



Luminescence behavior of Tb³⁺ ions in transparent glass and glass-ceramics containing CaF₂ nanocrystals

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ABSTRACT

Transparent glass-ceramics have been fabricated by heat treatment with 1.0 mol% Tb₂O₃-doped 45SiO₂–20Al₂O₃–10CaO–25CaF₂ aluminosilicate glass. The precipitated crystalline phase in the glass-ceramics is CaF₂ nanocrystals with a size of 15–27 nm and dispersed in the amorphous phase. Both photo- and radioluminescence measurements show that the increase of Tb³⁺ 545 nm line intensity by a factor of 4 and 3.5 is obtained in glass-ceramics with respect to the as-made glass, respectively.

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1. Introduction

Glass is an attractive scintillating material because of its low cost, large-volume production possibility and easy shaping of elements [1–3]. Glass, however, being the lack of long range order and the presence of many point defects gives rise to trapping sites responsible for non-radiative recombinations [2,3]. In comparison to crystalline scintillators, glass-based scintillators have been less frequently studied. One of the reasons is that activators generally require a crystalline environment to scintillate efficiently. This is mainly because the probability of radiative recombination of excitons in ordered (crystalline) environment is usually larger than that in the disordered (amorphous) environment [4].

The oxyfluoride glass-ceramics doped with rare earths were researched widely in the past decades, since such materials provide a desirable low phonon energy fluoride environment for active rare earth ions while maintaining the advantages of an oxide glasses, such as high mechanical strength, chemical durability and thermal stability. The glass-ceramics of this kind usually contain much smaller crystalline phases as the nanosized Pb_xCd_{1–x}F₂ or PbF₂ crystals in the glass hosts that they can improve the optical properties with no loss of the transparency [5,6]. However, both CdF₂ and PbF₂ are poisonous so that they

could not be used extensively in view of the environment issue. In 1998, Dejneka developed a new glass-ceramics containing LaF₃ nanocrystals [7], and now the fact that the efficiency of β-induced luminescence of this kind of glass-ceramic is comparable or nearly equal to that of the Schott IQI-301 product is encouraging [8]. However, the cost of LaF₃ materials is an obstacle for its practical application, some relative nanocrystals such as NaYF₄ and Sr₂GdF₇ have been precipitated in transparent glass-ceramics [9,10]. The transparent glass-ceramics containing MF₂ (M = Ca, Sr and Ba) nanocrystals recently have been aroused more interest owing to both the lower cost and less poison of MF₂ raw materials [11–17]. Furthermore, crystalline CaF₂ is highly transparent from 0.13 to 9.5 μm and gives a better matching of refractive index with the aluminosilicate glassy host [15]. A good example is the Eu²⁺-doped glass-ceramic containing CaF₂ nanocrystals where the Eu²⁺ has higher luminescence than in the as-made glass by Fu et al. [12].

Tb³⁺-activated silicate glass scintillators usually has higher luminescence than that of Eu³⁺- or Ce³⁺-activated [18], furthermore the characteristic emission of Tb³⁺ ions is around 550 nm, convenient for a direct coupling with silicon detectors and sensitive to human eyes. The response of Tb³⁺-activated glass is considerably slower than its Ce³⁺-doped counterpart, but does not demonstrate the self-quenching phenomenon that occurs in Ce³⁺-doped glass when Ce³⁺ is oxidized to Ce⁴⁺ [19], probably the oxidation of Tb³⁺ to Tb⁴⁺ is less thermodynamically favored. It implies that Tb³⁺-doped glass can be drawn into fiber easier than that of Ce³⁺-doped and it is more useful for application in

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radiography and nondestructive testing [18,20]. At present, however, little attention has been paid to the Tb^{3+} -doped oxyfluorine aluminosilicate glass and glass ceramic. In this work, the aluminosilicate glass was successfully fabricated, and the corresponding glass-ceramics were obtained by appropriate heat treatment of the as-made glass. X-ray diffraction (XRD), optical transmission, and luminescence behavior under both UV and X-ray have been investigated on the as-made glass and glass-ceramics.

2. Experimental

The aluminosilicate glass with composition of 45SiO_2 – $20\text{Al}_2\text{O}_3$ – 10CaO – 25CaF_2 – $1.0\text{Tb}_2\text{O}_3$ was prepared from analytical reagent SiO_2 , Al_2O_3 , CaCO_3 , CaF_2 and 4N-purity grade Tb_4O_7 raw materials. The batches of the raw materials were melted at 1400 – 1450°C for 2 h in a platinum crucible in the normal atmosphere. The melts were poured into a preheated stainless steel mold. The resultant glass was annealed in a muffle furnace at 600°C for 3 h to release the inner stress. The glass samples (denoted as 1.0TbG) with a regular size of $20\text{ mm} \times 20\text{ mm} \times 2\text{ mm}$ were finally obtained after cutting and polishing. The glass samples were then heated and held for another 4 h at 650, 675, 700 and 725°C to induce crystallization and form transparent glass-ceramics, denoted as GC650, GC675, GC700 and GC725, respectively.

Crystalline phase was identified by Bruker D8 X-ray diffraction by using $\text{Cu K}\alpha$ radiation with 2θ from 10° to 60° . Ultraviolet–visible transmission spectra were measured using a JASCO V-570 spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer luminescence spectrometer LS55 using a Xe lamp as an excitation source. The fluorescence decay time was measured on an Edinburgh Instruments FLS920 spectrofluorimeter with the time correlated single-photon counting technology. Radioluminescence (RL) spectra were performed by X-ray Excited Spectrometer, FluorMain, where an F-30X-ray tube (W anticathode target) was the X-ray source, and operated under 80 kV and 6 mA. Luminescence spectra were recorded with 44 W plate grating monochromator and Hamamatsu R928-28 photomultiplier with the data acquired by a computer. All the measurements were carried out at room temperature.

3. Result and discussions

3.1. Spectroscopic properties of Tb^{3+} -doped glass

Fig. 1 shows the excitation (monitor at 545 nm) and emission spectra (under the 4f–5d excitation of Tb^{3+} 225 nm) of the as-made glass, respectively. And a scheme of Tb^{3+} energy level and relative transitions are also depicted in Fig. 2. The emission spectra of Tb^{3+} are composed of two groups of transition: the blue emission bands centered at 381, 415, 437 and 459 nm attributed to $^5\text{D}_3 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$ and 3), and the green emission bands centered at 488, 545, 586 and 620 nm assigned to $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$ and 3). As shown in Fig. 1, the intensity of blue emission is much stronger than that of green one, which indicates that the dopant concentration of terbium ion is low. When the dopant concentration of terbium is higher, the blue emission will quench firstly, and then the green one will also quench by further adding Tb^{3+} ions. More details of Tb^{3+} luminescence in silicate glass can be referred to references elsewhere [21].

3.2. XRD diffraction and transmission

Fig. 3 shows the XRD patterns of the as-made glass and glass-ceramics heat treated at different temperatures for 4 h. The as-made glass is completely amorphous with no crystalline

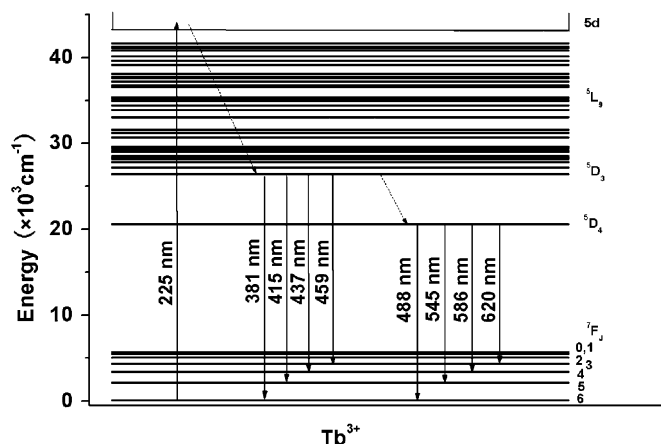


Fig. 2. Scheme of Tb^{3+} ions energy level and transitions.

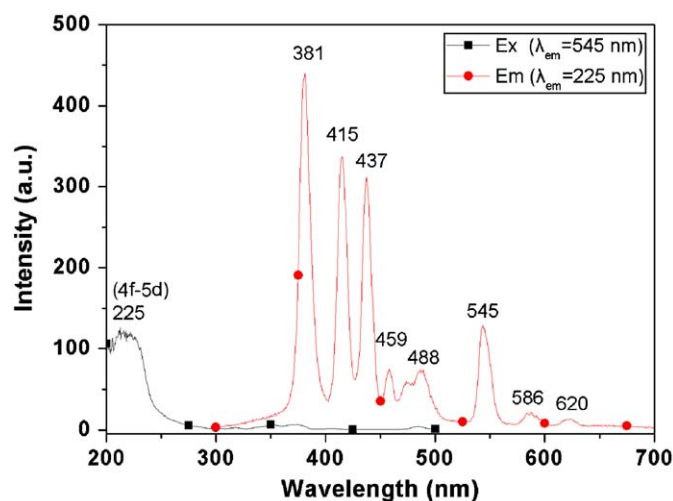


Fig. 1. Excitation and emission spectra of the as-made glass.

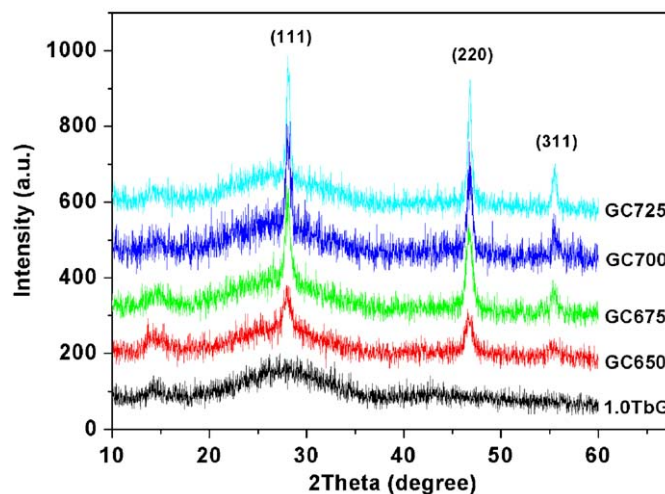


Fig. 3. XRD patterns of the as-made glass and glass-ceramics.

diffraction peaks. After heat treatment, the diffraction peaks of glass-ceramics can be easily assigned to cubic CaF_2 crystalline phase and indexed as (111), (220) and (311) in Fig. 3, respectively. Moreover, the width of the peaks becomes sharper with higher heat-treatment temperature, which indicates the gradual formation of CaF_2 nanocrystals in the glass-ceramics.

From the obtained peak width of XRD patterns, the crystal size of CaF_2 in glass-ceramics can be calculated by the Scherrer formula

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta},$$

where D_{hkl} is the crystal size at the vertical direction of (hkl), λ is the wavelength of X-ray ($\text{Cu K}\alpha$: 1.541 Å), θ the angle of diffraction, β the full-width at half-maximum (FWHM) of the diffraction peak and the constant $K = 0.89$. The volume fraction of the crystalline phase (crystallinity) in the glass ceramic was estimated by the ratio of integrating the area of the peaks and the total area of the XRD pattern from 10° to 60° [6,11].

The crystal size and the volume fraction of CaF_2 nanocrystals in glass-ceramics were plotted as a function of heat-treatment temperature in Fig. 4. With the increase of heat-treatment temperature, the CaF_2 nanocrystals sizes increases from about 15 up to 27 nm. While the volume fraction of CaF_2 nanocrystals in glass-ceramics increase sharply when the temperature increases

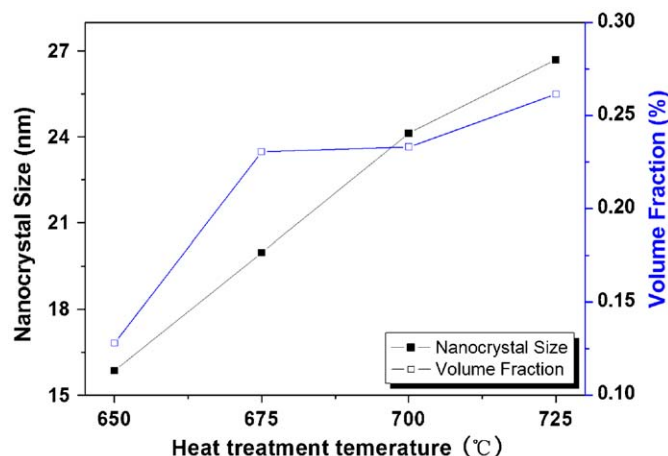


Fig. 4. CaF_2 nanocrystal size and volume fraction as a function of heat-treatment temperature in glass-ceramics.

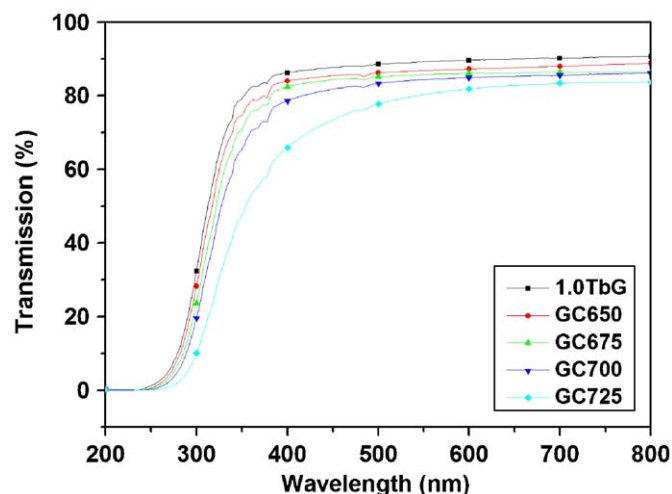


Fig. 5. Transmission spectra of the as-made glass and glass-ceramics.

up to 675°C and then increase slowly over 675°C , and the volume fraction keeps around 25%.

Fig. 5 shows the transmission spectra of the as-made glass and glass-ceramics in the range 200–800 nm. The as-made glass has the highest transparency, the transparency of glass-ceramics gets slightly lower with the increase of heat-treatment temperature. The faster nucleation and growth rate of CaF_2 nanocrystals in glass-ceramics can be confirmed with the elevated heat-treatment temperature, resulting in the larger size and higher crystallization fraction, but these glass-ceramics still retains good transparency, since the nanosize of CaF_2 is much smaller than the wavelength of the visible light [11,12].

It is worth to note that the cut-off wavelength of the glass-ceramics, compared to the as-made glass, is obviously red-shift with the increase of the heat-treatment temperature. It may be correlative with the reduction number of nonbridge fluorine (NBF) in the residual glassy phase when the CaF_2 crystalline phase precipitates [6]. The similar red-shift of cut-off wavelength has been observed in the $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramics where the ZnAl_2O_4 crystals precipitates, and the author attributing it to the reduction number of nonbridge oxygen (NBO) [22].

3.3. PL spectra analysis

Fig. 6 shows the PL spectra of the as-made glass and glass-ceramics under 225 nm excitation, and the integrated intensity of green ($^5\text{D}_4 \rightarrow ^7\text{F}_j$), blue ($^5\text{D}_3 \rightarrow ^7\text{F}_j$) as well as the ratio of $^5\text{D}_4$ to $^5\text{D}_3$ are plotted as a function of heat-treatment temperature in Fig. 7. In case of the as-made glass, the blue emission dominates over the green one. The intensity of blue emission decreases sharply when the as-made glass is ceramised, and then it increases with the increase of the heat-treatment temperature. While the green emission was always enhanced up to 725°C . Moreover, the line intensity of Tb^{3+} 545 nm equal approximately to that of 381 nm when the heat-treatment temperature is 700°C (sample GC700), and the intensity of 545 nm emission is stronger than that of 381 nm when the heat-treatment temperature is 725°C (sample GC725).

It is well known that the probability of radiative recombination of excitons in ordered crystalline environment is usually larger than that in the disordered amorphous environment [4]. As demonstrated in both Figs. 3 and 4, the crystal size and the volume fraction of CaF_2 nanocrystals in the glass-ceramics increases with the increase of heat-treatment temperature, which implied that more Tb^{3+} ions have been entered to the fluorine

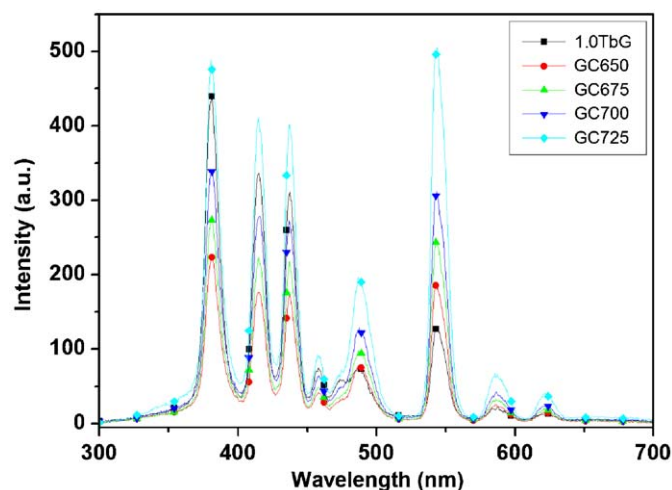


Fig. 6. PL spectra of the as-made glass and glass-ceramics.

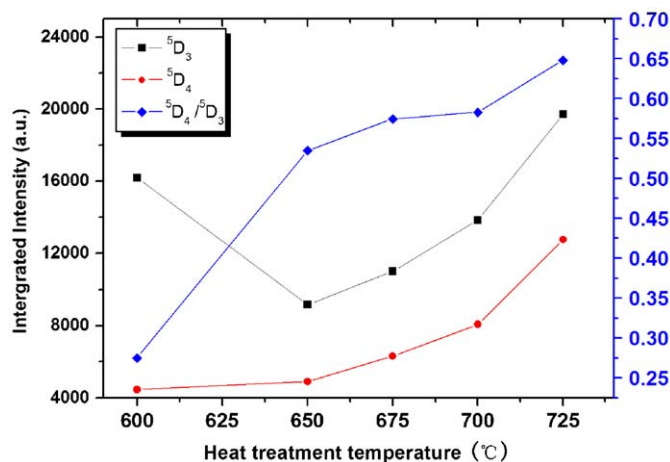


Fig. 7. Dependence of integrated intensity of $^5D_4 \rightarrow ^7F_j$, $^5D_3 \rightarrow ^7F_j$ and their ratios on heat-treatment temperature.

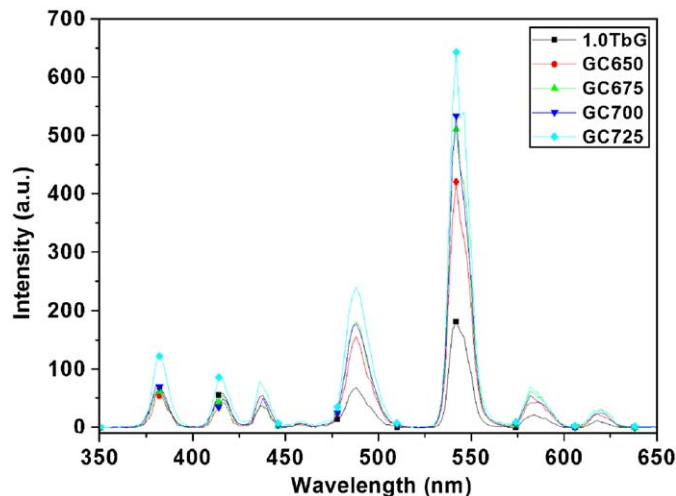


Fig. 9. RL spectra of the as-made glass and glass-ceramics.

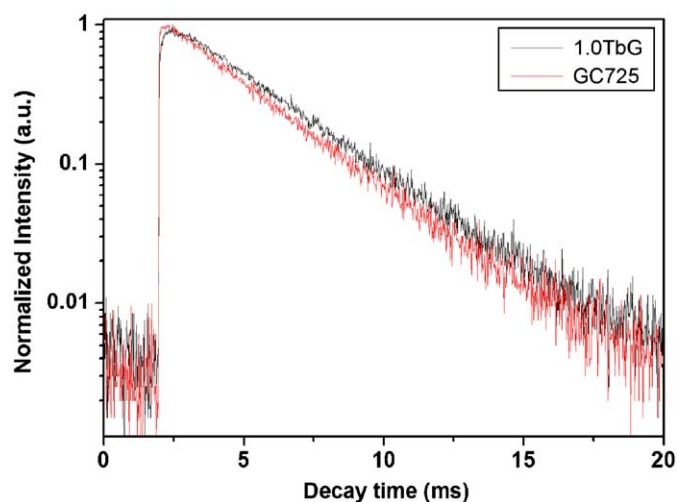


Fig. 8. Decay curves of the as-made glass and glass-ceramics.

environment, resulting in the formation of $\text{CaF}_2:\text{Tb}^{3+}$ nanocrystals [12]. CaF_2 crystals have a very low phonon energy of 320 cm^{-1} [23], compared to that of silicate-based host (the energy of Si–O vibration is $\sim 1100\text{ cm}^{-1}$), the excited Tb^{3+} , therefore, have a reduced multiphonon decay rate, resulting in an increased radiative emission rate. The higher is the heat-treatment temperature, the more is the $\text{CaF}_2:\text{Tb}^{3+}$ nanocrystals. As a result, the stronger emission of Tb^{3+} has been observed in glass-ceramics. The concentration of Tb^{3+} embedded in CaF_2 nanocrystals may be increased with the increasing temperature, so the concentration quenching of $\text{Tb}^{3+}(^5D_3 \rightarrow ^7F_j)$ by cross-relaxation in the form of $\text{Tb}^{3+}(^5D_3) + \text{Tb}^{3+}(^7F_6) \rightarrow \text{Tb}^{3+}(^5D_4) + \text{Tb}^{3+}(^7F_0)$ appeared in the sample GC725 [21].

3.4. Decay time

Fig. 8 shows luminescence decay curves of the 5D_4 state of Tb^{3+} in the as-made glass and the GC725 glass ceramic by monitoring the $^5D_4 \rightarrow ^7F_5$ emission of Tb^{3+} . The decay curves could be fitted to a single exponential function, yielding the lifetime of 2.8 ms for the as-made glass and 3.2 ms for the GC725 glass ceramic. The probable reason for increment in lifetime is that in the glass ceramic Tb^{3+} ions are the mixed sites of oxides and fluoride, however on ceramisation as sizeable number of Tb^{3+} ions are in

fluoride sites of low phonon energy which reduces the non-radiative relaxation and enhances the lifetimes [14].

3.5. RL spectra analysis

Fig. 9 shows the RL spectra of the as-made glass and glass-ceramics. With the increase of the heat-treatment temperature, both the green and blue emission of Tb^{3+} resembles that under UV excitation. The increase of 545 nm line intensity by a factor of 3.5 is obtained in the GC725 sample with respect to the as-made glass. Moreover, the emission band corresponding to the $^5D_4 \rightarrow ^7F_5$ transition is split into two distinct peaks in the sample GC725, which indicates that the Tb^{3+} had incorporated into CaF_2 nanocrystals [9,10]. The enhancement of Tb^{3+} luminescence under X-rays excitation attributes to the $\text{CaF}_2:\text{Tb}^{3+}$ nanocrystals with lower phonon energy, as explained in the case of UV excitation. Therefore, it may provide us an effective way to improve scintillating performance of some oxide glasses by annealing the as-made glass.

4. Conclusions

A novel transparent glass-ceramics containing CaF_2 nanocrystals have been fabricated by heat treatment from the $45\text{SiO}_2\text{--}20\text{Al}_2\text{O}_3\text{--}10\text{CaO--}25\text{CaF}_2\text{--}1.0\text{Tb}_2\text{O}_3$ as-made glass. Photo- and radio- luminescence results show that the increase of Tb^{3+} 545 nm line intensity by a factor of 4 and 3.5 is enhanced in glass-ceramics than the as-made glass, respectively. The main reason lies in the fact that Tb^{3+} preferring to precipitate in the CaF_2 crystals and forms the $\text{CaF}_2:\text{Tb}^{3+}$ nanocrystals with low phonon energy. The further enhancement of Tb^{3+} 545 nm line intensity may be optimized by codoping Gd_2O_3 as sensitizer and adding higher content of Tb^{3+} ions in the future work.

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