SNRU Journal of Science and Technology

Journal home page: snrujst.snru.ac.th

Investigation CeF_3 Doped SiO_2-Al_2O_3-BaF_2-Gd_2O_3 Glasses Effect on Luminescence and Scintillation Properties

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Received: 23 January 2021; **Revised:** 3 May 2021; **Accepted:** 12 May 2021; **Available online:** 1 September 2021

Abstract

Scintillating glasses with host compositions (in mol.%) of $50SiO_2$ - $20Al_2O_3$ - $15BaF_2$ - $15Gd_2O_3$ doped with CeF_3 (0.50, 1 and 1.50 wt.%) were prepared by melt-quenching method under a CO reducing atmosphere. The emission band of the Ce^{3+}: 5d - 4f transition in the spectral region 350 – 570 nm found in the photo- and radio-luminescence spectra. The integral scintillation efficiency was approximately 180% of the $Bi_4Ge_3O_{12}$ (BGO) scintillator excited under X-ray irradiation. Light yield (LY) measured under excitation with α particles and γ - rays. The 1 wt.% CeF_3 glass shows a LY of 1969 photons/MeV at 662 keV γ - rays, while the value of 228 photons/MeV was obtained at 5.50 MeV α particles and compared with BGO crystal. Photoluminescence decay kinetics displayed a few tens of nanoseconds decay time.

Keywords: Light yield; Luminescence; Scintillating glass

1. Introduction

Scintillating glass are materials that can change the energy of particles or X/γ-quanta with high energy into UV-Visible light. Scintillators have received much attention recently because they widely used in various fields, such as experimental nuclear physics, particle physics, nuclear medicine, medical imaging of positron emission tomography (PET), X-CT, oil exploration and environmental studies [1]. Currently, the main purpose of the development of scintillator materials is the high light yield, scintillator glass is new hope because of it easily formed and inexpensive.

The Cerium (Ce^{3+}) is the best rare earth suitable for doping into scintillator material because it exhibits high light yield and fast decay time properties under 5d-4f transition, while the other rare-earth ions show the slow decay time under 4f-4f transition [1, 2]. So, improvement glass host is aim of research. Generally, the scintillating glass formula often adds high density element into the glass structure to raise radiation absorption that affects light yield value. Therefore, this research mixes BaF_2 (density 4.89 g cm^{-3}) in a glass formula in order to increase the density of the glass host due to high density glass effect on absorption X/γ ray [3]. Furthermore, the fluorine group from CeF_3 and BaF_2 can reduce OH group vibration, which enhances the luminescence efficiency of scintillating glass [4]. This research is distinct due to an improved glass formula and doping CeF_3 (fluorine group decreases OH vibration).

The important properties of scintillator materials are high light yield (LY), fast decay time and good radiation hardness. In this work, Ce^{3+} was doped in oxide glass matrices that glass formula was

$50SiO_2$ - $20Al_2O_3$ -$15BaF_2$ -$15Gd_2O_3$ (in mol.%). The first step was the preparation of the glass matrix by the melt-quenching method under CO reducing atmosphere and the second step, sample was annealed and cool down in the furnace. The samples were studied luminescence properties by UV/Vis spectrum, photoluminescence (excitation and emission) and photoluminescence decay time. The scintillation properties were investigated by radioluminescence (RL) and light yield (LY), the samples were compared with $Bi_4Ge_3O_{12}$ (BGO) crystal as a reference scintillator. The BGO crystal often refers to RL&LY compared with scintillating glass because the aim of the development of scintillating glass is close luminescence efficiency of crystal due to crystal scintillator for commercial use.

2. Materials and methods

The glass host with the composition of $50SiO_2$ - $20Al_2O_3$ - $15BaF_2$ - $15Gd_2O_3$ (mol%) doped with CeF_3 0.50, 1 and 1.50 wt.% was prepared by the melt-quenching method. The starting materials were reagent-grade SiO_2, $Al(OH)_3$, BaF_2, Gd_2O_3 and CeF_3. The chemical powders were mixed homogeneously in an agate mortar and melted in an alumina crucible under a CO reducing atmosphere at 1600 ºC for 30 min. After that, the melt was poured on a preheated plate mold (stainless steel) and annealed at 700 ºC for 3 h let cooling down in the furnace at a natural cooling rate ambient temperature. The melt poured in the mold had no effect on the stainless steel and composition of glass because the melt immediately solidified due to different temperatures between the melt and preheated plate. The samples were polished size about $7 \times 7 \times 1$ mm^3 and then applied to all testing. The density of all samples was 4.21 g cm^{-3} because of same glass host by the Archimedes method.

Absorption spectra was measured on Hitachi U2900 spectrophotometer. Photoluminescence emission (PL) and excitation (PLE) spectra were reported by Shimadzu RF- 5301PC spectrofluorophotometer. Radioluminescence (RL) spectra was obtained from X-Rays Induced Optical Luminescence (Inel x-ray generator with 2 kW Cu-anode, spectrum was detected by fiber optics spectrometer, QE65000 Ocean Optics). Photoluminescence decay (PL decay) curves were detected by Horiba DeltaPro fluorescence life time system.

Light yield (LY) measurements were tested under the excitation of 5.50 MeV alpha particles from ^{238}Pu source and 662 keV γ - rays from ^{137}Cs source using photomultiplier (Photonis XP5200B PMT anode), the signal was transmitted to CANBERRA 2005 preamplifier and Tennelec TC243 spectroscopy amplifier. The program for analysis, Tukan 8k MCA was applied in order to record the pulse height spectra. The photoelectron yield, defined as number of photoelectrons per MeV (phe/MeV) of energy accumulated in the glass, observed from position of the photopeak (5.50 MeV alpha particles and 662 keV γ - rays) was detected in the glass scintillator. Scintillating glass was compared efficiency with BGO crystal reference [5].

3. Results and Discussion

Fig. 1 presents the absorption spectra of glass doped with CeF_3 and the absorption lines of Ce^{3+} displayed absorption edge about 380 nm and the energy level $4f \rightarrow 5d$ transitions of the Ce^{3+} ions [6]. The emission spectra excited at 275 and 340 nm and the excitation spectra of the Ce^{3+} emission as the glass doped CeF_3 sample are exhibited Fig. 2. The broad peak excitation bands (220 – 390 nm) were merged between $4f \rightarrow 5d$ transitions of the Ce^{3+} ions and $^8S_{7/2} \rightarrow {}^6I_J, {}^6P_{7/2}$ transitions of the Gd^{3+}ions. The wavelength of 275 nm peak in the excitation spectra of the Ce^{3+} emission shows that the energy transfer (ET) from the Gd^{3+} to Ce^{3+} ions replace in this scintillating glasses [7]. The Fig. 3 presents the energy transfer (ET) between Gd^{3+} and Ce^{3+} ions. Luminescence band of the Ce^{3+} $5d \rightarrow 4f$ transitions was observed in the range between 330 and 600 nm [8]. But note that the broad bands were inhomogeneous of Ce^{3+} in a glassy environment because of the amorphous structure of glass [9].

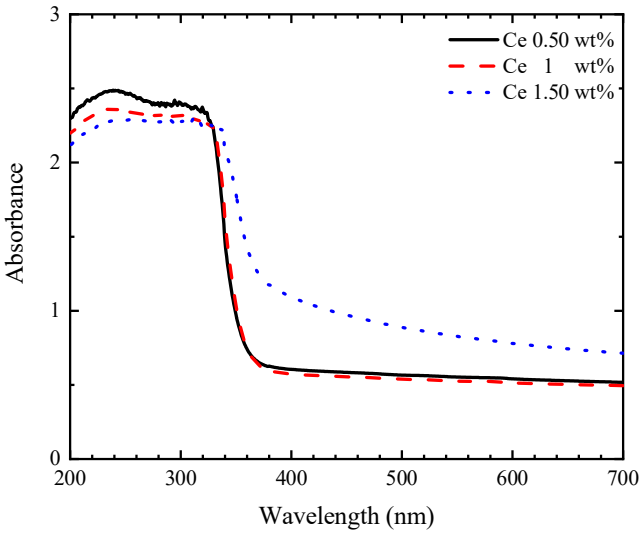

Fig. 1 Absorption spectra of the scintillating glasses.

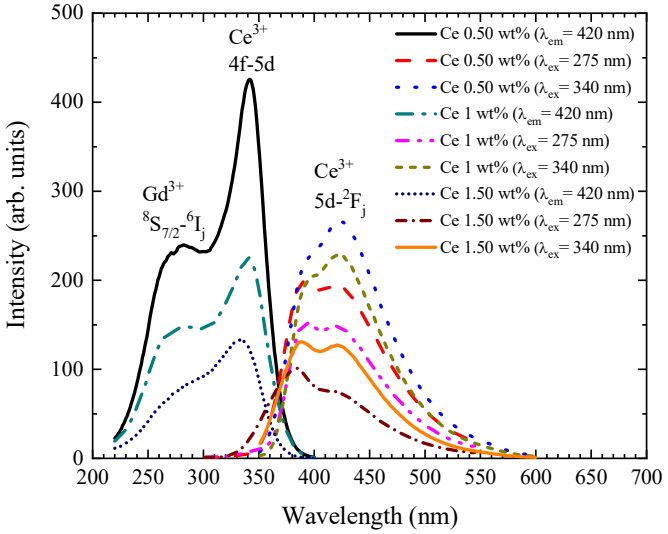

Fig. 2 Photoluminescence emission and excitation spectra of scintillating glasses.

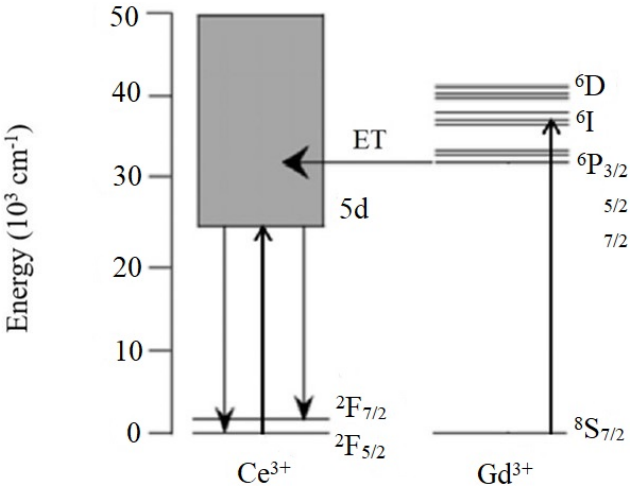

Fig. 3 Energy level diagram of Gd^{3+} and Ce^{3+}, energy transfer in scintillating glasses.

Radioluminescence (RL) spectra of all concentration samples and $Bi_4Ge_3O_{12}$ crystal are shown in Fig. 4. The scintillating glass of all samples are the similar shape and the testing was performed under the same conditions, therefore the spectra can be collated in this situation. The integral scintillation efficiency of the scintillating glass was defined from the ratio of the integrated intensity of its radioluminescence spectrum and the $Bi_4Ge_3O_{12}$ reference. The radioluminescence of the scintillating glasses was about 142%, 184% and 2% of the BGO crystal that were obtained from doping CeF_3 0.50, 1 and 1.50 wt%, respectively. The CeF_3 0.50 and 1 wt% displayed high energy emission of Ce^{3+} (5d-4f) from X-ray excitation because of the great density of the glass host [3]. However, CeF_3 1.50 wt% exhibited very low energy emission due to over doping of CeF_3.

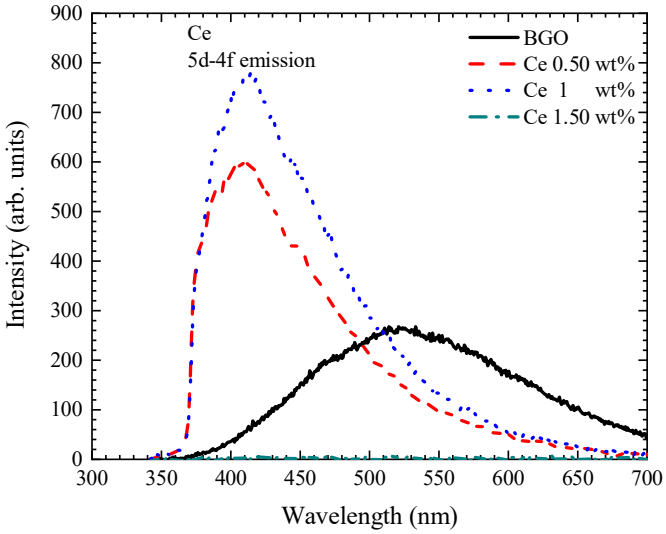

Fig. 4 Radioluminescence spectra of scintillating glasses and $Bi_4Ge_3O_{12}$ reference.

Pulse height spectra of 662 keV γ - rays from ^{137}Cs source tested scintillating glasses (doped CeF_3) and $Bi_4Ge_3O_{12}$ reference are shown in Fig. 5. The LY values of scintillating glasses and BGO crystal reference are displayed in Table 1. The CeF_3 1 wt% glass presents the highest LY value of about 1969 ph/MeV and 23% of BGO. The LY value measured under excitation by 5.50 MeV α particles from ^{238}Pu source, it found that CeF_3 1 wt% was 228 ph/MeV and 18% of BGO. Fig. 6 displays the pulse heigh spectra of 5.50 MeV α particles. The LY results show low efficiency of scintillating glasses because of trapping in the luminescence centers of glass structure [10].

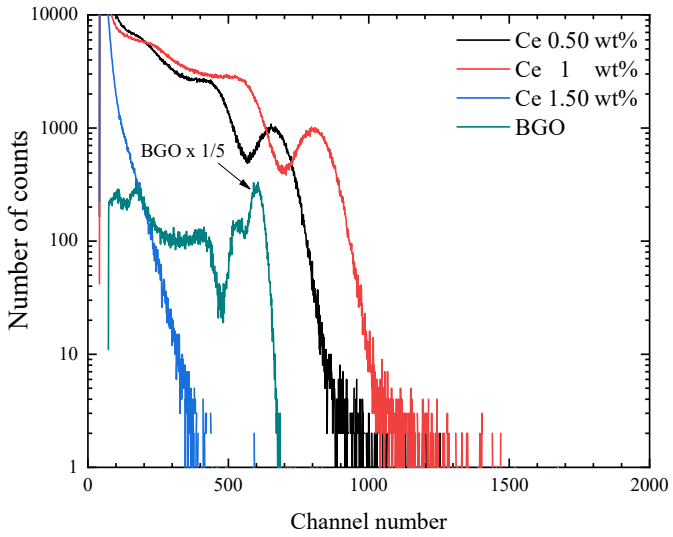

Fig. 5 Pulse height spectra of 662 keV γ - rays from ^{137}Cs source.

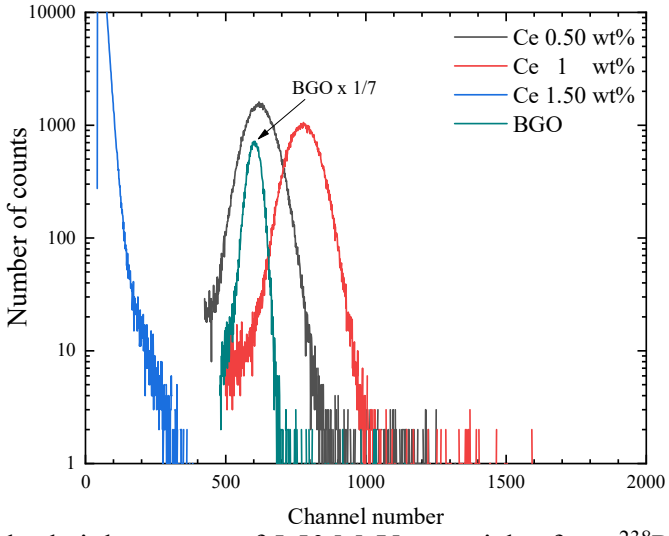

Fig. 6 Pulse height spectra of 5.50 MeV α particles from ^{238}Pu source.

Table 1 Light yield (LY) value was excited by γ and α of scintillating glasses.

Samples	**LY$_\gamma$ of 662 keV (ph/MeV)**	**LY$_\gamma$ (% of BGO)**	**LY$_\alpha$ of 5.50 MeV (ph/MeV)**	**LY$_\alpha$ (% of BGO)**
BGO	8500	100	1250	100
CeF_3 0.50 wt%	1610	19	182	15
CeF_3 1 wt%	1969	23	228	18
CeF_3 1.50 wt%	0	-	0	-

The PL decay of scintillating glass sample was excited at λ_{ex} = 286 nm as display in Fig. 7. This research chooses the CeF_3 1 wt% for plot decay curve because it exhibits the highest LY value. The decay curve of Ce^{3+} emission can be fitted with a double exponential equation as shown in equation (1);

$$I(t) = A_1^{\frac{-t}{\tau_1}} + A_2^{\frac{-t}{\tau_2}} + background \quad (1)$$

Where $I(t)$ luminescence intensity

A amplitude

t time

τ decay time

The relative intensity of the two components, calculated by equation (2);

$$Ii = \frac{A_i\tau_i}{A_1\tau_1 + A_2\tau_2} \; when \; i = 1, 2 \quad (2)$$

Results showed the decay times τ_1 = 22.39 ns (fast component) and τ_2 = 50.36 ns (slow component) with respective component intensities $I_i = (A_i\tau_i)/(\Sigma A_i\tau_i)$, namely, I_1 = 31.46% and I_2 = 68.54%, respectively. The distribution of dopant in the glass matrix was inhomogeneous, so the emission band was broad and the decay time value varied.

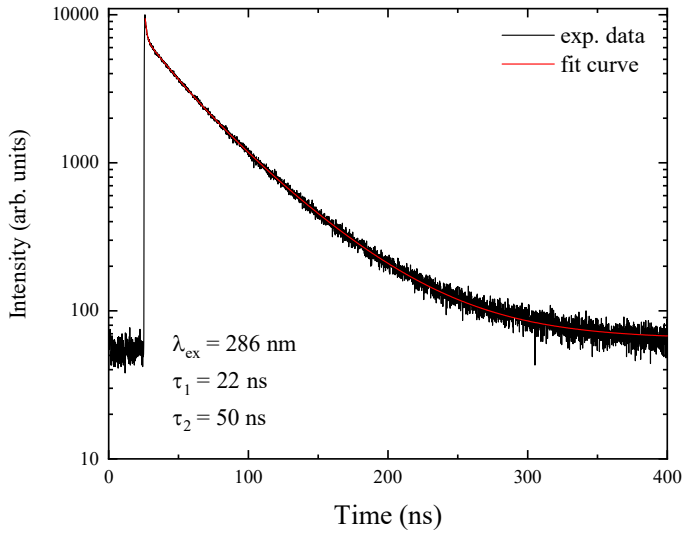

Fig. 7 Decay curve under excitation at λ_{ex} = 286 nm for the CeF_3 1 wt% scintillating glass sample.

4. Conclusion

The scintillating glasses showed intense blue emission of Ce^{3+} ions under UV excitation. The integral scintillation efficiency (radioluminescence) were 142%, 184% and 2% of the $Bi_4Ge_3O_{12}$ (reference) scintillator under X-ray irradiation from doping CeF_3 0.50, 1 and 1.50 wt%, respectively. For light yield (LY) value, the CeF_3 1 wt% displayed the highest LY value about 1969 ph/MeV (23% of BGO) for γ - rays and 228 ph/MeV (18% of BGO) for α-particles. The PL decay time of CeF_3 1 wt% showed a short decay time approximately τ_1 = 22.39 ns (fast component) and τ_2 = 50.36 ns (slow component).

5. Suggestions

Future study will improve glass formula in order to increase the efficiency of radioluminescence and light yield that are important properties of scintillating glass.

6. Acknowledgement

The authors would like to thank Assoc.Prof.Dr.Weerapong Chewpraditkul (KMUTT) and Prof.Dr.Danping Chen (SIOM) for their valuable discussion. Acknowledge for support of Scientific research equipment center of the Physics department MCRU. This research was financially promoted by the National Research Council of Thailand (No.52464). Finally, I would like to thank my mother for all of the inspiration and all of the encouragement.

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