# White-emitting Long-lasting Phosphor $Sr_2SiO_4$:$Dy^{3+}$

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A white-emitting long-lasting phosphor is synthesized by the conventional high temperature solid-state method. After irradiation by 185 or 210 nm UV light for 1 min, the $Dy^{3+}$-doped $Sr_2SiO_4$ phosphor emits white color long-lasting phosphorescence, and the phosphorescence can be seen with the naked eye in the dark clearly for more than 1 h even after the irradiation source has been removed. XRD, PL, and TL spectra are used to characterize this phosphor. It is considered that the long-lasting phosphorescence is due to persistent energy transfer from the e-traps to the $Dy^{3+}$ ions to create the white-emitting long-lasting phosphorescence.

Long-lasting phosphors can light up for a long time in the darkness after irradiation with sunlight or ultraviolet (UV) light. In recent years, the interests in these materials have been growing because of their potential application in dark environment display such as emergency signs, interior decoration, luminous paints, and graphic arts, etc.[1,2] Among them, the best performance of the long-lasting phosphorescence materials are $Eu^{2+}$-doped alkaline earth aluminate phosphors, for example, $SrAl_2O_4$ : Eu, Dy (green), $CaAl_2O_4$ : Eu, Nd (blue), and $Eu^{3+}$-doped oxysulfide yttrium, $Y_2O_2S$ : Eu, Ti, Mg (red).[2,3] Very recently, Kang and co-workers have reported a novel yellowish-orange afterglow phosphor, $Y_2O_2S$ : Ti, Mg.[4] Besides the blue, green, and red color long-lasting phosphors, white color long-lasting phosphors are also needed for various display.

Theoretically, we can get any color-emitting long-lasting phosphorescence by mixing the three primary color- (RGB) emitting long-lasting phosphors. For the white-light-emitting long-lasting phosphorescence, it can be also obtained 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.[5] Nevertheless, it is difficult to fabricate those persistent phosphors (RGB/YB) which have the similar phosphorescence decay ratios to ensure 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 $^4F_{9/2}$–$^6H_{15/2}$ transition and in the 570–600-nm region due to the $^4F_{9/2}$–$^6H_{13/2}$ transition, have attracted much attention because of its white light emission.[6,7] In this letter, we report some preliminary results on a $Dy^{3+}$-actived $Sr_2SiO_4$ white-light-emitting afterglow phosphor.

A series of $Sr_{2(1-x)}Dy_{2x}SiO_4$ phosphors have been synthesized by high temperature solid-state method. The starting materials were high-purity $SrCO_3$, $SiO_2$ and $Dy_2O_3$. The $Dy^{3+}$ dopants concentrations ranged from 1 to 5 mol % of $Sr^{2+}$ ions in $Sr_2SiO_4$. The starting materials was mixed and fired at 1200 °C for 6 h under flowing $N_2$ atmosphere.

Crystal structure of all synthesized powder samples were checked by a D/max-IIB X-ray diffractometer and XRD patterns matched the standard JCPDS files No. 39-1256. The excitation and emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a 150-W xenon lamp as excitation source. The afterglow intensity decay curve was measured on the same instrument. The thermoluminescence (TL) spectra were measured on a model FJ-427A1 TL meter. All measurements were carried out at room temperature (RT) except for the TL spectra.

Figure 1 presents the emission and excitation spectra of 3% $Dy^{3+}$-doped $Sr_2SiO_4$ sample under excitation at 210 nm and monitored at 480 nm. As shown in Figure 1, the emission spectrum of $Dy^{3+}$ has three groups of emissions located at 480, 573, and 664 nm, which correspond to the transitions of $^4F_{9/2}$–$^6H_{15/2}$ (blue), $^4F_{9/2}$–$^6H_{13/2}$ (yellow), $^4F_{9/2}$–$^6H_{11/2}$ (red), respectively.[8] Among the three emission peaks, the $^4F_{9/2}$–$^6H_{13/2}$ emission belongs to hypersensitive transition with $\Delta J = 2$, which is strongly influenced by outside environments of $Dy^{3+}$. Figure 1 also gives the excitation spectrum of 3% $Dy^{3+}$-doped $Sr_2SiO_4$, the peaks from 250 to 400 nm are due to $4f$–$4f$ transitions of $Dy^{3+}$,[9] while the broad band absorption peaking at 210 nm can be attributed to the charge transfer state of $Dy^{3+}$–$O^{2-}$.[10] Since this phosphor can emit efficiently yellow (573 nm) composition under the 250–400 nm excitation range, it is feasible to suggest that this phosphor has potential application in white-light-emitting diodes (LEDs).

An important result of the present work is that we have observed white-light-emitting long-lasting phosphorescence in $Sr_2SiO_4$ : $Dy^{3+}$ phosphors after stopping the excitation source. Figure 2A shows the afterglow intensity of 3% $Dy^{3+}$-doped $Sr_2SiO_4$ after the excitation source is stopped in logarithmic scale format. The phosphorescence emission intensity of all samples decreases quickly at first and then slowly. The long-lasting phosphorescence for the 3% $Dy^{3+}$-doped $Sr_2SiO_4$ phosphor can be seen with the naked eye in the dark clearly more than 1 h even after the UV irradiation has been removed. Moreover, we also see stronger white-emitting long-lasting phosphorescence in the dark under irradiation by a 185-nm UV lamp for 1 min.

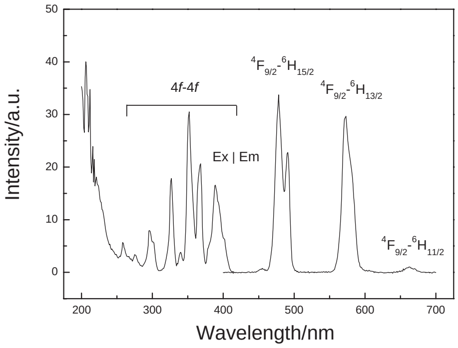

**Figure 1.** Emission ($\lambda_{ex} = 210$ nm) and excitation ($\lambda_{em} = 480$ nm) spectra of 3% $Dy^{3+}$-doped $Sr_2SiO_4$.

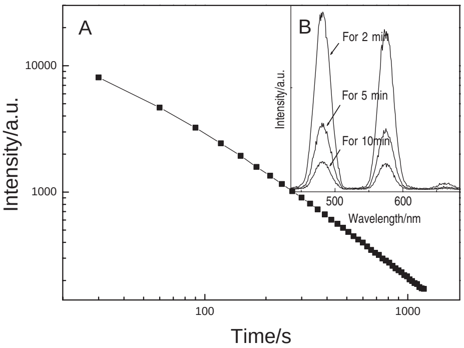

**Figure 2.** Afterglow intensity of 3% $Dy^{3+}$-doped $Sr_2SiO_4$ (A). Sample was irradiated by 210-nm UV light for 1 min before measurement. Inset (B) is the afterglow spectra of this phosphor after the excitation source is stopped at different times ($\lambda_{ex} = 185\,nm$, $t = 2, 5, 10\,min$).

It is interesting to note, however, that we do not get any long-lasting phosphorescence under irradiation by 300–400 nm UV light even for 10 min, indicating that the long-lasting phosphorescence is not directly rooted in $Dy^{3+}$.

As mentioned above, the $Dy^{3+}$-doped $Sr_2SiO_4$ phosphors show white-light-emitting long-lasting phosphorescence when illuminated under 210- or 185-nm radiation. The white color in our present work is the result of a mixture of two main emissions (480 and 573 nm). The color of the long-lasting phosphorescence would deviate from white color during the decay process if different emissions have distinctly different decay rations, so the afterglow decay rations of the two main emissions are crucial to the white-light-emitting long-lasting phosphorescence after the UV excited source has been removed. Figure 2B shows the afterglow spectra of 3% $Dy^{3+}$-doped $Sr_2SiO_4$ after the excitation source is stopped at different times ($t = 2, 5, 10\,min$). All of them contain two main emissions (480 and 573 nm). Moreover, those two emissions have the similar decay ratios because they originate from the same $^4F_{9/2}$ excited state. It is reasonable to ensure white-light-emitting long-lasting phosphorescence in $Dy^{3+}$-doped $Sr_2SiO_4$ phosphors all the time.

It is well known that trapping centers play an essential role for photoenergy storage in persistent, photostimulable, and thermostimulable phosphors. And TL spectrum has been a major technique for revealing trapping center.[11] The TL spectrum of $Sr_2SiO_4 : Dy^{3+}$ sample is shown in Figure 3. It consisted two main peaks located at 90 and 294 °C, corresponding to two different traps due to charge defects created in substituting $Sr^{2+}$ by $Dy^{3+}$.[2,12]

A detailed description of the phosphorescence mechanism can not be given at present. The long-lasting phosphorescence is assumed to be due to the thermostimulated recombination of holes and electrons which leave electrons or holes in a metastable state at room temperature.[2,13] On the basis of the above TL curve and the photoluminescence spectra results, it is therefore concluded that after irradiation by short UV light, the electrons in the valence band are excited to the conduction band and free electrons and holes are formed in the sample matrix. The excited electrons returned to the e-traps by nonradiation way, and stored in the e-traps which was created in the high temperature during synthesis process. Because the e-traps in a metastable state at room temperature, the excited electrons stored in it can be thermally released and turned back to the valence band edge. After stopping the excited source, a majority of excited electrons stored in the e-traps would be transferred to the $^4F_{9/2}$ state of $Dy^{3+}$ ions and create the characteristic emissions of $Dy^{3+}$ ions. When the decay ratio of the energy transfer from the e-traps to the $^4F_{9/2}$ state of $Dy^{3+}$ ion is proper, the white-light-emitting long-lasting phosphorescence of $Dy^{3+}$ can be obtained. Further studies will be needed in order to understand the mechanism.

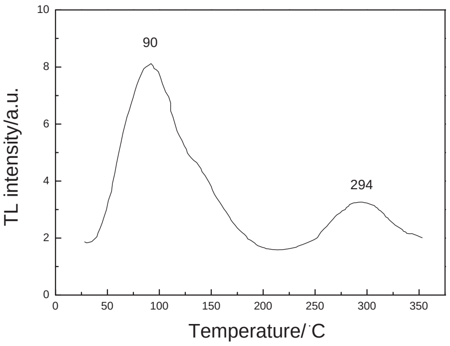

**Figure 3.** TL spectrum of 3% $Dy^{3+}$-doped $Sr_2SiO_4$.

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