



Effects of Ce^{3+} sensitizer on the luminescent properties of Tb^{3+} -activated silicate oxyfluoride scintillating glass under UV and X-ray excitation



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ABSTRACT

Novel Tb^{3+} or Ce^{3+} doped and $\text{Tb}^{3+}/\text{Ce}^{3+}$ codoped silicate oxyfluoride scintillating glasses were synthesized by melt-quenching method. The luminescent properties were studied by transmission spectra, photoluminescence excitation (PLE) and photoluminescence (PL) spectra, X-ray excited luminescence (XEL) spectra and luminescence decay curves in order to reveal the roles of Ce^{3+} sensitizer in the luminescence process of Tb^{3+} -activated silicate oxyfluoride scintillating glass under UV and X-ray excitation. As for $\text{Tb}^{3+}/\text{Ce}^{3+}$ codoped scintillating glasses, the Ce^{3+} ions strongly sensitized the luminescence of the Tb^{3+} ions by energy transfer process from Ce^{3+} to Tb^{3+} ions under UV excitation. The optimal doping concentration of Ce_2O_3 in $\text{Tb}^{3+}/\text{Ce}^{3+}$ codoped scintillating glasses can be determined to be 0.6 mol%. But under X-ray excitation, the enhancement of Tb^{3+} ions emission intensity caused by Ce^{3+} codoping is not as obvious as that under UV excitation, which is mainly due to the low energy transfer efficiency from host glass to Ce^{3+} ions. Under X-ray excitation, the intensity of 544 nm emission in $\text{Tb}^{3+}/\text{Ce}^{3+}$ codoped scintillating glasses with 0.6 mol% of Ce_2O_3 was 6 times than that of 500 nm emission in the commercial $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) crystals. The integral scintillation efficiency was about 83% of the BGO crystals. These results imply that the developed silicate oxyfluoride scintillating glasses in our case can be potential candidate for high-resolution medical X-ray imaging.

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1. Introduction

Glasses activated with rare-earth (RE) ions are attractive scintillating materials due to their advantages of low-cost, easy shaping of elements, possibility to incorporate activator ions at high concentrations and ease of manufacture in different sizes and shapes [1–3]. With regard to the research of scintillating glasses, Tb^{3+} -activated scintillating glasses have been the focus of many studies because of their high luminescent efficiency at around 540 nm, which is convenient for direct coupling with silicon detectors [4]. However, compare with scintillation crystal, the light yield of the scintillating glasses generally is low due to the presence of many trapping sites in the glass matrix, where electrons and holes can be entrapped, which will give rise to non-radiative recombination processes [5,6].

In order to improve the emission performance of Tb^{3+} ions in scintillating glass, some suitable sensitizers such as Ce^{3+} , Gd^{3+} , and Dy^{3+} are usually doped to the glass matrix [7–9]. Among these RE (Ce^{3+} , Gd^{3+} , and Dy^{3+}) ions, Ce^{3+} ion is not only a high efficiency emission center, but also has been proved to be an efficient sensitizer, especially for Tb^{3+} ions. The energy transfer of the different hosts between Ce^{3+}

and Tb^{3+} ions has been extensively investigated, such as borate glass [10], phosphate glass [11], aluminosilicate glass [12,13] and glass ceramics [14]. These discussions about energy transfer from Ce^{3+} ions to Tb^{3+} ions were carried out under the excitation of UV light, rare attention has been paid to the sensitizing effect of Ce^{3+} to Tb^{3+} under the high energy electrons or photons excitation. However, the application of these scintillating glasses are mainly operated under high energy electrons or photons excitation, so that to reveal the sensitizing effect of Ce^{3+} to Tb^{3+} under X-ray excitation is very necessary in order to prompt their practical application.

In this work, Tb^{3+} or Ce^{3+} doped and $\text{Tb}^{3+}/\text{Ce}^{3+}$ codoped silicate oxyfluoride glasses were successfully prepared by the melt-quenching method. The transmission spectra, photoluminescence excitation (PLE) and photoluminescence (PL) spectra, X-ray excited luminescence (XEL) spectra and luminescence decay curve were investigated systematically. In addition, energy transfer process between Ce^{3+} and Tb^{3+} ions and its influence on luminescent properties were discussed.

2. Experimental

The nominal compositions of the experimental glasses were listed in Table 1. The starting materials were analytical purity SiO_2 , BaF_2 , AlF_3 , BaCO_3 and high purity (99.99%) Gd_2O_3 , Tb_2O_3 , CeO_2 and Sb_2O_3 powders.

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Table 1
Nominal compositions of the experimental glass.

Glass samples	Composition (mol%)								Density (g cm ⁻³)
	SiO ₂	BaF ₂	BaO	AlF ₃	Gd ₂ O ₃	Sb ₂ O ₃	Tb ₂ O ₃	Ce ₂ O ₃	
HG	64	5.5	22	2	6	0.5	–	–	3.930 ± 0.005
Ce1	63.4	5.5	22	2	6	0.5	–	0.6	3.971 ± 0.006
Tb1	58	5.5	22	2	6	0.5	6	–	4.315 ± 0.003
TC1	57.8	5.5	22	2	6	0.5	6	0.2	4.319 ± 0.004
TC2	57.6	5.5	22	2	6	0.5	6	0.4	4.320 ± 0.003
TC3	57.4	5.5	22	2	6	0.5	6	0.6	4.326 ± 0.002
TC4	57.2	5.5	22	2	6	0.5	6	0.8	4.348 ± 0.005
TC5	57	5.5	22	2	6	0.5	6	1.0	4.356 ± 0.002
TC6	56	5.5	22	2	6	0.5	6	2.0	4.366 ± 0.006
TC7	55	5.5	22	2	6	0.5	6	3.0	4.376 ± 0.005
TC3-0S	57.9	5.5	22	2	6	–	6	0.6	4.412 ± 0.006

The role of appropriate amount of Sb₂O₃ is to reduce the tetravalent cerium to its trivalent one effectively in the synthesis process of glasses. About 20 g batches of well-mixed raw materials were melted at 1480 °C for 60 min in air. After melting, the liquid was cast into a preheated stainless-steel mold for quenching and annealed at 500 °C for 2 h to release its inner stress. Glass samples with the size of Φ20 × 2 mm were finally obtained after being cut and polished and used for the optical measurement.

Transmittance spectra were recorded with a Shimadzu UV-2700 UV–VIS spectrometer in the range of 200–750 nm. The PLE and PL spectra were collected using a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Luminescence decay curves were carried out with Fluorologs-3 Horiba Scientific spectrometer, with an iHR 320 single-emission monochromator, coupled to a R928 Hamamatsu photomultiplier. The excitation source was a 450 W pulsed Xe lamp. The XEL spectra (irradiated by W antiscatter target operating at 70 kV and 10 mA) were coupled to the OceanOptics QE Pro-FL spectrometer via optical lens and fibers. All the measurements were carried out at room temperature.

3. Results and discussion

The densities of glasses are shown in Table 1. It is well-known that high glass density can enlarge the X-ray absorption cross-section, which will increase the signal-to-noise ratio of image. As we expected, the densities of all Tb³⁺-activated silicate oxyfluoride scintillating glasses reach over 4.3 g/cm³, which indicate that present glasses are attractive as a potential scintillating materials.

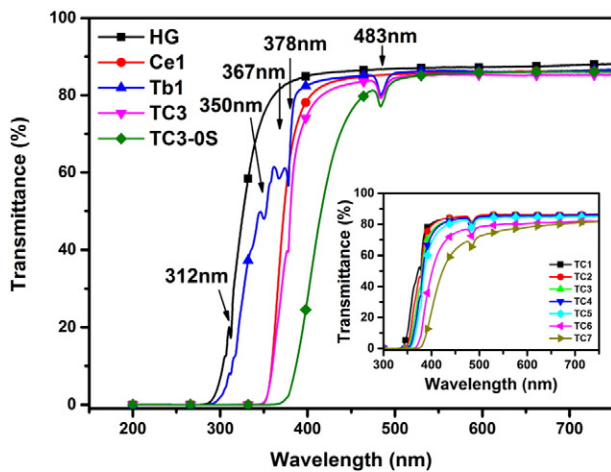


Fig. 1. Transmission spectra of the host glass (HG), Ce³⁺ doped glass (Ce1), Tb³⁺ doped glass (Tb1) and Tb³⁺/Ce³⁺ codoped glasses (TC3 and TC3-0S). Inset shows the transmission spectra of Tb³⁺/Ce³⁺ codoped glasses (TC1–TC7).

The transmission spectra of host glass, Ce³⁺ doped or Tb³⁺ doped and Tb³⁺/Ce³⁺ codoped scintillating glasses are presented in Fig. 1. The designed host glass (HG) without Ce³⁺ ions or Tb³⁺ ions has the shortest UV cut-off edge at approximately 294 nm. The characteristic absorption peak of Gd³⁺ ions can be found at 312 nm [8]. With the incorporation of Tb³⁺ ions into the host glass (Tb1), its cut-off edge shifts toward 309 nm, and several absorption peaks centered at 350, 367, 378 and 483 nm are observed, which associated with optical transitions from ⁷F₆ to ⁵L₉, ⁵L₁₀, ⁵G₆ and ⁵D₄ of Tb³⁺ ions, respectively [8]. For Ce³⁺ doped glass (Ce1), the Ce³⁺ ions exhibits a broad absorption band in the UV with an cut-off edge about 354 nm, which is caused by the 4f–5d transition of Ce³⁺ ions [15]. When Ce³⁺ ions are added into Tb³⁺ doped glass, the UV cut-off edge of glass sample TC3 shifts to 354 nm as well, which can be ascribed to the overlap of 4f–5d transition of Ce³⁺ ion on the f–f transitions of Tb³⁺ ion [16]. We further increase the Ce₂O₃ content, the UV cut-off edges of Ce³⁺/Tb³⁺ codoped glass samples shift to 383 nm, as shown in the inset of Fig. 1, which is associated with the absolute concentration of Ce⁴⁺ ions elevates in the samples with higher cerium concentration [15,17,18]. The detailed explanation is as follows: The absorption of Ce⁴⁺ ions is induced by a charge transfer states (CTS) from O²⁻ to Ce⁴⁺, and the position of the CTS band in oxide glasses commonly locates at longer wavelength in comparison to that of Ce³⁺ ions [12,13,19].

Here we would like to point out that the Ce³⁺ and Ce⁴⁺ ions normally coexist in the glasses because cerium is one of the most active elements among lanthanide. In our case, we prefer the Ce³⁺ in the glass, so we added appropriate amount of Sb₂O₃ during the synthesis process of glasses to reduce the tetravalent cerium to its trivalent one effectively. To see how reducing agent of Sb₂O₃ influence the concentration ratio of Ce³⁺ and Ce⁴⁺ in the glass, we further prepared the Tb³⁺/Ce³⁺ codoped glass without adding Sb₂O₃ (named as TC3-0S glass) to make a comparison. For TC3-0S glass, the UV cut-off edge shifts remarkably to 382 nm, which can be attributed to the presence of Ce⁴⁺ ions based on the above discussion. In our case, the cut-off edge of TC3 glass shifted to 354 nm by employing a reducing atmosphere with Sb₂O₃, indicating that cerium mainly exists as Ce³⁺ in glass samples.

The PLE and PL spectra for Tb³⁺ doped scintillating glass (Tb1) and host glass (HG) are illustrated in Fig. 2. The PLE spectrum is acquired by monitoring the green emission at 544 nm of Tb³⁺ ions. The overall excitation spectra are divided into two groups. The broad band around 244 nm is associated with the allowed 4f⁸ → 4f⁷5d¹ transition, and weak narrow bands located at 302 nm, 317 nm, 339 nm, 351 nm, 368 nm and 377 nm are assigned to the transitions from the ground state ⁷F₆ to ⁵H₆, ⁵H₇, ⁵L₈, ⁵L₉, ⁵L₁₀ and ⁵D₃ states, respectively [8,20]. In addition, another three excitation peaks located at 274 nm, 306 nm and 312 nm can be assigned to the characteristic ⁸S_{7/2} → ⁶I₁, ⁶P_{7/2}, _{5/2}

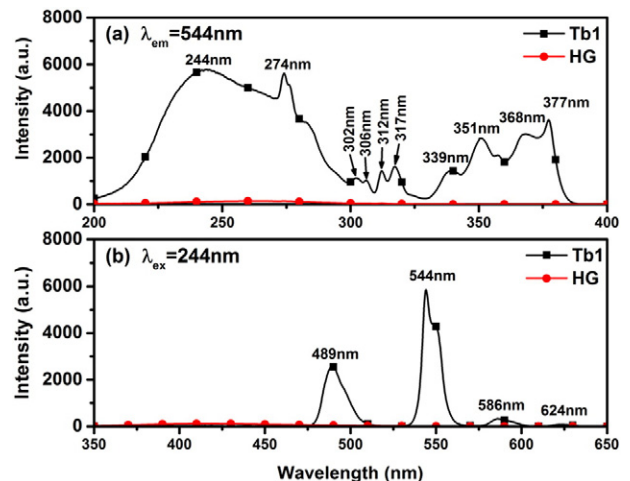


Fig. 2. PLE (a) and PL (b) spectra of Tb³⁺ doped glass (Tb1) and host glass (HG).

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