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Solid state reaction synthesis and photoluminescence properties of Dy^{3+} doped $Ca_3Sc_2Si_3O_{12}$ phosphor

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ABSTRACT

The white emission phosphor $Ca_3Sc_2Si_3O_{12}:Dy^{3+}$ was synthesized by the solid-state reaction. Phase analysis and characteristic luminescence properties are investigated by X-ray diffraction and photoluminescence spectra measurement. $Ca_3Sc_2Si_3O_{12}:Dy^{3+}$ phosphor shows strong absorption in 350–410 nm region and exhibits white emission with CIE chromaticity coordinates of (0.3425, 0.3343). Its emission intensity at 250 °C remained 74% of that measured at room temperature. Moreover, the activation energy is also calculated through the Arrhenius equation. The result shows that the thermostability of $Ca_3Sc_2Si_3O_{12}:Dy^{3+}$ is superior than that of commercial phosphor $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$. The outstanding luminescent properties indicate that $Ca_3Sc_2Si_3O_{12}:Dy^{3+}$ could be a potential white light emission phosphor.

1. Introduction

With the rapid development of the materials science and photoelectric technology in the last decades, white light-emitting-diodes (LEDs)-based, solid-state lighting is considered as the next generation of lighting source for its higher efficiency, energy saving, longer lifetime and environmental friendliness [1–3]. Up to now, two methods are used to obtain the white light. One is by using a blue LED chip and a yellow phosphor $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) [2]. However, due to the lack of a sufficient red emission in the visible spectrum, this combination leads to low color-rendering index (CRI) and high correlated color temperature (CCT) [3]. The other is coupling an ultra-violet (UV) LED with primary tricolor phosphors. However, multi-phosphors experience different light output degradation rates and there is a trade-off in luminous efficiency attributed to the reabsorption leading to unstable white light. Therefore, the tri-color white-LEDs still face large challenges [4]. Nowadays, white light emitting phosphors based on a single phase, which is considered as a possible method to enhance the chromatic stability and to avoid the above problems, have attracted much attention for application in white-LEDs [5–7]. As an efficient luminescent center, Dy^{3+} ion has been extensively studied to generate white light in various hosts owing to its two main emission parts: the blue band (470–500 nm) due to the $^4F_{9/2}$–$^6H_{15/2}$ transition and the yellow band (570–600 nm) due to the $^4F_{9/2}$–$^6H_{13/2}$ transition. Consequently, white light can be obtained by creating the appropriate mixture of blue and yellow emissions. Thus, there has been growing interest in developing Dy^{3+}-doped phosphors with high absorption in the UV to blue range, such as $Ca_3Si_2O_7:Dy^{3+}$ [8], $BaY_2ZnO_5:Dy^{3+}$ [9], $NaGd(MoO_4)_2:Dy^{3+}$ [10]. But searching a suitable host lattices for Dy doping with an appropriate mixture of blue and yellow emission is still a challenge. Recently, the green phosphor $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ (CSS:Ce) with the same structure of YAG, has attracted much attention for its excellent optical performance. It has been reported that CSS:Ce shows strong green emission under blue excitation and higher thermal stability beyond YAG:Ce [11]. However, to the best of our knowledge, the luminescence properties of Dy^{3+} ions doped CSS have not been reported. In this paper, the luminescence properties and concentration quenching mechanism of Dy^{3+} in CSS phosphor were discussed in detail.

2. Experimental

Phosphors with compositions of $Ca_{3-x}Sc_2Si_3O_{12}:xDy^{3+}$ ($0.01 \leq x \leq 0.03$) were synthesized *via* a standard solid-state reaction. The raw materials of $CaCO_3$ (A.R.), Sc_2O_3 (A.R.), SiO_2 (A.R.), and Dy_2O_3 (99.99%) were weighed in proper stoichiometric ratio, thoroughly mixed in an agate mortar with ethanol. Then, the mixtures were calcined at 1400 °C for 5 h in a reducing atmosphere (N_2:NH_3 = 4:3) with a heating rate of 5 °C/min. After these procedures, the disk was ground to powder for measurement.

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3. Measurements and characterization

Crystal structure of synthesized samples was identified by X-ray powder diffraction using a Rigaku D/max-2400 X diffraction with Ni-filtered Cu Kα radiation at room temperature. The photoluminescence (PL), photoluminescence excitation (PLE) spectra and the decay curves were measured by a FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source and double excitation monochromators. Thermal quenching was tested using a heating apparatus (TAP-02) in combination with PL equipment.

4. Results and discussion

Fig. 1 shows the XRD patterns of the CSS:xDy^{3+} ($0.01 \le x \le 0.03$) samples. All of the diffraction peaks matched well with the JCPDS file no. 74-1578 except for a small amount of Sc_2O_3. It is common that CSS prepared by the solid-state reaction method is formed accompanied by the by-product of Sc_2O_3 phase, which is mainly due to the low chemical activity of Sc_2O_3 [11].

Fig. 2(a) shows the excitation spectrum of $Ca_{2.975}Sc_2Si_3O_{12}$: 0.025Dy^{3+} phosphor monitored at 574 nm. A broad band (centered at 278 nm) can be observed which is attributed to the Dy–O charge transfer (C–T) transition. Also, there are several sharp excitation peaks between 320 and 470 nm centered at 324, 350, 365, 386, 425 and 450 nm assigned to the $^6H_{15/2} \rightarrow {}^6P_{3/2}$, $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^6H_{15/2} \rightarrow {}^4D_{5/2}$, $^6H_{15/2} \rightarrow {}^4M_{21/2}$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$ and $^6H_{15/2} \rightarrow {}^4J_{15/2}$ transitions, respectively [12]. Clearly, all of the peaks are attributed to the intra-4f forbidden transitions. It is well known that a suitable phosphor for UV-LEDs should have strong absorption from 350 to 410 nm, which is just the emission wavelength of UV-LED chips. Fig. 2(b) presents the emission spectra of the phosphors with various concentrations of Dy^{3+} upon an excitation at 350 nm. The characteristic emissions of Dy^{3+} are observed, including the peaks located at about 484, 574 and 660 nm which belong to the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (magnetic dipole transition), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (electric dipole transition) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$, respectively. What should be noticed is that the two general typical peaks are split in various degrees, which is caused by crystal field effects, whose magnitudes are closely related to the strength and symmetry of the crystal field effect of CSS. As the concentration increases, the intensity of Dy^{3+} emission increases rapidly and reaches a maximum at $x = 0.025$ and then remarkably decreases when Dy^{3+} content further increases due to the concentration quenching effect. The concentration quenching is due to the resonance between activators when the doping concentration reaches a critical value [13].

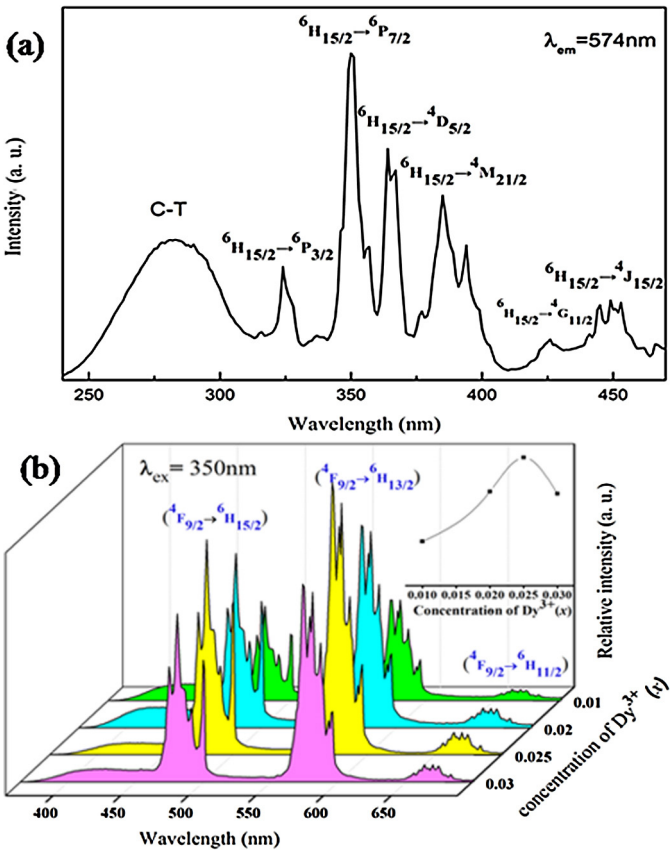

Fig. 2. (a) The PLE spectrum of CSS:0.025Dy^{3+} and (b) the PL spectra of CSS:xDy^{3+} ($0.01 \le x \le 0.03$).

Room temperature lifetimes depended on Dy^{3+} content of the luminescence of the $^4F_{9/2}$ are measured which are excited at 350 nm and monitored at 574 nm, as shown in Fig. 3. The corresponding luminescence decay curves are well fitted by a bi-exponential function [14]

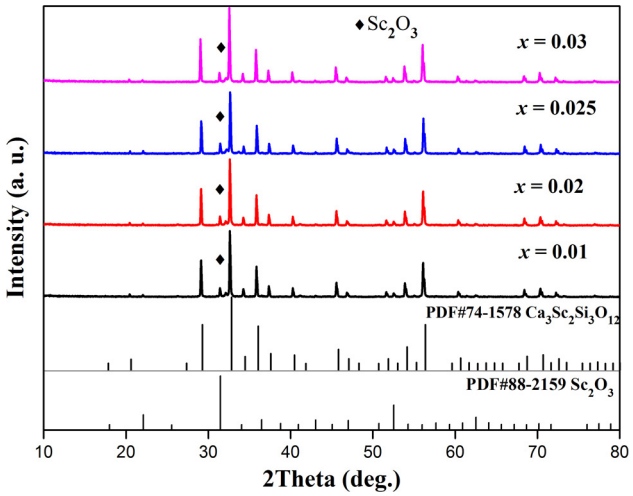

Fig. 1. The XRD patterns of the CSS:xDy^{3+} ($0.01 \le x \le 0.03$) samples.

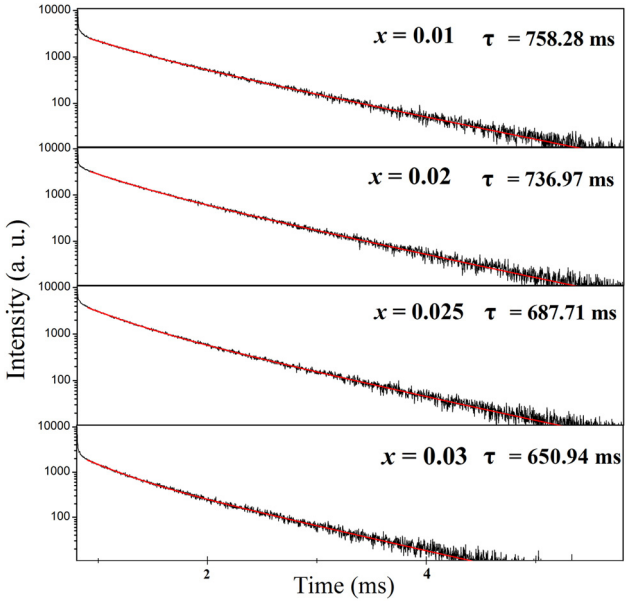

Fig. 3. The decay curves of CSS:xDy^{3+} ($0.01 \le x \le 0.03$).