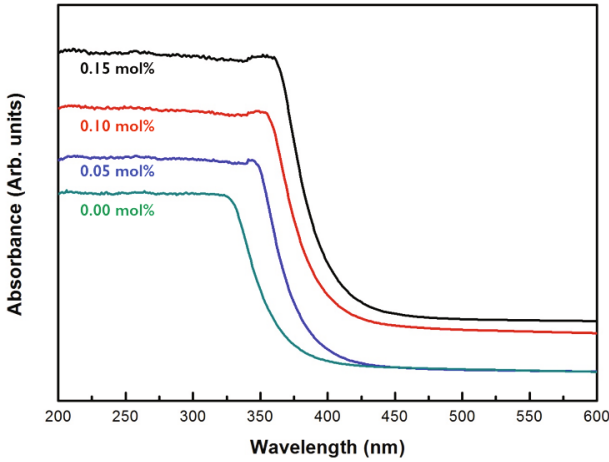


Fig. 4. (Color online) Absorption spectra of  $\text{CeF}_3$ -doped SBCG glasses.

### III. RESULTS AND DISCUSSION

Figure 4 shows the absorption edge of the SBCG:Ce glasses. The absorption edge of the 0.15 mol%  $\text{CeF}_3$ -doped SBCG glass was 375 nm because of the  $4f$ - $5d$  transition. The absorption edge shifted from 360 nm to 375 nm as the doping concentration of the  $\text{CeF}_3$  material increased [14]. The difference between the 0.05 mol%  $\text{CeF}_3$ -doped SBCG and 0.15 mol%  $\text{CeF}_3$ -doped SBCG was approximately 15 nm.

We measured the photo-induced excitation and emission spectra to understand the detailed luminescence properties. Figure 5 shows the excitation (black) and emission spectra (red and blue dotted) of the 0.15 mol%  $\text{CeF}_3$ -doped SBCG glass. The emission peak of the SBCG:Ce was 370 nm under two excitation peaks of 275 nm and 320 nm. The light yield under the excitation peak of 320 nm was almost 10 times higher than that under the excitation peak of 275 nm. The excitation peaks were 275 nm and 320 nm under an emission peak

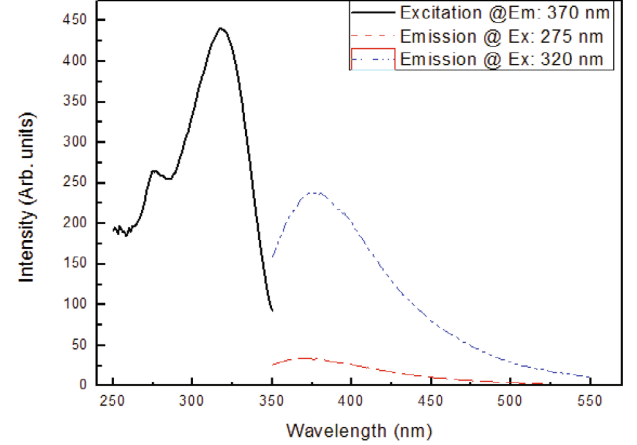


Fig. 5. (Color online) Photo-induced excitation (black line), and emission spectra under excitation peaks of 275 nm (red dots) and 320 nm (blue dots).

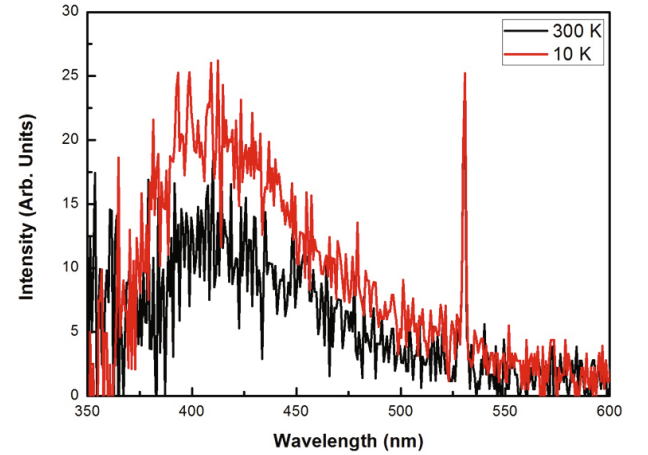


Fig. 6. (Color online) Laser-induced emission spectra of the 0.15 mol%  $\text{CeF}_3$ -doped SBCG glass at 10 K (red line) and 300 K (black line).

of 370 nm. These results were due to  $5d \rightarrow {}^2F_j$ , where  $j$  is  $5/2$  and  $7/2$ , and are consistent with a Ref. [14].

The luminescence property was studied for its temperature dependence by using the 266 nm laser source. The temperature dependence was studied in two experiments: comparing the light yield of laser-induced emission spectra, and comparing decay components by varying the temperature. Figure 6 shows the laser-induced emission spectra of the 0.15 mol%  $\text{CeF}_3$ -doped SBCG glass at 10 K (red line) and 300 K (black line). The emission peak did not change at either temperature, but the light yield at 10 K was almost 1.5 times higher than at 300 K.

The scintillation decay component of the 0.15 mol%  $\text{CeF}_3$ -doped SBCG glass was studied as the temperature was changed from 300 K to 10 K. The decay component curve was fitted to an exponential function:

$$y = A_1 \exp(-x/\tau_1) + y_0,$$

where  $A_1$  is the intensity contribution and  $\tau_1$  is the decay

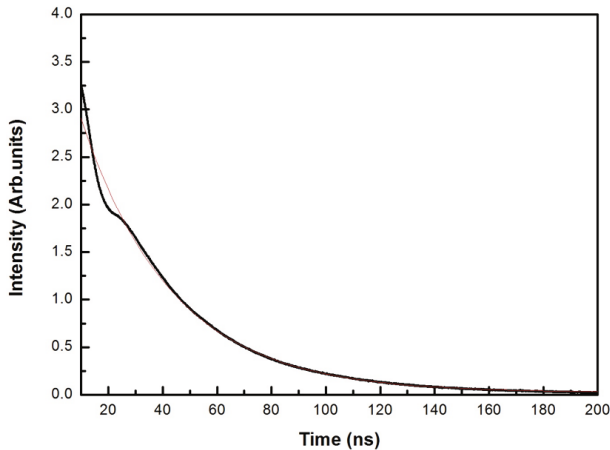


Fig. 7. (Color online) Decay component of 0.15 mol%  $\text{CeF}_3$ -doped SBCG glass at 300 K.

Table 1. Decay component of 0.15 mol%  $\text{CeF}_3$ -doped GCSB glass at different temperature.

Temperature (K)	Decay Time (ns)
300	34
250	37
200	38
150	40
100	40
50	41
10	41

time constant. The decay component of 0.15 mol%  $\text{CeF}_3$ -doped SBCG glass was approximately 34 ns at 300 K, as shown in Fig. 7. Table 1 summarizes the decay component dependence on the thermal quenching. The decay component increased with decreasing the temperature due to thermal quenching. Deep electron traps keep the energy, and this electron traps reduce the luminescence efficiency. This situation is remarkable at high temperatures [15].

As shown in Fig. 8, the X-ray induced emission spectra of the SBCG:Ce glasses had a broad emission peak between 350 nm and 550 nm. The 0.0 mol%  $\text{CeF}_3$ -doped SBCG showed no luminescence spectrum. The luminescence peak intensity of the 0.05 mol%  $\text{CeF}_3$ -doped SBCG of was highest at approximately 430 nm. The emission peak was related to the  $5d-4f$  transition [16]. The 0.05 mol%  $\text{CeF}_3$ -doped SBCG had the highest luminescence intensity among the samples. The luminescence intensity decreased with the doping concentration due to  $\text{CeF}_3$  concentration quenching [15].

The proton-induced emission spectra of the 0.10 mol% and 0.15 mol%  $\text{CeF}_3$ -doped SBCG glasses were measured by using a 100 MeV proton beam at the KOMAC accelerator facility. As shown in Fig. 9, the emission spectrum had two peaks at 430 nm and 490 nm. The

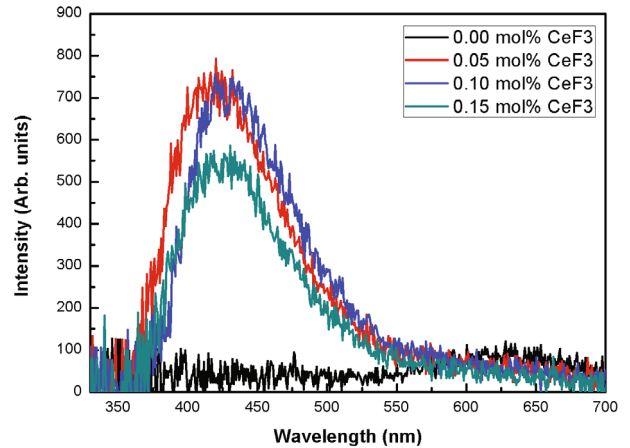


Fig. 8. (Color online) X-ray induced emission spectra of the SBCG:Ce glasses.

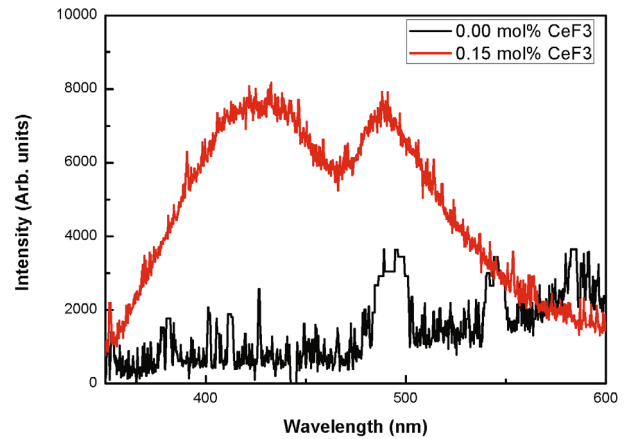


Fig. 9. (Color online) Proton-induced emission spectra of the 0.0 mol% (black line) and 0.15 mol% (red line)  $\text{CeF}_3$ -doped SBCG glasses.

peak of 490 nm was due to the base material since the 0.0 mol%  $\text{CeF}_3$ -doped SBCG also showed the peak at 490 nm. The proton beam energy is 100 MeV, which is 1000 times higher than X-ray energy. So we can observe the emission band of base material by using proton beam.

#### IV. CONCLUSIONS

The  $\text{CeF}_3$ -doped silicaborate-calcium-gadolinium glass scintillators ( $10\text{SiO}_2:(55-x)\text{B}_2\text{O}_3:10\text{CaO}:25\text{GdF}_3:x\text{CeF}_3$ ) were fabricated by using the melt-quenching technique. The optical properties were studied by using photo-, laser-, X-ray- and proton-induced luminescence spectra. The absorption peak of the  $\text{CeF}_3$ -doped silicaborate-calcium-gadolinium glass scintillator was approximately 360 nm. The emission spectrum had one broad one peak due to the  $4f-5d$  transition with photo-

laser-, X-ray, and proton source. The excitation peaks were located at 275 nm and 320 nm under an emission peak of 370 nm. The luminescence intensity at 10 K was 1.5 times higher than at 300 K with a 266 nm laser excitation. Thus the CeF<sub>3</sub>-doped silicaborate-calcium-gadolinium glass scintillator can be used as radiation detectors at not only room temperature but also low temperature. The decay component was increased with decreasing temperature. The 0.15 mol% CeF<sub>3</sub>-doped silicaborate-calcium-gadolinium glass scintillator had a decay time of 34 ns at room temperature. The CeF<sub>3</sub> doped silicaborate-calcium-gadolinium glass scintillators had a fast decay time and a broad emission peak in the blue range. We will fabricate a glass scintillator on the next step based on results of this study. Thus, it can potentially be applied as a radiation detector at nuclear and high energy physics, medical imaging, radiation monitoring, and homeland security.

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