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Color variation of photo-stimulated luminescence in strontium ortho-silicate with the assistance of trap centers

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ABSTRACT

A large enhancement of photo-stimulated luminescence by co-doping $\text{Tm}^{3+}/\text{Dy}^{3+}$ in α' - Sr_2SiO_4 was observed, upon the infrared (IR) stimulation at 980 nm after pre-exposure with Ultraviolet (UV) light. More interestingly, the color of PSL changes from green to yellow with substituting Dy^{3+} with Tm^{3+} . The results indicate that co-doping of Tm^{3+} generates a large number of traps peaking at 400 K, which able to immobilized the carriers permanently at room temperature and is more sensitive to IR light than other traps. It induced the redistribution of trap centers, especially around the emission center Eu_2 which located at another inequivalent site.

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1. Introduction

As one kind of electron trapping type materials, photo-stimulated luminescence (PSL) material has been attracting great interest due to the applications such as infrared sensors, dosimeters, and near infrared to visible converters [1]. PSL is a good alternative to thermaluminescence (TL) in radiation dosimetry due to several advantages. One of such advantages is the fact that stimulation method is completely optical, which makes it unnecessary to use a heating system for stimulating irradiated samples. Moreover, high sensitivity of PSL allows multiple readings because it is not necessary to stimulate all of the trapped charges and the readout process can be made very fast by increasing the stimulating light intensity [2].

Up to now, the commercial PSL phosphors with the strongest read-out intensity and largest storage capacity have been alkaline sulfide, such as SrS:Eu,Sm [3], CaS:Eu,Sm , which is chemically unstable [4]. Beyond that, many efforts have been made to search other PSL materials with different read-out emission color for overcoming the drawback of sulfides, e.g. BaFBr:Eu^{2+} [5], $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} [6], $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$, Tm^{3+} [1], and $\text{Sr}_2\text{SnO}_4:\text{Sm}^{3+}$ [7]. Unfortunately, their PSL intensity and storage capacity must be enhanced substantially to meet applications.

The Eu^{2+} activated strontium ortho-silicates (α' - Sr_2SiO_4) were first reported by Barry and Blasse et al. were intensively studied as phosphors for color-tunable white light emitting diodes (LEDs) [8,9]. Strontium ortho-silicate exists in two crystallographic modification, viz. α' - Sr_2SiO_4 (orthorhombic) and β - Sr_2SiO_4 (monoclinic). The transition between the β -phase and the high temperature

α' -phase occurs at 358 K involves the rearrangement of SiO_4 tetrahedra without disconnection of bonds. The α' - Sr_2SiO_4 phase can be stabilized at room temperature by partial replacement of strontium ions by barium ions. α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor had been studied with a view to make it an long persistent luminescence (LPL) phosphor by co-doping with Dy^{3+} ions [10]. However, α' - Sr_2SiO_4 hosted luminescence materials are rarely considered for PSL technology.

In this letter, a large enhancement of photo-stimulated luminescence by co-doping $\text{Dy}^{3+}/\text{Tm}^{3+}$ in α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ compared to the Dy^{3+} co-doped phosphor, was observed upon IR stimulation at 980 nm after pre-exposure in UV light. Moreover, we demonstrate a new strategy by controlling the distribution of trap centers to realize PSL color variation of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor.

2. Experimental

α' - $\text{Sr}_{2-x-y}\text{SiO}_4:\text{xEu}^{2+}, \text{yR}^{3+}$ ($\text{R}=\text{Dy, Tm}, \text{x}=0.004, \text{y}=0, 0.004$) phosphors were synthesized by a solid-state reaction method. Stoichiometric amounts of the starting materials were ground with acetone in an agate mortar to obtain a homogeneous mixture. As starting materials SrCO_3 (Aldrich, 99.9%), SiO_2 (Aldrich, 99.9%), Eu_2O_3 (Aldrich, 99.99%), Tm_2O_3 (Aldrich, 99.99%) and Dy_2O_3 (Aldrich, 99.99%) were used. The mixed powders were sintered at 1200 °C for 4 h under a flowing 95% N_2 –5% H_2 atmosphere in a tube furnace.

The phases of the samples were identified by X-ray powder diffraction (XRD) with Ni-filtered $\text{CuK}\alpha$ radiation. The spectra properties (emission, excitation and PSL spectra) of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{R}^{3+}$ were recorded on a F-7000 spectrometer. A 980 nm laser diode (500 mW) was used as a stimulating source. Persistent luminescence decay curve measurements were measured with a

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PR305 long afterglow instrument. The TL curves were measured with a FJ-427A TL meter (Beijing Nuclear Instrument Factory). Prior to the measurements, powder samples were first exposed to radiation by UV light (365 nm) for about 20 min, then heated from room temperature to 400 °C with a rate of 1 K/s.

3. Results and discussion

The phase purities of α' - $\text{Sr}_{2-x-y}\text{SiO}_4:\text{xEu}^{2+}, \text{yR}^{3+}$ ($x=0.0025$, $y=0, 0.0025$) were confirmed using X-ray powder diffraction (XRD). Fig. 1 presents the XRD pattern of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Tm}^{3+}$ as a representative sample. The results indicate that the structure of α' - Sr_2SiO_4 host lattice was unchanged upon the doping of Eu^{2+} ions or the co-doping of $\text{Dy}^{3+}/\text{Tm}^{3+}$. XRD patterns indicate that all compounds exhibit the same crystalline orthorhombic crystal system with a space group $Pnma$, as shown in Fig. 1(inset). In the crystal lattice, there are three crystallographically independent cation sites, namely, two Sr^{2+} sites, and one Si^{4+} site. Sr^{2+} ions occupy two kinds of polyhedral sites with nine and 10 coordinated oxygen atoms, respectively. Si atoms both occupy tetrahedral sites with four coordinated oxygen atoms. We can infer that Eu^{2+} ($R_9=0.130$ nm, $R_{10}=0.135$ nm) have a pronounced tendency to occupy Sr^{2+} ($R_9=0.131$ nm, $R_{10}=0.136$ nm) sites owing to the similar ionic radii between them. Comparing with ionic radius of Sr^{2+} , the ionic radii Si^{4+} (0.040 nm) is too small to be substituted by Eu^{2+} [11].

Fig. 2 shows the excitation and emission spectra of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$. Under 338 nm excitation, Eu^{2+} doped strontium silicate shows strong photoluminescence due to the transition from the lowest crystal field component of $4f^65d^1$ configuration of Eu^{2+} to the $4f^7$ ground state. Since Eu^{2+} ions replace Sr^{2+} ions two different types of luminescent centers (Eu_1 and Eu_2) in α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ can be expected. Based on covalency and crystal field arguments [12], the high energy emission band of Eu^{2+} can be assigned to the 10 coordinated site and the low energy band to the nine coordinated site. The excitation spectra of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ recorded for the two types of emission centers demonstrate different shapes and positions of the maxima. It is further confirmed that two emission bands originate from the f–d transition of different Eu^{2+} centers (Eu_1 and Eu_2) in α' - Sr_2SiO_4 [13].

As shown in Fig. 3(A and B), the emission spectra of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Tm}^{3+}$ do not show any transitions which could be attributed to Dy^{3+} or Tm^{3+} . It is found interestingly that two samples exhibit strong PSL with different colors upon IR stimulation at 980 nm after pre-exposure with UV light. Fig. 3(a and b) show that the corresponding PSL spectra of two samples with different stimulation times, which indicates that the PSL intensity is declining with increasing stimulation time. This result confirms that there do not exist an up-conversion process and it come from the release of the carriers in the traps of both samples under 980 nm stimulation. Comparing to the single doped sample (Fig. 2), a large enhancement of PSL by co-doping with $\text{Dy}^{3+}/\text{Tm}^{3+}$ is obtained, and it implies that the trap structure of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ is changed by co-doping rare earth ions. From the PSL spectra, it is safe to say that PSL also derived from Eu^{2+} ions in the above-mentioned two crystallographic Sr^{2+} sites, which suggests that both crystallographic sites are available for Eu_1 and Eu_2 to take part in both PSL processes. More noteworthy is that, with co-doping of Tm^{3+} (inset of Fig. 3b), the intensity ratio of the two emission bands changes as well as the color of PSL changes from green to yellow. Taking into account the above observations, it is can be speculated that there occurs a very significant change in the trap structure of host lattice because of the co-doping with different rare earth ions.

In order to probe the modifications occurring in the trap structure due to the rare earth ions co-doping, TL glow curves of

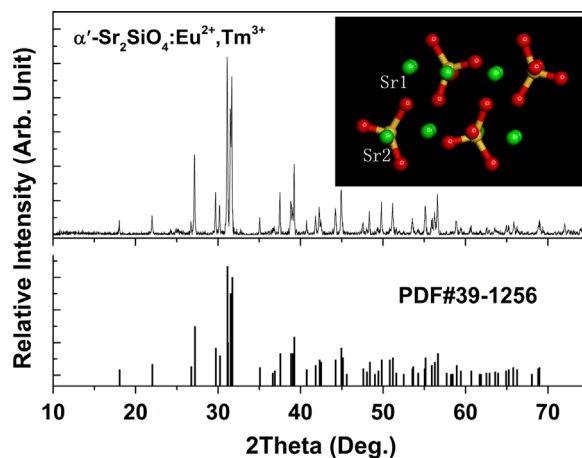


Fig. 1. XRD pattern of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Tm}^{3+}$. Inset: Crystal structure of α' - Sr_2SiO_4 .

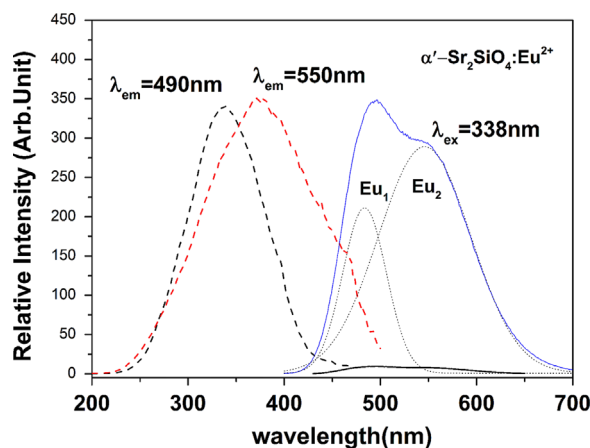


Fig. 2. Emission spectra (solid line) and excitation spectra (dash line) of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$.

the $\text{Dy}^{3+}/\text{Tm}^{3+}$ co-doped phosphors are compared with the Eu^{2+} single doped material. As shown in Fig. 4, the TL glow curve of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ exhibits two main components located at 415 and 500 K, respectively. For the deepest traps corresponding to the high-temperature band (T_3), the carriers trapped there are not assumed to be released by various treatments at room temperature to yield either LPL or PSL. Therefore, T_3 bands are not discussed here. It is obviously seen that both substitutions of Dy^{3+} and Tm^{3+} greatly change the TL properties as well as increase the overall TL intensity of α' - $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$. As we all known, there is a clear correlation between the TL and persistent luminescence intensity which can be established with simple TL measurements [14]. The effect of Dy^{3+} ions, which create new low-temperature T_1 band (306 K) corresponding to the shallow traps, explains in a straightforward manner the efficient persistent luminescence compared to other two samples (inset of Fig. 4).

For a storage phosphor, the traps should be relatively deep to preclude the thermal release of the intercepted carriers at room temperature, which have already found important application as photo-stimulated materials [15]. Utilizing the peak-shape method and the usual general order kinetics expression to fit TL glow curves [16], we successfully obtained the trap depth (E) of T_2 . The trap depth of T_2 is 1.352 eV, which able to immobilized the carriers permanently at room temperature. This kind of trap has a big absorption cross section for NIR light, which is more sensitive to 980 nm (~ 1.26 eV) stimulation. Hence, the 980 nm radiation is able to kick off the carriers from traps T_2 and subsequently exhibit the PSL phenomenon. Consequently, the performance of PSL is correlated to the generation of trap T_2 . Comparing with the T_2

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