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Luminescent properties of novel reddish-orange phosphor $LaInO_3$:Sm^{3+} for white light emitting diodes

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A novel reddish-orange luminescent material $LaInO_3$ doped with Sm^{3+} was synthesized by solid-state reaction. The crystal structure and photoluminescence properties were respectively discussed. The XRD pattern indicates that little amount of doped Sm^{3+} ions has nearly no effect on the host structure. The spectra reveal that the phosphor can be effectively excited under the excitation of near-UV or blue light to emit high intensity reddish-orange light at 600nm deriving from $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition of Sm^{3+}. The photoluminescence intensity is related to the concentration of Sm^{3+}, and the optimal Sm^{3+}-doped concentration is 4mol%. Due to its good luminescence performance, the phosphor $LaInO_3$:Sm^{3+} may be a potential candidate for white light emitting diodes.

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Keywords: Solid-state reaction, Phosphor, $LaInO_3$, LEDs

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1. Introduction

White light emitting diodes (LEDs) are considered a potential light source in the 21st century because of their advantages of high efficiency, low power consumption, long lifetime, and good reliability [1-3]. Presently the most commercial white LEDs are generated by blue InGaN chips in combination with YAG:Ce^{3+} phosphors [4]. But owing to the lack of red component in the white light, there are disadvantages to obtain white light through this method such as poor color rendering index and high color temperature [5]. One of the most approaches getting high-quality white light is to add red phosphors to the yellow phosphors [6]. Therefore the red phosphors play an important role in making white LEDs. The commercial red phosphors are based on sulfides. However, these phosphors have defects including chemical instability and low efficiency [7-8]. So it is necessary to exploit novel red phosphors to meet with the development of white LEDs. Rare indates are promising hosts due to their good stability and simple synthesis process. Meanwhile Sm^{3+} ions show main absorption under the excitation of near-UV light to emit red light in many hosts [9-10]. In this work, the reddish-orange phosphor powders of $LaInO_3$ doped with Sm^{3+} ions were synthesized by a solid-state reaction method and their luminescence properties were also investigated.

2. Experimental

A series of $La_{1-x}InO_3$:xSm^{3+} (x=0.01, 0.02, 0.03, 0.04, 0.05) samples were prepared by the conventional solid-state reaction. La_2O_3(A.R.), In_2O_3(99.99%) and Sm_2O_3(99.99%) were used as reagents for sample synthesis. All the raw materials with the stoichiometric proportion were weighed. When the powders were ground finely and mixed thoroughly in an agate mortar, the mixture was put into ceramic crucibles and preheated at 600℃ in air for 3h. Then it was annealed in atmosphere at 1300℃ for 6h and cooled naturally to room temperature. After that, the sintered sample was grounded and the $La_{1-x}InO_3$:xSm^{3+} phosphor was obtained.

The structure of the samples was examined by X-ray diffraction (XRD) using a D/MAX-2500PC X-ray diffractometer with Cu Kα radiation at 40 kV and 150 mA. The photoluminescence (PL) excitation and emission spectra were recorded with an RF-5301 molecular fluorescence spectrometer (excitation and emission slit width at 3nm). All these measurements were done at room temperature.

3. Results and discussion

3.1 Phase characterization

Fig. 1 shows the XRD pattern of $LaInO_3$:Sm^{3+} phosphor with 5 mol% Sm^{3+}. It can be seen that most peaks are indexed to the $LaInO_3$ phase, which agrees well with the reference (JCPDS card No. 09-0034). According to the JCPDS card, $LaInO_3$ has an orthorhombic crystal structure with the lattice parameters of a=1.140nm, b=0.8198nm and c=1.180 nm. The pattern demonstrated that there was no detectable phase change within the whole experimental range of Sm^{3+} concentration. This result indicates that Sm^{3+} has little influence on the matrix structure of $LaInO_3$ and doped Sm^{3+} ions do not form a new phase. For the same valence and comparable ionic radii of Sm^{3+}(0.108nm) and La^{3+}(0.118nm), it is believed that Sm^{3+} ions prefer to occupy La^{3+} ions sites in this reaction.

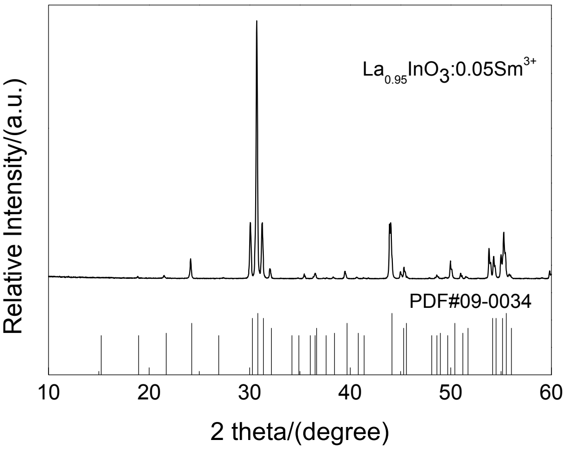

Fig. 1. XRD pattern of the sample $LaInO_3:Sm^{3+}$.

3.2 Excitation and emission spectra of $LaInO_3:Sm^{3+}$ phosphor

Excitation spectrum (λ_{em}=601nm) of $LaInO_3:0.05Sm^{3+}$ is shown in Fig. 2. It consists of one broad excitation band beyond about 358nm and some narrow bands below about 358nm. The former is attributed to the energy absorption of matrix and the charge transfer transition between O^{2-} and Sm^{3+} [11]. Due to the $[Xe]4f^5$ structure of the Sm^{3+} electron shell, the latter are absorption peaks originating from f-f transition of Sm^{3+}. Those excitation peaks are located at 362nm, 375nm, 405nm, 419nm, 479nm which respectively matches with the Sm^{3+} transition absorption of $^6H_{5/2}\rightarrow{}^4D_{15/2}$, $^6H_{5/2}\rightarrow{}^4L_{17/2}$, $^6H_{5/2}\rightarrow{}^4K_{11/2}$, $^6H_{5/2}\rightarrow{}^4M_{19/2}$, $^6H_{5/2}\rightarrow{}^4I_{13/2}$ [12]. Among all the peaks, the strongest absorption is at 405nm, and it indicates that this phosphor can be effectively excited by near-ultraviolet (UV) light emitting diodes. Moreover, the absorption peaks from about 460nm to 479nm are very strong, which shows that this kind of phosphor can be also well excited by blue light. Consequently, intense peaks at 405nm and 460nm to 479nm are better suited to the widely applied near-UV or blue LEDs.

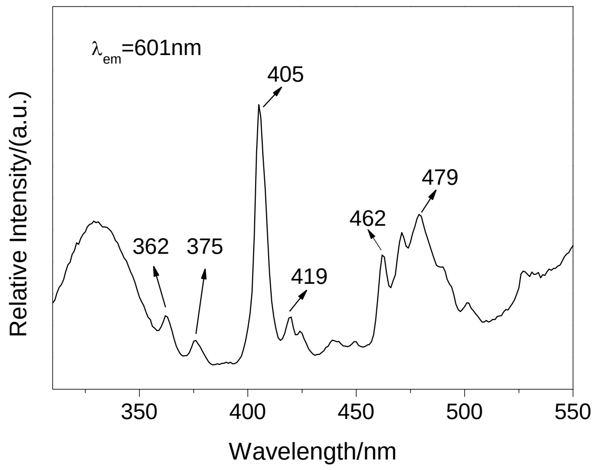

Fig. 2. The spectrum of the sample $LaInO_3:0.05Sm^{3+}$ (λ_{em}=601nm).

Fig. 3 presents the emission spectrum of $LaInO_3:0.05Sm^{3+}$ (λ_{ex}=405nm). As can be seen from this figure, the spectrum exhibits three major fluorescence emission peaks located at 562nm, 600nm and 647nm which stems from the $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ typical transitions of Sm^{3+}, respectively [13,14]. The strongest peak appears at 600nm, and it shows the sample can emit intense reddish-orange light under the excitation of near-UV light at 405nm.

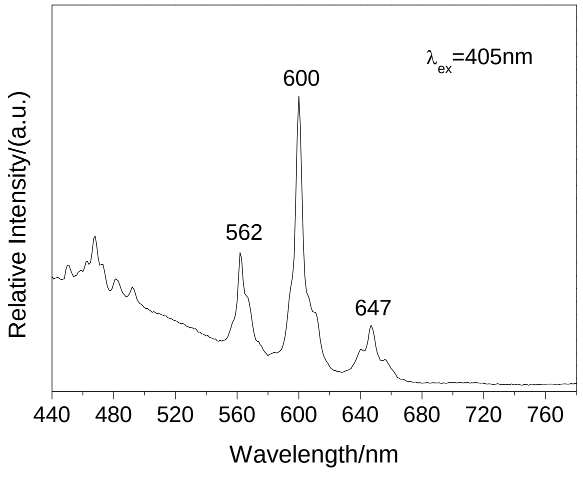

Fig. 3. The emission of the sample $LaInO_3:0.05Sm^{3+}$ (λ_{ex}=405nm).

3.3 The emission intensity of samples with respect to doped Sm^{3+} concentration

The effect of doped Sm^{3+} concentration on the emission spectra was also investigated. A series of samples with various concentrations of Sm^{3+} were synthesized. Fig. 4 gives the emission spectra of phosphors $La_{1-x}InO_3:xSm^{3+}$ (x=0.01, 0.02, 0.03, 0.04, 0.05) excited by the blue light at

462nm. For every phosphor, the strongest emission peak is at 600nm. The luminescent intensity varies with the increase of the Sm^{3+} content while the peak of emission position does not change. From the experimental result, the luminescence intensity of the phosphor reaches the maximum when the concentration of Sm^{3+} is 4mol%. The intensity will drop when the concentration of Sm^{3+} is below this concentration because of a few activator ions to shine. On the contrary, the luminescence intensity also reduces in excess of the optimum concentration of Sm^{3+} owing to concentration quenching.

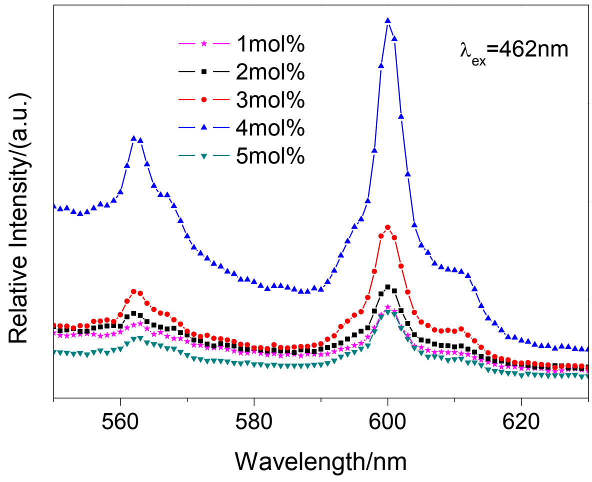

Fig. 4. The dependence of luminescence properties on Sm^{3+} concentration excited at 462nm.

The cause of concentration quenching for the phosphor $LaInO_3:Sm^{3+}$ is based on the following analyses. Firstly, the distance between Sm^{3+} ions will get shorter and the interaction of Sm^{3+} ions will increase, so that luminescence intensity drops with the increasing of Sm^{3+} concentration originating from the energy transfers and the enhancement of non-radiative relaxation among the neighboring Sm^{3+} ions. Secondly, related transfers of the Sm^{3+} energy levels chiefly happen from $^4G_{5/2}$ to ^6H_J from the luminescence principle. Therefore the quenching process is concerned with the cross-relaxation action through matched energy levels ($^4G_{5/2}+^6H_{5/2}\rightarrow^6F_{9/2}+^6F_{9/2}$) between neighboring Sm^{3+} centers [15]. This process of cross-relaxation levels of Sm^{3+} self-quenching is illustrated in Fig. 5. Because the energy between ΔE_1 ($^4G_{5/2}\rightarrow^6F_{9/2}$) and ΔE_2 ($^4H_{5/2}\rightarrow^6F_{9/2}$) is very close and matching, the energy level $^4G_{5/2}$ of Sm^{3+} ions can arrive at the $^6F_{9/2}$ level via a cross-relaxation process when it is excited. Thus many useful excited ions are consumed during this energy transfer, which leads to the appearing of concentration quenching and the reducing of photoluminescence intensity. In term of above investigation, the ideal activator concentration of Sm^{3+} is 4mol%.

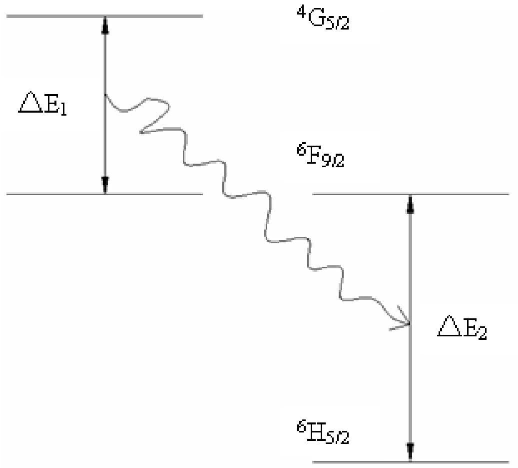

Fig. 5. Schematic diagram for the process of cross-relaxation levels of Sm^{3+} self-quenching.

4. Conclusions

Sm^{3+}-doped $LaInO_3$ phosphor was fabricated by conventional high temperature solid-state reaction technique at 1300℃. The photoluminescence spectra indicate that as-synthesized phosphor can be effectively excited by near-UV or blue LED chips to emit intense reddish-orange light located at 600nm. The optimal content of the Sm^{3+} concentration is 4mol% while too few or many Sm^{3+} ions will cause the decrease of luminescence intensity. Consequently, it is suggested that the novel reddish-orange phosphor $LaInO_3:Sm^{3+}$ may find application on fabrication for near-UV or blue chip-based white LEDs.

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