Influence of rare earth elements (Sc, La, Gd and Lu) on the luminescent properties of green phosphor Y₂SiO₅:Ce,Tb

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Abstract

Systematic studies on CL and PL for rare earths (Sc³⁺, La³⁺, Gd³⁺ and Lu³⁺) doped Y₂SiO₅:Ce,Tb phosphor were performed and the formula \( (Y_{0.965}R_{0.03}Ce_{0.005})_2SiO_5 \) (R = Sc, La, Gd and Lu) was applied to represent the compositions of the samples. Sensitizing influence of Ce³⁺ on Tb³⁺ can only be observed with the excitation of cathode rays and 355 nm UV. For the La³⁺ doped system, the PL intensity increased nearly 30% at \( x = 0.03 \); and for the Lu³⁺ doped system, the intensity increased about 20% at \( x = 0.20 \). Whereas doping of the Gd³⁺ and the Sc³⁺ reduced the intensity: at \( x = 0.3 \), the PL intensity decreased 10% for the Gd³⁺ doped system and about 25% for Sc³⁺. CL measurements showed that except the Sc³⁺, other rare earths doping improved the intensities: the La³⁺ doping made the intensity enhancement of about 10% at \( x = 0.03 \); the Gd³⁺ 35% at \( x = 0.1–0.3 \) and Lu³⁺ 25% at \( x = 0.1–0.2 \). For the Sc³⁺ doped samples, the CL intensity decreased about 25% at \( x = 0.2 \). The energy transfer processes were discussed for the Gd³⁺ doped samples. Two transfer processes from the Gd³⁺ to the Tb³⁺ were proposed: Gd³⁺ → Tb³⁺ and Gd³⁺ → Ce³⁺ → Tb³⁺.

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1. Introduction

Y₂SiO₅ is a good host material for both photoluminescent (PL) and cathodoluminescent (CL) phosphors [1]. Recently, Ce³⁺ or Tb³⁺ doped blue or green phosphors as well as Ce–Tb co-doped green phosphors were found a promising candidate for FED applications [2,3]. In our previous work [2–4], we reported the influence of Sc³⁺, La³⁺, Gd³⁺ and Lu³⁺ on the luminescence of both Y₂SiO₅:Ce³⁺ and Y₂SiO₅:Tb³⁺ and found the luminescence enhanced.

Like Y₂SiO₅:Ce and Y₂SiO₅:Tb, Ce³⁺–Tb³⁺ co-doped Y₂SiO₅ was also studied for a long time [5,6]. On the other hand, the energy transfer process from Ce³⁺ to Tb³⁺ was investigated in many phosphors including Y₂SiO₅:Ce³⁺,Tb³⁺ [6]. The early work mainly concerned the fundamental emission and excitation properties of Tb³⁺ and Ce³⁺ [7], but the results data on the rare earth replacements for Y in Y₂SiO₅:Ce,Tb has not been found. In order to make our research systematic, in the present work, not only the influence of Sc³⁺, La³⁺, Gd³⁺ and Lu³⁺ on the luminescence of Y₂SiO₅:Ce³⁺ and Y₂SiO₅:Tb³⁺ was studied, but the energy transfer processes Gd³⁺ → Tb³⁺ and Gd³⁺ → Ce³⁺ → Tb³⁺ were discussed.

2. Experimental

The purity of rare earth oxides as starting materials was over 99.99%. As the source of SiO₂, amorphous powder of

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luminescent purity was used. All starting materials were dried at 850 °C for several hours. Cerium oxalate was prepared by us; number of crystalline water was determined by TG analysis. Powder samples were prepared by the solid state reaction at high temperatures. Suitable amounts of dried starting materials were weighed and mixed by grinding in an agate mortar. Table 1 gives the masses of raw materials for samples with different composition. In order to obtain homogeneous mixtures, during the grinding, small amounts of acetone were added. Samples were fired at 1500 °C in reductive atmosphere (CO, produced from the burned carbon rods with high purity) for 6 h and BaF2 was used as flux.

The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/max 2000 X-ray powder diffractometer. The phases present were examined by analyzing the XRD patterns of the samples using a Powder X software [8]. PL was measured using a Hitachi F4500 fluorospectrometer and the function of energy calibration was applied for the spectral data collections. CL measurements were conducted by using a YFC-2 cathodoluminescentometer; the voltage of the electron beam was 10 kV and the current density was 1 µA/cm². The emission energy in the visible light range was integrated to represent the luminescence intensity.

3. Results and discussion

3.1. Phase presentation of (Y0.965Tb0.03Ce0.005)2SiO5

Fig. 1 shows the XRD pattern of (Y0.965Tb0.03Ce0.005)2SiO5, it matches well with JCPDS files of monoclinic Y2SiO5 (Card number: 36-1476). Two different monoclinic structures of Y2SiO5 have been found, the low temperature phase (X1) and the high temperature phase (X2). The X1 phase has the space group P21/c, whereas the space group B2/c is assigned to the X2. Previous studies found that the luminescent intensity of X1-Y2SiO5:Ce is much weaker than that of X2-Y2SiO5:Ce [4]. Y2SiO5:Ce prepared by solid state reaction were X2 phase, at high temperature only X2 phase can be gotten.

3.2. Luminescent properties of (Y0.965Tb0.03Ce0.005)2SiO5

In this paper, detailed research was conducted to investigate the influence of Tb3+ and Ce3+ contents on the luminescent properties of Y2SiO5, although the rough data have been available in the literature [9]. The luminescent properties of Y2SiO5:TB3+ were reported in our previous paper [4]. The excitation spectrum of this phosphor consists of 4f8 → 4f75d absorption bands of Tb3+ in the short UV wavelength region (230–300 nm) and the maximum position is at about 254 nm. The emission spectrum shows typical Tb3+ emissions originating from the 5D4 → 7Fj transitions and the highest emission at 546 nm is due to the 5D4 → 7F5 transition. The optimized concentration of Tb3+ obtained in Y2SiO5 is about 0.03 in cation mole ratio.

The luminescent properties of Y2SiO5:Ce were also previously reported [2,3,6,9]. The emission spectrum consists of a doublet peak with maximum at ca. 400 nm and it might be attributed to the 5d → 4f (3F4/2 and 3F5/2) transitions of Ce3+. The excitation spectrum contains three bands. The main band is at 355 nm and the other two bands are at 300 nm and 265 nm, respectively. All of which
can be ascribed to the transitions from the 4f ground state \( ^2F_{5/2} \) to the various 5d level split by the crystal field [10,11]. The optimized concentration of Ce\(^{3+}\) is about 0.005 in cation mole ratio.

It is found that the emission band of Ce\(^{3+}\) at 400 nm overlaps with the excitation peaks of Tb\(^{3+}\) at 360–380 nm (f–f transitions) (Fig. 2), thus the energy transfer process can take place from Ce\(^{3+}\) to Tb\(^{3+}\) and the transfer mechanism belongs to the multipolar interactions, which have been discussed in many works [7].

Fig. 3 represents the emission spectra of \((Y_{0.965}Tb_{0.03}\Ce_{0.005})_2SiO_5(a), (Y_{0.995}Ce_{0.005})_2SiO_5(b) and (Y_{0.97Tb_{0.03}})_2SiO_5(c)\) with the excitation at 355 nm. The emission spectrum of Ce\(^{3+}\)–Tb\(^{3+}\) co-doped sample shows both the emissions from Ce\(^{3+}\) and Tb\(^{3+}\), but compared with the Ce\(^{3+}\) or Tb\(^{3+}\) singly doped samples, the emission from Ce\(^{3+}\) is reduced and the emission from Tb\(^{3+}\) is dramatically increased. The Tb\(^{3+}\) emissions in Y\(_2\)SiO\(_5\):Tb\(^{3+}\) is very faint with the excitation at 355 nm UV light. The above results clearly show that with the excitation at 355 nm UV light, energy transfer from the Ce\(^{3+}\) to the Tb\(^{3+}\) occurs in the Y\(_2\)SiO\(_5\) matrix and bright green emission is obtained. With the cathode ray excitation, Tb\(^{3+}\) emission in Y\(_2\)SiO\(_5\) can also be sensitized by Ce\(^{3+}\). However, this sensitization cannot be observed with the excitation at 254 nm UV light, since the absorptions of Ce\(^{3+}\) in Y\(_2\)SiO\(_5\) does not appear in this UV range.

3.3. Photoluminescence of \((Y_{0.965-x}R_{x}Tb_{0.03}Ce_{0.005})_2SiO_5\) systems \((R = Sc, La, Gd and Lu)\)

\(R (R = Sc, La, Gd, and Lu)\) can substitute Y in Y\(_2\)SiO\(_5\) and form solid solutions. For different rare earth elements, the solid solution range varies. Our previous studies [3,9] indicated that the solid solution ranges are \(x < 0.65\) for the \((Y_{1-x}Sc_{x})_2SiO_5\) system, \(x < 0.05\) for the \((Y_{1-x}La_{x})_2SiO_5\) system, \(x < 0.4\) for the \((Y_{1-x}Gd_{x})_2SiO_5\) system and \(x < 0.35\) for the \((Y_{1-x}Lu_{x})_2SiO_5\) system, respectively. In the present work the luminescent properties were investigated only in the solid solution ranges.

When Sc\(^{3+}\), La\(^{3+}\), Gd\(^{3+}\) and Lu\(^{3+}\) replace Y\(^{3+}\) in the \((Y_{0.965}Tb_{0.03}Ce_{0.005})_2SiO_5\) phosphor respectively, the emission spectrum does not change, however the luminescent intensity varies. Fig. 4 shows the variations of PL intensity with the \(R^{3+}\) contents in the \((Y_{0.965-x}R_{x}Tb_{0.03}Ce_{0.005})_2SiO_5\) \((R = Sc, La, Gd and Lu)\) systems, where \(E_x = 355\) nm. The replacement of Y\(^{3+}\) by the La\(^{3+}\) and the Lu\(^{3+}\) causes increases of PL intensities by about 30% at \(x = 0.03\) for the La\(^{3+}\) and \(x = 0.20\) for the Lu\(^{3+}\). However, with the addition of the Gd\(^{3+}\) and the Sc\(^{3+}\), the luminescent intensity decreases. For the Gd\(^{3+}\) and the Sc\(^{3+}\) doped samples at \(x = 0.3\), the intensity is reduced about 10% and 25%, respectively. These results are similar to what we reported previously for the systems of \((Y_{0.965-x}R_{x}Ce_{0.005})_2SiO_5\)
and \((Y_{0.965-x}R_xTb_{0.03})_2\text{SiO}_5\) \((R = \text{Sc, La, Gd and Lu})\) [2–4].

### 3.4. Cathodoluminescence of \((Y_{0.965-x}R,Tb_{0.03}Ce_{0.005})_2\text{SiO}_5\) systems \((R = \text{Sc, La, Gd and Lu})\)

The cathodoluminescence measurements are carried out for the systems \((Y_{0.965-x}R_xTb_{0.03}Ce_{0.005})_2\text{SiO}_5\) \((R = \text{Sc, La, Gd and Lu})\). Fig. 5 exhibits CL spectrum of \((Y_{0.865}Gd_{0.10}Tb_{0.03}Ce_{0.005})_2\text{SiO}_5\), which is composed of the strong typical Tb\(^{3+}\) emission and the weak Ce\(^{3+}\) emission (located at 380–480 nm). The CL spectra of all the other samples are similar to it.

Fig. 6 shows the variations of cathodoluminescent intensity versus the \(R^{3+}\) content in the \((Y_{0.965-x}R_xTb_{0.03}Ce_{0.005})_2\text{SiO}_5\) systems. Except the Sc\(^{3+}\), the additions of La\(^{3+}\), Gd\(^{3+}\) and Lu\(^{3+}\) all improve the CL intensity. The optimized doping contents for La\(^{3+}\), Gd\(^{3+}\) and Lu\(^{3+}\) are at \(x = 0.03, 0.1–0.15\) and \(0.1–0.2\) and in the corresponding order the CL intensity increases about 10\%, 35\% and 25\%, respectively. For the Sc\(^{3+}\) doped samples, the CL intensity decreases about 15\% at \(x = 0.2\).

For the La\(^{3+}\) doped samples, both the PL and the CL intensities increase clearly, though the doping content is very limited. This phenomenon was also found for the La\(^{3+}\) doped Y\(_2\)SiO\(_5\):Ce and Y\(_2\)SiO\(_5\):Tb and the reason was discussed in the Refs. [2,4]. For the Gd\(^{3+}\) doped samples, the PL intensity was reduced, but the CL intensity was enhanced, similar to the situation observed from the Gd\(^{3+}\) doped Y\(_2\)SiO\(_5\):Ce and Y\(_2\)SiO\(_5\):Tb. It is proposed that the energy transfer process Gd\(^{3+}\) → Ce\(^{3+}\) → Tb\(^{3+}\) might occur and the details are discussed below.

### 3.5. Energy transfer in \((Y_{0.965-x}Gd_xTb_{0.03}Ce_{0.005})_2\text{SiO}_5\)

Energy transfer process (i.e. sensitization) is a quite common phenomenon in luminescent materials and also an effective way to improve luminescent efficiency. The energy transfer process between trivalent rare earth ions has been also proved efficient. It is reported in Ref. [12] that Gd\(^{3+}\) can transfer energy to other rare earths, such as Ce\(^{3+}\) and Tb\(^{3+}\). In this work, the Gd\(^{3+}\) doping reduced the PL for the Y\(_2\)SiO\(_5\):Ce,Tb, possibly because the replacement of Y\(^{3+}\) by Gd\(^{3+}\) modified the environment of the Tb\(^{3+}\) activator and this modification is not beneficial for the PL. However, the CL intensity was improved clearly by the Gd\(^{3+}\) doping, which implies that there are some ways for the Gd\(^{3+}\) to transfer the absorbed energy to the Tb\(^{3+}\).

For Gd\(^{3+}\), the energy difference between its ground state \(^8\text{S}_{7/2}\) and the lowest excited state \(^6\text{P}_{7/2}\) is larger than for all the other trivalent rare earth ions. Thus, it can readily transfer energy to other rare earth ions. The excitation peak of Gd\(^{3+}\) (\(^8\text{S}_{7/2}\) → \(^6\text{P}_{7/2}\)) appears at 275 nm and the emission at 310 nm [12], which overlaps the 300 nm excitation band of Ce\(^{3+}\) and the 4f\(^8\) → 4f\(^7\)5d transition of Tb\(^{3+}\) [13]. The mechanism of the energy transfer process Ce\(^{3+}\) → Tb\(^{3+}\) is well established [5,7,9] and the process Gd\(^{3+}\) → Ce\(^{3+}\) in Y\(_2\)SiO\(_5\) was also proved in Ref. [12,14]. Thus, it can be expected that in the system \((Y_{0.965-x}Gd_xTb_{0.03}Ce_{0.005})_2\text{SiO}_5\), the energy transfer process Gd\(^{3+}\) → Ce\(^{3+}\) → Tb\(^{3+}\) occurs, which is different from the process Ce\(^{3+}\) → Gd\(^{3+}\) → Tb\(^{3+}\) in LaPO\(_4\) and GdMgB\(_5\)O\(_{10}\) matrixes [6,7].

Fig. 7 shows the excitation spectrum of \((Y_{0.77}Gd_{0.20}Tb_{0.03})_2\text{SiO}_5\) monitored at 546 nm. The excitation peak of Gd\(^{3+}\) (\(^8\text{S}_{7/2}\) → \(^6\text{P}_{7/2}\)) appears at 275 nm. With the cathode rays excitation, the energy range of the secondary electrons is wide, thus it can excite both Tb\(^{3+}\) and Gd\(^{3+}\), and Gd\(^{3+}\) can transfer the energy to Tb\(^{3+}\). As a result, the CL intensity of \((Y_{0.97}Gd_xTb_{0.03})_2\text{SiO}_5\) phosphor increases. The similar phenomenon on Y\(_2\)SiO\(_5\):Ce was also reported in Ref. [12]. On the contrary, with the excitation of 254 nm UV light, only Tb\(^{3+}\) (rather than Gd\(^{3+}\)) is excited, therefore the improvement of the PL intensity can be observed. With the 275 nm UV light excitation, the Gd\(^{3+}\) ions absorb energy and transfer it to the Tb\(^{3+}\) ions, so the emission of Tb\(^{3+}\) increases. Fig. 8 presents
the decay curves of the Tb$^{3+}$ in \((Y_{0.97-x}Gd_xTb_{0.03})_2SiO_5\) with the various Gd$^{3+}$ contents \(x\) \((\lambda_{\text{EX}} = 275\,\text{nm}, \lambda_{\text{EM}} = 546\,\text{nm})\). It is well known that the decay curve can be represented by the following equation [15]:

\[
I = I_0 \exp\left(-\frac{t}{\tau}\right)
\]

where \(I\) and \(I_0\) are the luminescent intensities at time \(t\) and 0; \(\tau\) is defined as the luminescent lifetime. Based on Eq. (1) and decay curves, the lifetime values were calculated and presented in Fig. 9. The lifetime of Tb$^{3+}$ increases with the co-dopant Gd$^{3+}$ contents in our research range. The lifetime of Gd$^{3+}$ does not exhibit variation, for the content of Gd$^{3+}$ is several times more than that of Tb$^{3+}$. Only a small part of Gd$^{3+}$ ions take part in energy transfer process, lifetime is dominated by the residual Gd$^{3+}$ that does not take part in energy transfer process. The result gives further evidence for the energy transfer from Gd$^{3+}$ to Tb$^{3+}$. Therefore there are two routes for the Gd$^{3+}$ to trans-

Fig. 7. Excitation spectrum of \((Y_{0.77Gd_{0.20}Tb_{0.03}})_2SiO_5\) monitored at 546 nm.

Fig. 8. Decay curves of \((Y_{0.97-x}Gd_xTb_{0.03})_2SiO_5\) with various Gd$^{3+}$ content \(x\) \((\text{Ex} = 275\,\text{nm}, \text{Em} = 546\,\text{nm})\).

Fig. 9. Lifetime of the Tb$^{3+}$ as a function of the Gd$^{3+}$ doping contents.

Fig. 10. Schematic diagram of the energy transfer process in \((Y_{0.965-x}Gd_xTb_{0.03}Ce_{0.005})_2SiO_5\).

Fig. 11 shows the excitation spectrum of \((Y_{0.765Gd_{0.20}Ce_{0.005}Tb_{0.03}})_2SiO_5\) monitored at 546 nm, related to the \(^5D_4 \rightarrow ^7F_5\) transition of Tb$^{3+}$. The excitation bands from Tb$^{3+}$ and Ce$^{3+}$ as well as the excitation peak from Gd$^{3+}$ can be observed, which is in agreement with the energy transfer processes discussed above.

By analyzing the PL excitation and emission spectra, the energy transfer processes were confirmed, but the PL intensity was decreased with the addition of Gd$^{3+}$. It is because the PL measurements were conducted with the excitation of 355 nm UV light which was not at the excitation peak of the Gd$^{3+}$. With the cathode rays, all of the Tb$^{3+}$, Ce$^{3+}$ and Gd$^{3+}$ can be excited. Thus, with the addition of Gd$^{3+}$, the CL intensity of the phosphor was improved.
4. Conclusions

The PL and CL properties of Y$_2$SiO$_5$:Ce,Tb as well as Sc$^{3+}$, La$^{3+}$, Gd$^{3+}$ and Lu$^{3+}$ doped materials were investigated. The results can be summarized as follows.

1. The energy transfer process Ce$^{3+} \rightarrow$ Tb$^{3+}$ in the phosphor Y$_2$SiO$_5$:Ce,Tb was further confirmed. The transfer phenomenon can only be observed with the excitations at 355 nm (UV) and cathode rays.

2. The PL properties of the system (Y$_{0.965-x}$R$_x$Tb$_{0.03-}$Ce$_{0.005}$)$_2$SiO$_5$ (R = Sc, La, Gd and Lu) were investigated. For the Sc$^{3+}$ or Gd$^{3+}$ doped samples, the PL intensities decreased, whereas for the La$^{3+}$ doped samples, though the solid solution range was limited, the luminescent intensity increased nearly 30% at $x = 0.03$. The Lu$^{3+}$ doping increased the PL intensity about 20% at $x = 0.20$.

3. The CL measurements indicated that, except Sc$^{3+}$, the additions of La$^{3+}$, Gd$^{3+}$ and Lu$^{3+}$ improved the CL intensity. The La$^{3+}$ doping caused the CL intensity increase by about 10% at the optimized composition of $x = 0.03$; the Gd$^{3+}$ doping improved the intensity by about 30% at $x = 0.1$–0.15 and the Lu$^{3+}$ doping enhanced the intensity by about 20% at $x = 0.1$–0.2.

4. The energy transfer processes were discussed for the Gd$^{3+}$ doped samples. Two transfer processes from Gd$^{3+}$ to Tb$^{3+}$ were proposed: Gd$^{3+} \rightarrow$ Tb$^{3+}$ and Gd$^{3+} \rightarrow$ Ce$^{3+} \rightarrow$ Tb$^{3+}$.

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