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Effect of Tb^{3+} concentration and sensitization of Ce^{3+} on luminescence properties of terbium doped phosphate scintillating glass

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ABSTRACT

Phosphate glasses doped with different concentrations of Ce^{3+} and Tb^{3+} were prepared by high temperature melting method. Effects of Tb^{3+} concentration and sensitization of Ce^{3+} on photoluminescence and radio-luminescence properties of terbium doped phosphate glass have been investigated by absorption, excitation and emission spectroscopy. Results showed the phosphate glass exhibit high broad absorption band attribute to the allowed $4f^8$–$4f^75d$ transition of Tb^{3+}, which is beneficial for the 542 nm emission of Tb^{3+}. It is found that the emission intensity of Tb^{3+} at 542 nm increased as the concentration of Tb^{3+} and Ce^{3+}increasing. The suitable concentration of Ce^{3+} and Tb^{3+} in phosphate glass is 2 mol% and 10 mol% respectively, and the emission intensity of Ce^{3+}/Tb^{3+}-codoped phosphate glass at 542 nm shows 8 times stronger than that of the commercial $Bi_4Ge_3O_{12}$ (BGO) crystal at 500 nm. The phosphate glass doped with Ce^{3+} and Tb^{3+} ions would be potential candidates for scintillating material for static X-ray imaging.

1. Introduction

Tb^{3+}-doped scintillating glass is attractive material used in many applications such as thermal neutron detection and radiography [1], due to its many advantages like low-cost, manufacturing of large size and drawing for fiber [2–4]. However, compared with crystals, the energy transfer towards luminescence center efficiency is rather low in scintillating glass, which results in low light yield [5]. So far, many efforts have been devoted to enhance the luminescence intensity of Tb^{3+}-doped scintillating glass, such as choosing the matrix glass composition [3,4,6,7], deciding the suitable doping concentration of Tb^{3+} ions [8], and conforming the sensitization concentration of Gd_2O_3 or Ce_2O_3 [9–11]. In addition, glass ceramics were also fabricated to increase the luminescence intensity of Tb^{3+} [12,13].

It is reported that Tb^{3+}-actived silicate scintillating glass possessed higher luminescence intensity than the other glass, but with high concentration of rare earth ions it had troubles in fiber drawing due to its poor thermal stability [14]. In recent years, many attentions have been paid on phosphate scintillating glass [15–17], because it has many advantages such as high doping concentration of rare-earth ions, good radiative resistance and thermal stability for drawing fiber. However, some other important properties of phosphate glass have been ignored by these previous research work, such as low covalency and high transmittance in UV region, which can reduce the host absorption to the recombination energy of e–h pair in UV region and are beneficial for studying the 4f–5d transitions of Tb^{3+} ions and the sensitization of Ce^{3+} ions to the emission of Tb^{3+} ions [18].

It is well known that for the application of Tb^{3+}-doped scintillating glass, the light out is an important parameter for reducing radiative dose [19]. Further studies on increasing the emission intensity of Tb^{3+} in phosphate glass are valuable. Among the scintillating process [13], transferring excited electrons and holes to luminescence centers is critical, so the energy transfer (ET) efficiency can be greatly enhanced by increasing the absorption band of luminescence centers. In this paper, we studied the luminescence properties of phosphate glass with varied concentrations of Tb^{3+} and sensitization of Ce^{3+} with different Ce^{3+}/Tb^{3+} ratios. We have obtained suitable doping concentration of Ce^{3+} and Tb^{3+} ions in phosphate glass, and compared the emission intensity of glass samples with the commercial product BGO crystal.

2. Experimental

Precursor glasses with compositions showed in Table 1 were melted from commercial purity (usually 99.99%) oxides and phosphate in corundum crucibles, and the experimental errors were ±1%. About 200 g batches of well-mixed raw materials were melted at 1400 °C for 120 min under reducing atmosphere. After melting, the liquid was cast into a graphite mould and annealed for 2 h below the glass transition temperature and then cooled to room temperature at a rate of 30 °C/h. The glass samples obtained were polished for optical measurements with a thickness of 2 ± 0.02 mm.

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Table 1
The compositions of glass samples.

Glass (mol%)	P_2O_5	Al_2O_3	Li_2O	MgO	CeO_2	Tb_4O_7
Host glass	60	20	5	15	0	0
Tb1	60	19	5	15	0	1
Tb2	60	18	5	15	0	2
Tb3	60	15	5	15	0	5
Tb4	60	12	5	15	0	8
Tb5	60	10	5	15	0	10
Ce–Tb1	60	9	5	15	1	10
Ce–Tb2	60	8	5	15	2	10
Ce–Tb3	60	7	5	15	3	10
Ce–Tb4	60	5	5	15	5	10

The transmittance spectra of these samples were recorded with a PerkinElmer-Lambda 900UV/VIS/NIR spectrophotometer in the range of 200–500 nm, and the scan tread speed was 0.5 nm. Photoluminescence (PL) spectra were recorded on a PerkinElmer luminescence spectrometer LS55 using Xe lamp as excitation source and experimental errors of obtained data were about ±5%. Radioluminescence (RL) spectra were performed by X-ray Excited Spectrometer, where an F-30X-ray tube (W anticathode target) was the X-ray source, operated under 30 kV and 20 mA. The experimental errors of obtained data were about ±5%.

3. Results and discussion

The absorption spectra of un-doped host glass and that doped with different Tb^{3+} concentration are shown in Fig. 1. The absorption edge of un-doped host phosphate glass is in deep UV region at 220 nm, so the absorption peaks of Tb^{3+} in the region from 240 nm to 300 nm are observed which have not been found in silicate glass. In addition, the absorption spectra comprises of several other peaks at 283 nm, 301 nm, 316 nm, 350 nm, 378 nm and 484 nm. From the energy level of Tb^{3+} showed in the inset of Fig. 1, the high absorption peak at 248 nm is associated with the allowed $4f^8$–$4f^75d$ transition, and the other absorption peaks are ascribed to the forbidden transitions within the $4f^8$ configuration of Tb^{3+} ions. Additionally, the UV cut-off edges of glass samples shift from 220 nm to 230 nm with increment of the Tb^{3+} concentration, which may be due to the fact that the phenomenon of non-bridging oxygen (NBOs) in glass is presented by introducing of Tb^{3+} [20]. Moreover, the intensities of absorption peaks increase gradually as increasing the Tb^{3+} concentrations.

Fig. 2 shows the excitation spectra of phosphate glass doped with different Tb^{3+} concentrations by monitoring the green emission at 542 nm. The overall excitation spectra are divided into two groups. The highest broad band around 248 nm is associated with the allowed $4f^8$–$4f^75d$ transition, and the weak narrow bands located at 264 nm, 284 nm, 303 nm, 318 nm, 351 nm, 378 nm and 484 nm are respectively assigned to the transitions from the ground state to $^5F_2$, $^5F_4$, $^5H_6$, $^5H_7$, $^5D_2$, $^5D_3$, $^5D_4$ states. The intensity of excitation band at 248 nm is 3 times that of the excitation band at 378 nm, which shows that the allowed $4f^8$–$4f^75d$ transition can increase the emission intensity of Tb^{3+} at 542 nm through the relaxation process from 5d state to $^5D_4$ state. In addition, the excitation bands shift from 248 nm to 260 nm and become higher and broader with the increment of Tb^{3+} concentration. The reason is that the $4f^8$–$4f^75d$ transition is sensitive to the crystal field of the host [18], and increasing Tb^{3+} concentration can change the structure of phosphate glass.

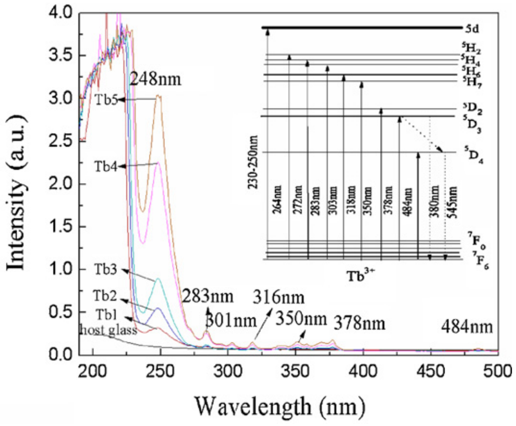

Fig. 1. Absorption spectra of un-doped host glass and glass doped with different Tb^{3+} concentration, and inset shows the energy level of Tb^{3+}.

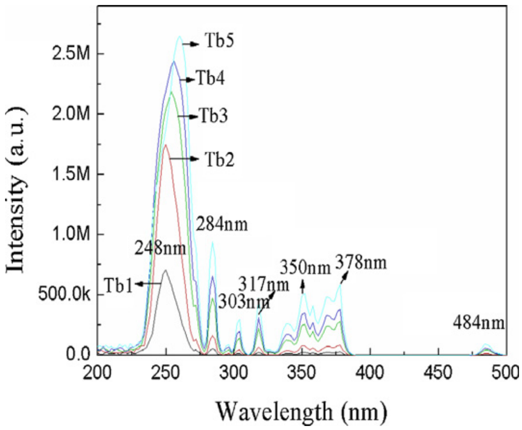

Fig. 2. Excitation spectra of phosphate glass doped with different Tb^{3+} concentration with emission at 542 nm.

The emission spectrum of phosphate glass doped with different Tb^{3+} concentrations is shown in Fig. 3, which is excited at 260 nm. The emission spectra of Tb^{3+} comprises of several peaks located at 487 nm, 542 nm, 547 nm, 582 nm, and 620 nm, which attribute to the transitions from the excited $^5D_4$ state to $^7F_6$, $^7F_5$, $^7F_4$, $^7F_3$ and $^7F_2$ states respectively [21]. In the emission spectrum of Tb^{3+}, the highest peak is located at 542 nm and its intensity increased as increasing Tb^{3+} ions concentration up to 10 mol%. Due to the solubility of phosphate glass, higher doped Tb^{3+} glass with concentration above 10 mol% cannot be produced and the intensity of 542 nm is not decreasing, but the rate of increase is slowed down at the concentration of 8 mol%.

From the energy level of Tb^{3+} in Fig. 1, it can be concluded that there are two non-radiative processes from $^5D_3$ to $^5D_4$ states: a fast cross-relaxation due to the resonance energy transfer (RET) through $^5D_3 \rightarrow {}^5D_4 = {}^7F_6 \rightarrow {}^7F_0$ and a multi-phonons assisted non-radiative relaxation due to the low energy gap between $^5D_3$ and

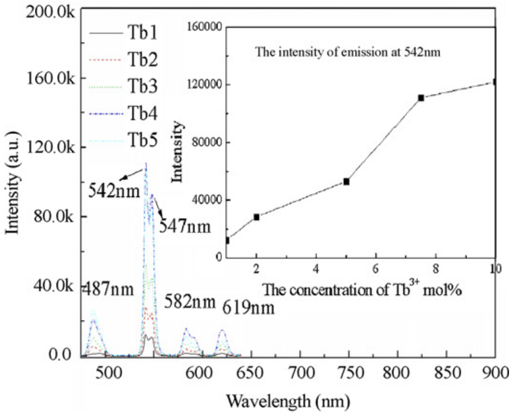

Fig. 3. Emission spectra of phosphate glass doped with different Tb^{3+} concentration with excitation at 260 nm.

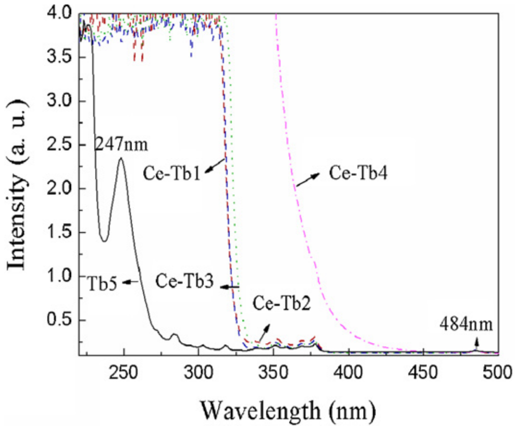

Fig. 4. Absorption spectra of Ce–Tb glass with different ratio of Ce^{3+}/Tb^{3+}.

$^5D_4$ states [21]. Among these two processes, cross-relaxation is proportional with the R^{-6}, where R is the distance between the close ions [21,22], and in most glasses, the critical value of Tb^{3+} concentration for cross-relaxation is 1 mol%. So, the phosphate glass doped with more than 1 mol% of Tb^{3+} ions is beneficial for using in static X-ray imaging, which the strongest emission band is located at 542 nm.

In addition, there are three effects on the emission of Tb^{3+} with the increment of its concentration in phosphate glass: (1) enhance the absorption intensity from ground state to 5d state and the multi-phonons non-radiative relaxation from 5d state to $^5D_3$ state; (2) increase the transition probability from $^5D_3$ state to $^5D_4$ state by cross relaxation; (3) when the concentration of Tb^{3+} arrives at a critical value, the concentration quenching would occur at $^5D_4$ state through the $^5D_4{:}^5D_4 \rightarrow {}^7F_6$:upper levels cooperative energy transfer [23]. Therefore, the emission intensity of Tb^{3+} at 542 nm increases with increment of Tb^{3+} ions concentrations and the rate of increment is slowed down at the concentration of 8 mol%, which due to the concentration quenching at $^5D_4$ state.

Furthermore, to enhance the emission intensity of Tb^{3+}-doped scintillating glass, we have studied the sensitization of Ce^{3+} to the luminescence behavior of Tb^{3+} by increasing the concentration ratio of Ce^{3+}/Tb^{3+}, where Tb^{3+} concentration was fixed at 10 mol%. Fig. 4 shows the absorption spectra of Ce^{3+}/Tb^{3+} co-doped phosphate glass with different Ce^{3+}/Tb^{3+} ratio. When adding Ce^{3+} ions into Tb^{3+}-doped glass, the UV absorption edges of glass samples Ce–Tb1, Ce–Tb2 and Ce–Tb3 shift from 230 nm to 330 nm, which ascribe to the 4f–5d transition of Ce^{3+} and the absorption bands of Tb^{3+} ranging from 247 nm to 330 nm are entirely suppressed. However, in Ce–Tb4 glass, the UV absorption edge shifts remarkably to 430 nm, and this phenomenon maybe due to the presence of Ce^{4+}[23], which has strong absorption bands at the region from 300 nm to 400 nm. Furthermore, the yellow color of the Ce–Tb4 glass also reveals the presence of Ce^{4+}.

The excitation spectra of Ce–Tb glass with different ratio of Ce^{3+}/Tb^{3+} are shown in Fig. 5. Compared with Tb5 glass, new broad excitation band ranging from 230 nm to 330 nm occurs in the Ce–Tb glass samples, which shows the presence of energy transfer from Ce^{3+} to Tb^{3+}. However, the intensity of excitation band at 260 nm in Tb5 glass is much higher than that in Ce–Tb glass samples. This is probably due to the fact that the excitation band at 260 nm in Tb5 glass is related with the direct 4f–5d transition. But in Ce–Tb glass, the excitation band at 260 nm is related with the energy transfer process from 5d state of Ce^{3+} to 4f state of Tb^{3+}, and the energy transfer efficiency is lower than 1. In addition, Fig. 5 shows that the intensities of excitation bands ranging from 230 nm to 330 nm increase gradually with increment of the Ce^{3+} concentrations, and then decrease when the phenomenon of concentration quenching occurs.

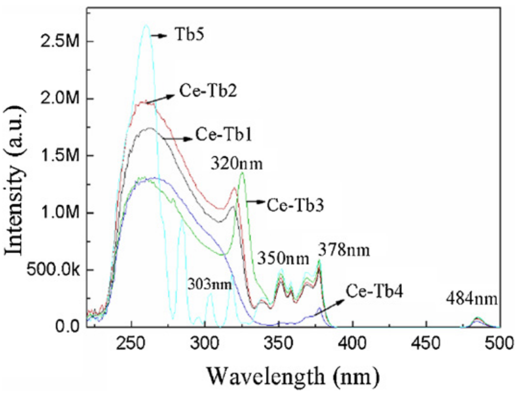

Fig. 5. Excitation spectra of Ce–Tb glass with different ratio of Ce^{3+}/Tb^{3+}.

The X-ray excited luminescence spectra of phosphate glass doped with different Tb^{3+} concentrations are shown in Fig. 6(a). Compared with the emission spectra excited by UV light, some emission bands at 547 nm and 620 nm disappear, which ascribes to the thermal quenching of the host glass [24]. Similarly, the emission intensity at 542 nm increases with the increment of Tb^{3+} concentrations up to 10 mol% and the rate of the increment is slowed down at the concentration of 8 mol%. The X-ray excited luminescence spectra of phosphate glass doped with different concentration ratio of Ce^{3+}/Tb^{3+} are showed in Fig. 6(b). A new emission band at 339 nm appears which is due to the transition from 5d state to 4f states of Ce^{3+} ions. Moreover, the 542 nm emission intensity in Ce–Tb2

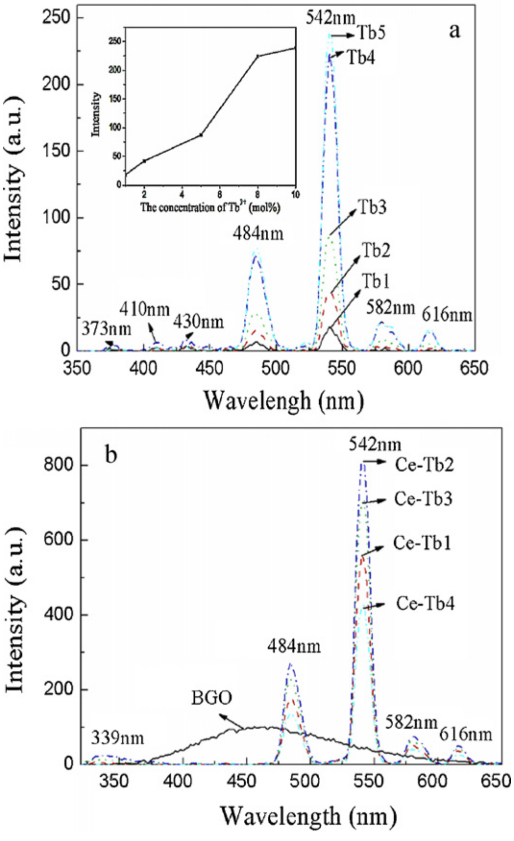

Fig. 6. (a) Emission spectra of phosphate glass doped with different Tb^{3+} concentration excited with X-ray; (b) emission spectra of Ce–Tb glass samples doped with different ratio of Ce^{3+}/Tb^{3+} and emission spectra of BGO crystal excited with X-ray.

glass is 3.2 times stronger than that in Tb5 glass. As said that X-ray excited luminescence is host sensitized luminescence [21], and the electron–hole pairs irradiated from X-ray will transfer energy to luminescence center. So adding Ce^{3+} into Tb^{3+}-doped glass can greatly enhance the transfer efficiency and increase the emission intensity of Tb^{3+}. However, due to the concentration quenching of Ce^{3+}, there is a suitable concentration of Ce^{3+} to inhibit the presence of Ce^{4+}. In this phosphate glass, the appropriate ratio of Ce^{3+}/Tb^{3+} is 2:10, which has the maximum 542 nm emission intensity. Furthermore, the X-ray excited luminescence intensity of Ce–Tb glass was compared with that of the commercial product $Bi_4Ge_3O_{12}$ crystal (BGO) in Fig. 6(b). The emission intensity of Ce–Tb2 glass at 542 nm is 8 times stronger than that of BGO crystal at 500 nm under the same experimental conditions, which is much useful for reducing radiative dose to obtain high-resolution X-ray imaging. In addition, the integral emission intensity of Ce–Tb2 glass is equivalent with that of BGO crystal, which shows that the new glass has the same energy transfer efficiency from X-ray to photons as compared with BGO crystal.

4. Conclusions

New phosphate scintillating glasses doped with different concentrations of Ce^{3+} and Tb^{3+} have been prepared. There is a strong broad absorption and excitation band associated with the allowed $4f^8$–$4f^7 5d$ transition of Tb^{3+} in phosphate glass, which is beneficial for the 542 nm emission of Tb^{3+}. It is found that increasing the concentration of Tb^{3+} and adding Ce^{3+} into the Tb^{3+}-doped phosphate glass can greatly increase the 542 nm emission intensity and the suitable concentration of Ce^{3+} and Tb^{3+} in phosphate glass is 2 and 10 mol%, respectively. The 542 nm emission intensity of Ce–Tb2 glass shows 8 times stronger than that of $Bi_4Ge_3O_{12}$ crystal at 500 nm, which shows that the Ce–Tb2 glass would be potential candidates for applied in static X-ray imaging.

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