

# Luminescence properties of novel red-emitting phosphor $\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$ for white light emitting-diodes

AN TANG<sup>1\*</sup>, TAO MA<sup>1</sup>, LIDUO GU<sup>2</sup>, YONGTAO ZHAO<sup>1</sup>, JUNHUI ZHANG<sup>1</sup>, HAOMING ZHANG<sup>1</sup>,  
FENGXIANG SHAO<sup>1</sup>, HONGSONG ZHANG<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, Henan Institute of Engineering, Zhengzhou, Henan 451191, China

<sup>2</sup>Department of Mechanics, Henan Mechanical and Electrical Vocational College, Zhengzhou, Henan, 451191, China

$\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$  red phosphors were synthesized by solid-state reaction and their luminescence properties were also studied through photoluminescence spectra. The excitation and emission spectra make it clear that the as-prepared phosphors can be effectively excited by near-ultraviolet (UV) 394 nm light and blue 466 nm light to emit strong red light located at 612 nm, due to the  $\text{Eu}^{3+}$  transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ . The luminescence intensity is dependent on phosphorus content, and it achieves the maximum at  $x = 0.4$ . Excessive phosphorus in the phosphors can result in reduction of luminescence intensity owing to concentration quenching. With the increasing content of phosphorus, the phosphors are prone to emit pure red light. This shows that the  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:0.04\text{Eu}^{3+}$  phosphor may be a potential candidate as a red component for white light emitting-diodes.

Keywords: *solid-state reaction; phosphor;  $\text{InNbO}_4$ ; LEDs*

© Wrocław University of Technology.

## 1. Introduction

White light emitting diodes (LEDs) have attracted a lot of attention for their long life, low energy consumption, high luminescence efficiency and environmental friendliness [1–3]. At present, the commercial white LEDs are mainly produced by the blue LED chips coated with yellow-emitting phosphors ( $\text{YAG}:\text{Ce}^{3+}$ ) [4]. However, there are at least two disadvantages in this kind of white LEDs, such as poor color rendering index ( $\text{CRI} < 80$ ) and high correlated color temperature ( $\text{CCT} > 4500 \text{ K}$ ), due to the shortage of red-emitting component. The conventional solution is adding a red-emitting phosphor to the unit of the white LEDs. In this approach, most red phosphors, for example  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ ,  $\text{CaS}:\text{Eu}^{2+}$  and  $\text{SrS}:\text{Eu}^{2+}$ , are based on sulfides which are chemically unstable and inefficient [5, 6]. Therefore, exploring novel red phosphors to overcome the above disadvantages is very necessary.

As a kind of good luminescence material, niobates are widely used. On one hand,  $\text{NbO}_4^{3-}$  ions can be self-activated due to charge transfer of Nb–O, and on the other hand, many activator and sensitizer ions can be doped into the host of niobates. Thus, niobates are regarded as ideal host materials for luminescence. These materials are applied in the field of X-rays [7, 8], and recently they have been reported to be used as ultraviolet luminescent materials [9, 10]. Currently, with the development of LED technology, people have been interested in niobates used in the area of LEDs due to their chemical stability and simple process of synthesis. In this work, a series of phosphors  $\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$  were prepared and their luminescence properties were also investigated.

## 2. Experimental

The powder samples with the composition of  $\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$  were synthesized by the conventional solid-state reaction. The stoichiometric amounts of starting materials  $\text{In}_2\text{O}_3$  (99.99 %),  $\text{Nb}_2\text{O}_5$  (A.R.),  $(\text{NH}_4)_2\text{HPO}_4$  (A.R.) and  $\text{Eu}_2\text{O}_3$

\*E-mail: tangan527@126.com

(99.99 %) were thoroughly mixed in an agate mortar. The mixtures were pre-calcined at 600 °C for 4 h in air, and re-calcined at 1255 °C for 6 h. The final samples were cooled down to room temperature in the furnace.

The crystal structure was identified by X-ray diffraction (XRD, D/MAX-2500PC) with CuK $\alpha$  radiation at 40 kV and 150 mA. The photoluminescence (PL) properties were measured by an RF-5301 molecular fluorescence spectrometer equipped with a xenon lamp as an excitation source, and the slit width for excitation and emission was 3 nm. All the measurements were carried out at room temperature.

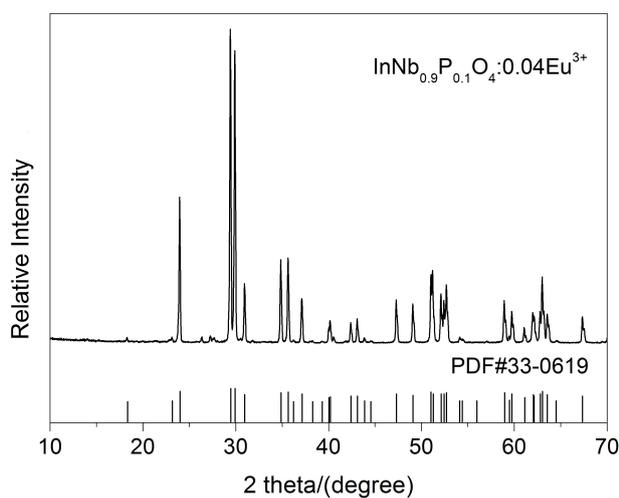


Fig. 1. XRD pattern of  $\text{InNb}_{0.9}\text{P}_{0.1}\text{O}_4:0.04\text{Eu}^{3+}$ .

### 3. Results and discussion

#### 3.1. Structural characterization

Fig. 1 shows the XRD pattern of  $\text{InNb}_{0.9}\text{P}_{0.1}\text{O}_4:\text{Eu}^{3+}$  sample. From the X-ray diffraction pattern, it is observed that all the diffraction peaks can be indexed well to the monoclinic phase of  $\text{InNbO}_4$  structure (JCPDS No. 33-0619). This clearly indicates that the synthesis of  $\text{InNb}_{0.9}\text{P}_{0.1}\text{O}_4:\text{Eu}^{3+}$  phosphor has been completed and no second phase appeared. The results suggest that the little amount of doped phosphonium ions and rare-earth ions have nearly no effect on the  $\text{InNbO}_4$  phase structure.

#### 3.2. Luminescence properties of phosphor $\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$

The excitation spectra of the  $\text{InNbO}_4:0.04\text{Eu}^{3+}$  and  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:0.04\text{Eu}^{3+}$  are shown in Fig. 2. In the spectra, the two strongest excitation peaks at 394 nm and 466 nm can be attributed to the  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  and  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  transitions of  $\text{Eu}^{3+}$ , respectively [11]. It implies that the phosphors can be effectively excited by radiations of near-UV and blue lights which match with the chips of white LEDs. Compared with the  $\text{InNbO}_4:0.04\text{Eu}^{3+}$  excitation spectrum, the peak position of the  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:0.04\text{Eu}^{3+}$  has not changed, but it has a stronger intensity. That is to say,  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:0.04\text{Eu}^{3+}$  can absorb more excitation energy and be used as luminescence material for white LEDs.

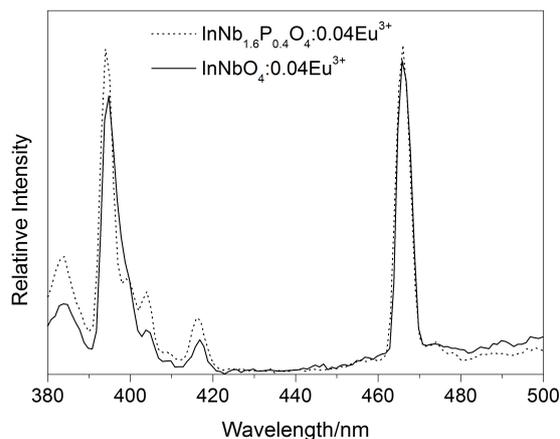


Fig. 2. Excitation ( $\lambda_{\text{em}} = 612 \text{ nm}$ ) spectra of  $\text{InNbO}_4:\text{Eu}^{3+}$  and  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:\text{Eu}^{3+}$ .

Fig. 3 presents the emission spectra of the  $\text{InNbO}_4:0.04\text{Eu}^{3+}$  and  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:0.04\text{Eu}^{3+}$ . There are two strong emission peaks in the spectra. One is the  $\text{Eu}^{3+}$  transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  at 612 nm and the other is  $\text{Eu}^{3+}$  transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  at 590 nm [12], but the former transition is much stronger than the latter one. It is believed that most  $\text{Eu}^{3+}$  ions are located within an asymmetric cation environment and the electric dipole transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  is dominant in the host lattice [13].

Photoluminescence relative intensity of  $\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$  ( $x = 0.0, 0.2, 0.4, 0.8, 1.0$ )

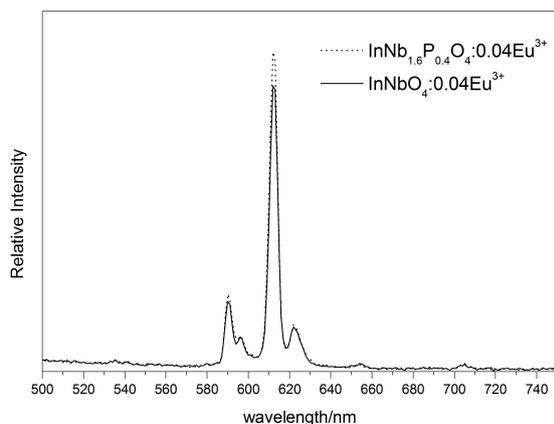


Fig. 3. Emission ( $\lambda_{\text{ex}} = 466$  nm) spectra of  $\text{InNbO}_4:\text{Eu}^{3+}$  and  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:\text{Eu}^{3+}$ .

phosphor due to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition for  $\text{Eu}^{3+}$  as a function of phosphorus content is exhibited in Fig. 4. It can be seen that the relative emission intensity is the highest when the value of  $x$  is about 0.4. If the content of phosphorus is larger than this value, the emission intensity of f-f transition for  $\text{Eu}^{3+}$  is obviously decreased as a result of concentration quenching, which is probably owing to higher number of new defects [14].

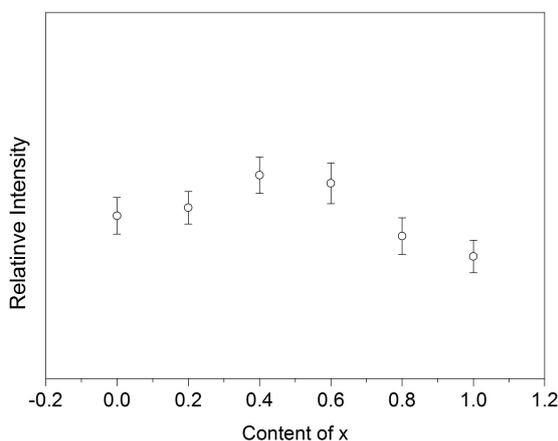


Fig. 4. Photoluminescence ( $\lambda_{\text{ex}} = 394$  nm) relative intensity of  $\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$  phosphor due to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition for  $\text{Eu}^{3+}$  as a function of phosphorus content.

According to the theory of 4f transition of rare-earth ions, the  $\text{Eu}^{3+}$  electric dipole transition of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  is sensitive to coordination environment, while the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  only manifests

magnetic dipole transition which is insensitive to the site symmetry [15]. Thus, the ratio of spectral line intensity between the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transitions, which is defined as  $I_{0-2}/I_{0-1}(\text{R/O})$ , can be used to analyze the symmetry information. Fig. 5 shows the R/O value variation for  $\text{Eu}^{3+}$  in the matrix  $\text{InNb}_{1-x}\text{P}_x\text{O}_4$  with different phosphorus additions. With the increasing of the phosphorus content, R/O value becomes larger gradually due to the reinforcement of covalence and polarizability in the host doped with P element. This means that crystal environment around  $\text{Eu}^{3+}$  will be distorted upon the addition of P element, and the R/O value will increase, which is profitable in getting pure red light.

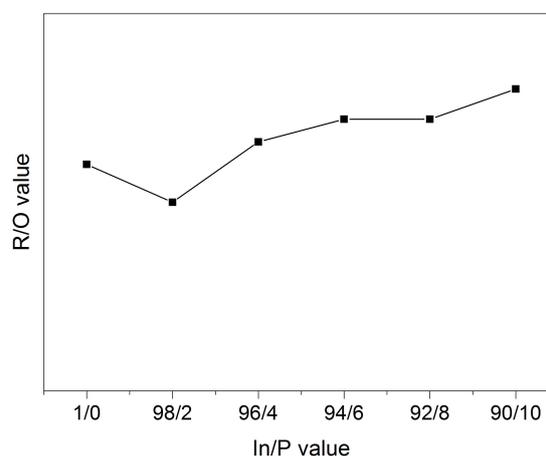


Fig. 5. R/O value variation for  $\text{Eu}^{3+}$  in the matrix of  $\text{InNb}_{1-x}\text{P}_x\text{O}_4$  with different phosphorus addition.

## 4. Conclusions

A novel series of red-emitting phosphors  $\text{InNb}_{1-x}\text{P}_x\text{O}_4:\text{Eu}^{3+}$  ( $x = 0.2, 0.4, 0.6, 0.8$ ) were successfully prepared by the conventional solid-state reaction at  $1255$  °C. The excitation spectra show that the phosphors can be effectively excited by near-UV light at 394 nm and blue light at 466 nm. The emission spectra indicate that the as-synthesized phosphors can emit red light at 612 nm when excited by near-UV or blue light. The R/O value increases with increasing the phosphorus content, and the luminescence intensity reaches the

maximum when x value is 0.4. Thus, the investigation shows that  $\text{InNb}_{1.6}\text{P}_{0.4}\text{O}_4:\text{Eu}^{3+}$  is an ideal red phosphor for near-UV and blue chip-based white LEDs.

### Acknowledgements

This work was supported by the Research Fund for the Doctoral Program of Henan Institute of Engineering (Grant No. D2013012).

### References

- [1] WANG B.L., LIN Y.T., JU H.D., *J. Alloy. Compd.*, 584 (2014), 167.
- [2] YANG F., LIANG Y.J., LIU M.Y., LI X.J., ZHANG M.F., WANG N., *Opt. Laser Technol.*, 46 (2013), 14.
- [3] ZHANG J.L., ZHANG X.G., GONG M.L., SHI J.X., YU L.P., RONG C.Y., LIAN S.X., *Mater. Lett.*, 79 (2012), 100.
- [4] CHEN F.M., LIU X.H., *Opt. Mater.*, 35 (2013), 2716.
- [5] FENG W.L., JIN Y., WU Y., LI D.F., CAI A.K., *J. Lumin.*, 134 (2013), 614.
- [6] LIAO J.S., LIU L.B., YOU H.Y., HUANG H.P., YOU W.X., *Optik*, 123 (2012), 901.
- [7] BRIXNER L.H., *Mater. Chem. Phys.*, 16 (1987), 253.
- [8] XIAO X.Z., YAN B., *J. Alloy. Compd.*, 421 (2006), 252.
- [9] LIU H., VASQUEZ O., SANTIAGO V.R., DIAZ L., FERNANDEZ F.E., LIU L., XU L., GAN F., *J. Lumin.*, 108 (2004), 37.
- [10] FUKADA H., KONAGAI M., UEDSA K., MIYATA T., *Thin Solid Films*, 517 (2009), 6054.
- [11] ZHOU L.Y., WEI J.S., GONG F.Z., HUANG J.L., YI L.H., *J. Solid State Chem.*, 181 (2008), 1337.
- [12] YANG Z.P., TIAN J., WANG S.L., YANG G.W., LI X., LI P.L., *Mater. Lett.*, 62 (2008), 1369.
- [13] GUO Y., SUN M., GUO W.M., REN F.Q., CHEN D.H., *Opt. Laser Technol.*, 42 (2010), 1328.
- [14] CI Z.P., WANG Y.H., ZHANG J.C., SUN Y.K., *Physica B*, 403 (2008), 670.
- [15] RAINHO J.P., CARLOS L.D., ROCHA J., *J. Lumin.*, 87 – 89 (2000), 1083.

Received 2014-12-09  
Accepted 2015-02-13