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journal homepage: [www.elsevier.com/locate/jnoncrysol](http://www.elsevier.com/locate/jnoncrysol)Spectroscopic properties of  $\text{Ce}^{3+}/\text{Tb}^{3+}$  co-doped high silica scintillating glassQingmin Chen<sup>a</sup>, Jingxin Ding<sup>a,b</sup>, Guanpeng Yao<sup>a</sup>, Hai Lin<sup>a</sup>, Chun Li<sup>a</sup>, Yanyan Zhou<sup>a,\*</sup>, Fanning Zeng<sup>a,\*</sup><sup>a</sup> School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China<sup>b</sup> Synthetic Single Crystal Research Center, Key Laboratory of Transparent and Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

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## ABSTRACT

$\text{Ce}^{3+}/\text{Tb}^{3+}$  co-doped high silica scintillating glasses were prepared by sintering porous glasses in CO reducing atmosphere. The uniformly distributed nanopores in the prepared glass are quite suitable for absorbing  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$  ions due to large specific surface. The main mechanism of absorbing of  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$  in high silica glass was hydrogen bonds. The calculated doping concentration of  $\text{Ce}^{3+}$  in the glass is agreed with measured densities, excitation spectrum as well as emission spectrum at room temperature. The emission spectrum proves that the intensity of  $\text{Tb}^{3+}$  could be enhanced by  $\text{Ce}^{3+}$ , and specially the intensity of highest peaks at 543 nm have been increased to 10 times stronger than those without  $\text{Ce}^{3+}$ . Moreover, with the  $\text{Ce}^{3+}$  concentration increased to 0.2 mol/L, the luminescence intensity increased to a maximum and then decreased due to the concentration quenching of  $\text{Ce}^{3+}$ . The process of energy transfer between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  and the concentration quenching were analyzed thoroughly in high silica glass.

## 1. Introduction

Scintillating glasses could be applied in the area of X-rays,  $\gamma$ -rays and neutrons detection. They are attractive scintillating materials due to advantages of easy shaping of elements, low production cost, the ease of manufacture in different sizes and shapes and possibility to incorporate activator ions compared to the crystal [1–3]. Many studies have been devoted to researching on scintillating glasses prepared by high temperature melting method [4–6], but they suffer from a wide range of concentration quenching because of rare earth (RE) polymer in the melting process, which decreases the emission intensity.

Taking these problems into consideration, a new approach to obtain intense luminescence glasses containing rare-earth ions was reported in this paper. Traditionally, RE ions were introduced directly by the common high-temperature melting method. On the contrary, an improved three-step process has been applied to prepare high silica glasses including preparing porous glass, adsorbing rare-earth ions and sintering in reducing atmosphere. High silica glasses, with properties nearly closed to silica glasses, have advantages of considerable optical, physical properties and chemical durability compared with other glass materials [7,8], which made high silica glass working in extreme conditions. What's more,  $\text{Tb}^{3+}$ -activated silicate glass with high light yield,

good transparency and intense emission around 540 nm are suitable for direct coupling with silicon detectors [9,10]. Additionally,  $\text{Ce}^{3+}$  ions give rise to the scintillation with a fast decay time of about 20–50 ns due to 5d-4f electron transition in  $\text{Ce}^{3+}$  doped glass [11]. A typical energy transfer between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  could benefit the emission of  $\text{Tb}^{3+}$ , and  $\text{Ce}^{3+}$  is utilized as sensitizer to enhance the luminescence properties [12].

In this work,  $\text{Ce}^{3+}/\text{Tb}^{3+}$  co-doped high silica scintillating glass were successfully fabricated by the aforementioned three-step progress. SEM, densities, photoluminescence excitation spectra and photoluminescence emission spectra have been investigated systematically. In addition, the energy transfer process, the absorption mechanism and their influence on spectroscopy properties were discussed.

## 2. Experimental

Reagent-grade chemicals  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$  were chosen to be the starting materials in solid-state reaction to produce initial glasses. The composition of the initial glass was 59 $\text{SiO}_2$ , 29 $\text{B}_2\text{O}_3$ , 10 $\text{Na}_2\text{O}$ , 2 $\text{Al}_2\text{O}_3$  (in wt%), and besides  $\text{Sb}_2\text{O}_3$  (1 wt%) were used as clarifier. The schematic diagram for detail preparation of high silica glass in experiment is described in Fig. 1. The raw materials were

\* Corresponding authors.

E-mail addresses: [724959885@qq.com](mailto:724959885@qq.com) (Y. Zhou), [zengfm@cust.edu.cn](mailto:zengfm@cust.edu.cn) (F. Zeng).<http://dx.doi.org/10.1016/j.jnoncrysol.2017.07.025>Received 6 May 2017; Received in revised form 23 July 2017; Accepted 27 July 2017  
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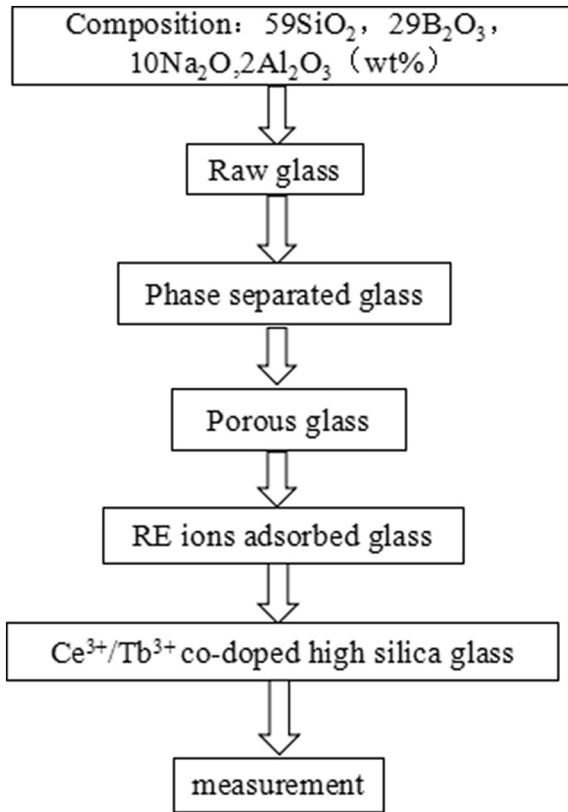


Fig. 1. Experimental proceeding chart.

**Table 1**  
Doping concentration of solutions and glass samples.

Glass samples	Sa1	Sa2	Sa3	Sa4	Sa5	Sa6
$c_s$ of $Tb^{3+}$ ions (mol/L)	0.2	0.2	0.2	0.2	0.2	0.2
$c_s$ of $Ce^{3+}$ ions (mol/L)	0	0.05	0.1	0.15	0.2	0.25
$c_g$ of $Ce^{3+}$ ions (ppm)	0	1952	3903	5855	7807	9759
Density $\rho$ (g/cm <sup>3</sup> )	2.1083	2.1179	2.1384	2.1506	2.1670	2.1792
Standard deviation (S.D.)	0.0107	0.0142	0.0123	0.0131	0.0115	0.0137

melted in a corundum crucible at 1450 °C for 3 h. The melt was then poured into a preheated at 650 °C stainless steel plate. Phase separation of the alkali borate and silica phases were performed at 580 °C for 30 h. The obtained phase-separated glass were cut to pieces and optically polished with the dimension of about 10 × 10 × 2 mm<sup>3</sup>. Then the phase separated glasses were soaked into hot (90 °C) acid solution to prepare porous glasses which was called high silica glass with over 96% SiO<sub>2</sub> contained [13]. In the preparation of Tb<sup>3+</sup>/Ce<sup>3+</sup> co-doped high silica glasses, the solution concentration of Tb(NO<sub>3</sub>)<sub>3</sub> was fixed to 0.2 mol/L (M) while the solution concentration of Ce(NO<sub>3</sub>)<sub>3</sub> was adjusted to the 0, 0.05, 0.1, 0.15, 0.2, 0.25 M listed in Table 1 and labeled as Sa1–Sa6 which were immersed into pre-prepared solutions for 6 h and dried at room temperature. After that these samples were sintered at 1000 °C in reducing atmosphere and annealed at the rate of 1 °C/min to the room temperature.

The SEM spectrum was measured by JXA-840 provided by JEOL. The photoluminescence excitation (PLE) and emission (PL) spectra were obtained using RF-5301PC spectrophotometer containing a spectral range from 300 nm to 600 nm. The densities were measured by Archimedes methods at room temperature which using the distilled water as an immersion liquid [14]. The high silica glass samples were polished optically before spectral measurements. All spectral measurements were carried out at room temperature.

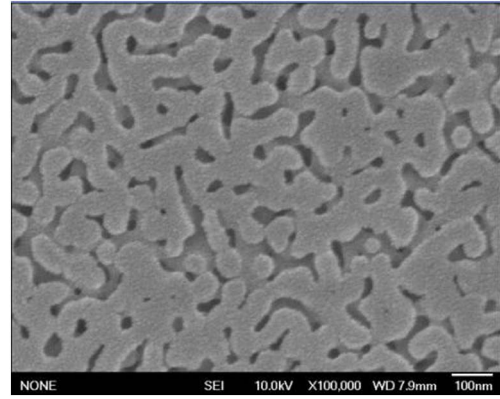


Fig. 2. SEM images of porous glass samples.

### 3. Results and discussion

#### 3.1. Mechanism of adsorption of RE ions by nanopores glass

As shown in Fig. 2, pores with an average size of 30 nm distribute uniformly in high silica glasses, which indicates the potential to absorb large amount of RE ions due to the large surface area and narrow pore size.

In the surface of nanopores, the network structure of original silicon tetrahedral was destroyed in the acid leaching process to form a hanging oxygen bond which connected to H<sup>+</sup> in the acid solution to form a siloxane ≡Si–OH. When the porous glass was leached into solution containing RE ions, the RE ions entered nanopores together with water molecules. RE ions existed in the form of hydrated complexes RE(H<sub>2</sub>O)<sub>n</sub><sup>m+</sup> in the solution, not in the form of a separate ionic state.

The interaction between the complex RE(H<sub>2</sub>O)<sub>n</sub><sup>m+</sup> and hydroxyl are Van der Waals and hydrogen in the surface of high silica glass [15,16]. Because bond energy of hydrogen bonds is stronger 5 to 10 times than that of Van der Waals, the main way of adsorption is hydrogen bond.

Fig. 3 shows the schematic diagram of nanopores surface adsorption and local amplified adsorption through hydrogen bonds. As shown in Fig. 3, there are two kinds of ways of hydrogen bonding. The one is the hydrogen of siloxane ≡Si–OH connected with oxygen atoms of RE(H<sub>2</sub>O)<sub>n</sub><sup>m+</sup>, and the other is the oxygen atom of siloxane ≡Si–OH connected with hydrogen atom of RE(H<sub>2</sub>O)<sub>n</sub><sup>m+</sup>.

When the adsorption is completed, the sintering process will be followed. According to H. Elmer's thermal dehydration theory about porous glass [17], shrinkage process of the RE ions doped porous glass occurs to make glass dense, which resulted in the decreasing of the specific surface area. And the covalent bond was formed as a bridge of RE ions as a bridge. As a result, the RE ions finally enter stably the glass network.

#### 3.2. Relationship between doping concentration in glass and density

The doping-concentrations in glass  $c_g$  can be obtained with the following Eq. (1) [18] and the results were shown in Table 1.

$$c_g = pc_s M / d(1 - p) \quad (1)$$

where  $p$  represents the porosity of porous glass,  $d$  stands for the density of sintering glass,  $c_s$  is the Ce<sup>3+</sup> ions concentration in solution,  $M$  is the relative atomic mass and  $p = 38\%$ ,  $d = 2.15$  g/cm<sup>3</sup>. And the standard deviation (S.D.) of density ( $\sigma_{\rho_i}$ ) is obtained by the Formula (2).

$$\sigma_{\rho_i} = \sqrt{1/n - 1 \sum_{i=1}^n (\rho_i - \bar{\rho})^2} \quad n = 6; i = 1, 2, \dots, 6; \quad (2)$$

The concentration of Ce<sup>3+</sup> doped in the prepared glasses was

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