Green long-after-glow luminescence of Tb^{3+} in Sr_2SiO_4*

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The green long-after-glow luminescence from Tb^{3+}-doped Sr_2SiO_4 phosphors, which are synthesized by the high temperature solid state reaction in a reductive atmosphere, is observed in this paper. The results show that under ultraviolet excitation, the obtained phosphors produce an intense green-lighting-emission from the Tb^{3+}, and the green-lighting long-after-glow luminescence related to Tb^{3+} can last half an hour after the irradiation source has been removed. Moreover, the effects of co-doping Li^+, Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+} with Tb^{3+} on the decay properties and thermoluminescence properties are investigated to confirm the long-after-glow mechanism.

Keywords: long-after-glow luminescence, Tb^{3+}, Sr_2SiO_4

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1. Introduction

Long-after-glow phosphor is a kind of energy-storing material, which can absorb the ultraviolet or visible light from the sunlight or artificial illumination, store the energy, and then release the energy as visible light that leads to a long lasting after-glow in the darkness. This material can be used in many fields, including emergency lighting display, interior decoration, multidimensional optical memory, and light sources.[1–7] Especially since the discovery of $SrAl_2O_4$:Eu^{2+}, Dy^{3+},[8] overwhelmingly extensive researches on the long lasting after-glow of Eu^{2+} in different after-glow materials such as aluminates,[8,9] borates,[10,11] and silicates[12,13] have been conducted to prolong their after-glow luminescence by tuning their broad band emission color and provide a fundamental understanding of the after-glow mechanism.[9]

Until now, the mechanism of long-after-glow luminescence Eu^{2+} has been rather well known and is consistent with the experimental results. It is found that the energy level lifetime of the luminescence center ion seems to be one of the critical points to the long-after-glow luminescence of rare-earth ions; it seems to determine the probability of transferring the charge (electron) from the excited levels of rare-earth to the conduction band (CB) of the host.[14] For instance, in the Eu^{2+}-actived long-lasting materials, when the excitation occurs to the 4f5d levels of Eu^{2+} located in (or close to) the CB, the lifetime of the 4f5d $\rightarrow$ 4f emission of Eu^{2+}, being about 1 μs, seems to be largely sufficient to allow efficient electron transfer to the CB. It easily results in the occurrence of long-lasting behavior. In contrast, for Ce^{3+}-doped phosphors, whose emission lifetime is a few tens of nanoseconds, it has been only occasionally found from among the long-after-glow luminescence materials.[15–18] On the other hand, in the case of luminescent materials doped with Tb^{3+}, the lifetime of the $^5D_4$ emitting level of Tb^{3+} is in the range of several milliseconds, which is much longer than that of Eu^{2+}. It reasons that in Eu^{2+}-actived host with long-after-glow, Tb^{3+} ion would be in favor of the capture of electrons to the CB to generate long-lasting luminescence.[15] In recent years, much work on Eu^{2+}-doped Sr_2SiO_4 has been reported, in which the observation of Eu^{2+} related-long after-glow can be found,[19,20] but there have been no reports on the long-lasting luminescence of Tb^{3+} in this silicate compound. So one of the purposes of this work is to examine the long-lasting phenomenon in Sr_2SiO_4:Tb^{3+} and further, to confirm the examinations.

In this paper, Tb^{3+}-doped Sr_2SiO_4 is synthesized by a solid-state reaction at 1350 °C in a reducing atmosphere. The crystal structure, photoluminescence, and after-glow properties are characterized and the effects of co-doped Li^+, Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+} on the decay properties are investigated. This work is motivated by not only the development of novel trivalent Tb-doped silicate phosphors, but also the interest to have a better understanding of the long-after-glow luminescence properties and the nature of trivalent rare-earth ions in these hosts.

2. Experiment

2.1. Sample synthesis

Sr_2SiO_4 phosphors were synthesized via a conventional solid-state reaction process. The $SrCO_3$ (A.R.), SiO_2 (A.R.), Tb_4O_7 (99.99%), Li_2CO_3 (A.R.), Dy_2O_3 (99.99%), Er_2O_3 (99.99%), Gd_2O_3 (99.99%), and Yb_2O_3 (99.99%) were used

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as the starting materials. Initially, the raw powders were weighed according to the nominal compositions of $Sr_{2-x}SiO_4$: xTb^{3+} ($x = 0.005$, 0.01, 0.015, denoted as Tb0.005, Tb0.01, Tb0.015). The co-doped samples were weighed according to the nominal compositions of $Sr_{1.98}SiO_4$:$0.01Tb^{3+}$, $0.01M$ ($M = Li^+$, Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+}, denoted as Tb–Li, Tb–Dy, Tb–Er, Tb–Gd, and Tb–Yb). Then the powders were mixed and milled thoroughly for 1 h. Finally, the powder mixtures were fired at 1350 °C for 4 h in a slightly reducing atmosphere (a mixture of 5% H_2 and 95% N_2) in a tube oven to prevent Tb^{3+} from being oxidized into Tb^{4+}. No fluxes were used in order to obtain accurate experiment results.

2.2. Characterization

The crystalline phases of the samples were investigated by X-ray powder diffraction (XRD) with a Rigaku D/max 2200 Diffractometer with Cu Kα ($\lambda = 1.542$ Å) radiation operated at 36 kV and 30 mA. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were investigated by an F-7000 Fluorescence Spectrophotometer (Hitachi) with an Xe lamp excitation. The slits of the emission and excitation lights were both 2.5 nm. The working voltage of the photomultiplier tube was 700 V and the scanning rate was 240 nm·min^{-1}. The after-glow spectrum and decay curves were also measured by an F-7000 Fluorescence Spectrophotometer. The samples were excited by an Xe lamp (285 nm) for 10 min and the measurement was carried out without any excitation. Quantitative thermoluminescence (TL) curves were measured using a Thermal Luminescence Meter System (a product of the Beijing Nuclear Instrument Factory) equipped with a temperature-controlled oven and a PC data acquisition system.

3. Results

3.1. Phase identification

The phase purity and crystallinity of the samples are monitored by X-ray powder diffraction (Fig. 1). As shown in the figure, the pure Sr_2SiO_4 and rare-earth ions-doped Sr_2SiO_4 samples show identical diffraction patterns, and no significant difference can be observed. According to the JCPDF standard card No. 038-0271, the patterns can be indexed to monoclinic Sr_2SiO_4 structure with space group $P\,21/n$. The cell parameters are $a = 0.9753$ nm, $b = 0.7078$ nm, and $c = 0.5661$ nm. In Tb^{3+}-doped Sr_2SiO_4, the doping Tb^{3+} can be considered to substitute for the site Sr^{2+} ions, because the ionic radius of Tb^{3+} (0.092 nm) is slightly smaller than that of Sr^{2+} (0.118 nm). Moreover, in the co-doped samples, the Dy^{3+} (0.0912 nm), Er^{3+} (0.089 nm), Gd^{3+} (0.094 nm), and Yb^{3+} (0.101 nm) can also substitute for the site Sr^{2+} ions. Li^+ was used for charge compensatory additives.

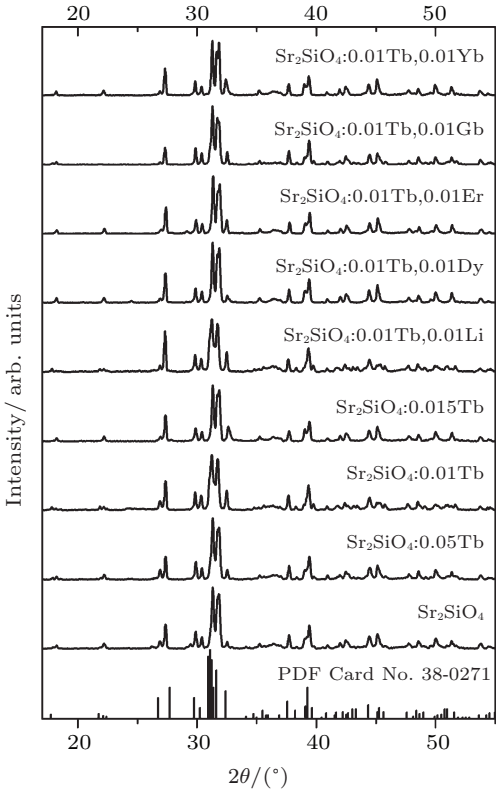


Fig. 1. XRD patterns of Sr_2SiO_4 phosphors and Tb^{3+}singly doped and co-doped Sr_2SiO_4 samples, indexed according to the JCPDS card No. 038-0271.

3.2. Photoluminescence analysis

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the $Sr_{1.99}SiO_4$:$0.01Tb^{3+}$ sample are shown in Fig. 2. Under excitation at 285 nm, the transitions from $^5D_3$ to ^7F_J states, located in a range from 370 nm to 450 nm, and the transitions from $^5D_4$ to ^7F_J ($J = 6$, 5, 4, 3) states of Tb^{3+} located at 486, 546, 551, 587, and 625 nm, respectively, can be observed. The most prominent emission peak located at 548 nm, which combined with other peaks give an efficient green output. The excitation spectrum is recorded when 546-nm emission of Tb^{3+} is monitored. The spectrum consists of two overlapping broad bands with maxima at 285 nm and 228 nm, whose bands may be assigned to the 4f–4f5d transition and the host absorption, respectively. Under excitation at 228 nm, the emission spectra also present the characteristic line emission bands of the $^5D_3$–^7F_J and $^5D_4$–$^7F_{3-6}$ transitions of Tb^{3+}.

After removing the UV excitation source, the Tb^{3+}-doped Sr_2SiO_4 sample exhibits a green long-after-glow, which could be observed by the naked eye for about half an hour in darkness. Figure 3 presents the long after-glow emission spectrum of Sr_2SiO_4:0.01Tb phosphors. It shows that the long-after-glow spectrum consists of two main peaks at 486 nm and 546 nm and is coincident with the PL spectrum in Fig. 2.

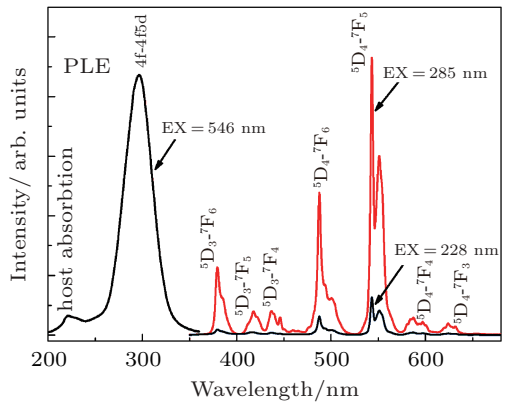


Fig. 2. (color online) PLE ($\lambda_{em} = 546$ nm) and PL ($\lambda_{ex} = 285$ nm and 228 nm) spectra and the emission spectra of the Sr_2SiO_4:0.01Tb phosphors.

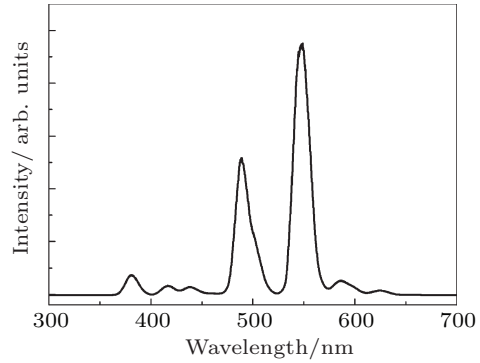


Fig. 3. Long-after-glow emission spectrum of Sr_2SiO_4:0.01Tb phosphors after 285-nm irradiation.

4. Discussion

To reveal the long-after-glow mechanisms in our case, the co-doped phosphors with trivalent rare-earth ions Dy^{3+}, Er^{3+}, Gd^{3+}, Yb^{3+}(RE^{3+}) are synthesized, and the after-glow intensity decay curves and TL are measured.

The after-glow intensity decay curves of the phosphor co-doped with Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+} are shown in Fig. 4. The decay curves of long-after-glow phosphors contain a fast decay process and a slow decay process. In general, the slow decay process determines the duration of the after-glow.[21–24] The computer-aided simulations of the experimental data are conducted to reveal the lifetimes of the prepared phosphors. All the decay curves can be expressed by the double exponential equation as follows:

$$I(t) = I_0 + A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right),$$

where I and I_0 are the after-glow intensities; A_1 and A_2 are the constants; t is the time; τ_1 and τ_2 are the decay constants of the rapid and the slow decay components, respectively. The parameters of the fitting results are listed in Table 1.

By co-doping trivalent ions Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+} (RE^{3+}), the after-glow time can be enhanced to one hour, which is twice as great as that of Tb0.01. It indicates that the trapping centers are created by the trivalent rare-earth ions including the Tb^{3+}.

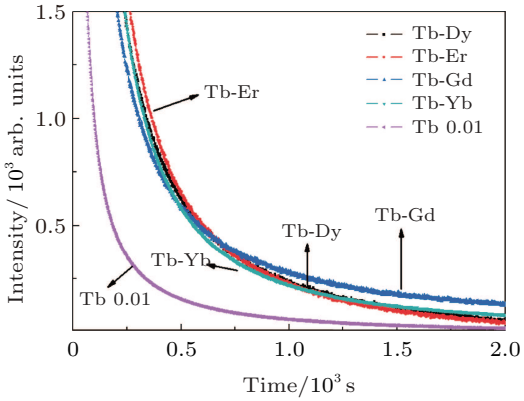


Fig. 4. (color online) After-glow intensity decay curves of RE^{3+} co-doping phosphors.

Table 1. Fitting parameters of the decay curves with different co-doping RE^{3+} ions.

Samples	I_0	A_1	τ_1/s	A_2	τ_2/s
Tb0.01	59.04	9325.70	19.98	2031.62	167.15
Tb–Dy	59.27	17624.47	44.48	2709.89	335.34
Tb–Er	41.78	19977.84	50.44	2883.27	338.51
Tb–Gd	117.73	15514.77	38.96	2317.98	334.32
Tb–Yb	71.72	14614.44	47.54	2906.12	301.36

The thermoluminescence (TL) technique has proven to be the most suitable one to reveal the nature of trapping centers.[25] TL curves are measured (Fig. 5) to confirm the above discussion, and to gain an insight into the influences of different traps on the origin of the long-after-glow in the phosphor.

The TL curve of the Tb^{3+}-doped Sr_2SiO_4 sample is found to be a broad peak located at 336 K with another broad band which is higher than 420 K. The former peak may be ascribed to being related to the defects that are created by the incorporation of Tb^{3+} into the Sr_2SiO_4 host. Ordinarily, the TL band at somewhere between 343 K and 420 K is suitable for long-after-glow materials to free the trapped carriers slowly by thermal energy at room temperature.[26] The TL temperature, which is higher than 420 K, is too deep to free the carriers trapped. With the codopants of Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+}, the intense TL peak at 340 K increases. It means that more trap centers, which are responsible for the long-after-glow, are aggregated in Sr_2SiO_4. Moverover, new TL peaks appear with the codopant, and the peaks are located in a range from 380 K to 397 K. It indicates that the codopants of Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+} introduce new traps into the phosphor.

Consequently, with the codopant of Li^+, the intense TL peak at 351 K decreases immediately, and no new TL peak appears. The decay curves of Tb^{3+}–Li^+ co-doping phosphor are also shown in Fig. 6 to confirm the influence of Li^+. It shows that with the co-doping of Li^+, the values of τ_1 and τ_2 decrease to 2.52 s and 50.66 s, respectively. It is harmful for the long-after-glow of Tb^{3+}.

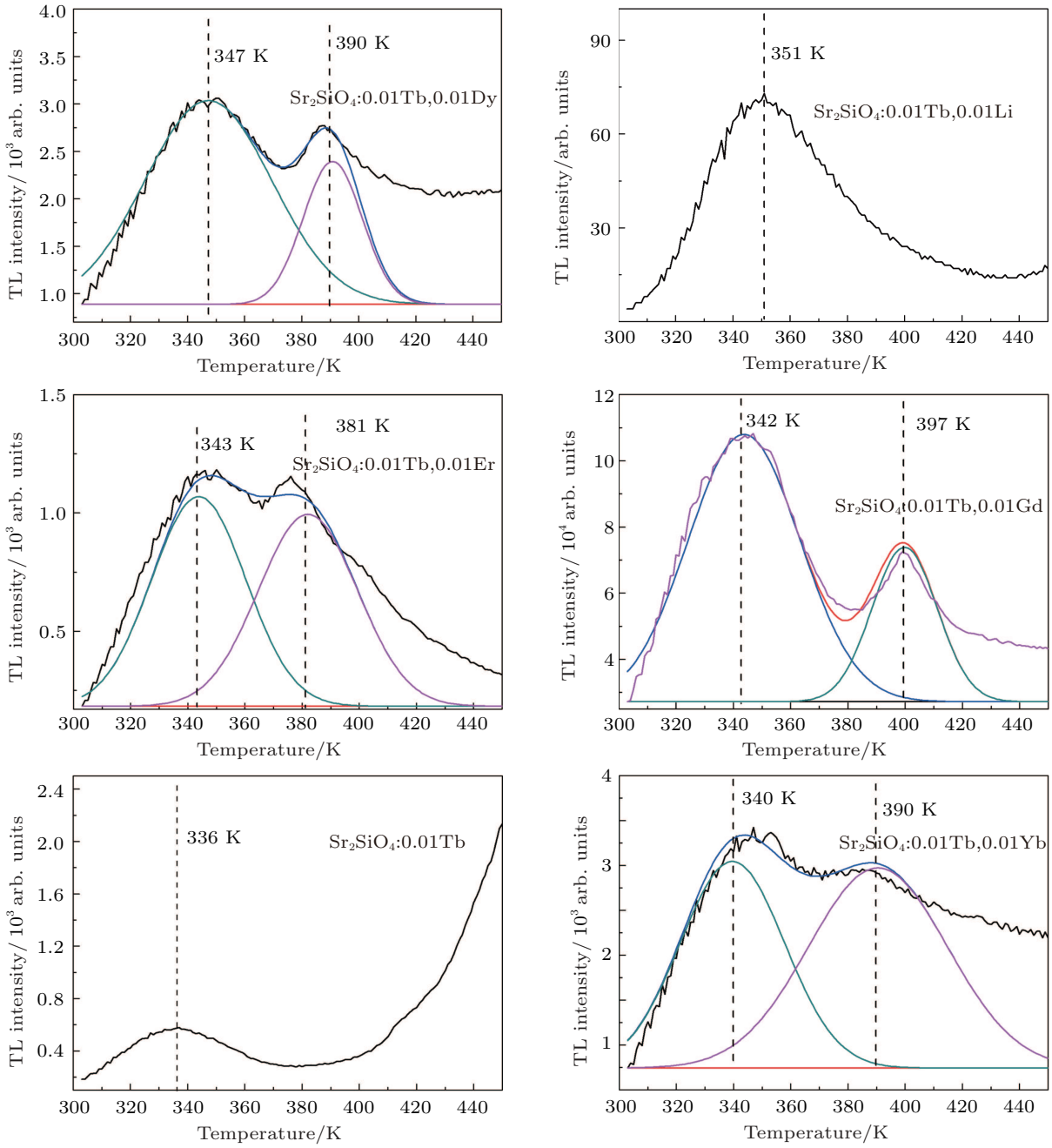


Fig. 5. (color online) Thermoluminescence curves of Tb^{3+} singly doped and co-doped Sr_2SiO_4 samples.

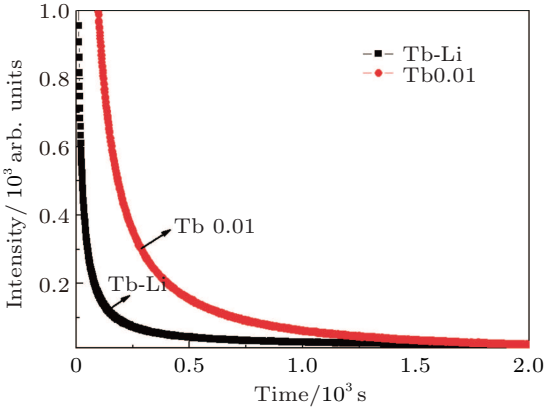


Fig. 6. (color online) After-glow intensity decay curves of Li^+ co-doping phosphors.

Theoretically, if there are adequate hole and/or electron traps with suitable depth values within the host lattice, a long-after-glow emission can be observed in the impurity-doped phosphors. Due to the nonequivalent substitution of M^{3+} for M^{2+}, an excess positive charge in the lattice must be compensated to maintain the electroneutrality in the phosphor.[27–31] In our case, two Tb^{3+} ions substitute for three Sr^{2+} ions in the matrix to balance the charges of these phosphors, which create two Tb_{Sr} positive defects and one V''_{Sr} negative defect ($2Tb^{3+} + 3Sr^{2+} \rightarrow 2\ Tb_{Sr} + V''_{Sr}$). The Tb_{Sr} plays the role of an electron trapping center, and the V''_{Sr} may serve as the hole trapping center. When the phosphors are excited by a UV irradiation source, electrons in Tb^{3+} are excited from the 4f states to 4f5d

states, thereby creating holes in the 4f states. The relatively long lifetime allows efficient electrons to transfer to the CB, and then the electrons are captured by the electron trapping centers (Tb_{Sr}). Simultaneously, the holes are captured by the hole trapping centers (V''_{Sr}). Through the thermal disturbance at room temperature, the electrons are released, forming electron trapping centers, and transfer back to the emitting level of Tb^{3+} which then recombine with the holes at a slow release rate.

As the above discussion indicates, the trivalent Tb ions not only play the role of an activator but also act as an auxiliary dopant to create trapping centers. Moreover, with the codopants of Dy^{3+}, Er^{3+}, Gd^{3+}, and Yb^{3+}, the nonequivalent substitution of RE^{3+} for Sr^{2+} results in aggrandizement of the density of trapping centers and the creation of new traps, which is of benefit to the long-after-glow of $Tb^{3+}$and the prolongation of the long-after-glow decay time. Generally, alkali metal ions such as Li^{+} are readily used for charge compensatory additives,[32] which means that the co-doping of Li^{+} avoids the Tb_{Sr} and V''_{Sr} caused by the nonequivalent substitution, which thus reduces the density of trap centers and the long-after-glow decay time.

5. Conclusions

In this paper, Sr_2SiO_4:Tb^{3+} phosphors are successfully synthesized by a conventional solid-state reaction process in a reducing atmosphere; it exhibits an intense green emission and long-after-glow when excited by UV irradiation. The Tb^{3+}-related long-after-glow can be considered to result from the recombination of holes and electrons trapped caused by the trivalent Tb ions, which could be reduced by codoping with charge compensatory additives, Li^{+} ion, and enhanced by codoping with trivalent rare-earth ions.

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