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Journal of Solid State Chemistry 179 (2006) 266–269

JOURNAL OF SOLID STATE CHEMISTRY

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White-light-emitting long-lasting phosphorescence in Dy^{3+}-doped $SrSiO_3$

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Received 17 July 2005; received in revised form 11 October 2005; accepted 20 October 2005
Available online 23 November 2005

Abstract

We report on a luminescent phenomenon in Dy^{3+}-doped $SrSiO_3$ long-lasting phosphor. After irradiation by a 254-nm UV lamp for 5 min, the Dy^{3+}-doped $SrSiO_3$ phosphor emits white light-emitting long-lasting phosphorescence for more than 1 h even after the irradiation source has been removed. Photoluminescence, long-lasting phosphorescence and thermoluminescence (TL) spectra are used to explain this phenomenon. Photoluminescence spectra reveal that the white light-emitting long-lasting phosphorescence originated from the two mixtures of Dy^{3+} characteristic luminescence, the 480-nm blue emission ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and the 572-nm yellow emission ($^4F_{9/2} \rightarrow {}^6H_{13/2}$). TL spectra shows that the introduction of Dy^{3+} ions into the $SrSiO_3$ host produces a highly dense trapping level at 377 K (0.59 eV), which is responsible for the long-lasting phosphorescence at room temperature. A possible mechanism of the long-lasting phosphorescence based on the experimental results is proposed. It is considered that the long-lasting phosphorescence is due to persistent energy transfer from the electron traps to the Dy^{3+} ions, which creates the persistent luminescence of Dy^{3+} to produce the white light-emitting long-lasting phosphorescence.

Keywords: Phosphor; Afterglow; Luminescence; $SrSiO_3$:Dy^{3+}

1. Introduction

Long-lasting phosphorescence, a phenomenon due to the thermal stimulated recombination of holes and electrons at traps, which leave holes or electrons in a long-lived excited state at room temperature, is an interesting phenomenon in which the material persists for a long time after the removal of the excitation source [1]. Based on this intrinsic merit, much interest was aroused in various rare earth ion-doped crystals and glasses excited by UV or infrared femtosecond laser, and their applications for luminous glass, emergency signs, watches and graphic arts, etc [2–6].

However, progress in these fields was rather slow. It has taken almost 100 years to extend the persistence time from minutes to tens of hours. One of the reasons is that it is hard to introduce proper traps in these materials. Till now, the best performance of the long-lasting phosphorescence materials are Eu^{2+}-doped alkaline-earth aluminate phosphors, i.e., $SrAl_2O_4$:Eu,Dy (green), $CaAl_2O_4$:Eu,Nd (blue), and Eu^{3+}-doped oxysulfide yttrium, Y_2O_2S:Eu,Ti,Mg (red) [7–9]. Besides the blue, green and red color long-lasting phosphor, white light-emitting long-lasting phosphors are also needed for potential applications. This present work is aimed at searching for the white light-emitting long-lasting phosphors.

Theoretically speaking, we can get any color-emitting long-lasting phosphorescence by mixing the three primary colors (RGB)-emitting long-lasting phosphors. For white light-emitting long-lasting phosphorescence, one can also obtain by mixing a blue and a yellow light-emitting long-lasting phosphors as well as the integration of the InGaN blue LED chip and a yellow-emitting phosphor to obtain the white light-emitting diodes (LEDs) [10]. However, it is difficult to fabricate those persistent phosphors (RGB/YB) which have similar phosphorescence decay ratios to ensure the white light-emitting long-lasting phosphorescence all the time.

Dy^{3+} ions, which have the luminescence lines in the 470–500 nm region due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and in

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0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.10.025

the 570–600 nm region due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, have attracted much attention because of its white light emission [11–14]. In this paper, we report on a novel white light-emitting afterglow phosphor $Sr_{1-x}Dy_xSiO_3$. It was found that long-lasting phosphorescence indirectly came from the luminescence of Dy^{3+} ions.

2. Experimental

Powder samples were prepared by the conventional high-temperature solid-state technique. The starting materials were high-purity $SrCO_3$ (>99.9%), SiO_2 (>99.99%) and Dy_2O_3 (>99.99%). The Dy^{3+} dopant concentrations ranged from 0 to 5 mol% of Sr^{2+} ions in $SrSiO_3$. After having taken the starting materials in metrological proportions and homogenized thoroughly, the mixture was sintered at 1300 °C for 3 h using alumina crucibles with alumina lids in air atmosphere with subsequent air cooling to get the products.

Crystal structure of all synthesized powder samples were checked by D/max-IIB X-ray diffractometer and XRD patterns matched quite well with the standard JCPDS files no. 36-0018. The excitation and emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The afterglow decay curve measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer. Quantitative thermoluminescence (TL) spectra were measured on a model FJ-427A1 TL meter (made by Beijing Nuclear Instrument Factory, China) with a heating rate of 2 K/s from room temperature to 673 K. Before measurement, 0.025 g powder samples were pressed into pellets (5 mm diameter and 1 mm thickness), then exposed to a standard UV lamp peak at 254 nm for 5 min. All measurements were carried out at room temperature except for the TL spectrum.

3. Results and discussion

A series of $Sr_{1-x}Dy_xSiO_3$ samples have been synthesized with the dopant level ranging from 0.5 to 5 mol%. The concentration quenching occurs when Dy^{3+} is doped at above 1 mol%. The photoluminescence spectra of 1 mol% Dy^{3+}-doped $SrSiO_3$ sample under excitation at 350 nm and monitored at 572 nm are shown in Fig. 1, respectively. As shown here, the emission spectrum of Dy^{3+} has three groups of emissions located at 480, 572 and 664 nm, which correspond to the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow), $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (red), respectively [15]. Among the three emission peaks, the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission belongs to hypersensitive transition with $\Delta J = 2$, which is strongly influenced by outside environments of Dy^{3+}. Fig. 1 also gives the excitation spectrum of 1 mol% Dy^{3+}-doped $SrSiO_3$, the peaks which range from 250–400 nm are due to $4f$–$4f$ transitions of Dy^{3+} [16], while the broad band absorption peaking at 210 nm can be attributed to the charge transfer state of Dy^{3+}–O^{2-} [17]. Since this phosphor can efficiently emit yellow composition under the 300–400 nm excitation range, it is feasible to suggest that this phosphor has a potential application in white LEDs.

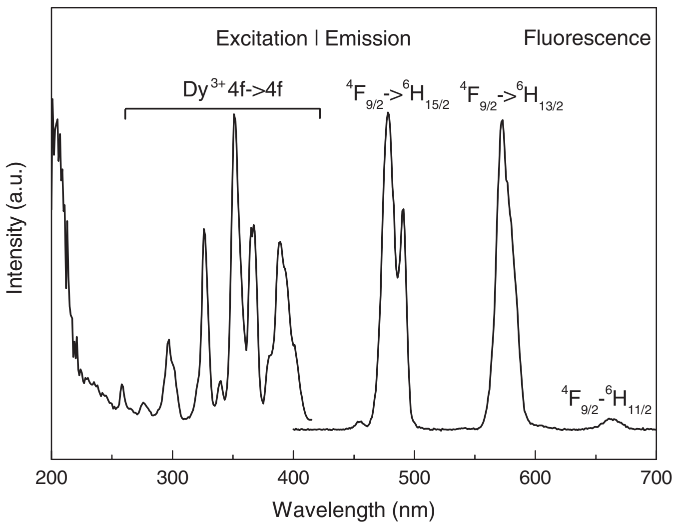

Fig. 1. Emission ($\lambda_{ex} = 350$ nm) and excitation ($\lambda_{em} = 572$ nm) spectra of 1 mol% Dy^{3+}-doped $SrSiO_3$.

An important new result of the present work is that we have observed obvious white light-emitting long-lasting phosphorescence in $SrSiO_3$:Dy^{3+} phosphors. Fig. 2 shows the afterglow spectra of 1 mol% Dy^{3+}-doped $SrSiO_3$ after the excitation source is switched off at different times. These decay curves were measured by a Varian Cary Eclipse fluorescence spectrophotometer. The excitation light of the sample was blocked when the sample had been exposed for 5 min under 254-nm UV lamp and the emitted afterglow from it was recorded over a time period of 300–1200 s in the kinetic analysis mode of the spectrometer system. The scan interval is set to 30 s. The phosphorescence emission intensity of all the samples decreases quickly at first and then slowly, which can be fitted to a single-exponential function: $I = At^{-n}$. The long-lasting phosphorescence for the 1 mol% Dy^{3+}-doped $SrSiO_3$ phosphor can be seen with the naked eye in the dark (0.32 mcd/m^2) clearly for more 1 h even after the UV irradiation has been removed. Moreover, we have also observed stronger white light-emitting long-lasting phosphorescence under irradiation by 185-nm UV lamp for several minutes. It is interesting to note, however, that we do not get any long-lasting phosphorescence under irradiation by 365-nm UV light even for 10 min, indicating that the long-lasting phosphorescence is not directly rooted in the luminescence of Dy^{3+} ions.

As mentioned above, the Dy^{3+}-doped $SrSiO_3$ phosphors show white light-emitting long-lasting phosphorescence when illuminated with a 254-nm UV lamp. The white color in our present work is the result of a mixture of two main emissions of Dy^{3+} ions (480 and 572 nm). The color of the long-lasting phosphorescence would deviate from white color during the decay process if different emissions have

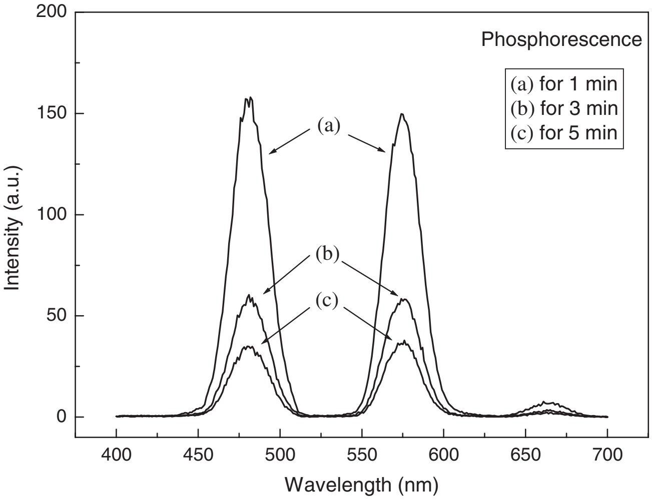

Fig. 2. Long-lasting phosphorescence spectra of 1 mol% $\mathrm{Dy^{3+}}$-doped $\mathrm{SrSiO_3}$ after the excitation source is switched off at different times ($\lambda_{\mathrm{ex}} = 254\,\mathrm{nm}$, $a = 1$, $b = 3$, $c = 5$ min).

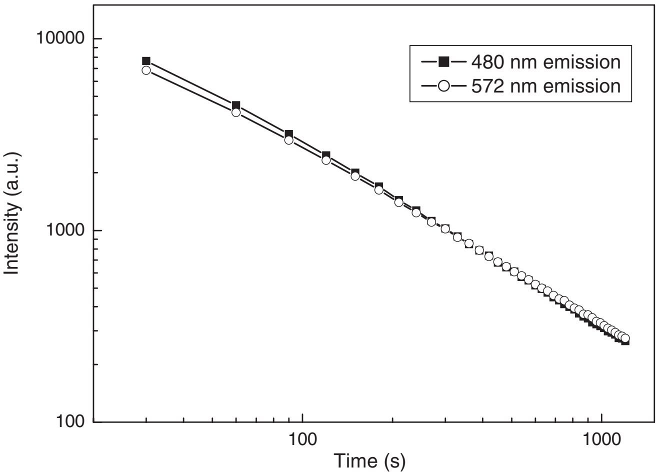

Fig. 3. Afterglow decay curves of 1 mol% $\mathrm{Dy^{3+}}$-doped $\mathrm{SrSiO_3}$ at 480 and 572 nm. The sample was irradiated by 254-nm UV light for 5 min before measurement.

distinctly different decay ratios, so the afterglow decay ratios of the two main emissions are crucial to the white light-emitting long-lasting phosphorescence after the UV excited source has been removed. Fig. 3 shows the afterglow intensity decay curves of the phosphorescence at 480 and 572 nm in the 1 mol% $\mathrm{Dy^{3+}}$-doped $\mathrm{SrSiO_3}$ phosphor sample. The two emissions have similar decay ratios because the two emissions originate from the same $^4F_{9/2}$ excited state, and the yellow emission (572 nm) intensity to blue emission (480 nm) intensity approach unity. These results clearly indicate that the color of the white light-emitting long-lasting phosphorescence of $\mathrm{Dy^{3+}}$-doped $\mathrm{SrSiO_3}$ phosphor remains the same throughout the decay time.

It is known that trapping centers play an essential role for photo energy storage in persistent, photostimulable, and thermostimulable phosphors [18]. It is also reported that long-lasting phosphorescence phenomenon is observed in $\mathrm{Ce^{3+}}$-doped $\mathrm{BaAl_2O_4}$ and $\mathrm{Tb^{3+}}$-doped $\mathrm{CaAl_2O_4}$ phosphors, due to the $\mathrm{Ce^{3+}/Tb^{3+}}$ ions chemically nonequivalent substitution of $\mathrm{Ca^{2+}}$ ions to produce suitable defect-related traps [19,20]. In our present case, from the viewpoint of ionic radii, it is reasonable to suggest that, the $\mathrm{Dy^{3+}}$ ions ($r_{\mathrm{Dy^{3+}}} = 0.091\,\mathrm{nm}$) are expected to occupy the $\mathrm{Sr^{2+}}$ ($r_{\mathrm{Sr^{2+}}} = 0.113\,\mathrm{nm}$) sites in the $\mathrm{SrSiO_3}$ host and no $\mathrm{Dy^{3+}}$ ion is expected to occupy the $\mathrm{Si^{4+}}$ sites ($r_{\mathrm{Si^{4+}}} = 0.041\,\mathrm{nm}$). Due to these chemically nonequivalent substitutions, an excess of positive charge in the host lattice must be compensated. One possible way of charge compensation mechanism is that two $\mathrm{Dy^{3+}}$ ions replace three $\mathrm{Sr^{2+}}$ ions to balance the charge of these phosphors, which create two $\mathrm{Dy_{Sr}^{\circ}}$ positive defects and one V_{Sr}'' negative defect [19–21],

$$2\mathrm{Dy^{3+}} + 3\mathrm{Sr^{2+}} \rightarrow 2\mathrm{Dy_{Sr}^{\circ}} + V_{\mathrm{Sr}}''.$$

In order to explain the phenomenon of $\mathrm{Dy^{3+}}$-doped in the $\mathrm{SrSiO_3}$ host, it is necessary to take the TL spectrum into consideration. Fig. 4 shows the TL curves of $\mathrm{Dy^{3+}}$-doped and -undoped $\mathrm{SrSiO_3}$ samples. No peak could be detected in the undoped phosphor. On the contrary, two glow peaks are located at 377 and 513 K in the $\mathrm{Dy^{3+}}$-doped $\mathrm{SrSiO_3}$ phosphor, corresponding to two different traps formed due to charge defects created in substituting $\mathrm{Sr^{2+}}$ by $\mathrm{Dy^{3+}}$ [6,18–20]. The depths of the traps were calculated to be 0.59 and 1.14 eV for 377 and 513 K, respectively [22]. To the best of our knowledge, the dominant peaks are situated above room temperature (323–393 K) if materials show excellent long-lasting phosphorescence performance [7,23]. Therefore, the highly dense trapping level at 377 K (0.59 eV) is responsible for the long-lasting phosphorescence at room temperature in our present case.

The detailed description of long-lasting phosphorescence mechanism is not yet known. The long-lasting phosphorescence phenomenon is assumed to be due to the

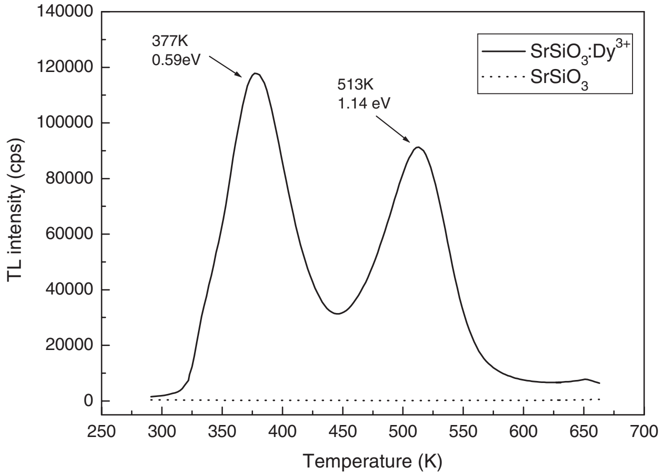

Fig. 4. Thermoluminescence spectrum of $\mathrm{Dy^{3+}}$-doped (solid line) and undoped (dot line) $\mathrm{SrSiO_3}$.

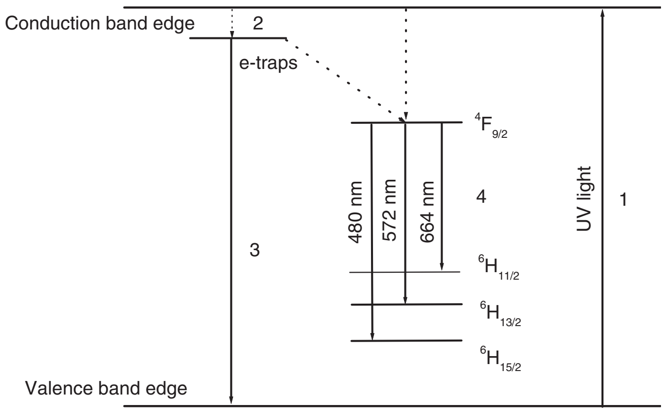

Fig. 5. The possible process of the origin of the long-lasting phosphorescence in the $SrSiO_3$: Dy^{3+} phosphor.

thermostimulated recombination of holes and electrons which leave electrons or holes in a metastable state at room temperature [24]. On the basis of the above TL curve and the photoluminescence spectra results, it is reasonable to postulate that, (a) when Dy^{3+} doped into $SrSiO_3$ host, due to the chemically nonequivalent substitution, Dy^{3+} ions act as a role of creating the electron traps during the high-temperature synthesis process; (b) the long-lasting phosphorescence originates energy transfer from the electron traps to the Dy^{3+} ions, which give birth to the characteristic emissions of Dy^{3+}. The possible process can be displayed in Fig. 5. After irradiation by UV light, the electrons in the valence band are excited to the conduction band and free electrons and holes are formed in the sample host. The holes or electrons were trapped by defect centers, released by heat at room temperature, and recombined with electrons or holes trapped by other defect centers (step 1). One part of the excited electrons returned to the electron traps by the nonradiative way, and got stored in the electron traps which was created at high temperature during the synthesis process (step 2). Because the electron traps are in a metastable state at room temperature, the excited electrons stored in it can be thermally released and be turned back to the valence band edge (step 3). After turning off the excited source, a majority of excited electrons stored in the electron traps would be transferred to the $^4F_{9/2}$ state of Dy^{3+} ions and would create the characteristic emissions of Dy^{3+} ions (step 4). When the decay ratio of the energy transfer from the electron traps to the $^4F_{9/2}$ state of Dy^{3+} ions is proper, the white light-emitting long-lasting phosphorescence of Dy^{3+} can be obtained.

4. Conclusions

In conclusion, a white light-emitting afterglow phosphor with the chemical formula $Sr_{1-x}Dy_xSiO_3$ synthesized by conventional solid-state method is reported in this paper. Long-lasting phosphorescence from Dy^{3+} was observed with the naked eye (0.32 mcd/m^2) for about 1 h in the dark clearly even after the UV lamp had been removed. The long-lasting phosphorescence is considered to be due to energy transfer from the electron traps to the Dy^{3+} ions. These findings are important in the context of Dy^{3+} nonequivalent substitution for white light-emitting long-lasting phosphorescence materials available.

Acknowledgments

This present work was supported by the National Natural Science Foundations of China (Grant nos. 50472077 and 20171018), the Natural Science Foundations of Guangdong Province (Grant nos. 013201 and 36706).

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