Hydrothermal synthesis and vacuum ultraviolet excited photoluminescence properties of (Y, La)VO₄:Eu³⁺ phosphors

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Abstract. The Y₀.95₋ₓLaₓVO₄:5%Eu³⁺ (0≤x≤0.15) phosphors were synthesized successfully by mild hydrothermal method at 200°C and their photoluminescence properties under ultraviolet (UV) and vacuum ultraviolet (VUV) excitation were studied. Monitoring at 619nm, a strong broad absorption was enhanced by co-doping of La³⁺ into the YVO₄:Eu³⁺ lattices at about 260nm in the UV excitation spectra. The VUV excitation spectra also showed the enhanced excitation bands at about 156nm and 200nm. Under 254nm or 147nm excitation, it was found that Y₀.95₋ₓLaₓVO₄:Eu³⁺ phosphors showed strong red emission at about 615nm and 619nm corresponding to the electric dipole 5D₀→7F₂ transition of Eu³⁺, resulting in good color purity. The improvement of luminescence intensity of YVO₄:Eu³⁺ was also observed after partial substituting Y³⁺ by La³⁺ and the optimal luminescence intensity appeared with incorporation of 2.5mol% La³⁺. The reasons of this enhancement were investigated and discussed in details.

1. Introduction
In recent research, rare earth doped phosphors have been widely studied for their numerous applications in PDPs and Hg-free lamps [1-3]. In these applications, small phosphor particles of less than 5µm in diameter are required [4]. Particularly, the nanosized phosphors have received much attention [5] for its much effect on the efficiency of luminescent devices. Hydrothermal method has been regarded as one of the most effective soft chemical routes to prepare nanomaterials at low temperature without milling or calcinations that could effectively save energy [6-8]. An excellent performance of displays and lamps requires phosphors with high quality for sufficient brightness, good colorimetric purity and long-term stability. YVO₄ has ZrSiO₄ structure, belonging to the space group I₄₁/amd [9]. It is well known that YVO₄:Eu³⁺ has been considered as a candidate of red phosphors and widely studied because of its good color purity, which is resulted from the noncentrosymmetric site of Eu³⁺ ion [10]. Moreover, nanosized YVO₄:Eu³⁺ has attracted much research, in K.Riwotzki and M.Haase’s work [11], they have synthesized YVO₄:Ln (Ln=Eu, Sm, Dy) nanoparticles with size from about 10 to 30nm by a hydrothermal method. In Zhang’s group [12], they have obtained YVO₄:Eu³⁺ nanopowders by sol–gel combustion method and reported that the luminescence intensity of the YVO₄:Eu³⁺ samples under 365nm excitation enhanced remarkably by the incorporation of Li⁺ ions. But there are few reports about the enhanced luminescence intensity of the YVO₄:Eu³⁺ under VUV excitation.
In our previous work [13], the YVO₄:Eu³⁺ nanophosphors at different pH values were synthesized by a mild hydrothermal method and their photoluminescence were evaluated under UV and VUV regions. When pH value was 7, the optimal luminescence intensity appeared. But the low efficiency of YVO₄:Eu³⁺ was still a problem for the application in PDPs and Hg-free lamps. By co-doping the La³⁺, the photoluminescence of many systems have been enhanced, such as Y₂SiO₅:Ce [14], Y₂O₃:Eu [4], and YBO₃:Eu [15].

In this study, the Y₀.⁹₅₋ₓLaxVO₄:0.₀⁵Eu³⁺ (0 ≤ x ≤ 0.₁₅) phosphors were synthesized at a low temperature by hydrothermal process. The PL properties were investigated under UV and VUV excitation.

2. Experimental
The phosphor samples Y₀.⁹₅₋ₓLaxVO₄:0.₀⁵Eu³⁺ (0 ≤ x ≤ 0.₁₅) were synthesized using a mild hydrothermal method. The starting materials were high purity Y₂O₃ (99.99%), La₂O₃ (99.99%), Eu₂O₃ (99.99%), and V₂O₅ (99%). Y₂O₃, La₂O₃ and Eu₂O₃ were entirely dissolved in nitric acid, and V₂O₅ was entirely dissolved in hydrochloric acid, obtaining a clear starting mixed solution by mixing the two solutions. The final pH value of the mixed solution was 7 through adding ammonia into the solution under vigorous stirring. Then, the mixture was transferred into a Teflon-lined stainless steel autoclave with a filling capacity of 40% distilled water. The hydrothermal reaction lasted 10 h at 200°C. Finally, the autoclave was cooled naturally and the product was filtered and dried in air.

The phase of synthesized phosphors were identified using a Rigaku D/max-2400 X-ray diffractometer with Ni-filtered Cu Kα (λ = 1.54178Å) radiation and the morphology and microstructure were observed by scanning electronic microscope (SEM, Hitachis-4800). The UV emission and excitation spectra were measured using an Edinburgh Instruments FLS920T. The VUV emission and excitation spectra were measured by the vacuum monochromator (VM504, Acton Research Corporation, ARC), and the VUV excitation spectra were corrected by dividing the excitation intensity of sodium salicylate. All the measurement conditions were at temperature.

3. Results and discussion
3.1. The crystal phase and SEM micrograph of Y₀.⁹₅₋ₓLaxVO₄:0.₀⁵Eu³⁺ (0 ≤ x ≤ 0.₁₅) phosphors

Figure 1 showed the crystal phase of hydrothermal (HT) Y₀.⁹₅₋ₓLaxVO₄:0.₀⁵Eu³⁺ (0 ≤ x ≤ 0.₁₅) phosphors and solid-state reaction (SR) Y₀.⁹₅VO₄:0.₀⁵Eu³⁺. Except for Y₀.₈La₀.₁₅VO₄:0.₀⁵Eu³⁺ with some small
peaks signed by symbol ‘*’, all the patterns of HT Y_{0.95}La_{0.05}VO_{4}:0.05Eu^{3+} and SR Y_{0.95}VO_{4}:0.05Eu^{3+} were consistent with a pure tetragonal phase YVO_{4} (JCPDS No. 17-0341). Compared with SR Y_{0.95}VO_{4}:0.05Eu^{3+}, the broadening of the peaks were obviously observed. SEM micrograph of Y_{0.90}V_{0.05}O_{4}:5%Eu^{3+} phosphor particles prepared by HT method was given in figure 2. From the figure, it can be seen that the particles have a narrow size distribution with a slight agglomerate phenomenon, and the particles showed spherical-like shape and their main size distribution was around 40nm.

3.2. PL properties of (Y, La)VO_{4}:Eu^{3+} phosphors

![Figure 3](image-url)

**Figure 3.** UV excitation spectra of (a) Y_{0.95}VO_{4}:5%Eu and (b) Y_{0.925}La_{0.025}VO_{4}:5%Eu, and the UV excitation spectra in 350-400nm regions is magnified in the insert.

Figure 3 gave the UV excitation spectra of Y_{0.925}La_{0.025}VO_{4}:5%Eu and Y_{0.95}VO_{4}:5%Eu^{3+}. The UV excitation spectra monitored by Eu^{3+} 5D_{0}–7F_{2} at 619nm showed a broad band with the maxima at about 260nm and some sharp lines in the longer wavelength region. Below 350nm, the peaks ranging from 200 to 350nm were assigned to the overlap of VO_{4}^{3-} absorption and Eu^{3+}–O^{2-} charge transfer, the former was ascribed to a charge transfer from the oxygen ligands to the central vanadium atom inside the VO_{4}^{2-} group, which agreed well with Ref. [16-18]. The sharp lines in the longer wavelength region were due to the f–f transitions within 4f^{6} configuration of Eu^{3+}. Among them, the peak at 398nm with 7F_{0}–5L_{6} transition was most prominent, which accorded with previous report [19]. With the mol concentration of La^{3+} ranging from 0.025 to 0.15, the UV excitation spectra were similar to each other. It was observed that the peaks at about 260nm have improved with the introduction of La^{3+}. In Wang et al.’s work [15], the (Y, Ln)BO_{3}:Eu^{3+} (Ln=Sc^{3+}, Bi^{3+}, La^{3+}) phosphors were synthesized and the reasons of enhanced photoluminescence of YBO_{3}:Eu^{3+} were explained. The possible reason of the enhancement might be the different charge-to-radius ratio between Y^{3+} and La^{3+}. The charge-to-radius ratio of La^{3+} was smaller than that of Y^{3+}, when La^{3+} was substituted into the Y^{3+} site in the lattice, the tight binding of the oxygen electrons toward Y^{3+} was expected to be leased. Thus, the Eu^{3+}–O^{2-} CT band was enhanced.
Figure 4 showed the emission spectra of $Y_{0.95}V_2O_4:5\%Eu^{3+}$ and $Y_{0.925}La_{0.025}V_2O_4:5\%Eu^{3+}$ samples under 254nm excitation. The samples exhibited strong red luminescence. The emission spectra contained exclusively the characteristic emission of Eu$^{3+}$, namely, the $5D_0-7F_1$ (594nm), $5D_0-7F_2$ (609nm, 615nm, 619 nm), $5D_0-7F_3$ (654nm), and $5D_0-7F_4$ (697nm and 700nm), respectively. The emission spectra were dominated by the Eu$^{3+}$ $5D_0-7F_2$ hypersensitive electric-dipole transition with the sharp peaks at 615nm and 619nm, which was due to the low symmetry local site of Eu$^{3+}$ in the YVO$_4$ host lattices [20, 21]. Also, the dependence of the emission intensity of Eu$^{3+}$ varied with the concentration of La$^{3+}$. The results were shown in figure 5, which was the curve of the $5D_0-7F_2$ emission of Eu$^{3+}$ at 619nm upon the doping concentration in crystalline $Y_{0.95-x}La_xVO_4:5\%Eu^{3+}$. It was found that the emission intensity of Eu$^{3+}$ first increased with increasing the concentration of La$^{3+}$, reaching a maximum at $x=2.5$ mol%, then decreased with the doping concentrations. Thus the optimum emission intensity was obtained by substitution of 2.5mol % La$^{3+}$ for Y$^{3+}$ sites.

Monitoring by 619 nm emission, the VUV excitation spectra of $Y_{0.95}V_2O_4:5\%Eu^{3+}$ and $Y_{0.925}La_{0.025}V_2O_4:5\%Eu^{3+}$ were shown in figure 6. The excitation spectra were similar. Below 200 nm, the excitation spectra had a broad band with the maxima at about 156 nm. The strong broad band at about 156nm could be assigned to be the host absorption band. Also, the broad band centred at 157 and 173nm was assigned to host absorption in LaVO$_4$/Eu$^{3+}$ [22]. Above 200nm, the result was similar to the UV excitation spectra discussed above. In 100-200nm regions, the peaks at about 200nm improved with the incorporation of La$^{3+}$. This may be the absorption of La-O at about 200nm, which is consistent with Ref. [23].
Figure 6. VUV excitation spectrum of $Y_{0.95}VO_4:5\%Eu^{3+}$ (a) and $Y_{0.925}La_{0.025}VO_4:5\%Eu^{3+}$ (b).

Figure 7. Emission spectra of (a) $Y_{0.95}VO_4:5\%Eu^{3+}$ and (b) $Y_{0.925}La_{0.025}VO_4:5\%Eu^{3+}$.

Figure 8. The emission intensity of Eu$^{3+}$ at different concentrations under 147 excitation.

Figure 7 showed the emission spectra of $Y_{0.95}VO_4:5\%Eu^{3+}$ and $Y_{0.925}La_{0.025}VO_4:5\%Eu^{3+}$ samples under 147nm excitation, and the emission spectra consisted with the characteristic emission of Eu$^{3+}$ discussed above. Figure 8 gave the emission intensity of Eu$^{3+}$ at 619nm at different La$^{3+}$ concentrations, the optimum emission intensity was also at x=2.5 mol%, and the commission international declared standards (CIE) chromaticity coordinations were calculated to be (0.671, 0.329) closing to the standard of the National Television System Committee (NTSC), which defines CIE color chromaticity coordinations as (0.67, 0.33). In addition, the enhancement may result from the
contribution of La$^{3+}$ which played an intermediate role in the energy transfer process from HA band to Eu$^{3+}$, the further study need to go on.

4. Conclusions
In summary, La$^{3+}$ doped YVO$_4$:Eu$^{3+}$ phosphors had been successfully synthesized at 200°C through a hydrothermal process without further calcining treatment. SEM image observations showed that these phosphors are nanoparticles with the average size of 40nm. Their PL properties were investigated in UV/VUV region, respectively. In the excitation spectra, the broad band at about 156 nm was assigned to the host absorption band, and the peaks ranging from 200 to 350nm were assigned to the absorption of VO$_4^{3-}$ and Eu$^{3+}$–O$^{2-}$ charge transfer. The strongest emission peak of Y$_{0.95-x}$La$_x$VO$_4$:0.05Eu$^{3+}$ was observed at about 619nm, and the optimum emission intensity was at x=2.5 mol%.

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