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Color-tunable luminescence properties and energy transfer of Tb^{3+}/Sm^{3+} co-doped $Ca_9La(PO_4)_5(SiO_4)F_2$ phosphors

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HIGHLIGHTS

- The ET mechanism has been confirmed by the luminescence spectra and fluorescence decay curves.
- The ET interaction mechanism was determined to be dipole–quadrupole interaction.
- The emission color of as-prepared phosphor could be adjusted from green to yellow.

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ABSTRACT

The $Ca_9La(PO_4)_5(SiO_4)F_2:Tb^{3+},Sm^{3+}$ phosphor with apatite structure has been successfully synthesized by high temperature solid-state reaction, and its luminescence properties as well as energy transfer mechanism has been investigated in detail. The energy transfer (ET) efficiency increases with increasing Sm^{3+} doping content, that was confirmed by the luminescence spectra and fluorescence decay curves of corresponding ions. The ET interaction mechanism was determined to be dipole–quadrupole interaction. The emission color of $Ca_9La(PO_4)_5(SiO_4)F_2:Tb^{3+},Sm^{3+}$ phosphor could be adjusted from green (0.272, 0.489) to yellow (0.363, 0.395) area through controlling the dopant ratio of Tb^{3+}/Sm^{3+}. The above results indicate that the $Ca_9La(PO_4)_5(SiO_4)F_2:Tb^{3+},Sm^{3+}$ phosphor has a great potential in white light-emitting diodes application.

1. Introduction

In the past few decades, white light-emitting diodes (*w*-LED) have superseded conventional incandescent or fluorescent lamps, and become the next generation light source due to the high luminous efficiency, longer operational lifetime, low power consumption, thermal resistance, environment-friendly and wide application prospects [1–9]. Generally, the commercial phosphor converted w-LEDs can be formed by combining a blue GaN chip with a yellow-emitting phosphor or coupling near-ultraviolet (n-UV) InGaN-based chips with the RGB tricolor phosphors. Although both methods of white light realization are efficient, this kind of w-LED severely limits the white quality due to the lack of sufficient red emission, as a result the red-emitting phosphors are necessary to improve the performance of the white light blends in terms of correlated color temperature (CCT) and color-rendering index (CRI) [10–13]. Therefore, it is necessary to explore alternative red or tunable phosphors which have excellent chemical stability and suitable excitation wavelength in the *n*-UV range.

Apatite-type phosphors have attracted considerable attention as luminescence materials host due to the efficient luminescence, excellent chemical and thermal stabilities [14]. As the member of apatite structure compound, $A_{10}[PO_4]_6Z_2$, which is isostructural with nature fluorapatite, wherein A represents divalent cations such as Ca^{2+}, Ba^{2+}, Mg^{2+}, Mn^{2+}, Sr^{2+}, can be considered. For this compound, the alkali metal ions like Na^+, K^+, and Ag^+ or rare earth ions can occupy the A-site and then form a coupling isomorphic replacement. Z is mainly occupied by the F^-, Cl^- or OH^- ions [15,16]. In the light of the capability of being substituted by versatile ions and forming solid solutions of apatite structure, it is significant and valuable to study on the apatite structure compounds. As it is known, Tb^{3+} ions always emit bright green light and Sm^{3+} ions emit mainly in red region, which have been widely investigated to apply for near-ultraviolet (*n*-UV) LEDs [17–19]. By changing the Tb^{3+} and Sm^{3+} ratio in the co-doped material, one can adjust the luminescent color. In addition, Tb^{3+} could be acted as a good

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sensitizer to enhance the luminescence efficiency of Sm^{3+} ions. Recently Y.Il Jeon et al. studied $Ca_2La_8(GeO_4)_6O_2:Tb^{3+}/Sm^{3+}$ nanocrystalline phosphor, as the Sm^{3+} ion concentration increases, the Commission International de I'Eclairage chromaticity coordinates shift towards warm white-light region due to the energy transfer from Tb^{3+} to Sm^{3+} ions [20]. W. Xie et al. investigated $CaLa_2(MoO_4)_4:Tb^{3+}/Sm^{3+}$ phosphor, and tunable phosphors from blue to warm-white-light were obtained owing to energy transfer from Tb^{3+} to Sm^{3+} [21].

As far as we know, the luminous performance and energy transfer mechanism of Tb^{3+} and Sm^{3+} co-doped $Ca_9La(PO_4)_5(SiO_4)F_2$ (CLPSF) phosphors have not been reported. Hereafter, we evaluate the apatite-type phosphor $Ca_9La(PO_4)_5(SiO_4)F_2:Tb^{3+},Sm^{3+}$ with color tunable luminescence properties. The mechanism of energy transfer from Tb^{3+} to Sm^{3+} in the phosphors was systematically investigated by photoluminescence excitation (PLE), emission (PL) spectra and lifetime measurement. These results indicate that $Ca_9La(PO_4)_5(SiO_4)F_2:Tb^{3+},Sm^{3+}$ phosphor can act as a potential tunable phosphor in the *w*-LEDs application.

2. Experimental procedures

A series of $Ca_9La_{1-x-y}(PO_4)_5(SiO_4)F_2:xTb^{3+}$, ySm^{3+} phosphors were prepared by a solid-state synthesis technique. The constituent raw materials were chosen as $CaCO_3$ (A.R.), La_2O_3 (A.R.), $(NH_4)_2HPO_4$ (A.R.), SiO_2 (A.R.), NH_4HF_2(A.R.), Sm_2O_3 (99.99%) and Tb_4O_7 (99.99%), these raw materials were produced in Beijing Chemical Plant. After mixing and thoroughly grinding, the stoichiometric mixture was placed into an alumina crucible and annealed at 1380 °C in the air atmosphere for 4 h. (The excess of 50% mol of NH_4HF_2 is necessary to compensate the loss of F source at high temperature.) Then, the samples were furnace-cooled to room temperature naturally. Finally, the products were ground again into powder samples for measurement.

The X-ray diffraction (XRD) patterns were recorded using an X-ray powder diffractometer (D8, Advance, Bruker, Germany) with Cu-Kα radiation (λ = 0.15406 nm) operated at 40 kV and 30 mA. Epy room temperature excitation and emission spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer PL system equipped with a xenon lamp (400 V, 150 W) as excitation source. A 400 nm cutoff filter was used in the measurement to eliminate the second-order emission of source radiation. The lifetimes were recorded on a spectrofluorometer (FS5, Edinburgh, England), and the temperature luminescence decay curves were obtained from a spectrofluorometer (Horiba, JobinYvon TBXPS) using a tunable pulse laser radiation as the excitation. All the measurements were carried out at room temperature.

3. Results and discussion

The phase purity of as-prepared samples was checked by analysis of the XRD patterns as shown in Fig. 1. It can be seen that all of the diffraction peaks are matched well with the JCPDS card No. 15-876 regardless of the dopant content [22]. This indicates that the Tb^{3+} and Sm^{3+} ions incorporated in the host structure does not cause any significant change in the crystal structure of the host matrix. In this structure, the Ca^{2+}/La^{3+} ions have two different coordination numbers (CN). Ca/La(1) site is nine-fold coordinated and Ca/La(2) cite is seven-fold coordinated. Based on the effective ionic radii and charge balance of cations with different CN, the activators Tb^{3+}/Sm^{3+} ions are expected to occupy the Ca/La sites randomly in the host, because the effective ionic radii of Tb^{3+}/Sm^{3+} is closest to that of La^{3+} ions.

Fig. 2(a) shows the PLE and PL spectra of $Ca_9La_{0.8}(PO_4)_5(SiO_4)F_2$:0.20 Tb^{3+} phosphor. The excitation spectrum was monitored at an emission wavelength of 545 nm related to the $^5D_4$–$^7F_5$ transition of Tb^{3+} ions. In addition, several weak sharp lines were observed to appear at 319, 348, 358 and 377 nm, which could be assigned to transitions from the $^7F_6$ ground state to the excited states of Tb^{3+} $^5D_{1,0}$, ^5G_J, and $^5L_{10}$ levels. Furthermore, the PL spectrum recorded under the excitation of 377 nm gives the typical characteristic optical transitions $^5D_4$–^7F_J (J = 6, 5, 4, and 3) of Tb^{3+} ions at 484, 545, 583 and 621 nm. The $^5D_3$–^7F_J (J = 5, 6) emission of Tb^{3+} at 421 and 435 nm are also observed in $Ca_9La_{0.8}(PO_4)_5(SiO_4)F_2$:0.20 Tb^{3+} due to the lower vibration frequency of phonon in this matrix [23–26]. The PLE and PL spectra of $Ca_9La_{0.8}(PO_4)_5(SiO_4)F_2$:0.20$Sm^{3+}$ are shown in Fig. 2(b). The left curve on the left is the PLE spectrum which was monitored at the emission wavelength of 600 nm for the $^4G_{5/2}$ to $^6H_{7/2}$ transition of Sm^{3+} ions, and some observable features can be assigned to the transition from the $^6H_{5/2}$ ground state to the $^4I_{11/2}$ (471 nm), $^4G_{9/2}$ (439 nm), $^6P_{5/2}$ (417 nm), $^6G_{11/2}$ (402 nm), $^6P_{7/2}$ (374 nm), $^4D_{5/2}$ (361 nm), and (4 K, 4L)$_{17/2}$ (345 nm) [27–29]. The presence of intense absorption band from 300 to 500 nm displays that $Ca_9La(PO_4)_5(SiO_4)F_2:Sm^{3+}$ phosphor can be used as a potential phosphor for UV/NUV LED lighting. Under the excitation of 407 nm, the characteristic emission consists of three bands corresponding to the transitions from the $^4G_{5/2}$ excited state to the $^6H_{5/2}$ (564 nm), $^6H_{7/2}$ (600 nm), and $^6H_{9/2}$ (647 nm). As shown in Fig. 2(a) and (b), a significant spectral overlap is observed between the emission band of Tb^{3+} and the absorptions of Sm^{3+}, that indicates the possible energy transfer from Tb^{3+} to Sm^{3+} in $Ca_9La(PO_4)_5(SiO_4)F_2$ host.

In order to obtain the color-tunable emission and further investigate

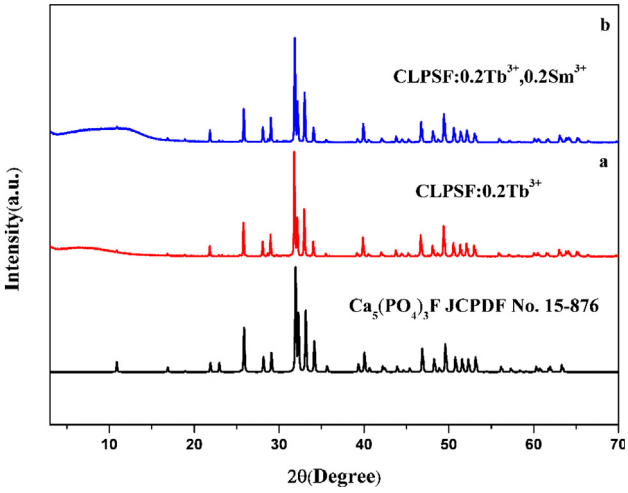

Fig. 1. XRD patterns of CLPSF:0.2 Tb^{3+} (a), CLPSF:0.2 Tb^{3+}, 0.2Sm^{3+} (b), and the standard data for $Ca_5(PO_4)_3F$ (JCPDS card No. 15-876) is shown as a reference.

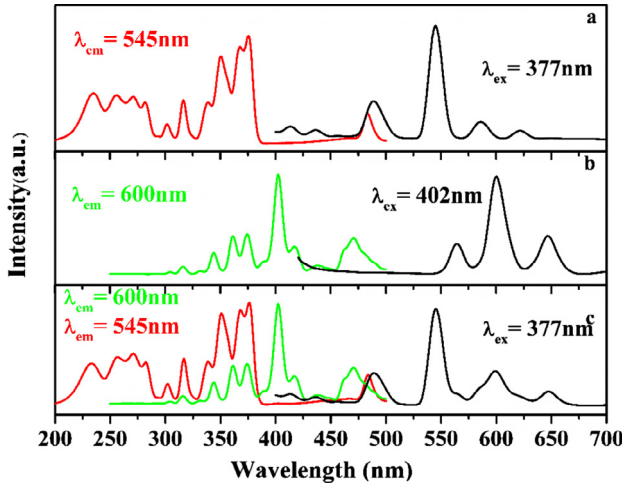

Fig. 2. PLE (left) and PL (right) spectra for CLPSF:0.2 Tb^{3+} (a), CLPSF:0.2Sm^{3+} (b), and CLPSF:0.2 Tb^{3+}, 0.2Sm^{3+} (c) samples. The corresponding monitoring wavelengths are also shown in the figure.