

Preparation and photoluminescence properties of praseodymium-activated LaInO_3 used as a red-emitting phosphor

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Rare-earth Pr^{3+} doped LaInO_3 red-emitting phosphors were synthesized by a conventional high temperature solid-state method at atmosphere. X-ray diffraction (XRD) and molecular fluorescence spectrometer were made use of to characterize the crystal structure and photoluminescence properties of the phosphors, respectively. The XRD analysis indicates that the phosphor presents pure crystalline phase. The excitation spectrum illustrates that the phosphor has several sharp peaks at 444nm ($^3\text{H}_4 \rightarrow ^3\text{P}_2$), 468nm ($^3\text{H}_4 \rightarrow ^1\text{I}_6$), 477nm ($^3\text{H}_4 \rightarrow ^3\text{P}_1$) and 488nm ($^3\text{H}_4 \rightarrow ^3\text{P}_0$). At the same time, the emission spectrum shows that there are two strong emission peaks in the as-prepared phosphor located at 611nm ($^1\text{D}_2 \rightarrow ^3\text{H}_4$) and 622nm ($^3\text{P}_0 \rightarrow ^3\text{H}_6$) under the excitation of blue lights. The positions of the emission peaks do not change with different doping concentration of Pr^{3+} but the emission intensity. The intensity firstly increases and finally decreases with the increasing of Pr^{3+} concentration. The optimal doping concentration of Pr^{3+} -doped LaInO_3 is checked to be 0.4mol% and at this concentration, the intensity reaches the maximum value. The results offer a red-emitting phosphor possibly used in the production of white LEDs.

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1. Introduction

White light-emitting diodes (LEDs) which have been paid more attention to are praised as an important lighting source in the 21st century because they are efficient, energy-saving and environmentally friendly [1-5]. A commercial white LED can be realized though the following two methods [6-13]. One is by combining an InGaN chip of blue LED with a yellow phosphor $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and the other is by combining a single near-ultraviolet (UV) LED chip with red-green-blue (RGB) phosphors. Along with the semiconductor development, both of blue and near-UV LEDs can bring an efficient solid-state light, but the efficiency of many RGB phosphors excited by UV or blue light is not high [14-18]. Particularly, red-emitting phosphors used in white LEDs are relatively both rare and inefficient [19-21]. For example, the current red-emitting phosphors are mainly $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. Compared with green phosphor $\text{ZnS}:\text{Cu}^+, \text{Al}^{3+}$ and blue phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, the phosphor $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ has poor absorption and short working time owing to the toxic gas release of sulfide in the near UV region [22-25]. So it is a significant work to exploit high efficient and good stable red phosphors for white LEDs.

It is well known that the photoluminescence (PL) properties of a phosphor are related to the host materials. Of

late, some hosts of red phosphors including silicates, aluminates, tungstates, molybdates and indates are studied [26-32]. These red phosphors doped with rare-earth ions possess some advantages such as improving the color rendering index (CRI) and overcoming the drawback of instability. Among the above hosts, indate is a potential material for white LEDs due to its ideal stability and easy synthesis. When it is doped with rare-earth ions, it exhibits special optical properties. For instance, Tang et al. prepared $\text{LaInO}_3:\text{Eu}^{3+}$ red phosphor and found that it could be excited by near UV or blue light to emit strong red light at 612nm [33]. However, there have been few studies on the PL properties of indates doped with other rare-earth ions. Trivalent praseodymium (Pr^{3+}) has been investigated to show a very good PL property as an activator. Cho et al. has reported that $\text{CaTiO}_3:\text{Pr}^{3+}$ can be observed an intense emission peak at 613nm [34]. Besides, Xiong et al. obtained phosphor $\text{NaGd}(\text{WO}_4)_2:\text{Pr}^{3+}$ used in the blue LED emitting deep red light located at 649nm and presented the transition from deep to pinky red with the increasing of Pr^{3+} concentration [35]. Enlightened by the exploitation described above, Pr^{3+} -activated LaInO_3 is considered as a red-emitting phosphor for white LEDs. Therefore, in the present work, $\text{LaInO}_3:\text{Pr}^{3+}$ phosphor has been prepared and its photoluminescence properties has also been investigated.

2. Experimental

2.1. Synthesis of samples

A batch of red-emitting phosphors $\text{LaInO}_3:\text{Pr}^{3+}$ were prepared by a traditional solid-state reaction method in a high temperature atmosphere. High purity reagents (99.99%) of indium oxide (In_2O_3), lanthanum oxide (La_2O_3) and praseodymium (Pr_6O_{11}) were used as the raw materials for the production of the samples. These materials were weighed by an appropriate stoichiometric ratio and ground finely in agate mortar. Next the homogeneous mixture was put into a corundum crucible. Consequently it was pre-sintered at 600°C for 3h and sintered at 1300°C for 6h in an electric stove. At last this work reaped the samples of $\text{LaInO}_3:\text{Pr}^{3+}$ by means of removing the composition from the cooling stove.

2.2. Characterization of structure and photoluminescence

The structure of the as-prepared samples was characterized by powder X-ray diffraction (XRD) through a Shimadzu diffractometer with the 2θ range of all the data from 10° to 60° using $\text{Cu K}\alpha$ radiation at 40kV and 150mA. The photoluminescence properties were examined with an RF-5301 molecular fluorescence spectrometer under a Xe lamp as the source of excitation. The excitation and emission slit width were located at 3nm during the examination. The above performances were all carried out at room temperature.

3. Results and discussion

3.1. XRD analysis

The XRD profile of $\text{LaInO}_3:0.004\text{Pr}^{3+}$ phosphor is shown in Fig. 1. The pattern is consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) No. 09-0034. These diffraction peaks can be classified as the orthorhombic phase with the lattice parameters $a=1.140\text{nm}$, $b=0.8198\text{nm}$ and $c=1.180\text{nm}$. XRD indicated that there were few impurity peaks detected in the pattern and the Pr^{3+} doped sample in the range of finite concentration did not make the host structure altered. This phenomenon demonstrates that the activator Pr^{3+} had been incorporated with the host LaInO_3 . What's more, the ionic radii of Pr^{3+} (0.113nm) and La^{3+} (0.118nm) are nearly equal and they have the same valence, so it can be concluded that Pr^{3+} ions in the host tend to replace the sites of La^{3+} .

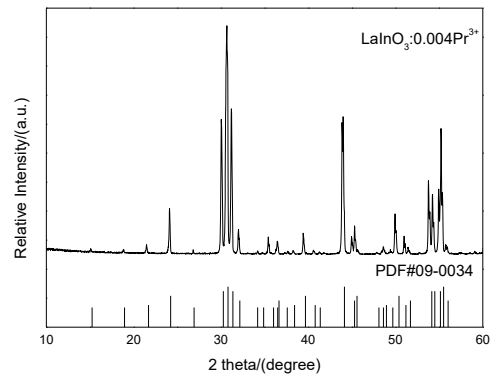


Fig. 1. XRD pattern of the sample $\text{LaInO}_3:0.004\text{Pr}^{3+}$

3.2. Photoluminescence characterization of $\text{LaInO}_3:\text{Pr}^{3+}$

Fig. 2 represents the excitation spectrum of $\text{LaInO}_3:0.004\text{Pr}^{3+}$ monitored at 622nm. It can be seen that there are several peaks in the spectrum located at about 444nm, 468nm, 477nm and 488nm, which are ascribed to the transitions of Pr^{3+} from $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{H}_4 \rightarrow ^1\text{I}_6$, $^3\text{H}_4 \rightarrow ^3\text{P}_1$, $^3\text{H}_4 \rightarrow ^3\text{P}_0$, respectively [36-39]. Additionally, the excitation bands from 440nm to 500nm are plentiful and spectral regions are corresponding to the emission wavelength of blue LED chip, so the obtained phosphors may be used to realize the manufacture of LEDs.

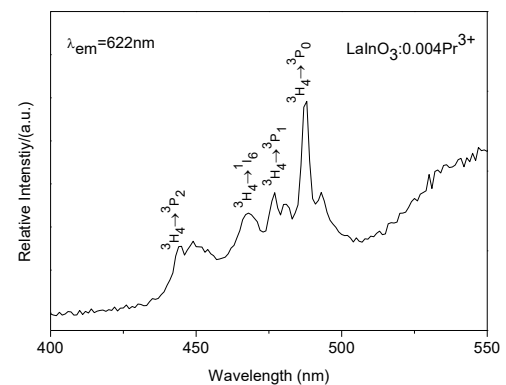


Fig. 2. Excitation spectrum of $\text{LaInO}_3:0.004\text{Pr}^{3+}$

Fig. 3 displays the emission spectrum of $\text{LaInO}_3:0.004\text{Pr}^{3+}$ under the excitation wavelength at 468nm. Two dominant sharp peaks are observed in the spectrum and they are at 611nm and 622nm, respectively corresponding to the Pr^{3+} transitions of $^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{H}_6$ [40-42]. Both of the peaks, the emission intensity of 611nm is stronger than that of 622nm, which illustrates that the phosphor can emit red light when it is excited by the blue light.

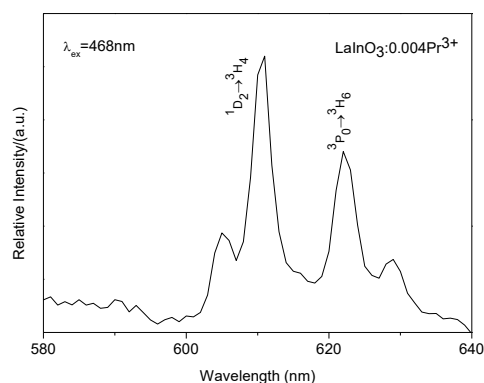


Fig. 3. The emission spectrum of the phosphor $\text{LaInO}_3:0.004\text{Pr}^{3+}$ excited at 468nm

3.3. Effect of Pr^{3+} dopant concentration on the luminescence properties

For the purpose of exploring the optimal doping content of Pr^{3+} , some $\text{LaInO}_3:\text{xPr}^{3+}$ ($\text{x}=0.002, 0.004, 0.006, 0.008, 0.01$) phosphors were prepared. Fig. 4 describes the influence of Pr^{3+} concentration on luminescence properties and the emission intensity dependence of $\text{LaInO}_3:\text{xPr}^{3+}$ on the doping content (x) is plotted out in the inset of Fig. 4. It can be found that the doping concentration of Pr^{3+} does not change the position of emission peaks. Furthermore, the emission intensities of the phosphors increase with the addition of the Pr^{3+} and will drop after the concentration exceeding 0.4mol% because of the effect of concentration quenching. Herein, the optimum concentration of Pr^{3+} in the phosphor $\text{LaInO}_3:\text{xPr}^{3+}$ is 0.4mol%.

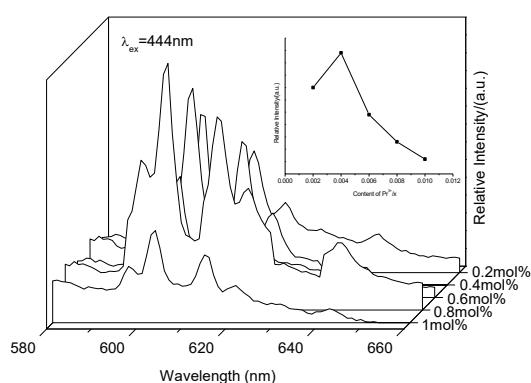


Fig. 4. Influence of Pr^{3+} concentration on luminescence properties (The inset shows the emission intensity at different content of Pr^{3+})

According to the interrelated theories [43-48], the concentration quenching comes out owing to the multipole-multipole interaction of ions in inorganic materials. It can be described this interaction using the relation between the emission intensity and concentration of activator ions. When the energy transfer appears in the activators, the type of the interaction would be speculated by the below equation:

$$\frac{I}{X} = K[1 + \beta(x)\frac{\theta}{3}]^{-1}$$

where I is the emission intensity, x is the concentration of activator, K and β are constants for a certain host under the same excitation state, and the value of θ determines the type of multipolar interactions. The variables of $\theta=6, 8$ and 10 present dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions, respectively. In order to calculate the value of θ , Fig. 5 gives the relation between $\lg(I/x)$ and $\lg(x)$. Here I is the emission intensity at 611nm with the excitation of 444nm light. From the graph, the slope of fitting linear is about -1.7 and θ is nearly 6 , thus the concentration quenching of emission intensity in the studied phosphors belongs to the result of dipole-dipole interactions.

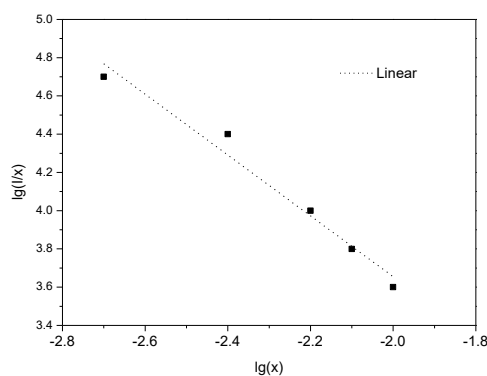


Fig. 5. The curve of $\lg(I/x)$ versus $\lg(x)$ in the phosphors $\text{LaInO}_3:\text{Pr}^{3+}$

4. Conclusions

Red-emitting phosphors $\text{LaInO}_3:\text{Pr}^{3+}$ were prepared via a high temperature solid-state reaction method in atmosphere. The obtained phosphors have no impurity phase with an orthorhombic crystal structure. The excitation spectrum of the phosphor has several sharp bands at 444nm, 468nm, 477nm and 488nm due to the Pr^{3+} transitions. Under the blue light excitation, the phosphors can emit red lights located at 611nm and 622nm as a result

of the Pr^{3+} corresponding transitions of $^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{H}_6$. The doping concentration of Pr^{3+} does not cause the change of peak positions except for the emission intensity. The maximum emission intensity lies at the Pr^{3+} concentration of 0.4mol%. When the doping concentration is over this value, the intensity will decrease owing to the concentration quenching. This quenching is possibly described as the result of dople-dople interactions. Consequently, it is suggested that the phosphor $\text{LaInO}_3:\text{Pr}^{3+}$ may find some application in the fabrication of white LEDs.

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