New synthesis technology for high efficiency
Eu:YV$_{1-x}$P$_x$O$_4$ nanophosphor

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Highly efficient Eu:YV$_{1-x}$P$_x$O$_4$ phosphor particles, $\sim$200 nm in size, were synthesized using a new synthesis technique. The resulting particles exhibited higher photoluminescence efficiency than the micron-sized commercial sample, highlighting their high quality. To the best of our knowledge, such high efficiency has not been achieved without a surface and heat treatments. In addition to the photoluminescence spectrum, high resolution transmission electron microscopy (HRTEM) demonstrated perfect crystallinity with clear lattice fringes.

Key-words : Asymmetry ratio, Structural distortion, Local environment of Eu$^{3+}$ ion

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1. Introduction

The current advances in information display technology have led to increases in the demand for luminescent materials with improved characteristics. In particular, rare earth-doped phosphors exhibit interesting spectral properties with a size reduction. Nowadays, the size of commercial phosphors is in the micrometer range and there is significant expectation of superior performance using nanosized phosphors to replace the existing commercial ones. The significance of the particle size for panel efficiency was discussed by Justel and Nikol.1 They highlighted the particle size dependence on the brightness, resolution and maintenance. Cho et al. also reported the particle size dependent display panel efficiency.2 In this concern, various attempts have been made to prepare nanosized phosphor particles with a controlled size and shape. Although hydrothermal methods appear to be a promising approach, the lower quantum efficiency and significant aggregation are a limitation to their industrial applications.3 Recently, Kakihana’s group successfully synthesized high efficient YVO$_4$:Eu red emitting phosphor particles ranging in size from $\sim$30 to $\sim$250 nm using a polymerizable complex (PC) method. According to their report, although, the photoluminescence intensity of the as-grown particles was improved at least 3 fold by a subsequent heat treatment the PC method is not suitable for mass production due to the polyesterification process.4 This paper presents synthesis of high efficient nano Eu:YV$_{1-x}$P$_x$O$_4$ phosphor by LPP process in which cellulose is used as a template. The use of cellulose pulp brings many advantages such as; distinct porous structure of cellulose fibrils may allow the physical absorption of the metal ion contained in solution into the cellulose inner space. The presence of abundant of functional groups on the cellulose chain enables immobilization of metal ions via electrostatic (ion-dipole) interactions between electron-rich oxygen atoms of the polar hydroxyl groups and electropositive metal ions, thus reducing segregations of particular metal ions. This makes cellulose a promising material to be used for preparation of multi-component materials with compositional homogeneity.5 In addition, the cellulose pulp can enable application of high synthesis temperature as it is more stable than other polymer complex resulting in higher crystallinity and purity without aggregation. On the other hand, we performed a rapid heating process. It is believed that this rapid heating process enhanced the particle crystallinity, particularly at the surface since each particle was individually surrounded by high carbon containing cellulose structure and during the burning of this structure released extra thermal energy may enhanced particle surface smoothness and crystallinity. Furthermore, since the cellulose is inexpensive raw material, new synthesis technique will be a general and powerful tool for the preparation of nano phosphors for display and fluorescent lamp applications.

As usual, two competitive effects, radiative and nonradiative recombinations, determine the efficiency of phosphors. On one hand an increase of the europium concentration improves the probability of energy transfers to europium and thus radiative recombination. But on the other hand, there is also an increase of the probability of energy transfer between europium ions which leads to nonradiative recombination. In addition, it was reported that by partial replacement of VO$_4^{3-}$ ions with PO$_4^{3-}$ ions, a new series of yttrium phosphate–vanadates (YV$_{1-x}$P$_x$O$_4$) have emerged with better luminescent properties.6 Thus, by varying the concentration of each component one can specify the optimum composition for high efficiency.

This paper reports the synthesis of high efficient Y(P,V)O$_4$:Eu, which is one of the most important red emitting phosphors in fluorescent lamp and display applications.7 The diversity of this study comes from the high luminescence efficiency of the resulting nanoparticles (approximately 100.5% compared to the micron size commercial sample). To the best of our knowledge, there are no reports of the achievement of such a high efficiency without any surface or heat treatments. This approach may offer a practical way of eliminating surface defects caused mostly by adsorbed chemical species or low crystallinity.

2. Experimental

The synthesis of YPV:Eu nanophosphors was achieved using a liquid phase precursor (LPP) method.8 Raw materials; (VO(SO$_3$)$_3$)}
\( n\text{H}_2\text{O}, \geq 99.9\%) \), phosphoric (\( \text{H}_3\text{PO}_4, 99.9\% \)), yttrium chloride (\( \text{YCl}_3 \cdot 6\text{H}_2\text{O}, \geq 99.9\% \)) and europium chloride (\( \text{EuCl}_3 \cdot 6\text{H}_2\text{O}, \geq 99.9\% \)) were dissolved in deionized water. Aqueous solutions of those metal salts were mixed according to a predetermined molar ratio of \( \text{Eu:YV}_{1-x}\text{P}_x\text{O}_4 \) and 100 g of cellulose pulp was impregnated into 100 ml of the resulting mixture solution. The impregnated pulp was dried at 80°C in a dry oven, and then rapidly calcined at 800°C for two hours to remove the cellulose template. Finally, the calcined powder was heated from room temperature to 1150°C at a heating rate of 200°C h\(^{-1}\) in air.

The excitation and emission spectrum was measured at room temperature using a xenon lamp (500 W) as the source of the PL spectrophotometer (PLE/PL Drasa PRO 5300, Korea) over the range 220–450 and 350–700 nm, respectively. The crystallinity and phases purity of the synthesized samples was analysed by powder X-ray diffraction (Rigaku) with CuK\(\alpha\) radiation (\( \lambda = 0.15406 \text{nm} \)) operating at 40 kV - 30 mA at a scanning rate 2\(\theta\)/min in the 2\(\theta\) range of 15–80. The elemental content was analyzed by inductively coupled plasma atomic emission spectrometer (Perkin-Elmer Optima 3000 DV ICP-AES). The surface morphology and crystallinity of the resulting particles were observed by scanning electron microscopy (FESEM, XL-30, Philips) and high resolution transmission electron microscopy (HR-TEM, JEOL 300 kV).

3. Results and discussion

Field emission scanning electron microscopy (FESEM) was used to examine the morphology and particle size of the sample and commercial product. In the case of the present sample, the particles were spherical in shape and \( \sim 200 \text{nm} \) in size. In contrast, the commercial product showed large irregular shaped particles, \( \sim 5-7 \mu\text{m} \) in size (Fig. 1(a, b)).

Figure 2 shows HRTEM micrographs of \( \text{Eu:YV}_{1-x}\text{P}_x\text{O}_4 \) sample revealing smooth surface and perfect crystalline structure with well defined lattice fringes (Fig. 2(a, b)).

The XRD patterns of the present sample (Fig. 3) showed a pure tetragonal xenotime phase was obtained and all recorded peaks were between the standard \( \text{YVO}_4 \) (JCPDS, 72-0274) and \( \text{YPO}_4 \) (JCPDS, 11-0254) pattern, agreeing with the Vegard law.\(^7\)

ICP analyses resulted in 9.1% Eu, 11% P, 17.5% V and 62.5 Y in weight percent. Atomic weight percent of each component was calculated and resulting composition was determined as \( \text{Y}_{0.99}\text{P}_{0.50}\text{V}_{0.484}\text{O}_4:\text{Eu}_{0.085}\). Although the composition described according to ICP result seem nonstoichiometric, it is very difficult to clarify the composition truly because a probable sort of impurity phase cannot be seen in the XRD pattern. On the other hand, it is expected that ICP analysis may usually involve some errors.

Figure 4 shows the excitation (\( \lambda_{\text{exc}} = 618 \text{nm} \)) and emission spectra (\( \lambda_{\text{exc}} = 254 \text{nm} \)) of the Eu:YV\(_{1-x}\)P\(_x\)O\(_4\) samples. In these figures, the luminescence intensities were normalized with respect to the micron sized commercial product. The excitation spectrum exhibited a broad band extending from 225–350 nm, corresponding to the charge transfer from oxygen ligands to the central vanadium atom inside the VO\(^{4+}\) group ions and weak bands at 380 and 395 nm in the longer wavelength region, originating from the f–f transitions of the Eu\(^{3+}\) ions (Fig. 4(a)). The intensity of those latter peaks was weak because of multiphonon relaxations.\(^8\) The emission spectra consisted three peaks assigned to \( ^{3}\text{D}_0\rightarrow^{2}\text{F}_1 \) magnetic dipole transitions and \( ^{3}\text{D}_0\rightarrow^{2}\text{F}_2,4 \) forced electric dipole transitions (Fig. 4(b)).

![Fig. 1. FE-SEM images of the YPV(LPP) samples and commercial product.](image1.png)

![Fig. 2. HR-TEM observations of the YPV(LPP) samples (a) surface state and (b) lattice structure.](image2.png)
The present sample exhibited \( \sim 100\% \) emission intensity at 621 nm compared to the micron-sized commercial product without line broadening. According to Judd–Ofelt theory, as the intensity of transitions different J-number levels depends on the local environment of europium ion the more insight into possible structural change surrounding \( \text{Eu}^{3+} \) ion could be gained by considering the ratios of the integrated intensities of \( ^5D_0-^7F_2 \) and \( ^5D_0-^7F_1 \) transitions. This ratio is called as asymmetry ratio since \( ^5D_0-^7F_2 \) electric dipole transitions are very sensitive the asymmetry of the coordination polyhedron of \( \text{Eu}^{3+} \) ion.\(^{9,12}\)

Table 1 shows the calculated asymmetry ratios \((R)\) of the micron sized commercial product, the present sample and previous work.\(^4\) The size of present sample is at least ten times smaller than that of commercial product. It was expected that the differences in particle size may induce changes in crystal field experienced by \( \text{Eu}^{3+} \) ions as a large fraction of \( \text{Eu}^{3+} \) ions would reside on or toward the surface of nanoparticles.\(^{12}\) However, the \( R \) value of the present sample is comparable to that of commercial product. In the case of previous work, the \( R \) value is \( \sim 2 \) fold larger indicating the higher asymmetry of \( \text{Eu}^{3+} \) ions due to structural distortions. On the other hand, even if present sample has distorted structure due to size matter, a line broadening should appear on the luminescence spectrum.\(^9\) Those results suggest that the present sample exhibits high crystallinity and less structural distortions as a consequence of high synthesis temperature. In addition, a large fraction of \( \text{Eu}^{3+} \) ions on surface is known as luminescence quencher. Therefore, it is expected that extra thermal energy released during the burning of cellulose may be enhanced the incorporation of \( \text{Eu}^{3+} \) ions into the inner shell of the particle surface.

### 4. Conclusion

In this paper, \( \text{Eu}^{3+} \)-doped \( \text{Eu}:\text{Y}_{1-x} \text{P}_{x} \text{O}_4 \) nanophosphor particles, \( \sim 200 \text{nm} \) in size, were obtained at \( 1150°C \) using cellulose pulp. Strong \( ^5D_{0}^2^7F_2 \) emission of \( \text{Eu}^{3+} \) ions was observed at 621 nm, and its intensity was \( \sim 100\% \) of the commercial product. The comparable asymmetry ratios \((R)\) and the absence of line broadening on the luminescence spectrum indicated less structural distortion and high crystallinity of the present sample.

### References