Valence regulation of cerium ions in borosilicate (borogermanate) glass scintillator synthesized in air atmosphere

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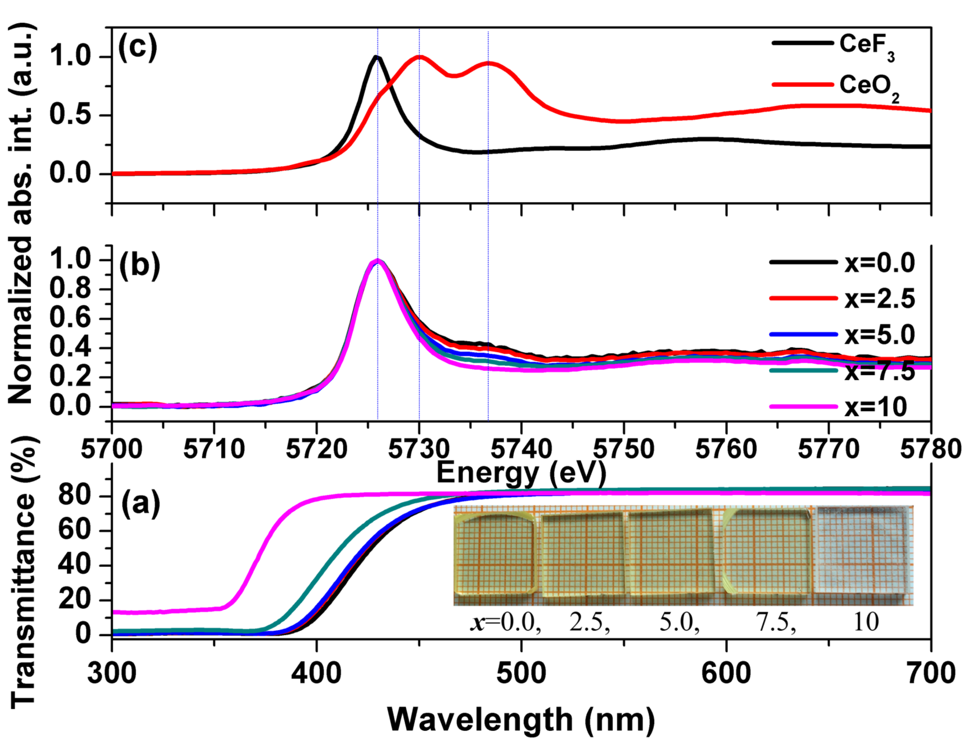
Introduction

The Circular Electron Positron Collider (CEPC) is a large international scientific facility proposed by the Chinese particle physics community. Glass scintillator is considered to be one of the most important candidates for crystals in view of cost, size and shape, and fiber-drawing technology. The fast decay time of glass scintillators is realized by doping with cerium ions. However, both Ce^{3+} and Ce^{4+} coexist in the developed glass scintillators, and only Ce^{3+} is reported to attribute to both light yield and fast decay time.

In this work, we have successfully synthesized colorless and transparent cerium-activated borosilicate (germanium) scintillation glass systems in air. It was found that in the borosilicate system, the glass component Al_2O_3 is one of the key components in the synthesis of colorless and transparent scintillation glass in air. The regulation of the valence state of cerium ions in Ce^{3+}-activated borosilicate glasses by different silicon sources and aluminum sources (especially aluminum nitride) and their luminescence properties were systematically studied. However, in the borogermanate system, the synthesis of colorless and transparent borogermanate glass in air can be realized by external doping with an appropriate amount of Si_3N_4. Lots of experimental results revealed that the synthesis of transparent colorless borogermanate glasses in air is easier to control than that of borosilicate one under the same conditions. The light yield of the glass is higher than 800 ph/MeV, and the energy resolution is 26.77%. . It would be a potential possibility for the proposal of SiPM coupling with glass scintillators in the hadron calorimeter (HCAL) of CEPC.

1. Role of Al^{3+} on tuning optical properties

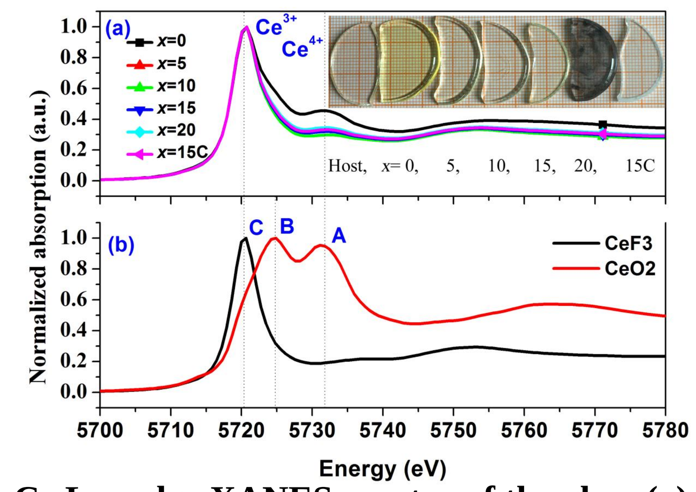


Transmittance spectra (a), Ce L_{III}-edge XANES spectra of borosilicate glasses (b), and reference compounds CeF_3 as well as CeO_2 (c)

- The optical transmittance of all glasses is higher than 80% in the 470-700 nm. The observed continuous blue shift is associated with the enhanced concentration ratios of Ce^{3+} to Ce^{4+} ions. Because the 4f-5d electronic transition of Ce^{3+} ions and the charge transfer band of O_2--Ce^{4+} should be responsible for the light absorption in this wavelength region
- The normalized XANES spectra of borosilicate glasses show the evident characteristic features of both Ce^{3+} and Ce^{4+} ions. The glass exhibits the best match to CeF_3. With decrease of Al_2O_3 content and increase of BaO, the intensity of ~5737 eV peak increases, indicating the increase of Ce^{4+} concentration in the borosilicate glass.

2. Si source on tuning optical properties

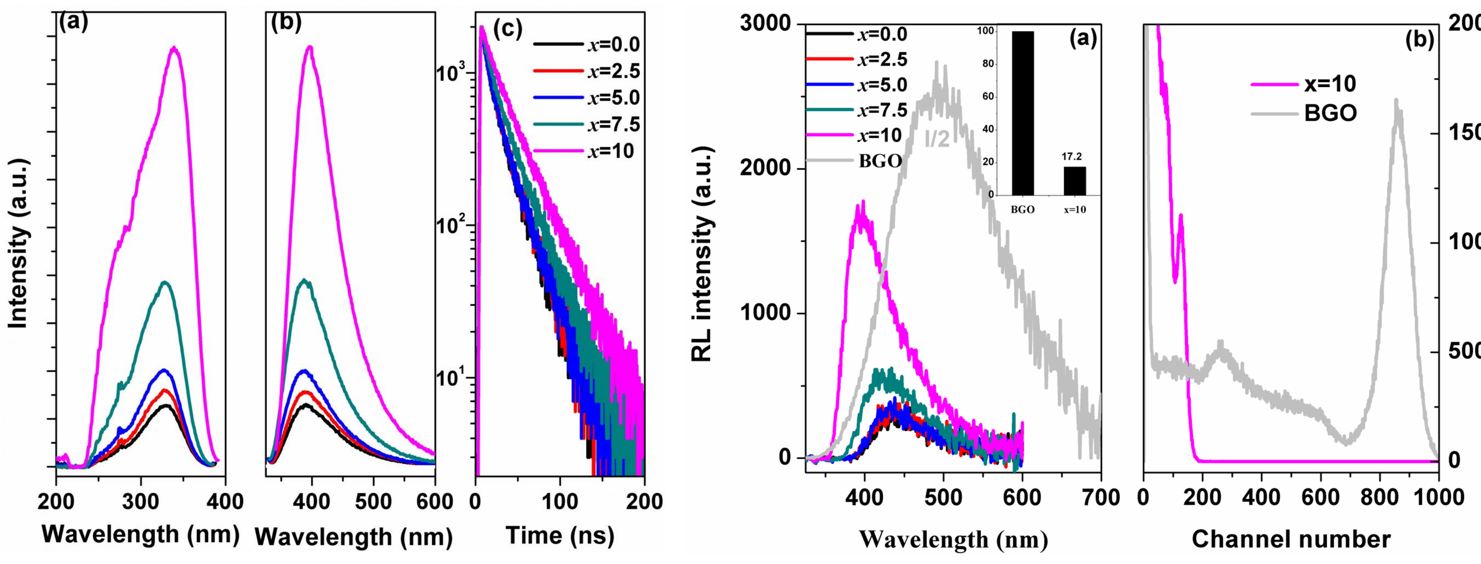
No.	B_2O_3	SiO_2	SiC	Al_2O_3	Gd_2O_3	CeF_3	Density (g/cm³)	Lifetime (ns)	Ex/Em (nm)	Δλ (nm)
Host	30	25	0	10	35	0	4.878	-	-	-
x=0	30	25	0	10	34	1	4.858	22.93	326/386	60
x=5	30	20	5	10	34	1	4.926	27.06	329/387	56
x=10	30	15	10	10	34	1	4.882	28.37	331/388	57
x=15	30	10	15	10	34	1	4.880	28.52	331/390	59
x=20	30	5	20	10	34	1	4.969	28.66	332/391	59
x=15C	30	10	15	10	34	1	4.940	29.30	335/394	59



Ce L_{III}-edge XANES spectra of the glass (a) and XANES spectra of Ce^{4+} and Ce^{3+} samples (b)

- The XANES spectra of glass scintillators show the characteristic features of both Ce^{3+} and Ce^{4+} ions. The x=0 glass one prepared without any SiC or C incorporation exhibits much higher Ce^{4+} concentration compared to the other samples.
- The attractive reducing effect of the proper quantities of SiC is able to be illustrated by the colour of borosilicate glasses scintillators due to the absorption edge differences in visible light. The colour of borosilicate glass scintillator changes from heavy yellow, light yellow, even to nearly completely colourless.

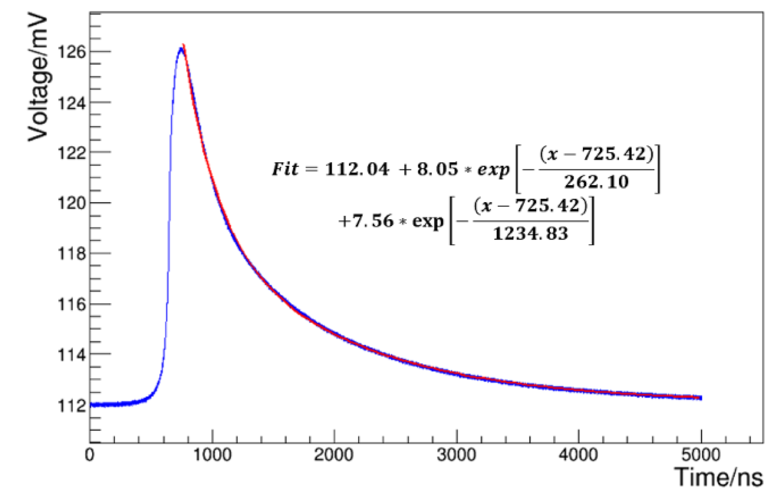
3. PL and Scintillation properties



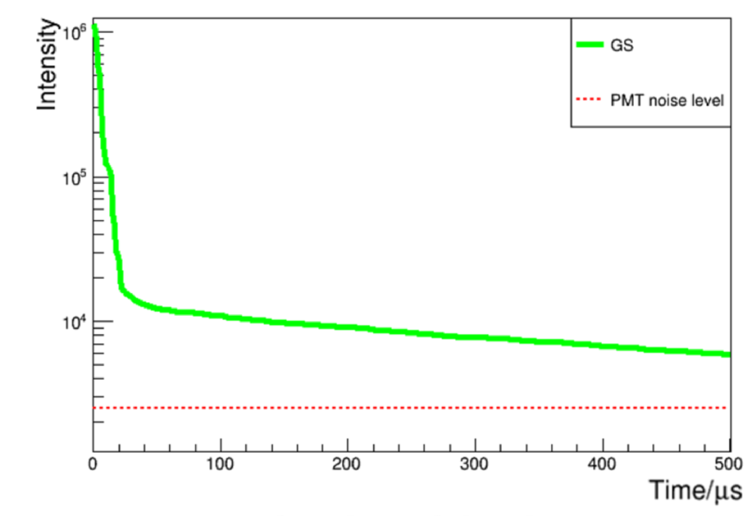
Excitation, emission spectra, PL decay curves, XEL spectra and energy spectra

- The integral emission intensity of the glass is enhanced by about 6.7 times, which is mainly resulted from the increasing concentration of Ce^{3+} ions tuned by the full replacement of BaO by Al_2O_3.
- All the emission decay curves of Ce^{3+} ions follow well the double-exponential rule. In XEL, integral emission intensity of the glass is about that of 17.2% BGO crystal. Under ^{137}Cs Gamma source, the light yield of the glass is about 14.7% of that of the BGO crystal.

4. Time properties



Scintillating decay time curve of the glass



Afterglow of the glass

- The decay time of the fast and slow components is 262.10 ns (18%) and 1234.83 ns (82%), respectively. The fast component is attributed to the 5d-4f transitions of Ce^{3+} in host glass and the energy transport to Ce^{3+} center results in the slow component.
- The parameter $k = F_0 / F_{100}$ is defined to illustrate afterglow, where F_0 is the highest frequency, F_{100} is the frequency after 100 μs. The afterglow k values of the glass is 299.44. As a comparison, the afterglow k value of GAGG single crystal is 11.65. Most of the electrons and holes are captured by the traps in the glass, which prevents the photons from escaping from the glass.

5. Conclusions

- **A colorless Ce^{3+}-activated borosilicate scintillating glass was successfully synthesized in air atmosphere by replacing all BaO with Al_2O_3 and adding Si source as a reducing agent.**
- **Both the PL and XEL intensity of the optimized borosilicate glass scintillators are enhanced by a factor of 6.5 and 7.7, respectively.**
- **Its integral XEL intensity is about 17.2% BGO, with a light yield of ~800 ph/MeV estimated by gamma ray spectroscopy. And the scintillating decay times of the glass are 262.10 ns (18%) and 1234.83 ns (82%), respectively. And the light decreased faster than GAGG crystal.**
- **It would be a potential possibility for the proposal of SiPM coupling with glass scintillators in the HCAL of CEPC.**

Acknowledgement

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