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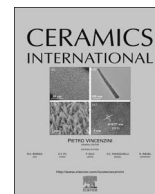
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Fast Ce³⁺-activated borosilicate glass scintillators prepared in air atmosphere



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ABSTRACT

We report a simple synthesis method of a transparent and colorless Ce³⁺-activated borosilicate glass scintillator by conventional melt-quenching method in air atmosphere. The optical transmittance and X-ray absorption near edge spectroscopy (XANES) spectra imply that ceric ions (Ce⁴⁺) can be effectively reduced to cerous one (Ce³⁺) in borosilicate glass scintillator by substituting 40–60 mol% SiC for SiO₂. Compared to the x=0 glass scintillator, both the photo- and radioluminescence intensity of the optimized borosilicate glass scintillator (x=15 C) are enhanced by a factor of 6.5 and 7.7, respectively. The integral radioluminescence intensity of the x=15 C borosilicate glass scintillator resulted from the combined reduction effect of both SiC and graphite powder is about that of 14% bismuth germinate (BGO) crystal.

1. Introduction

With comparison to scintillating crystals and ceramics utilized in medical imaging, homeland security, and high energy physics engineering, Ce³⁺-activated glass scintillators with properties of fast decay and high density may be potential candidates owing to the remarkable superiorities in cost-effective and large-volume production, as well as easy shaping of elements [1–3]. The incorporation of Ce³⁺ into the borosilicate glass is usually adopted for the large solution capacity of rare-earth oxides and the extreme chemical stability for nuclear waste immobilization [4]. Therefore, Ce³⁺-activated borosilicate glasses enriching gadolinium oxide have been extensively attracted for the purpose of detecting high-energy rays by many scholars these days [5–8]. However, an indispensable reduction atmosphere, either CO or H₂/N₂ mixed gases, must be supported to reduce Ce⁴⁺ to Ce³⁺ as completely as possible during glass synthesis. It has been confirmed that only Ce³⁺ ions can give rise to efficient luminescence, while Ce⁴⁺ shows no luminescence. And the optical absorption bands of Ce⁴⁺ is observed to extend from far UV to the visible region, up to 500 nm [8], which quenches the emission intensity of Ce³⁺ ions. The rigorous requirement of indispensable reduction atmosphere not only complicates the synthesis conditions, but increases the corresponding production cost.

To the best of our knowledge, controlling the oxidation state of

cerium (Ce³⁺) in the glass materials quenched in air atmosphere is considerably difficult [9–11], which may be linked to the existed lots of defects in glass materials with the intermediate- and long-range disorder structure. Following the successful tunability of the oxide states of cerium in borogermanate glass scintillators by adding 0.31 mol% Si₃N₄ in air atmosphere [9], we get the similar success by substituting 40–60 mol% SiC for SiO₂ in borosilicate glass scintillators in this work. It is found that the combined reduction effect of SiC and graphite powder further attribute to improve the optical properties of borosilicate glass scintillators. And the reduction effect was also observed by both optical transmittance and XANES spectra, a detailed study on the luminescent properties was supported by the static photoluminescence (PL) and dynamic emission decay curves, as well as radioluminescence (RL) spectra under X-ray excitation.

2. Experimental methods

Borosilicate glass scintillators with the nominal composition of 30B₂O₃-(25-x)SiO₂-xSiC-10Al₂O₃-34Gd₂O₃-1CeF₃ (x=0, 5, 10, 15 and 20) in Table 1 were synthesized in air atmosphere by melt-quenching method according to the reported procedure in our previous works [9,10]. The raw materials such as H₃BO₃ (99.99%), SiO₂ (99.99%), Al₂O₃ (99.99%) and CeF₃ (99.99%) were all purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd. The reagents such as SiC (99.

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Table 1Glass composition (mol%), density, lifetime, the strongest excitation/ emission wavelength, and the Stokes shift of Ce^{3+} ions.

No.	B_2O_3	SiO_2	SiC	Al_2O_3	Gd_2O_3	CeF_3	graphite	Density (g/cm^3) ^a	Lifetime (ns) ^b	Ex/Em (nm)	$\Delta\lambda$ (nm)
Host	30	25	0	10	35	0		4.878	–	–	–
$x=0$	30	25	0	10	34	1		4.858	22.93	326/386	60
$x=5$	30	20	5	10	34	1		4.926	27.06	329/387	56
$x=10$	30	15	10	10	34	1		4.882	28.37	331/388	57
$x=15$	30	10	15	10	34	1		4.880	28.52	331/390	59
$x=20$	30	5	20	10	34	1		4.969	28.66	332/391	59
$x=15\text{C}$	30	10	15	10	34	1	1.0 wt.%	4.940	29.30	335/394	59

^a Measured by Archimedes' principle.^b Evaluated by a sum of two exponential methods [9].

9%) and Gd_2O_3 (99.99%) were purchased from Shanghai Jingchun Reagent Co. Ltd., and Jiangxi Ketai Advanced Materials Co. Ltd., respectively. The addition of extra 1 wt.% graphite powder to the $x=15$ glass to obtain the $x=15\text{C}$ glass is aimed to check the combined reduction effect of both SiC and graphite powder on the luminescent properties of borosilicate glass scintillators.

All borosilicate glass scintillators with the same thickness of about 2 mm are polished on a UNIPOL-802 polishing equipment (Shenyang Kejing Auto-instrument Co. Ltd., Shenyang, China) for optical properties measurement. UV–vis transmittance spectra were collected in 200–800 nm wavelength regions on a Lambda 750 S UV/VIS spectrometer (Perkin-Elmer, Wellesley, USA). Ce L_{III} -edge X-ray absorption near edge structure (XANES) spectra were carried out on the 1W2B beamline of Beijing Synchrotron Radiation Facility (BSRF, Beijing, China). Data process and analysis using linear combination fitting (LCF) method were performed on Athena software to evaluate the concentrations of Ce^{3+} and Ce^{4+} in borosilicate glass scintillators [12]. Static PL spectra were measured by an FLS980 spectrometer (Edinburgh Instr., Livingston, UK) equipped with a 450 W Xe lamp as an excitation source, and dynamic emission decay curves were done on a nanosecond hydrogen flash lamp (nF920 with 1.5 ns pulse width) by applying deconvolution from the lamp pulse with the excitation and emission wavelength at 330 and 390 nm, respectively. RL spectra (irradiated by Cu K_α X-rays operating at 30 kV and 3 mA) were also collected on the mentioned FLS980 spectrometer coupled by means of optical lens and fibers to guide the radioluminescence light.

3. Results and discussion

Fig. 1(a) shows transmittance spectra of borosilicate glass scintillators. The UV cut-off edge of the designed host glass without any cerium ions locates at about 318 nm, while it shifts dramatically towards 395 nm activated with 1 mol% CeF_3 ($x=0$). This observation is associated with the contribution of cerium dopants: both the electronic

transition of Ce^{3+} from the 4f ground state to its 5d excited state and the charge transfer band of $\text{O}^{2-}\text{-Ce}^{4+}$ [8]. However, a blue-shifting of the cut-off edges is observed from 395 ($x=0$), 360 ($x=5$), 355 ($x=10$), 358 ($x=15$) to 353 nm ($x=20$) induced by an increasing content of substituting SiC for SiO_2 . The strong reduction nature of SiC that reduces Ce^{4+} to Ce^{3+} ions can be judged from the above-mentioned blue-shifting of the cut-off edges. Moreover, the $x=15\text{C}$ glass scintillator is obtained by adding 1 wt% graphite powder to the $x=15$ one, and its cut-off edge is nearly located at 352 nm, which must be associated with the combined reduction effect of both SiC and graphite agents.

Fig. 1(b) and (c) display the emission spectra and decay curves of Gd^{3+} 312 nm emission excited by 276 nm, respectively. The content of Gd_2O_3 is purposely designed to be as high as 34 mol% due to the following considerations: (i) to enhance the glass density to enlarge the absorption capacity of the incident high-energy rays, and (ii) to construct efficient energy transfer routine from Gd^{3+} sensitizers to Ce^{3+} activators. As summarized in Table 1, the glass density is found to be about 4.9 g/cm^3 , which is close to the basic density requirement of a practical scintillator, i.e. 5.0 g/cm^3 . Additionally, the highly efficient energy transfer from Gd^{3+} to Ce^{3+} can be confirmed by the complete vanishing of the featured emission peak at 312 nm of Gd^{3+} ions, and the dramatic decreasing in the corresponding decay times.

Upon monitoring the emission/excitation wavelength listed in the last second column in Table 1, the corresponding excitation and emission spectra of Ce^{3+} -activated borosilicate glass scintillators are shown in Fig. 2(a) and (b), respectively. All excitation and emission spectra show the similar profiles except for slight difference in the positions and intensities of emission band. The excitation spectrum comprises two groups of broad bands in 235–290 and 290–385 nm wavelength regions due to the characteristic absorption transitions of Ce^{3+} ion from the 4f level to its excited states $5d_{3,4,5}$ and $5d_{1,2}$, respectively [9,10]. Upon excitation of the 4f-5d_{1,2} level, the Ce^{3+} emission spectrum with maxima at around 390 nm is observed from 325 to 650 nm. The emission intensity of Ce^{3+} ions clearly increases with x values except for the $x=15$ glass scintillators, and the highest emission intensity is the $x=15\text{C}$ glass scintillator. With comparison to the $x=0$ glass scintillator, the integral emission intensity of the $x=10$ and $x=15\text{C}$ glass scintillators is enhanced by a factor of 4.8 and 6.5, respectively. Regarding the RL spectra in Fig. 2(d), the trend of emission intensity is very similar to the emission spectra. The maximum RL intensity is also the $x=15\text{C}$ glass scintillator, whose integral emission intensity is about that of 14% BGO, being higher than that of the $x=0$ glass scintillator by a factor of 7.7. This attributes to the higher concentration of the reduced Ce^{3+} ions, which results in the lower self-absorption of Ce^{4+} ions, as depicted in the optical transmittance spectra in Fig. 1(a).

Fig. 2(c) gives the emission decay curves ($\lambda_{\text{ex}}=330$ nm, $\lambda_{\text{em}}=390$ nm) of Ce^{3+} -activated borosilicate glass scintillators. All emission decay curves of Ce^{3+} ions follow well the double-exponential rule rather than the single-exponential one. Thus, the mean lifetimes of emission decay curves can be evaluated by a sum of two exponential functions [9,10]. The evaluated values of the mean lifetime are about

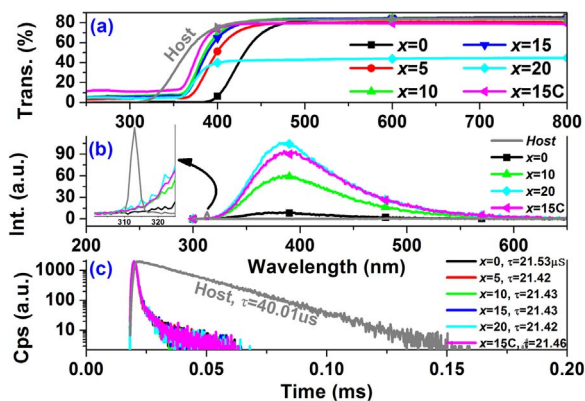


Fig. 1. Transmittance spectra (a), emission spectra excited by 276 nm (b) and decay curves of Gd^{3+} 312 nm emission under 276 nm excitation (c). Inset b shows the emission spectra of Gd^{3+} ions in 300–330 nm wavelength regions.

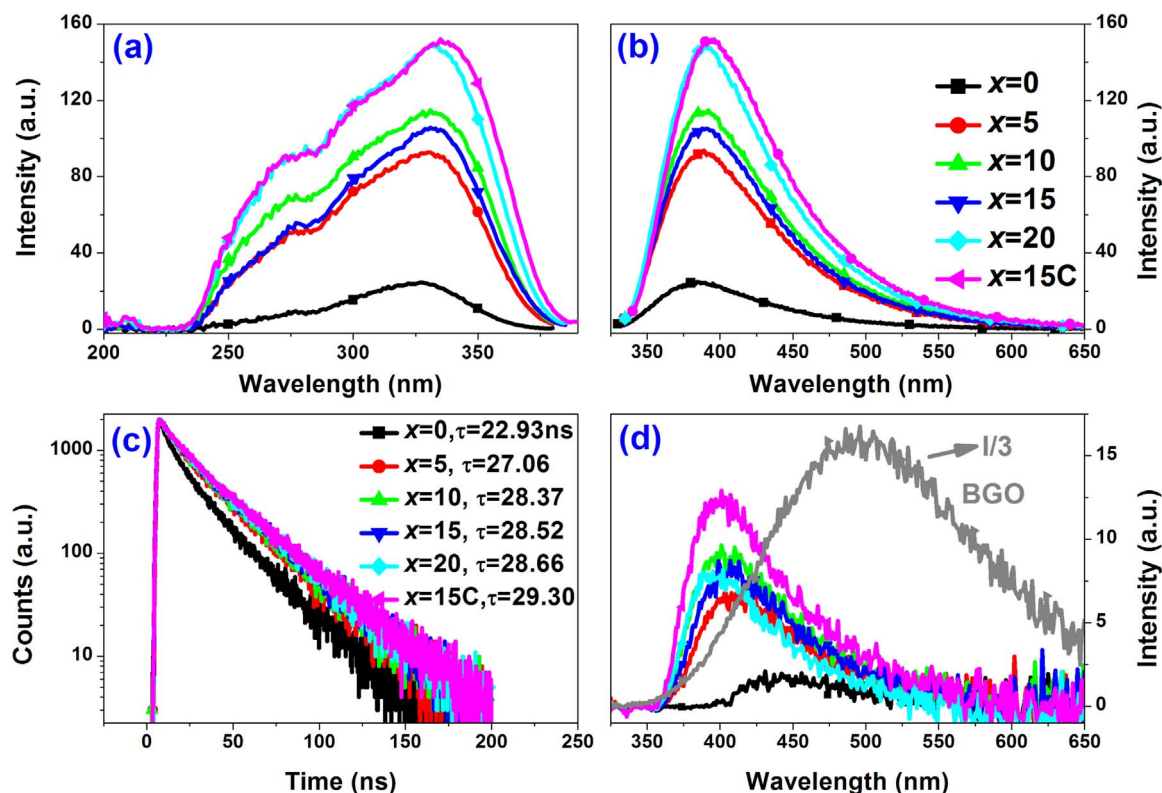


Fig. 2. Excitation (a), emission (b) spectra, emission decay curves (c) and RL spectra (d).

22.93, 27.06, 28.37, 28.52, 28.66 ns and 29.30 ns, respectively. The lifetimes clearly increase with the substitution ratios of SiC for SiO₂, they are in accordance with the presented PL and RL spectra. It suggests that the developed dense and fast borosilicate glass scintillators may be potential in the fields of both nuclear medical imaging and high energy physics engineering.

To further understand the reduction effect induced by substituting SiC for SiO₂ on the optical properties of Ce³⁺-activated borosilicate glass scintillators, we present the normalized Ce L_{III}-edge XANES spectra in Fig. 3(a), where the standard trivalent and tetravalent Ce compounds, i.e. CeF₃ and CeO₂ crystalline powder are also compared in Fig. 3(b). The XANES spectra of borosilicate glass scintillators show the characteristic features of both Ce³⁺ and Ce⁴⁺ ions. Compared to the other glass scintillators, the $x=0$ one prepared without any SiC or C incorporation exhibits much higher Ce⁴⁺ concentration indicated by the relatively higher Ce⁴⁺ absorption for the black curve shown in Fig. 3(a); while the Ce⁴⁺ concentration differences in the other glass

scintillators (colored curves) are difficult to distinguish. By using a LCF method, the concentration of Ce³⁺ ions in borosilicate glass scintillators are estimated to be 71.0% ($x=0$), 83.8% ($x=5$), 87.5% ($x=10$), 85.1% ($x=15$), 82.4% ($x=20$) and 83.8% ($x=15C$), respectively. Failure to clearly distinguish the Ce³⁺ concentrations ($\sim 85 \pm 2.6\%$ range) by XANES in the glass scintillators prepared with different SiC ratios is attributed to the low (1 mol%) Ce doping ratio and small probing volume using ~ 6 keV X-ray photons, which exhibits a shallow penetration depth estimated to be $< 20 \mu\text{m}$, significantly smaller than the 2 mm thickness of borosilicate glass scintillators that can be fully probed by transmission/absorption measurements using visible light wavelengths shown in Fig. 1(a). The attractive reducing effect of the proper quantities of SiC is able to be illustrated by the colour of borosilicate glass scintillators due to the absorption edge differences in visible light, as presented in the inset of Fig. 3(a). The colour of borosilicate glass scintillator changes from heavy yellow ($x=0$), light yellow ($x=5, 10$ and 15), even to completely colorless ($x=15C$). However, the colour of the $x=20$ glass scintillator is dark black due to the excessive SiC, which heavily degrades the optical transmittance property (Fig. 1(a)), and results in the lower light yield (Fig. 2(d)).

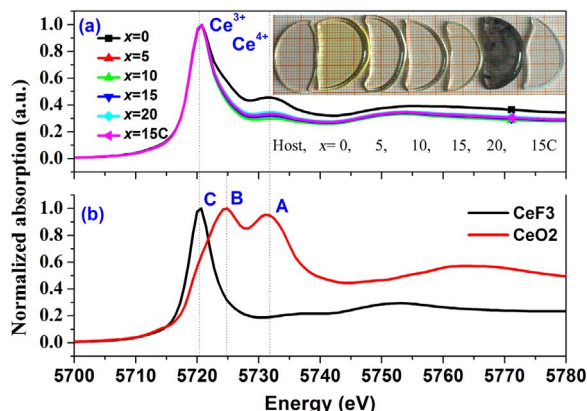


Fig. 3. Ce L_{III}-edge XANES spectra of borosilicate glass scintillators (a) and XANES spectra of Ce⁴⁺ and Ce³⁺ reference samples (b). Inset (a) shows the digital photographs.

4. Conclusions

We have successfully synthesized transparent and colorless borosilicate glass scintillators featured with a density of $\sim 4.9 \text{ g/cm}^3$ and decay time of about 28–29 ns in air atmosphere by substituting 40–60 mol% SiC for SiO₂. More than 80% concentration of Ce³⁺ ions exist in borosilicate glass scintillators by the substituting method. Both PL and RL intensity of the optimized borosilicate glass scintillators are enhanced by a factor of 6.5 and 7.7, respectively. And the highest RL intensity ($\sim 14\%$ BGO) can be easily tuned by the combined reduction effect of both SiC and graphite powder. The proposal of combined reduction effect will guide us to design and synthesize other scintillating materials in air atmosphere in the future.

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