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Design, synthesis and characterization of a novel orange-yellow long-lasting phosphor: Li_2SrSiO_4:Eu^{2+}, Dy^{3+}

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ABSTRACT

A novel orange-yellow long-lasting phosphor (LLP) Li_2SrSiO_4:Eu^{2+}, Dy^{3+} was developed. The incorporation of the orbitals of Dy^{3+} in the formation of the discrete level associated with oxygen vacancy ($V_{\ddot{o}}$) causes a change in the number of traps, which largely extends the thermoluminescence characteristics and evidently improves the long persistent luminescence property of the phosphor. Both fluorescence and phosphorescence spectra of Li_2SrSiO_4:Eu^{2+}, Dy^{3+} reveal broad and intensive emission extending from 500 to 700 nm with a peak at about 567 nm, this indicates that photoluminescence(PL) and long-lasting luminescence (LLL) are from the same Eu^{2+} ions center. After the removal of UV light, the afterglow of the sample with the optimum doping concentration can persist over 15 h above the recognizable intensity level (≥ 0.32 mcd/m^2).

1. Introduction

Long-lasting phosphor (LLP), of which long persistent phenomenon can persist for a long time after removal of excitation source, is a kind of energy-storing material, which can be used in many fields, including safety indication [1], radiation detection [2,3], road signs [4], as well as optical storage [5]. Great progress on LLP has been made in the past decades, prolonging the persistence time from seconds to many hours, and providing a fundamental understanding of the long-lasting mechanism.

Currently, divalent europium doped silicate is a kind of the most excellent long-lasting phosphors, due to its chemicophysical stabilization and excellent phosphorescence, such as $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} (blue) [6], $Ca_2ZnSi_2O_7$: Eu^{2+} (green) [7], and $Ca_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} (green) [8]. Unfortunately, the majority of them are mainly restricted to the emission color from blue to green region, in other words, the long-wavelength emission from yellow to red of LLP is lacking. Although many researchers have discovered a few new LLPs with longer wavelength emission such as SrS:Eu^{2+}, Pr^{3+} (orange-red) [9], $Ca_2Si_5N_8$:Eu^{2+}, Tm^{3+} (orange) [10], and $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} (orange-yellow) [11]. To our best knowledge, the chemical property of sulfides is unstable, the physical property of aluminates is weak, and the preparation condition of nitrides is rigorous. Therefore there is an intense desire for exploring new Eu^{2+}-doped silicates with emission color from yellow to red.

Eu^{2+} ion as a well-known activator with an electron configuration of $4f^65d^1$ presents the usual broad emission band, which can be shifted from UV to red region in different host lattices. Fortunately, the PL property of Eu^{2+} doped Li_2SrSiO_4 matrix with long-wavelength emission was reported [12–14]. It motivated us to explore the LLL properties of this phosphor. In this work, the LLL properties of this orange-yellow emissive long-lasting phosphor Li_2SrSiO_4:Eu^{2+}, Dy^{3+} were investigated. The improvement of orange-yellow LLL property was realized by the incorporation of Dy^{3+}. Oxygen vacancy ($V_{\ddot{o}}$) can be significantly enhanced to more efficiently capture and release charge carriers, which is attributed to the stabilization of $V_{\ddot{o}}$ reinforced by doping Dy^{3+} ions. The mechanism for the origin of LLL phenomenon was discussed, as well as the reason for enhancement of LLL phenomenon which was also discussed briefly.

2. Experimental

2.1. Preparation of Li_2SrSiO_4:Eu^{2+} and Li_2SrSiO_4:Eu^{2+}, Dy^{3+} phosphors

A series of silicates phosphors, $Li_2Sr_{0.997-x}SiO_4$:0.003Eu^{2+}, $x$$Dy^{3+}$ ($x = 0, 0.002, 0.003, 0.004, 0.005$), were prepared by solid-state reaction method. The original materials are $SrCO_3$ (A.R.), Li_2CO_3 (99.99%), SiO_2 (99.99%), and Dy_2O_3 (99.99%). The stoichiometric mixture of raw materials was homogeneously mixed and ground, then the crucible with the mixture was placed in the furnace and sintered at 950 °C for

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10 h in a flowing 95% N_2–5% H_2 atmosphere. After annealing, the samples were cooled to room temperature in the furnace, and ground again into powder for measurements.

2.2. Measurement procedure

The phases of samples were identified by X-ray powder diffraction (XRD) with Ni-filtered CuKα radiation (λ = 0.15406 nm) at a scanning step of 0.02° in the 2θ range from 10°–80°. Emission and excitation spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. Afterglow decay curves were measured by a PR305 long persistent luminescence instrument after the sample was irradiated by 254 nm UV light for 20 min. TL curves were measured with an FJ-427A TL meter (Beijing Nuclear Instrument Factory). Prior to the measurements, 0.002 g samples were first pre-irradiated by UV light (254 nm) for about 20 min, then heated from room temperature to 400 °C with a rate of 1 K/s. All measurements were carried at room temperature except the TL glow curves.

3. Results and discussion

3.1. XRD analysis

The phase structure of all prepared samples was systematically checked by X-ray diffraction (XRD). Fig. 1 shows the typical XRD patterns of $Li_2Sr_{0.997\text{-}x}SiO_4$:0.003$Eu^{2+}$, $x$$Dy^{3+}$ (x = 0, 0.002, 0.003, 0.004, 0.005) samples. By comparing with JCPDS Card no. 47-0120, which is also plotted in the bottom of Fig. 1, all the observed peaks can be indexed to the pure phase of Li_2SrSiO_4. No phase transformation or impurity is observed, when the doping concentration of Dy^{3+} ions is equal to or less than 0.5%.

3.2. Photoluminescence properties

Both $Li_2Sr_{0.997}SiO_4$:0.003Eu^{2+} and $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+} show bright and efficient orange-yellow emission under UV excitation. The excitation and the emission spectra of $Li_2Sr_{0.997}SiO_4$:0.003Eu^{2+} and $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+} are shown in Fig. 2. Under the excitation of 397 nm, these phosphors show broad and intensive emission extending from 500 to 700 nm with a peak at 567 nm. This indicates the crystal field strength has a strong splitting effect on the emission of Eu^{2+} [15]. Monitored at 567 nm, the excitation spectra show a broad excitation band from 250 to 550 nm, which are attributed to the transition from the ground state to the $4f^65d^1$ of Eu^{2+} ions. Meanwhile the PL intensity of $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+} is much lower than that of $Li_2Sr_{0.997}SiO_4$:0.003Eu^{2+}, which may be attributed to a portion of carriers captured by a large number of defects generated by the introduction of Dy^{3+} ions into $Li_2Sr_{0.997}SiO_4$:0.003Eu^{2+}, under the excitation of 397 nm.

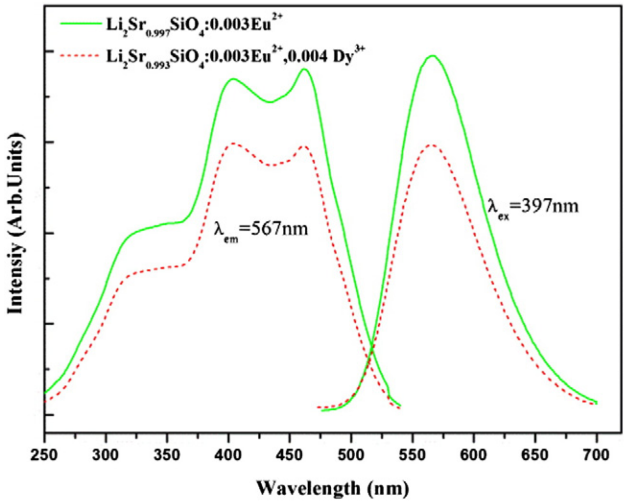

Fig. 2. PL spectra excited at 397 nm and PLE spectra monitored at 567 nm of $Li_2Sr_{0.997}SiO_4$:0.003Eu^{2+} and $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+}.

3.3. Afterglow decay curves of Li_2SrSiO_4:Eu^{2+} and Li_2SrSiO_4:Eu^{2+}, Dy^{3+}

As indicated above, when excited using a UV lamp, both $Li_2Sr_{0.997}SiO_4$:0.003Eu^{2+} and $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+} samples emit orange-yellow light; however after the excitation source was switched off, only Li_2SrSiO_4:Eu^{2+}, Dy^{3+} yielded orange-yellow LLL. In other words, the orange-yellow LLL phenomenon in the series Li_2SrSiO_4:Eu^{2+}, Dy^{3+} samples exposed to 254 nm UV light for 20 min can be observed for several hours with the naked eye in the dark. The LLL decay curves of the $Li_2Sr_{0.997\text{-}y}SiO_4$:0.003$Eu^{2+}$, $y$$Dy^{3+}$ ($0.002 \le y \le 0.005$) are shown in Fig. 3. A series of experiments show that the $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+} sample has the longest duration of afterglow. It can be seen that, after removing the UV lamp excitation, the $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+} sample with higher orange-yellow LLL intensity can last more than 15 h above the recognizable intensity level (0.32 mcd m^{-2}). As seen in inset A of Fig. 3 the photo of the prepared $Li_2Sr_{0.993}SiO_4$:0.003Eu^{2+}, 0.004Dy^{3+} sample was also taken at 1 min after the removal of the 254 nm UV light. In order to make a comparison, the LLL decay curve of $Li_2Sr_{0.997}SiO_4$:0.003Eu^{2+} was also measured and was plotted in Fig. 3. The duration of afterglow is only 2 min, leading to the afterglow decay curve resembling a vertical

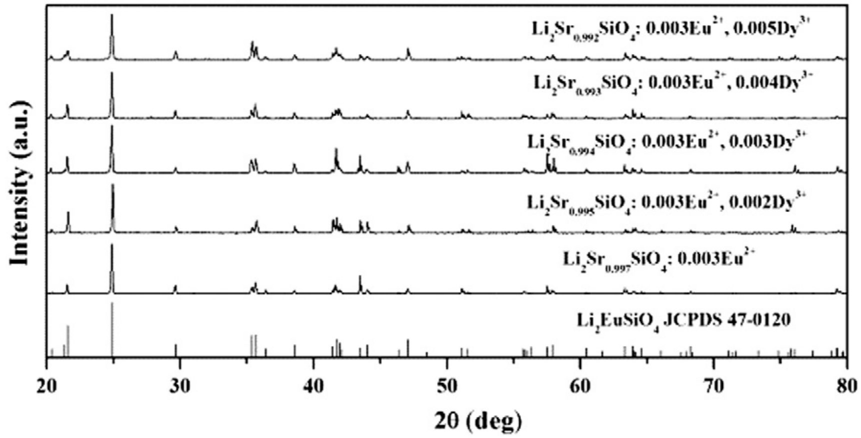

Fig. 1. XRD patterns of $Li_2Sr_{0.997\text{-}x}SiO_4$:0.003$Eu^{2+}$, $x$$Dy^{3+}$ (x = 0, 0.002, 0.003, 0.004, 0.005) and JCPDS Card No.47-0120.