

# Effect of synthesis conditions on Ce<sup>3+</sup> luminescence in borate glasses



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## ABSTRACT

Cerium exhibits two stable valence states, i.e. Ce<sup>3+</sup> and Ce<sup>4+</sup>. In glassy hosts, Ce<sup>4+</sup> strongly deactivates the Ce<sup>3+</sup> luminescence and therefore it becomes essential to employ reducing conditions in the glass synthesis. In the present work, we report a systematic study on the effect of different synthesis conditions on Ce<sup>3+</sup> luminescence properties in borate glasses. In the air atmosphere synthesized glasses, strong Ce<sup>4+</sup> charge transfer (CT) transitions have been observed, which led to poor luminescence properties with quantum yield less than 1%. The Ce<sup>3+</sup> luminescence significantly improved in glasses prepared under reducing synthesis atmosphere suggesting effective reduction of Ce<sup>4+</sup> ions to the Ce<sup>3+</sup> state. In both mild to strong reducing conditions, the decay profiles were single exponential with decay lifetime of about 46 ns. Among the studied synthesis conditions, the glass prepared under strong reducing condition using carbon enclosed double crucible plus 0.5 wt.% carbon doping showed best performance with luminescence quantum yield of about 42%, which is one of the highest value in the glassy hosts reported so far.

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## 1. Introduction

Ce<sup>3+</sup> doped inorganic materials such as glasses and crystals are widely used as phosphors for displays and lightings as well as the high energy radiation scintillators [1–3]. It is due to the superior light yield of Ce<sup>3+</sup> ions arising from its parity allowed 5d–4f transitions. Moreover, the absence of cross-relaxation mechanisms and an insignificant multiphonon relaxation of excitation population due to the wide separation of 5d–4f energy levels have established Ce<sup>3+</sup> as one of the most efficient luminescent ion. Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>: Ce<sup>3+</sup>, LaCl<sub>3</sub>: Ce<sup>3+</sup>, LSO: Ce<sup>3+</sup> and some glasses activated with Ce<sup>3+</sup> ions are widely commercialized as efficient phosphors and radiation scintillators [1–5].

The redox reaction of cerium allows two stable valence states, i.e. Ce<sup>3+</sup> and Ce<sup>4+</sup>, whose equilibrium depends on the host material as well as on the synthesis conditions [6]. Ce<sup>4+</sup>, owing to its strong charge transfer (CT) absorption (Ce<sup>4+</sup> + e<sup>-</sup> → Ce<sup>3+</sup>) in the UV–visible spectral region can act as a quenching center for the Ce<sup>3+</sup> luminescence (Fig. 1). In the case of the glasses, the Ce<sup>4+</sup> CT occurs at longer wavelength region and effectively overlaps the Ce<sup>3+</sup> 4f–5d transitions [7]. Therefore special precautions such as the reducing synthesis atmosphere, selection of appropriate precursor chemicals, and doping with reducing agents are necessary in the synthesis of Ce<sup>3+</sup> doped glasses. Reisfeld and Hormadaly used (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> as a precursor chemical for Ce<sup>3+</sup> and added mannitol as the reducing agent in the batch to maintain the reducing atmosphere during the synthesis of Ce<sup>3+</sup> doped borate glass [8]. Chewpraditkul et al. used CeO<sub>2</sub> as the precursor dopant

chemical and the melting was carried out in CO reducing atmosphere [7]. In other reports, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was used as a precursor chemical and the melting was carried out under N<sub>2</sub> plus graphite lumps; whereas, only N<sub>2</sub> atmosphere was also used as the reducing atmosphere together with the oxide precursor chemicals in the glass synthesis [6,9]. From all these studies, it can be seen that the different reducing conditions were employed in the glass synthesis, which creates mild to strong reducing effects. There is no systematic study on the influence of such varied synthesis conditions on Ce<sup>3+</sup> luminescence properties in the glass, which is highly important to precisely optimize the synthesis process.

In this work, we present a systematic investigation on the effect of different synthesis conditions on the Ce<sup>3+</sup> luminescence properties in a calcium–aluminum–lanthanum–borate glass system. We studied various synthesis conditions, such as reducing atmosphere (5% H<sub>2</sub> gas flow, melting in carbon enclosed double crucibles, etc.), direct doping of carbon or aluminum metal as a reducing agent in the batch, and the use of CeO<sub>2</sub> or CeF<sub>3</sub> precursor dopant chemicals, and investigated its influence on the Ce<sup>3+</sup> luminescence, decay lifetime and luminescence quantum yield.

## 2. Experimental

High temperature melt-quenching method was used for the glass synthesis with base composition of 55 B<sub>2</sub>O<sub>3</sub>–20 CaO–10 Al<sub>2</sub>O<sub>3</sub>–15 La<sub>2</sub>O<sub>3</sub> in mol%. The doped samples were obtained by substituting the 0.5 mol% of La<sub>2</sub>O<sub>3</sub> with an equivalent amount of the dopant contents. CeO<sub>2</sub> (99.99%) and CeF<sub>3</sub> (99.99%) were used as precursor chemicals for the dopants. The melting was carried out in covered alumina

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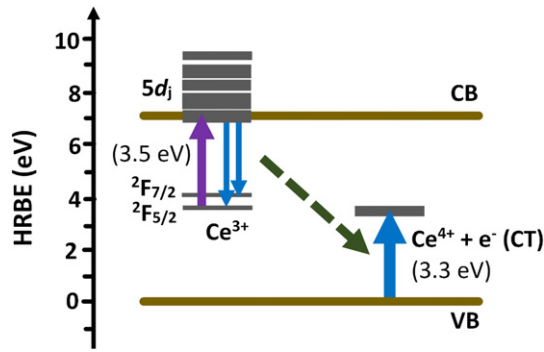


Fig. 1. Host referred electron binding energy (HRBE) diagram of  $\text{Ce}^{3+}$  ions in studied borate glass explaining the  $\text{Ce}^{3+}$  quenching mechanism by  $\text{Ce}^{4+}$  ions.

crucibles using different synthesis conditions and the details are presented in Table 1.

The glass samples G-1 and G-2 were prepared under normal air atmosphere, G-3 was prepared in 5%  $\text{H}_2$ –95%  $\text{N}_2$  reducing atmosphere, and the samples G-4 to G-6 were prepared in strongly reducing CO atmosphere provided by putting the covered batch crucible in a carbon filled enclosing crucible. For further reducing action, additional dopants were incorporated in the batch, such as the carbon powder (99.9%) or the Al metal (99.9%) as specified in Table 1. All the ingredients were mixed thoroughly using a mortar–pestle and melted at 1350 °C for 45 min. The melt was then quenched on a warm stainless steel mold. The cast glasses were annealed at 600 °C for stress removal and cooled slowly to room temperature. The well-annealed glasses were cut and polished in  $10 \times 10 \times 2 \text{ mm}^3$  dimensions for various measurements.

Optical absorption spectra were recorded using a Shimadzu 3600 spectrophotometer in the wavelength range of 180–800 nm. To avoid the saturation effect due to the strong absorption in the UV region, absorption spectra were also measured using thin samples (~200  $\mu\text{m}$  thickness). Photoluminescence (PL) and PL excitation (PLE) spectra of the studied glasses were recorded using a Shimadzu RF-5300 spectrophotometer in the 200–700 nm wavelength region. The PL quantum yield was measured using a 10 in. integrating sphere (Labsphere Inc., LMS-100) attached with a multi-channel CCD detector (Ocean Optics Inc., USB 2000) and a 372 nm LD (Nichia Co. Ltd., NDHU110APAE3) excitation source. Signals were calibrated using a standard halogen lamp (Labsphere, SCL-600) and an auxiliary halogen lamp for absolute spectral power distribution and absorption losses. The systematic error in quantum yield measurement is less than 5%. The PL decay curves were recorded using a PL lifetime measurement setup (Hamamatsu-Photonics, Quantarus Tau) equipped with a picosecond LED ( $\lambda_p$ : 340 nm; temporal resolution ~0.5 ns).

### 3. Results and discussion

#### 3.1. Optical absorption spectra

Fig. 2 shows the UV–visible optical absorption spectra of the studied glasses. The base glass absorption spectrum is also presented in the

Table 1

Sample identification name and the respective reducing conditions used in glass synthesis.

Sample name	G-1	G-2	G-3	G-4	G-5	G-6
Dopant precursors	$\text{CeO}_2$	$\text{CeO}_2$	$\text{CeO}_2$	$\text{CeO}_2$	$\text{CeF}_3$	$\text{CeF}_3$
Additional dopants	–	C (0.5 wt.%)	–	Al <sup>a</sup> (0.5 wt.%)	–	C (0.5 wt.%)
Synthesis atmosphere	Air	Air	5% $\text{H}_2$	CO	CO	CO

<sup>a</sup> In glass G-4, the additional Al metal doping was compensated with the  $\text{Al}_2\text{O}_3$  contents in the batch to maintain the glass stoichiometry.

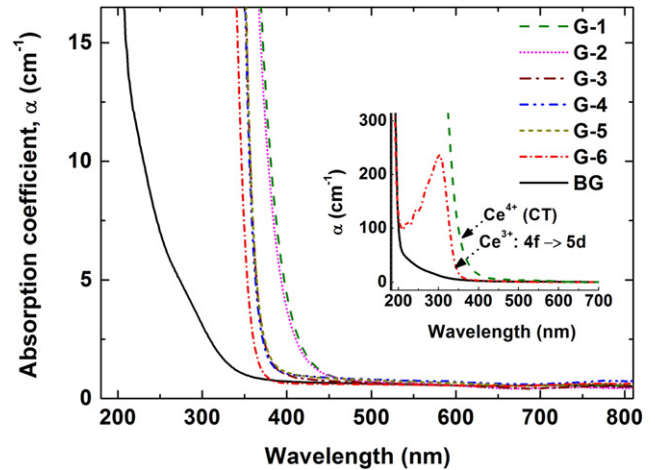


Fig. 2. Optical absorption spectra of the studied glasses (thickness ~2 mm). Inset: Absorption spectra recorded using thin samples (thickness ~200  $\mu\text{m}$ ).

figure for reference. In the cerium doped glasses, a strong absorption is observed in the UV region, thereby shifting the UV absorption band to the longer wavelength region. In the air atmosphere synthesized G-1 glass sample, this band shift is maximum, whereas it is least in the G-6 glass prepared under CO reducing atmosphere. Inset shows the absorption spectra of the G-1, G-6 and the base glass samples recorded using thin (~200  $\mu\text{m}$ ) specimens. In the case of air atmosphere synthesized G-1 glass, the absorption is very strong starting at about 400 nm and is attributed to the charge transfer (CT) transitions of the  $\text{Ce}^{4+}$  ions ( $\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}$ ) [10]. The presence of such intense CT absorption incorporates yellowish tint in the air atmosphere synthesized G-1 as well as the G-2 glasses. This suggests that the addition of carbon doping in the G-2 glass batch has very small reducing effect owing to its air atmosphere synthesis condition. Whereas, the G-3 to G-6 glasses prepared under reducing atmosphere conditions are all clear with no visible coloration. The absorption spectra of the thin specimen of these glasses showed well-resolved five absorption bands due to the  $\text{Ce}^{3+} 4f \rightarrow 5d_j$  transitions ( $j = 1-5$ ) as represented in the absorption profile of the G-6 glass sample in the inset of Fig. 2. This clearly demonstrates that the reducing atmosphere is highly advantageous in the glass synthesis to effectively reduce the  $\text{Ce}^{4+}$  ions in to the  $\text{Ce}^{3+}$  state.

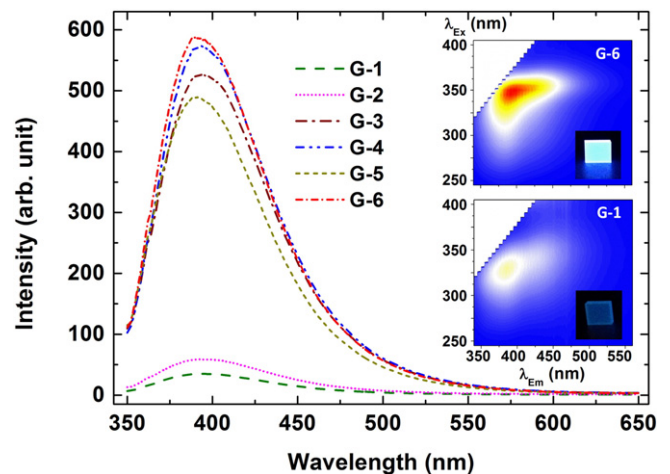


Fig. 3. PL spectra of the studied glasses ( $\lambda_{\text{exc}}$ : 345 nm). Inset shows the PL-PL mapping of G-1 and G-6 glasses along with their PL glow images.

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