

Energy transfer and red phosphorescence in strontium aluminates co-doped with Cr^{3+} , Eu^{2+} and Dy^{3+}

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Abstract

Cr^{3+} activated red long persistent phosphorescence through persistence energy transfer from Eu^{2+} to Cr^{3+} has been reported in strontium aluminates co-doped with Cr^{3+} , Eu^{2+} and Dy^{3+} . The decay processes of the red long persistent phosphorescence at 693 nm emission exhibit strong behavior of f–d band of Eu^{2+} , indicating the occurrence of energy transfer from Eu^{2+} to Cr^{3+} . Lifetime measurements of the blue band show that the energy transfer rates increase with the increase of the Cr^{3+} concentration. There are several phases observed in the strontium aluminates. Energy transfer occurs only for the Eu^{2+} and Cr^{3+} ions that located in the same phase in the host. In $\text{SrAl}_{12}\text{O}_{19}$ phase, the Eu^{2+} ions emit blue light centered at 400 nm and prefer to transferring energy to the Cr^{3+} that yields 688 nm emission, while in the $\text{Sr}_2\text{Al}_6\text{O}_{11}$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phases, the Eu^{2+} ions emit at 460 and 490 nm, respectively, and transfer the energy to the Cr^{3+} ions that give emission at 693 nm. It is found that the persistent phosphorescence only consists of the 490 and 693 nm bands, indicating the dominant contribution to the phosphorescence is from the ions in the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Oxide long-persistent phosphors have been synthesized in recent years. They have better formability and longer persistent time compared to previous sulfide phosphors. The activated emission centers, however, are limited in rare earth ions.

The examples are $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} and $\text{CaAl}_2\text{O}_4:\text{Tb}^{3+}$, Ce^{3+} crystalline materials [1–3] and Tb^{3+} or Eu^{2+} co-doped glass systems [4–6]. Transition metal ions, e.g. Cr^{3+} , have been widely used in luminescent materials; however, there are only limited reports for the ions applied to persistent phosphors. To our best knowledge, there are no reports on Cr^{3+} ions for this application. On the other hand, blue and green long persistent phosphors are obtained using

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oxides, but better red oxide phosphors are still in search.

In this paper, Cr^{3+} ions are introduced as activators in phosphorescence materials and the Eu^{2+} , Dy^{3+} , Cr^{3+} co-doped strontium aluminates samples have been prepared. Their emission and excitation spectra have been investigated and red long persistent phosphorescence observed. The effects of different compositions of Sr and Al in the host system on the optical properties of the co-doped system have been studied.

2. Experimental

The starting materials are SrCO_3 (A.P.), Al_2O_3 (A.P.), H_3BO_3 (A.P.), Eu_2O_3 (99.9%), Dy_2O_3 (99.9%) and Cr_2O_3 (G.P.) powders. The powder samples are prepared for different nominal compositions: $\text{SrO} \cdot 2\text{Al}_2\text{O}_3$ (SA_2), $\text{SrO} \cdot 3\text{Al}_2\text{O}_3$ (SA_3), $\text{SrO} \cdot 4\text{Al}_2\text{O}_3$ (SA_4), $\text{SrO} \cdot 5\text{Al}_2\text{O}_3$ (SA_5), $\text{SrO} \cdot 6\text{Al}_2\text{O}_3$ (SA_6) and $4\text{SrO} \cdot 7\text{Al}_2\text{O}_3$ (SA_7). All samples are co-doped with 1 at% Eu, 2 at% Dy and different concentrations of Cr from 0 to 5 at%. A proper amount of H_3BO_3 is added to serve as a flux. The mixtures are ground for 1 h, then pre-fired at 1000°C for 4 h in the air, and finally sintered at 1300°C for 4 h in reducing atmosphere.

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra are measured at room temperature with a Hitachi Spectra-fluorometer (F-4500). In fluorescence lifetime measurements, the third harmonic (355 nm) of a Nd-YAG laser (Spectra-Physics, GCR 130) is used as an excitation source, and the signals are detected with a Tektronix digital oscilloscope (TDS 3052).

3. Results and discussion

Fig. 1 shows the emission spectra for 1 at% Eu, 2 at% Dy and 5 at% Cr co-doped with SA_2 , SA_3 , SA_4 , SA_5 and SA_6 , respectively, under 330 nm excitation. The positions of the blue emission bands of Eu^{2+} and the red emission lines of Cr^{3+} vary in different samples, indicating the formation of different phases in the $\text{SrO-Al}_2\text{O}_3$ system.

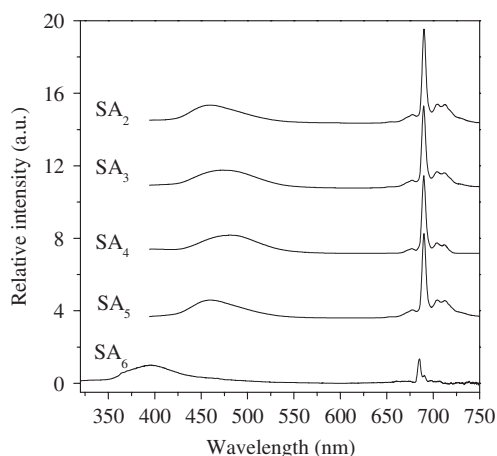


Fig. 1. Emission spectra for SA_2 , SA_3 , SA_4 , SA_5 and SA_6 co-doped with 1 at% Eu, 2 at% Dy and 5 at% Cr under 330 nm excitation.

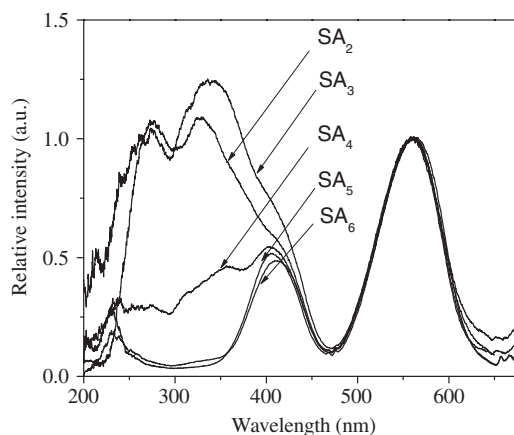


Fig. 2. Excitation spectra ($\lambda_{\text{em}} = 693 \text{ nm}$) of SA_2 , SA_3 , SA_4 , SA_5 and SA_6 co-doped with 1 at% Eu^{2+} , 2 at% Dy^{3+} and 5 at% Cr^{3+} .

According to the positions of the blue bands, the bands at 400, 460, and 490 nm can be attributed to Eu^{2+} transitions in $\text{SrAl}_{12}\text{O}_{19}$ [7], $\text{Sr}_2\text{Al}_6\text{O}_{11}$ [8], and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phases [8,9], respectively. The sharp emissions in red are R lines due to the transitions of Cr^{3+} ions in different compositions. Obviously, the R lines are located at 688 nm in $\text{SrAl}_{12}\text{O}_{19}$ phase and at 693 nm in other phases.

Fig. 2 depicts the excitation spectra of samples SA_n ($n = 2, 3, 4, 5$ and 6) when Cr^{3+} emission lines are monitored. In the spectra, the bands peaking at

420 and 570 nm originate from $^4A_2-^4T_1(F)$ and $^4A_2-^4T_2(F)$ transitions of Cr^{3+} , respectively. The excitation bands between 275 and 350 nm UV region originate from f–d transitions of Eu^{2+} . It is exhibited that the UV excitation bands grow remarkably with the decrease of n number for the SA_n samples. When the value of n is 2, the concentration quench occurs between Eu^{2+} ions. It is because of the decrease of n number that results in the decrease of volume of a crystal unit cell, leading to the increase of Eu^{2+} numbers in unit volume, and then enhancing the excitation bands in the case of energy transfer from Eu^{2+} to Cr^{3+} . However, persistent phosphorescence spectra of these samples show 490 and 693 nm emissions only, indicating the dominant contribution of $Sr_4Al_{14}O_{25}$ phase to the phosphorescence. For this reason, we will pay more attention on the luminescence and phosphorescence properties of $Sr_4Al_{14}O_{25}:Cr^{3+}$, Eu^{2+} , Dy^{3+} in the following sections.

Fig. 3 represents emission spectra of S_4A_7 co-doped with 1 at% Eu^{2+} , 2 at% Dy^{3+} and x at% Cr^{3+} ($x = 0.5, 1, 2, 3, 4$ and 5) under 330 nm excitation, where the intensities of the blue bands are normalized. An afterglow spectrum of S_4A_7 : 1 at% Eu^{2+} , 2 at% Dy^{3+} and 1 at% Cr^{3+} (line L1) is also presented in Fig. 3. As we know, 330 nm can excite Eu^{2+} only but not Cr^{3+} , the strong red

emission of Cr^{3+} should be the result of energy transfer from Eu^{2+} . It can be seen that Cr^{3+} emission intensity increases with the increase of Cr^{3+} concentration up to 4 mol%, indicating increase of energy transfer efficiencies from Eu^{2+} to Cr^{3+} with increasing Cr^{3+} concentration. The intensity of red emission peak reaches a maximum when the concentration of Cr^{3+} is 4%. Higher than this concentration, the intensity of the red emission started to decrease due to concentration quenching. There are also different phases including $Sr_2Al_6O_{11}$ with a blue band at 460 nm and $Sr_4Al_{14}O_{25}$ at 490 nm of Eu^{2+} in the emission spectra. However, the afterglow emission (line L1) occurs in $Sr_4Al_{14}O_{25}$ phase only with a blue band at 490 nm of Eu^{2+} and the red lines at 693 nm of Cr^{3+} . It is believed that only $Sr_4Al_{14}O_{25}$ phase contributes to the afterglow.

To further find the evidence of energy transfer, the blue fluorescence lifetimes of Eu^{2+} in S_4A_7 co-doped with 1 at% Eu^{2+} , 2 at% Dy^{3+} and x % Cr^{3+} ($x = 0, 0.5, 1, 2, 3$ and 4) are measured, as shown in Fig. 4. The decays can be described as a single exponential and the fitting results of the lifetimes to the exponential function are listed above each decay curve. It is clearly observed that the lifetimes become shorter with the increase

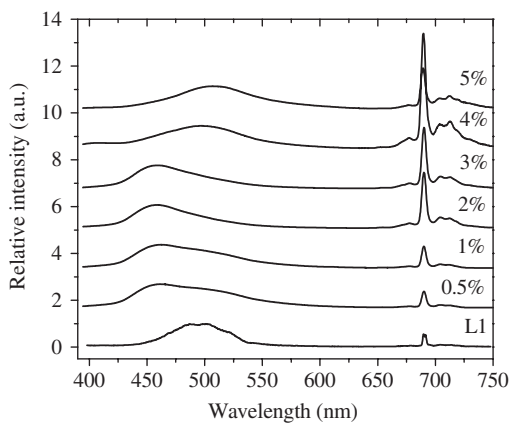


Fig. 3. Normalized emission spectra ($\lambda_{ex} = 330$ nm) of S_4A_7 co-doped with 1 at% Eu^{2+} , 2 at% Dy^{3+} and x % Cr^{3+} ($x = 0.5, 1, 2, 3, 4$ and 5) and an afterglow spectrum of S_4A_7 : 1 at% Cr^{3+} , 1 at% Eu^{2+} , 2 at% Dy^{3+} (line L1).

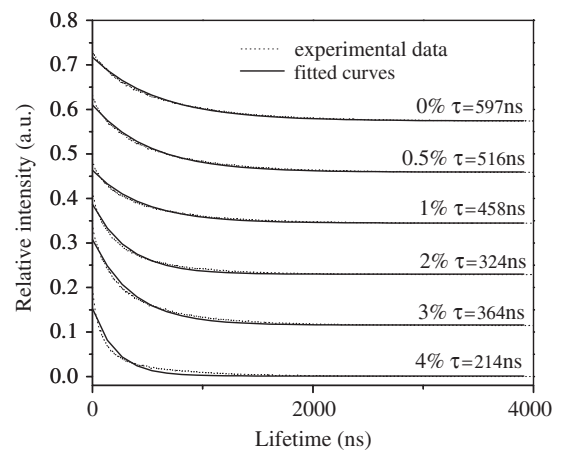


Fig. 4. The fluorescence decay curves of Eu^{2+} (490 nm emission) in S_4A_7 co-doped with 1 at% Eu^{2+} , 2 at% Dy^{3+} and x % Cr^{3+} ($x = 0, 0.5, 1, 2, 3$ and 4). The lifetimes listed above the curves obtained from single exponential fitting.

of the Cr^{3+} concentration as a result of energy transfer from Eu^{2+} to Cr^{3+} .

An important result of the present work is the long-lasting red phosphorescence observed in above-mentioned Eu^{2+} , Dy^{3+} , and Cr^{3+} co-doped strontium aluminates. Fig. 5 shows the decay curves of the phosphorescence at 490 and 693 nm of Sr_4Al_7 :1% Cr^{3+} , 1% Eu^{2+} and 2% Dy^{3+} phosphor sample after radiation with xenon lamp for 5 min. It is found that the red afterglow of Cr^{3+} decays faster than the blue one. In the previous reports regarding strontium aluminates phosphors (e.g. SrAl_2O_4 :Dy, Eu [10–12]), the researchers have believed that the co-doped Dy^{3+} works as the hole trap centers and prolongs the afterglow. In the strontium aluminates co-doped with Dy^{3+} , Cr^{3+} and Eu^{2+} , Dy^{3+} may also act as trap centers, which capture the free holes. Because the Cr^{3+} replaces Al^{3+} , there exist two types of Dy^{3+} , one surrounded mainly by Al called Dy1 and the other by Cr called Dy2. The former may deeper energy levels than the latter. Eu^{2+} is mainly surrounded by Dy1, whereas Cr^{3+} is certainly surrounded by Dy2. Based on energy transfer theory, the red phosphorescence mainly originates from those Cr^{3+} ions located at short distance to Eu^{2+} ions, so that the decay rates of the red afterglow are determined by both Dy1 and Dy2 traps. In contrast, the blue phosphorescence mainly originates from those Eu^{2+} ions that

located at long distance to Cr^{3+} ions, so that the decay rates of the blue one are dominantly determined by the Dy1 trap centers.

4. Conclusions

In conclusion, Cr^{3+} activated red long persistent phosphors have been prepared and persistence energy transfer observed. In the system of Cr^{3+} , Eu^{2+} , Dy^{3+} co-doped $\text{SrO-Al}_2\text{O}_3$, the energy transfer from Eu^{2+} to Cr^{3+} only occurs in the same phase. The Eu^{2+} ions emit blue light at 400 nm and prefer to transferring energy to the Cr^{3+} ions that yield 688 nm emission in $\text{SrAl}_{12}\text{O}_{19}$ phase, while in the $\text{Sr}_2\text{Al}_6\text{O}_{11}$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phases, the Eu^{2+} emissions peak at 460 and 490 nm, respectively, and transfers the energy to the Cr^{3+} ions that give emission at 693 nm. The emission lines at 693 nm increases following the increase of the Eu^{2+} concentrations under 330 nm excitation. The lifetimes of Eu^{2+} emitting at 490 nm become shorter with the increase of the Cr^{3+} concentrations. Persistent phosphorescence is obtained through persistent energy transfer in these systems and shows only 490 and 693 nm emissions, so the ions in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase make a dominant contribution to the phosphorescence.

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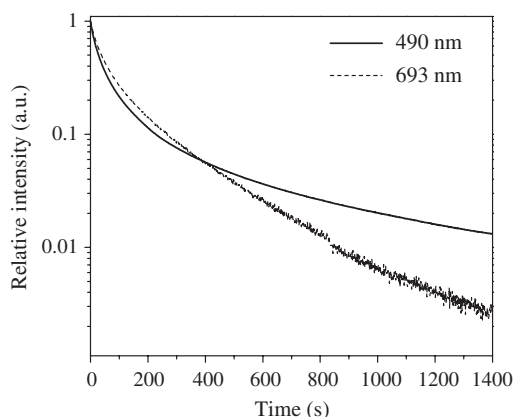


Fig. 5. Decay curves of the phosphorescence at 490 and 693 nm of Sr_4Al_7 :1% Cr^{3+} , 1% Eu^{2+} and 2% Dy^{3+} after radiation with xenon lamp for 5 min.

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