The investigation on the relationship between the R/O ratio of Eu³⁺ in orthophosphates and the excitation wavelengths

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Abstract

Orthophosphates doped with Eu^{3+} were widely investigated for their excellent photoluminescence properties for lighting and displays applications. In this work, we successfully synthesized orthophosphates $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$), $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$), $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06, 0.09$) and studied their excitation and emission spectra. The obtained emission spectra of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$) showed that the integrated intensity ratios of $^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ of Eu^{3+} were similar under 393 nm and 147 nm excitation, and higher than that under 254 nm excitation. The similar phenomena were observed in $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$) and $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06, 0.09$). We interpreted this phenomenon based on the theory of energy transfer.

Keywords: A. Inorganic compounds; D. Luminescence; D. Optical properties

1. Introduction

Recently, Eu^{3+} is widely used as a red-emitting activator and applied in fluorescent lamp, light emitting diode (LED), plasma display panels (PDPs) and Hg-free fluorescent lamps for its $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric-dipole transition in the red region with a finite spectral width [1-2]. However, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ red emission of Eu^{3+} belongs to the forbidden transition, and the allowed $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic-dipole transition emission of Eu^{3+} locates in the orange region [3-4]. Therefore, how to tune the emission intensity ratio of $^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ (R/O) of Eu^{3+} becomes a necessary task to realize the actual applications. Indeed, the ratio of R/O strongly depends on both the crystal structural defects and the energy transfer pathway [5-6]. Considering the energy transfer pathway of phosphor is different under different wavelengths excitation, in this paper, we mainly investigate the relationship between the R/O intensity ratio of Eu^{3+} and the different excitation wavelengths.

Orthophosphates are chosen as the phosphor host for their stable crystal structure, the good optical transparency and the efficient absorption properties in the ultraviolet (UV) and vacuum ultraviolet (VUV) region [7-9]. In this work, in order to eliminate the effect of selective excitation, orthophosphate $\text{K}_3\text{La}(\text{PO}_4)_2:\text{Eu}^{3+}$, $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Eu}^{3+}$, $\text{GdPO}_4:\text{Eu}^{3+}$ are chosen because the rare earth (RE) ions in these three phosphates have only one crystallographic site, and hence the doping Eu^{3+} ions occupy only one site. Therefore, the R/O intensity ratio of Eu^{3+} mainly depends on the excitation wavelengths. In addition, the RE ions are surrounded by seven O ions in $\text{K}_3\text{La}(\text{PO}_4)_2$ and $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Eu}^{3+}$, six of

which are in near inversion symmetric positions [10,11]. Accordingly, the geometric symmetry of the REO_7 polyhedron would be easily be interfered, so the R/O intensity ratio of Eu^{3+} changes.

In this work, the photoluminescence (PL) properties of $\text{K}_3\text{La}(\text{PO}_4)_2:\text{Eu}^{3+}$, $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Eu}^{3+}$, $\text{GdPO}_4:\text{Eu}^{3+}$ were investigated under near-ultraviolet (NUV), UV and VUV excitation. The main reason for choosing these three excitation wavelengths is that the characteristic excitation peaks of Eu^{3+} f-f transition locate in the NUV region [12,13], the charge transfer (CT) band of $\text{O}^{2-}-\text{Eu}^{3+}$ is in the UV (around 250 nm) region [14,15], and the VUV excitation mainly involves the energy transfer from the host to Eu^{3+} under VUV excitation [16,17]. It is obvious that the energy transfer pathway are different under NUV, UV and VUV excitations. We investigate in details the energy transfer process through analyzing the relationship between the R/O ratio of Eu^{3+} in orthophosphates and the excitation wavelengths in the three energy regions mentioned above.

2. Experimental

Three series of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$), $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$) and $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06, 0.09$) were prepared by mixing stoichiometric quantities of K_2CO_3 (2N), La_2O_3 (5N), Gd_2O_3 (4N), Eu_2O_3 (4N) and $(\text{NH}_4)_2\text{HPO}_4$ (98.5 %, excess of 5-15 mol %). Excess of $(\text{NH}_4)_2\text{HPO}_4$ was added to compensate the evaporation loss at high temperature. The mixtures were ground thoroughly and preheated at 400 °C for 1 h, cooled and reground. Then the resulting

mixtures were heated respectively at 1200 °C, 950 °C and 1100 °C for several hours to obtain the phosphors $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$, $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ and $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$.

All the samples were checked by X-ray diffraction (XRD) using Rigaku diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. UV excitation and emission spectra were measured by a Xe lamp (FLS-920T). VUV excitation and emission spectra were measured by FLS-920T fluorescence spectrophotometer with a VM-504-type vacuum monochromator using a deuterium lamp as the lighting source. The VUV excitation spectra were corrected with sodium salicylate, the quantum efficiency of which was almost constant in the region of 120-200 nm. All the measurements were performed at room temperature.

3. Results and discussion

3.1 XRD patterns

The XRD patterns of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$, $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$, and $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ are plotted in Fig.1, together with the corresponding JCPDS data No.47-0468, 49-1085 and 26-0660, respectively. The diffraction peaks of the obtained samples are consistent with the corresponding JCPDS files, indicating that all our samples are single phase. The diffraction peaks of $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ and $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ shift slightly to the small angle region in comparison with the JCPDS No.49-1085 and 26-0660, respectively. On the contrary, the diffraction peaks of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ shift to the large angle side in contrast to the JCPDS No.

47-0468. The main reason for such peak shifts is the ionic radius: $\text{La}^{3+} > \text{Eu}^{3+} > \text{Gd}^{3+}$. This phenomenon is consistent with the Vegard's law, demonstrating that the Eu ions are doped into the Gd and La ions sites.

3.2. PL spectra of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$)

When the Eu^{3+} concentration of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ is changed between 0.03 mol and 0.09 mol, the excitation spectra are similar except the excitation intensity is changed. As a typical example, the VUV-UV excitation spectra of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ are show in Fig.2. The VUV excitation spectrum is obtained by monitoring the 617 nm emission. The UV excitation spectra are measured with the excitation wavelength of 589 nm and 617 nm, respectively. According to the previously reported VUV absorption of $\text{M}_3\text{La}(\text{PO}_4)_2$ ($\text{M}=\text{Na}, \text{K}, \text{and Rb}$) [18], the broad bands below 200 nm can be assigned to the host absorption. The broad band with the maximum at about 254 nm is the CT band of $\text{O}^{2-}-\text{Eu}^{3+}$. The sharp peaks from 295 nm to 400 nm are attributed to the 4f-4f transitions of Eu^{3+} . The strongest sharp peak locates at 393 nm and belongs to the ${}^7\text{F}_6 \rightarrow {}^5\text{L}_6$ characteristic transition of Eu^{3+} [19]. More detailed assignment is tabulated in Table.1. Monitoring the 589 nm and 617 nm emission, the obtained UV excitation are similar and only the intensity of the 4f-4f peaks and the CT band is different, which indicates that the Eu^{3+} ions in $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ occupy one site.

Considering that the emission spectra of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$) are similar in profile under the same wavelength excitation, three typical emission spectra of

$\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ are displayed in Fig.3 with the excitation wavelengths of 393 nm, 254 nm and 147 nm, respectively. In the following, we will discuss these three emission spectra in details.

Under 393 nm excitation, two emission peaks are observed with the maxima at 589 nm and 617 nm, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=1, 2$) transitions of Eu^{3+} , respectively. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ red emission belongs to the electric-dipole transition and the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ orange emission to the magnetic-dipole transition. The integrated intensity ratio of R/O of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$) under 393 nm excitation is shown in Table.2. The intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ red emission is higher than that of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ orange emission. According to the excitation spectrum of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ discussed above in Fig.2, the wavelength at 393 nm corresponds to the $^7\text{F}_6 \rightarrow ^5\text{L}_6$ characteristic transition of Eu^{3+} . This means that the electrons can be excited directly from $^7\text{F}_6$ to $^5\text{L}_6$ energy level under 393 nm excitation, and then relax to the low energy level emitting a visible light. The electric-dipole forbidden transition intensity is higher than the allowed magnetic dipole transition, which demonstrates that the doping Eu^{3+} ions locate at a low symmetric site, so the choose law of electric dipole transition is broken. According to ref.[10, 11], the La sites in $\text{K}_3\text{La}(\text{PO}_4)_2$ deviate slightly from the inversion symmetry since and 6 of the 7 surrounding O ions are close to inversion positions. In this view, the intensity of the forbidden electric-dipole transition should be low, contradicting our experimental results. The most possible reason for the high electric-dipole emission should be the distortion of EuO_7 polyhedron caused by the partial replacement of La^{3+} by Eu^{3+} . The ionic radii of

La^{3+} and Eu^{3+} in REO_7 polyhedron are 1.10 Å and 0.95 Å [20], respectively. The doping of Eu^{3+} results in the contraction of the $\text{K}_3\text{La}(\text{PO}_4)_2$ crystal lattice. Since, the electric-dipole red emission of Eu^{3+} is sensitive to the distortion of EuO_n polyhedron and is easily affected by its surroundings, and hence the intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ red emission has higher intensity under 393 nm excitation.

Under 254 nm excitation, the emission spectrum of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ contains two peaks with maxima at 592 nm and 617 nm, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=1, 2$) transitions of Eu^{3+} , respectively. The integrated intensity ratio of R/O of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$) is around 0.99 (see Table.2). The intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ orange emission is slightly higher than that of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ red emission, which is contrary to that under 393 nm excitation. Considering Eu^{3+} ions occupy only one crystalline site, the probability of selective excitation can be excluded. Therefore, the change of the R/O ratio can be ascribed to the different energy transfer process. According to the excitation spectra discussed in Fig.2, the excitation energy is absorbed mainly by the $\text{O}^{2-}\text{-Eu}^{3+}$ CT band under 254 nm excitation. In other words, the electrons transfer from the 2p-orbits of O^{2-} to the 4f-orbits of Eu^{3+} , and then the $\text{Eu}^{3+}+e$ excitation state forms leading to the expansion of the Eu ions electron cloud and increasing the repulsive force between the atoms. This is contrary to the contraction of the crystal volume for the doping of Eu^{3+} . At last, the change of the EuO_7 symmetry is small. As a consequence the main emission of Eu^{3+} is dominated by the the allowed magnetic-dipole transition under 254 nm excitation.

Under 147 nm excitation, two peaks with maxima at 590 nm and 617 nm are observed in the emission spectrum of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ and can be assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0, 1, 2$) transitions of Eu^{3+} , respectively. The strongest emission belongs to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} . The integrated intensity ratio of R/O of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$) is around 1.45 (see Table.2). This ratio is the same with that obtained under 393 nm excitation, but is different from that obtained under 254 nm excitation. It's obvious that the intensity ratio of R/O is changed under different wavelengths excitation. This phenomenon is interesting. In order to confirm that the results are not unique, the emission spectra of $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$) and $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06, 0.09$) were measured under the different wavelengths excitation.

3.3. PL spectra of $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$)

Fig.4 displays the VUV-UV excitation spectra of $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ as an typical for the series of $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$). The VUV excitation spectrum is obtained by monitoring the 617 nm emission. The UV excitation spectra are measured by monitoring the 589 nm and 617 nm emission, respectively. Two strong excitation bands and several sharp peaks are observed in the VUV-UV excitation spectra. The strong band around 147 nm is assigned to the absorption of PO_4^{3-} group [21]. The band with the maxima at 260 nm belongs to the CT band of $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$. The peak at 274 nm comes from the $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ ($J=11/2, 9/2, 7/2$) transition of Gd^{3+} [22-23]. The other sharp peaks correspond to the 4f-4f transitions of Eu^{3+} . The strong sharp peak at 393 nm is

originated from the ${}^7F_6 \rightarrow {}^5L_6$ characteristic transition of Eu^{3+} . Monitoring different Eu^{3+} emissions, the obtained UV excitations are similar except the intensity of 4f-4f bands and CT band is different, which indicates that the Eu^{3+} ions in $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ occupy only one site.

The emission spectra of $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$) are similar in profile. Hence we show the emission spectra of $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ under 393 nm, 260 nm and 147 nm excitation in Fig.5. The shapes and the positions of the emissions are similar under the three excitations. The emission peaks at 589 nm, 617 nm, 652 nm can be assigned to the ${}^5D_0 \rightarrow {}^7F_J$ ($J=1, 2, 3$) transition of Eu^{3+} . Under 393 nm, 260 nm and 147 nm excitation, the integrated intensity ratios of R/O of $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$) are shown in Table.3. The ratios of R/O under 147 nm and 393 nm excitation are similar and are higher than that under 260 nm excitation. This phenomenon is consistent with $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$).

3.4. PL spectra of $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06, 0.09$)

The excitation spectra of $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06$ and 0.09) are similar. The VUV-UV excitation spectra of $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ is given in Fig.6. The VUV excitation spectrum of $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ is obtained by monitoring the 614 nm emission. The UV excitation spectra are obtained by monitoring the 593 nm and 614 nm emission, respectively. The excitation band in the region of 120-163 nm is attributed to the absorption of PO_4^{3-} group [24]. The band around 251 nm is the CT band of $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$.

The sharp peak at 393 nm belongs to the ${}^7F_6 \rightarrow {}^5L_6$ transition of Eu^{3+} . In these two UV excitation spectra, the excitation position are completely same and only the intensity of the 4f-4f bands and the CT band is different. This indicates the Eu^{3+} ions in $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ occupy only one site.

Fig.7 plots the emission spectra of $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ under 393 nm, 251 nm and 147 nm excitation. Four emission peaks with the maxima at 593 nm, 621 nm, 651nm and 698 nm are observed and respectively belongs to the ${}^5D_0 \rightarrow {}^7F_J$ ($J=1, 2, 3, 4$) transition of Eu^{3+} . Under 393 nm, 251 nm and 147 nm excitations, the integrated intensity ratios of R/O for $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06$ and 0.09) are shown in Table.4. The ratios of R/O under 147 nm excitation is similar to that under 393 nm excitation, but is higher than that under 251 nm excitation. This results are consistent with that observed in $\text{K}_3\text{La}(\text{PO}_4)_2:\text{Eu}^{3+}$ and $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Eu}^{3+}$. Now, we may ask why the integrated intensity ratio of R/O is high under 147 nm excitation. One of the reasons should be the penetration depth of VUV radiation and the surface defects of the phosphors. According to Modi's work [25], the depth of incident radiation are all restricted to 8.0 nm (10-250 eV). Considering the penetration depth of VUV radiation can be affected by the photon energy, diffusion to the surface, dielectric permittivity of materials and incident angle, the penetration depth of VUV radiation in our experiment is less than 10 nm [26]. In this case, the VUV light excite only parts of the phosphor particles near the surface area. Moreover, defects exit on the surface of the phosphor particle, which leads to the distorted EuO_n polyhedron on the surface. So the forbidden ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} can be released and has high

emission intensity, thus the ratios of R/O under 147 nm excitation is higher.

4. Conclusions

The relationship between the ratio of R/O of Eu^{3+} in orthophosphates and the excitation wavelengths was investigated. The integrated intensity ratio of R/O of Eu^{3+} under UV excitation is lower than that under 393 nm and 147 nm excitation. Under 393 nm excitation, the high integrated intensity ratio of R/O attributes to the direct electron transition from $^7\text{F}_6$ to $^5\text{L}_6$ energy level of Eu^{3+} , and the electric-dipole red emission of Eu^{3+} is sensitive to the distortion of EuO_n polyhedron. Under 147 nm excitation, the high integrated intensity ratio of R/O is a consequence of the shallow penetration depth of VUV radiation and the distorted EuO_n polyhedron near the surface.

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References

- [1] G. Wakefield, E. Holland, P.J. Dobson, J. L. Hutchison, *Adv. Mater.* 13 (2001) 1557.
- [2] Y. Jin, J. Zheng, *Mater. Lett.* 114 (2014) 4.
- [3] U. Rambabu, N.R. Munirathnam, T.L. Prakash, S. Buddhudu, *Mater. Chem. Phys.* 78, (2003) 160.
- [4] U.Rambabu, S. Buddhudu, *Opt. Mater.*, 17 (2001) 401.
- [5] Q. Dong, Y. Wang, Z. Wang, X. Yu, B. Liu, *J. Phys. Chem. C.* 114 (2010) 9245.
- [6] J. Shin, S. Choi, S. Hong, S. Kwon, S. Seo, H. Kim, Y. Song, D. Yoon, *J Alloy Compd.* 509 (2011) 4331.
- [7] Xueyan Wu and Hongpeng You, *Mater. Res. Bull.*, 37 (2002) 1531.
- [8] Yu-Sheng Tang and Shu-Fen Hu, *Applied Physics Letters.* 90 (2007) 151108.
- [9] Xinguo Zhang, Liya Zhou, Menglian Gong, *Optical Materials.* 35(2013) 993.
- [10] H.Y-P. Hong, S.R. Chinn, *Mater. Res. Bull.*, 11 (1976) 421.
- [11] D. Zhao, F. F Li, *Acta Crystallogr E.* E66 (2010) i64.
- [12] Arunachalam Lakshmanan, R.S. Bhaskar, Preema C. Thomas, R. Satheesh Kumar, V. Siva Kumar, M.T. Jose, *Materials Letters.*, 64 (2010) 1809.
- [13] Dongseok Kang, Hyoung Sun Yoo, Sang Hoon Jung, Hyunki Kim, and Duk Young Jeon, *J. Phys. Chem. C.*, 115(2011) 24334.
- [14] R. Sankar and G. V. Subba Rao, *Journal of The Electrochemical Society.*, 147 (2000) 2773.
- [15] Kyong-Gue Lee, Byung-Yong Yu, Chong-Hong Pyun, Sun-Il Mho, *Solid State*

Communications., 122 (2002) 485.

- [16] René T. Wegh, Harry Donker, Koenraad D. Oskam, Andries Meijerink, *Science*, 283 (1999) 663.
- [17] Xiaoqing Zeng, , Seoung-Jae Im, Sang-Hun Jang, Young-Mo Kim, Hyoung-Bin Park, Seung-Hyun Son, Hidekazu Hatanaka, Gi-Young Kim, Seul-Gi Kim, *J. Lumin.* 121 (2006) 1.
- [18] B. Finke. L. Schwarz, P. Gurtler, M. Kraas, M. Joppien, J. Becker, *J. Lumin.* 60&61 (1994) 975.
- [19] R.Y. Wang, *J. Lumin.* 106 (2004) 211.
- [20] R. D. Shannon, *Acta.Cryst.* A32 (1976) 751.
- [21] W. Liu, D. Wang, Y. Wang, J. Zhang, H. Tao, *J. Am. Ceram. Soc.* 96 (2013) 2257.
- [22] X.X. Li, Y.H. Wang, *J. Lumin.* 1000 (2007) 122.
- [23] Y.H. Wang, T. Endo, E.Q. Xie, D.Y. He, B. Liu, *Microelectron. J.* 35 (2004) 357.
- [24] Z. Tian, H. Liang, H. Lin, Q. Su, B. Guo, G. Zhang, Y. Fu, *J Solid State Chem.* 179 (2006) 1356.
- [25] M. Modi, G. Lodha, P. Srivastava, A. Sinha, R. Nandedkar, *Phys Rev B.* 74 (2006), 045326/1.
- [26] M. Terekhin, A. Vasil'ev, M. Kamada, E. Nakamura, S.Kubota, *Phys Rev B.* 52 (1995) 3117.

Table captions

Table.1: Transition energies of Eu^{3+} in the excitation spectra of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$.

Table.2: Integrated intensity ratios of R/O of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$)

under 254 nm, 393 nm and 147 nm excitation.

Table.3: Integrated intensity ratios of R/O of $\text{K}_3\text{Gd}_{1-y}(\text{PO}_4)_2:y\text{Eu}^{3+}$ ($y=0.03, 0.06, 0.09$)

under 393 nm, 260 nm and 147 nm excitation.

Table.4: Integrated intensity ratios of R/O for $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06$ and 0.09)

under 251 nm, 393 nm and 147 nm excitation.

Figure captions

Fig.1: XRD patterns of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$, $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$, and $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$.

Fig.2: VUV-UV excitation spectra of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ ($\lambda_{\text{em}}= 617 \text{ nm}$, $\lambda_{\text{em}}= 589 \text{ nm}$).

Fig.3: Emission spectra of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ under 393 nm, 254 nm and 147 nm excitation.

Fig.4: VUV-UV excitation spectra of $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ ($\lambda_{\text{em}}= 617 \text{ nm}$, $\lambda_{\text{em}}= 589 \text{ nm}$).

Fig.5: Emission spectra of $\text{K}_3\text{Gd}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ under 393 nm, 260 nm and 147 nm excitation.

Fig.6: VUV-UV excitation spectra of $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ ($\lambda_{\text{em}}= 614\text{nm}$, $\lambda_{\text{em}}= 593 \text{ nm}$).

Fig.7: Emission spectra of $\text{Gd}_{0.94}\text{PO}_4:0.06\text{Eu}^{3+}$ under 393 nm, 251 nm and 147 nm excitation.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table.1: Transition energies of Eu^{3+} in the excitation spectra of $\text{K}_3\text{La}_{0.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$

Excitation maximum (nm)	transition
290, 296	${}^7\text{F}_0 \rightarrow {}^5\text{F}_2$
317, 325, 341	${}^7\text{F}_{0,1} \rightarrow {}^5\text{H}_3, {}^5\text{H}_6$
360, 372	${}^7\text{F}_{0,1} \rightarrow {}^5\text{D}_4$
381	${}^7\text{F}_{0,1} \rightarrow {}^5\text{D}_j, {}^5\text{L}_7$
393, 395	${}^7\text{F}_{0,1} \rightarrow {}^5\text{L}_6$

Table.2: Integrated intensity ratios of R/O of $\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x=0.03, 0.06, 0.09$)

under 254 nm, 393 nm and 147 nm excitation.

$\text{K}_3\text{La}_{1-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ x	R/O		
	$\lambda_{\text{ex}}=254\text{nm}$	$\lambda_{\text{ex}}=393\text{nm}$	$\lambda_{\text{ex}}=147\text{nm}$
0.03	1.00	1.42	1.45
0.06	0.99	1.45	1.47
0.09	0.98	1.40	1.41

Table.3: Integrated intensity ratios of R/O of $K_3Gd_{1-y}(PO_4)_2:yEu^{3+}$ ($y=0.03, 0.06, 0.09$)
under 393 nm, 260 nm and 147 nm excitation.

$K_3Gd_{1-y}(PO_4)_2:yEu^{3+}$ y	R/O		
	$\lambda_{ex}=260nm$	$\lambda_{ex}=393nm$	$\lambda_{ex}=147nm$
0.03	1.44	1.71	1.71
0.06	1.49	1.70	1.79
0.09	1.40	1.65	1.69

Table.4: Integrated intensity ratios of R/O for $\text{Gd}_{1-m}\text{PO}_4:m\text{Eu}^{3+}$ ($m=0.03, 0.06$ and 0.09)
under 251 nm, 393 nm and 147 nm excitation.

$\text{Gd}_{1-m}\text{PO}_4:\text{Eu}_m$ m	R/O		
	$\lambda_{\text{ex}}=251\text{nm}$	$\lambda_{\text{ex}}=393\text{nm}$	$\lambda_{\text{ex}}=147\text{nm}$
0.03	0.68	0.99	0.83
0.06	0.68	0.85	0.85
0.09	0.70	0.92	0.83