Emission characteristics of Pr^{3+}-doped $InNbO_4$ used as a red-emitting phosphor for white LEDs

A. TANG[a*], L. GU[b], H. ZHANG[a], Y. ZHAO[a], H. CHEN[a], H. ZHANG[a]

[a]*Department of Mechanical Engineering, Henan Institute of Engineering, Zhengzhou, Henan 451191, China*

[b]*Department of Mechanics, Henan Mechanical and Electrical Vocational College, Zhengzhou, Henan, 451191, China*

A series of red-emitting $InNbO_4:Pr^{3+}$ phosphors were prepared by a solid-state reaction method in air. The crystal structure, size distribution and luminescence properties were also characterized by powder X-ray diffraction (XRD), laser particle size analyzer and molecular fluorescence spectrometer, respectively. The XRD pattern of the phosphor depicted a single phase formation of the phosphor and the crystal structure had no change with the addition of Pr^{3+}. The particle distribution exhibited a narrow size distribution with the average diameter of 2.0μm fitting in with the coating demand of making LED. Study on the excitation spectrum illustrates that the phosphor has the several excitation peaks from 449nm to 470nm in accordance with the excitation of blue LED chip. Analyzing the emission spectrum shows that the phosphor can emit intensive red lights at 606nm and 614nm due to the $^1D_2 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_6$ transitions of Pr^{3+} ions respectively under the blue light at 466nm. The emission intensity can be enhanced by adding the content of Pr^{3+} and attains the maximum with the Pr^{3+}-doped concentration of 0.3mol%. The results indicate that the phosphor $InNbO_4:Pr^{3+}$ would be a promising red-emitting phosphor which is used as a kind of phosphor-converted materials for white LEDs.

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Keywords: Red-Emitting phosphor, Photoluminescence properties, $InNbO_4$, White LEDs; Solid-state reaction

1. Introduction

At present how to save energy and environmental pollution has been of catholic concern. In the realm of solid-state lighting, white light-emitting diodes (LEDs) with low energy consumption and no mercury have recently attracted much interest because of their enormous potentials in the energy conservation and environmental protection[1-5]. Besides, white LEDs have advantages of long lifetime and high reliability[6-8], thus these sources are promising for next-generation lighting technology. Currently white LEDs have been widely used as new generation lighting source in many fields such as display devices, cameras, mobile phones and architecture lightings [9-12]. Nowadays there are two general approaches to produce white LEDs: combining blue LED chip with a yellow phosphor of $YAG:Ce^{3+}$ and mixing Red/Green/Blue (RGB) emissions from RGB phosphors excited by near ultraviolet (NUV) LED chip[13-15]. In the above two methods, the red-emitting phosphors, with a high thermal and chemical stability, which can efficiently absorb lights from NUV TO blue region are needed to make the white light better. Today the commercial red-emitting phosphors are based on sulfides, like $Y_2O_2S:Eu^{3+}$, $CaS:Eu^{3+}$. Unfortunately, these phosphors have some drawbacks, e.g. low luminescent efficiency, poor chemical stability and short working lifetime[16-20]. So searching for excellent red-emitting phosphors to meet with the need of white LEDs development is urgent.

The activators in red-emitting phosphor materials for white LEDs mainly are rare earth ions. Among those ions, many researches have been focused on Eu^{3+} ions doped in silicates, phosphates, tungstates and molybdates, etc[21-25]. Those Eu^{3+}-doped compounds have intense emissions of red light due to the $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+}[26]. However, the absorption lines of Eu^{3+} are very sharp and sometimes cannot satisfy the wavelength demands of LED chip emissions[27], which probably causes prepared phosphors with low red-emitting efficiency. Hence, for the purpose of searching of red-emitting phosphors for white LEDs with high efficiency, some work has been done on Pr^{3+} activator. It is well known that Pr has two valent states of Pr^{3+} and Pr^{5+}. But only Pr^{3+} is used as activator in luminescent materials. The energy levels of Pr^{3+} consist of several metastable mulriple structures which are $^3P_{0,1,2}$, $^1D_2$ and $^1G_4$[28]. These energy levels can make efficient emissions of red, blue and green lights. Which color the Pr^{3+} emits depends on crystal structure of matrix. Jang et al. reported that Pr^{3+}-doped $Y_3Al_5O_{12}:Ce^{3+}$ yellow phosphor can emit red light, which brings about the improvement of color rendering index (CRI)[29]. Dabre et al. synthesized $Sr_2ZnWO_6:Pr^{3+}$ phosphor and found that the phosphor has the typical emission spectra in the region from blue to red light[30]. In the above analysis, some materials doped with Pr^{3+} can be possibly considered as a sort of novel materials for white LEDs.

Considered as a luminescence material, niobate has high stability and no complicated prepared process, which are extensively used in the X-rays[31,32]. For recent years, several attempts have been made to use niobates in the area of ultraviolet luminescent materials[33,34]. With a view to develop the technology of LED, exploiting niobates for white LEDs is a meaningful task. In this paper, Pr^{3+}-doped $InNbO_4$ phosphors were systemically synthesized and their photoluminescence properties were also investigated.

2. Experimental

2.1 Preparation of $InNbO_4:Pr^{3+}$ phosphors

The phosphor $InNbO_4:Pr^{3+}$ was prepared by the general solid-state reaction in air. High-purity indium oxide (In_2O_3, 99.99%), niobium oxide (Nb_2O_5, analytical grade) and praseodymium oxide (Pr_6O_{11}, 99.99%) were used as raw materials. Stoichiometric starting powders were weighed and thoroughly ground in an agate mortar for 25min, then the homogeneous mixture was transferred to a corundum crucible and preheated at 600℃ for 4h in a electric furnace. Next it was calcined at 1255℃ for 6h and cooled with the furnace. Finally the phosphor $InNbO_4:Pr^{3+}$ was gotten.

2.2 Measurements of samples

X-ray diffractions (XRD) of the powders were tested on a Shimadzu diffraction system with the scanning angle from 10℃ to 70℃ under Cu Kα radiation at 40 kV and 150 mA in order to identify the crystal structure of the samples. The particle size distribution was examined on a Rise-2002 laser particle size analyzer with the dispersant of distilled water. Photoluminescence spectra of excitation and emission were taken with an RF-5301 molecular fluorescence spectrometer using a Xe lamp as the source of excitation under the excitation and emission slit width at 3nm. The above measurements were done at room temperature.

3. Results and discussion

3.1 Analysis of XRD and size distribution

The XRD pattern of as-obtained $InNbO_4:Pr^{3+}$ sample was shown in Fig. 1. The diffraction peaks of the sample agree well with the Joint Committee on Powder Diffraction Standards (JCPDS) No. 33-0619 and no other impurity phases could be found. Thus it is illustrated that a single phase of $InNbO_4:Pr^{3+}$ was obtained with no shift of diffraction peaks. According to the PDF#33-0619 card, $InNbO_4$ is monoclinic crystal structure with a space group P2/a(13). The unit cell parameters are a=0.5143nm, b=0.5774nm and c=0.4837nm.

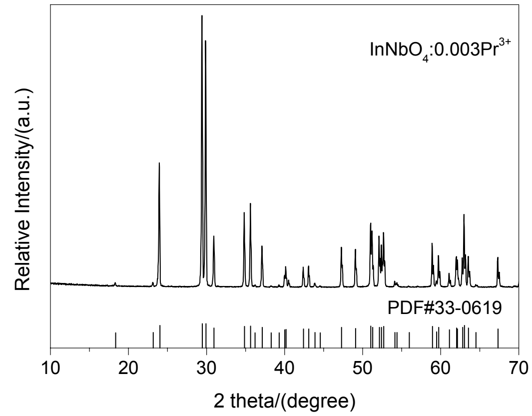

Fig. 1. XRD pattern of sample $InNbO_4:0.003Pr$

Fig. 2 presents the particle size distribution of $InNbO_4:Pr^{3+}$. The particles of the sample have a narrow size distribution and the average diameter approximates to 2.0μm, which is propitious to the coating for the production of solid-lighting devices[35].

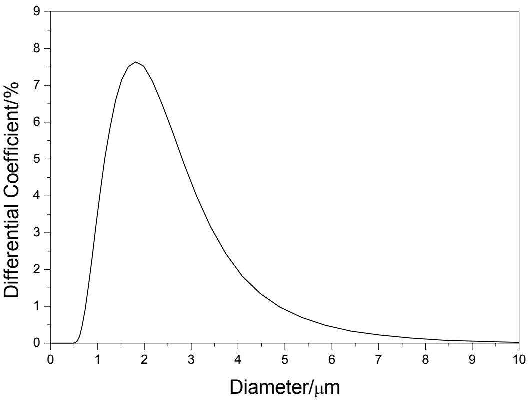

Fig. 2. Particle size distribution of $InNbO_4:Pr^{3+}$

3.2 The spectra of the excitation and emission of $InNbO_4:Pr^{3+}$

The excitation spectrum of the phosphor $InNbO_4:Pr^{3+}$ monitored at 614nm is shown in Fig. 3. There are four sharp peaks in the spectrum corresponding to the transitions of Pr^{3+} different energy levels. These transitions are $^3H_4 \rightarrow {}^3P_2$(λ=449nm), $^3H_4 \rightarrow {}^3P_1$(λ=477nm), $^3H_4 \rightarrow {}^3P_0$ (λ=489nm) and $^3H_4 \rightarrow {}^1D_2$ (λ=583nm)[36]. Among the transitions, $^3H_4 \rightarrow {}^3P_2$ and $^3H_4 \rightarrow {}^1D_2$ belong to supersensitive transition, which is sensitive to their surroundings of host and related to the partial symmetry. This sharp transition peak cannot be found under the Pr^{3+}

occupying central symmetry. Several low intensity peaks from 449nm to 470nm were also observed owing to the splitting patterns of energy levels in the excitation state[37]. The cleavage effect originates from different secondary energy levels which are connected to the doping of Pr^{3+} resulting in the crystal field of $InNbO_4$ matrix. In the upper wavelength, the range from 449nm to 470nm pertains to the blue LED chip, which illustrates that as-synthesized phosphor $InNbO_4:Pr^{3+}$ could be excited by this type of LED.

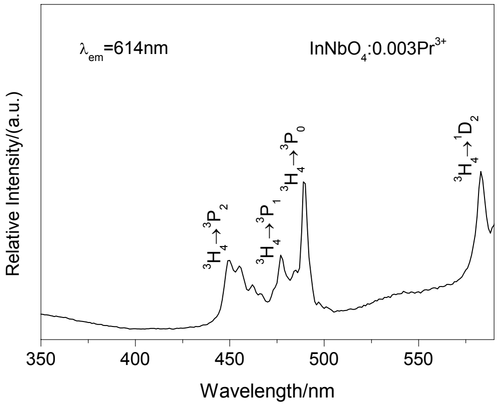

Fig. 3. Excitation spectrum of the phosphor $InNbO_4:0.003Pr^{3+}$

Fig. 4 displays the emission spectrum of the phosphor $InNbO_4:0.003Pr^{3+}$ excited with the blue light excitation at 466nm. Two main emitting peaks at 603nm and 614nm are observed in the spectrum, which come from the Pr^{3+} transition of $^1D_2\rightarrow{}^3H_4$ and $^3P_0\rightarrow{}^3H_6$, respectively. Both of the strong transitions are the region of red light. That is to say, the phosphor $InNbO_4:0.003Pr^{3+}$ can emit red light when excited by blue light.

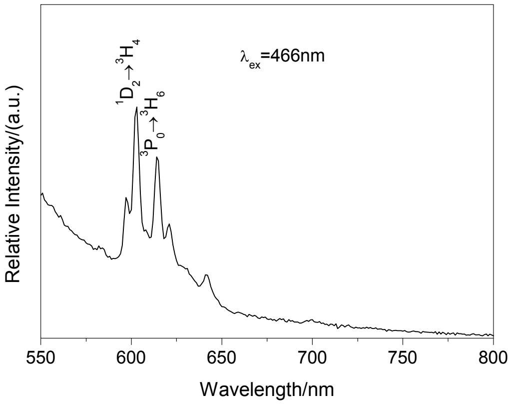

Fig. 4. Emission spectrum of the phosphor $InNbO_4:0.003Pr^{3+}$

3.3 Effect of Pr^{3+}-doped concentration on the luminescence properties

The amount of dopant exerts a influence on the luminescence properties in rare earth ion doped phosphor[38,39]. Fig. 5 gives photoluminescence emission spectra of $InNbO_4:Pr^{3+}$ phosphors with different Pr^{3+} concentrations. It can be seen that all the phosphors exhibit the same position of peak except the intensity of emission peak. In other words, the Pr^{3+}-doped content only results in the change of intensity.

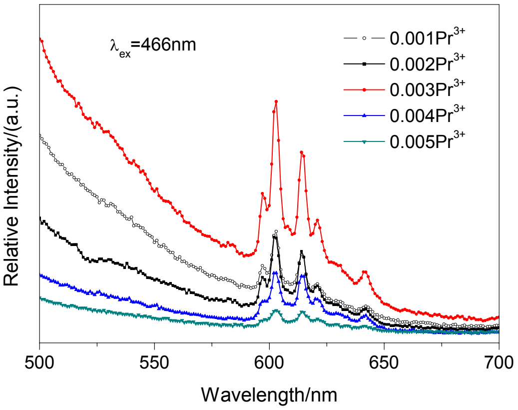

Fig. 5. Emission spectra of $InNbO_4:xPr^{3+}$ phosphors under the excitation at 466nm

With the increasing of Pr^{3+} dopant, the emission intensity of the phosphor increases in the starting stage and it reaches the maximal value with the doping concentration of 0.3mol%. Subsequently, the intensity drops quickly. This phenomenon is described as Fig. 6. It is reported that other rare earth ions have an high doping concentration in the related hosts[40]. For example, He et al. found that the optical Eu^{3+} concentration in the KBiPMo:Eu^{3+} phosphor reaches up to 80mol%[41]. Compared with these doping ions, Pr^{3+} has a lower doping concentration, probably because the distance of Pr^{3+} is very short, which easily leads to the occurrence of concentration quenching. For this experiment, the best doping concentration is 0.3mol%. More or less Pr^{3+} ions are harmful to the improvement of luminescence intensity.

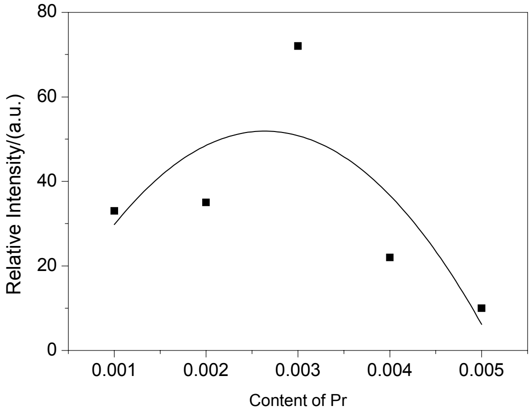

Fig.6. The effect of content of Pr^{3+} on the photoluminescence intensity

4. Conclusions

In conclusion, Pr^{3+}-activated indium niobate, $InNbO_4:Pr^{3+}$ phosphors were synthesized by using solid-state reaction. Meanwhile, the structure, size distribution and photoluminescence properties were investigated. The as-prepared phosphors have a single $InNbO_4$ phase and narrow size distribution. The phosphor can be excited by the blue wavelength lights from 449nm to 470nm in the excitation spectrum. With the blue light excitation of 466nm, the phosphor performs strong red emission at 606nm and 614nm responding to the respective $^1D_2 \rightarrow {^3H_4}$ and $^3P_0 \rightarrow {^3H_6}$ transitions of Pr^{3+} ions. The luminescence intensity of the phosphor considerably increased with the beginning adding Pr^{3+} concentration and reached the ultimate value with the doping Pr^{3+} concentration of 0.3mol%. Exceeding this concentration, the concentration quenching could be observed. The main excitation peaks of obtained phosphors match with the wavelength of blue LED chips and the phosphors can emit intensive red light. Thus, the phosphor $InNbO_4:Pr^{3+}$ may be a potential candidate of red-emitting phosphor for white LEDs.

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*Corresponding author: tangan527@126.com