Ce³⁺-Gd³⁺ co-doped high efficiency oxide glasses and transfer efficiency from Gd³⁺ to Ce³⁺*

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The rare earth Ce³⁺ ion doped SiO₂-B₂O₃-BaO-Gd₂O₃ system is synthesized by high-temperature melting method. The density, transmission, excitation spectra and scintillating properties of the glasses are investigated. The results indicate that all the samples have good physical and scintillating properties. The emission peak wavelength of all samples is 390 nm under X-ray radiation. Gd³⁺ ions have a negative impact on scintillating properties when its concentration reaches a certain level. Gd³⁺ ions sensitize the luminescence of Ce³⁺ ions, and the ideal concentration is 15 mol% for Gd³⁺ ions. Also the decay characteristics of Ce³⁺ and Gd³⁺ ions are investigated. These samples have potential practical applications in high energy physics.

Scintillating glasses are promising alternatives to single crystals and ceramic scintillators for applications in high energy physics and in X-ray computed tomography (X-CT) for industrial and medical imaging. The main advantages of scintillating glasses[1] are the possibility of low-cost production, the ease of manufacture for different sizes and shapes, such as fibers[2,3], and the composition of glasses can be adjusted at a broad arrangement. Compared with crystals[4], scintillating glasses have some disadvantages, such as low transfer efficiency, low density and low light yield. However, density and light yield are two important features for scintillators in some applications.

In high energy physics, densely Ce³⁺-doped fluoride glasses were investigated as a kind of possible alternative material for electromagnetic calorimeters[5]. At higher concentrations of Ce³⁺ ions, an unfavorable combination of low transfer efficiency and quenching of Ce³⁺ emission due to the interaction between closely occurring elementary excitations was noted[6]. The latter effect was noticed in CeF₃ single crystal scintillators[7]. The SiO₂-B₂O₃-BaO-Gd₂O₃ system glasses with high density and luminescence properties have been reported[8]. In this paper, we get a high efficiency scintillating glass which can be used in high energy physics and can replace crystal scintillators.

In this paper, Ce³⁺-doped oxide scintillating glasses with different concentrations of rare-earth ions are prepared. The density, transmission, photon yield, radiation wave length, decay times of Gd³⁺ and Ce³⁺ ions , luminescence properties under X-Ray and ultraviolet (UV) excitation are investigated. Also, the transfer efficiency from Gd³⁺ to Ce³⁺ is investigated through fitting the decay curves of Gd³⁺ ions.

Compositions of the studied glasses are shown in Tab.1. They were prepared using high purity (99.9%) SiO₂ and Gd₂O₃ as starting materials, while B₂O₃, BaO and Ce³⁺ ions were introduced from reagent grade H₃BO₃, BaCO₃ and CeF₃. Then, they were carefully mixed in appropriate proportions, and 20 g batches were placed in corundum crucibles and melted under a 95%N₂/5%H₂ atmosphere at 1450 °C for 30 min. The melts were constantly poured onto a preheated stainless-steel plate and pressed into the glasses with 7 mm thickness, then annealed at 450 °C for 2 h followed by cooling in the furnace at its natural cooling rate. The glasses were cut and polished to 3 mm thickness for various spectroscopic measurements.

The densities of different samples were measured by Archimedes' method. UV transmission spectra were measured by Perkin-Elmer Lamda 35 spectrometer. Luminescence spectra under UV excitation were measured by Hitachi F-4500 spectrometer. The scintillation light output was measured using an 60 keV/c X-ray beam. All the above measurements

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were performed at room temperature.

Tab.1 Compositions of glasses

Serial number	Glass name	Glass composition (mol %) Glass matrix	Ce_2O_3	Density (g • cm^{-3})
1	SBBG0	$35SiO_2$-$35B_2O_3$-$15BaO$-$15Gd_2O_3$	0.0	4.262
2	SBBG1	$40SiO_2$-$39B_2O_3$-$15BaO$-$5Gd_2O_3$	1.0	3.433
3	SBBG2	$38SiO_2$-$36B_2O_3$-$15BaO$-$10Gd_2O_3$	1.0	3.889
4	SBBG3	$35SiO_2$-$34B_2O_3$-$15BaO$-$15Gd_2O_3$	1.0	4.347
5	SBBG4	$33SiO_2$-$31B_2O_3$-$15BaO$-$20Gd_2O_3$	1.0	4.798
6	SBBG5	$27SiO_2$-$27B_2O_3$-$15BaO$-$30Gd_2O_3$	1.0	5.494

The densities of different samples are also shown in Fig.1. All samples have high density as expected. Particularly, the density of SBBG5 is nearly 5.5 g/cm³. The high density indicates the glasses can be a promising candidate for scintillating applications.
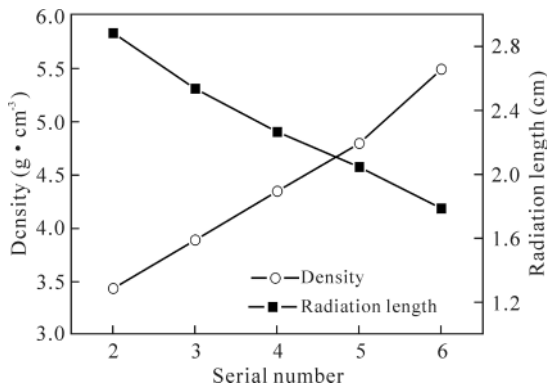

Fig.1 Density and radiation length of samples

Radiation length depends on glass density and mass absorption coefficient. According to reported result[9], the radiation length L is

$$L = 1/(dm) = (dm)^{-1} , \tag{1}$$

where m is mass absorption coefficient (cm²/g), and d is glass density (g/cm³). The radiation lengths of all samples are listed in Fig.1.

It is obvious that Gd_2O_3 has a remarkable effect for improving the density and radiation length. The decrease in the radiation length is due to the increase of the density of glasses.

Transmission spectra of glass base and the doped glass are shown in Fig.2, where the sample of SBBG0 is glass base. As can be seen, the UV absorption edges for glass base are located at about 313 nm. By comparison, the UV absorption edges of Ce^{3+}-doped glasses are located at 350 nm, whereas all Gd^{3+} absorption bands in Ce^{3+}-doped glasses in the shorter frequency range disappear due to the overlapping effect of Ce^{3+} absorbing band. And they are all determined by the lowest 4f-5d transition of Ce^{3+} ions.

The red shift of the UV cut-off position is observed as shown

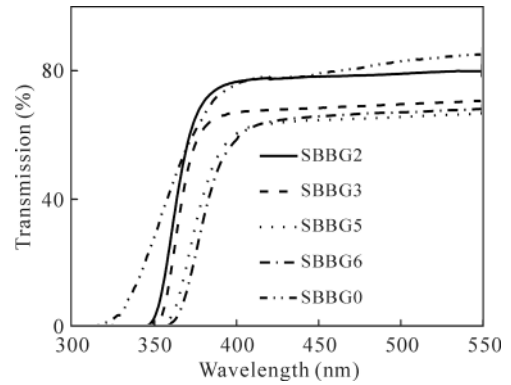in Fig.2. At beginning, the transmission shifts toward longer wavelength with increasing Gd_2O_3[10].

Fig.2 Transmission spectra of doped glasses with different amounts of Gd_2O_3 and glass base

Excitation spectra (λ_{em}=390 nm) of glass samples (SBBG2-SBBG5) and emission spectrum (λ_{ex}= 270 nm) of SBBG0 sample are shown in Fig.3. Two main excitation peaks are located at 270 nm and 340 nm (29411 cm^{-1}), respectively, which can be attributed to the $^8S_{7/2}\rightarrow^6I$ transition of Gd^{3+} ion and the 4f-5d transition of Ce^{3+} ion[11]. Also the emission spectrum peaks are located at 313 nm (31948 cm^{-1}), which can be attributed to the $^6P_{7/2}$-^6I transition of Gd^{3+} ions. It demonstrates the efficient energy transfer from Gd^{3+} ion to Ce^{3+} ion.
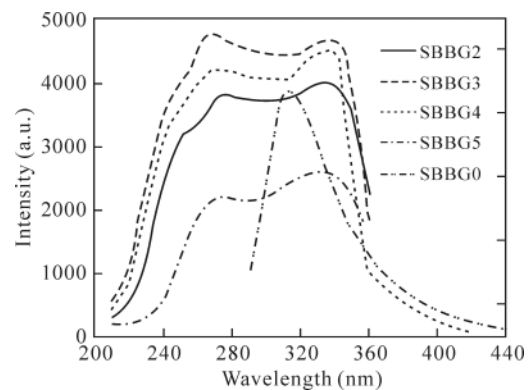

Fig.3 Excitation spectra (λ_{em}= 390 nm) of glass samples (SBBG2-SBBG5) and emission spectrum (λ_{ex}= 270 nm) of SBBG0 sample

The emission spectra for different concentrations of Gd^{3+} ions under X-ray excitation are presented in Fig.4. With the increase of the concentration of Gd^{3+} ions, the intensity of emission of Ce^{3+} increases. The results imply that Gd^{3+} ions sensitize the luminescence of Ce^{3+} in these matrices, and Gd^{3+} ions can transmit energy to Ce^{3+} efficiently. However, at higher Gd^{3+} ion concentrations reaching 15 mol%, a decrease in the emission peak intensity of Ce^{3+} is clearly observed due

to the concentration quenching effect. The efficiency energy transfer from Gd^{3+} to Gd^{3+} increases, and thus the efficiency energy transfer from Gd^{3+} to Ce^{3+} decreases.

The measurements of excitation spectra and emission spectra under X-ray excitations indicate that the $Gd^{3+} \rightarrow Ce^{3+}$ energy transfer in the phosphate glass matrices occurs.
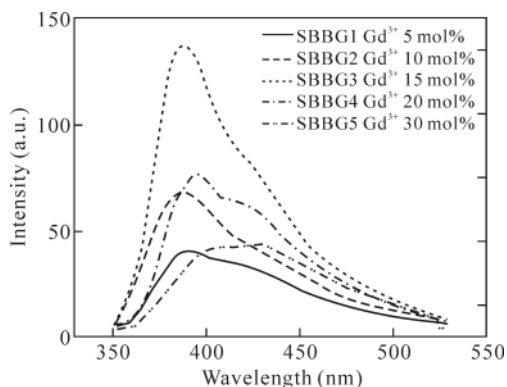

Fig.4 Emission spectra of samples with different amounts of Gd_2O_3 under X-ray radiation

Fig.5 shows the decay curves of the SBBG3 and SBBG5 glasses under H_2 lamp pulse excitation. Their decay curves may be fitted using double-exponential function[8], and the lifetimes are 33.6 ns and 21.0 ns, respectively. The lifetimes of all samples are listed in Tab.2.
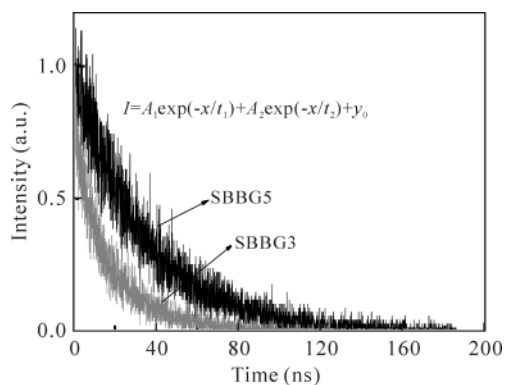

Fig.5 Decay curves of SBBG3 and SBBG5

Tab.2 Lifetime of Ce^{3+} ions

Glass name	SBBG1	SBBG2	SBBG3	SBBG4	SBBG5
Decay time (ns)	36.2	19.9	16.9	27.3	33.6

The high density and high light output indicate that the present glasses are very attractive. The emission of Ce^{3+} is an allowed 5d-4f transition and has a typical decay constant of less than 50 ns. So the glasses have extensive applications in high energy physics experiments.

Fig.6 shows the decay curves of Gd^{3+} ions. The decay of Gd^{3+} may be considered to be due to two contributions: (i) the cross relaxation to Ce^{3+}, which is characterized by a tem-

poral parameter τ_{cr}; (ii) the one-site radiative and non-radiative decay, which is characterized by the parameter $\tau_{one-site}$. The decay curves can be expressed as[12]:

$$I(t) = I_0 \exp[-(t/\tau_{cr})^{3/s} - t/\tau_{one-site}] , \qquad (2)$$

where $I(t)$ and I_0 are the luminescence intensities during the decay and at $t=0$, respectively, s is a parameter to describe the distance dependence of the cross relaxation process, and $s=6$, 8, and 10 denote the electric dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions between luminescent centers, respectively[13]. The one-site decay constant $\tau_{one-site}$ is assigned as a fixed value of 1.61 ms from the decay of the only doped Gd^{3+}. τ_{cr} from the data fitted with $s=6$ by rearranging Eq.(2) into a linear form while taking natural logarithms of both sides are summarized in Tab.3. Therefore, the fitting is consistent with dipole-dipole transfer between Gd^{3+} and Ce^{3+}. With the increase of Gd^{3+} concentration, the parameter τ_{cr} increases rapidly. But at higher Gd^{3+} ion concentrations reaching 15 mol%, a decrease of the parameter τ_{cr} is clearly observed, which indicates a fast cross relaxation from Gd^{3+} to Ce^{3+} since the interaction of Ce^{3+} and Gd^{3+} changes from long to short distance. However, with the increase of Gd^{3+}, the efficiency energy transfer from Gd^{3+} to Gd^{3+} increases, and thus the efficiency energy transfer from Gd^{3+} to Ce^{3+} decreases.
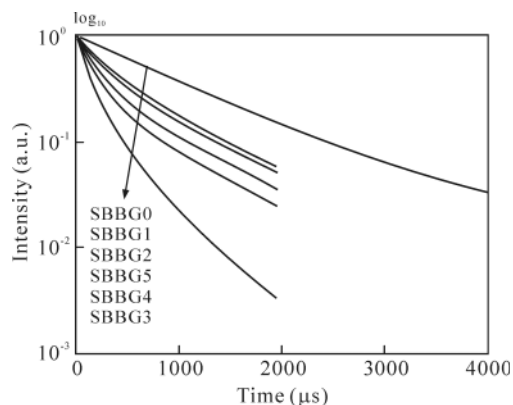
Fig.6 Decay curves of Gd^{3+} ions

Tab.3 Lifetime of Gd^{3+} ions and efficiency of $Gd^{3+} \rightarrow Ce^{3+}$ transfer (η_{ETE})

Glass name	SBBG1	SBBG2	SBBG3	SBBG4	SBBG5
$\tau_{cr}(\mu s)$	468	421	133	245	314
η_{ETE} (%)	71.1	73.9	91.7	84.8	80.5

In Fig.7, the energy levels of Gd^{3+} and Ce^{3+} ions are schematically shown to explain the energy transfer mechanism in the Gd^{3+}/ Ce^{3+} co-doped glasses. Gd^{3+} emission mainly occurs at 312 nm which is due to the electric-dipole transition of $^6P_{7/2} \rightarrow {}^8S_{7/2}$. Due to the forbidden nature of the ^6I and ^6D transitions, only when Gd^{3+} is sufficiently excited via energy

transfer from the host lattice, can Gd^{3+} further transfer energy to Ce^{3+}. Energy transfer occurs, because the ^6I and $^6P_{7/2}$ states of Gd^{3+} are higher than 5d state of Ce^{3+} as shown in Fig.6, which is known as the resonance condition[14]. Resonance takes place, because the emission of Gd^{3+} overlaps with the 312 nm absorption peak of Ce^{3+}.

When Ce^{3+} ions are excited by UV light or X-Ray, electronic transition of 5d → ^2F_J is observed in these glasses, where $J = 5/2$ and 7/2. Gd^{3+} ions can also be excited to ^6I, then decay to the $^6P_{7/2}$ level rapidly, and the energy in the $^6P_{7/2}$ level of Gd^{3+} is transferred to the 5d level of Ce^{3+} by resonant energy transfer[15] which can enhance the luminescence of Ce^{3+}.
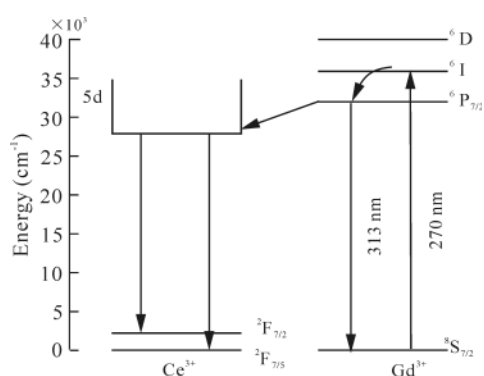

Fig.7 Energy level diagram of Ce^{3+} and Gd^{3+} emissions

In summary, an oxide glass host with higher density, better transmittance, good glass forming stability and chemical durability is obtained from SiO_2-B_2O_3-BaO-Gd_2O_3 system. Radiation length is between 1.79 cm and 2.89 cm, the emission peak is located at 390 nm, and the radioluminescence efficiency of Ce^{3+}-doped glasses increases along with Gd^{3+} concentration. The maximum radioluminescence intensity is achieved when the Gd^{3+} concentration is about 15 mol%. Decay time is about 10 ns to 40 ns. With these favorable characteristics, the present glasses suggest the potential application in high energy physics and particle physics.

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