Luminescence and structural properties of self-assembled Y(V,P)O₄:Eu³⁺@amorphous-K-VO₃ core/shell nanophosphors

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A Liquid-Phase Precursor method followed by a 5% KOH solution treatment was employed for the facile synthesis of Y(V,P)O₄:Eu³⁺@amorphous-K-VO₃ core/shell nanophosphors with non-stoichiometric composition Yₓ(V₀.₄₄P₀.₅₆)O₄:Euₙₓ₋₁ (x = 0.855, 0.875, 0.90 and 0.965). It was observed that this non-stoichiometric composition approach leads to the control of the size, shape and unit cell parameters depending upon the Y concentration. The shell layer of 2–7 nm formed by alkaline solution treatment at room-temperature was observed by Transmission Electron Microscope (TEM). The particle size grew up by 20–50 nm and the luminescence properties were enhanced by 9–31% after the KOH solution treatment. In contrast, the micro-sized Y(V,P)O₄:Eu³⁺ phosphors treated by the KOH solution did not show any change in their luminescence properties. This KOH solution treatment opens new possibilities to facilely synthesize Y(V,P)O₄:Eu³⁺@amorphous-K-VO₃ core/shell nanophosphors with highly stable properties and improved luminescence.

Key-words : Nanophosphors, Nanoparticle, Surface treatment, Core/shell

1. Introduction

During last two centuries, vanadium materials have been widely used in structural, mechanical, optical, electro-optical, catalysis and biological applications, since vanadium doped materials show superior properties in strength, durability, thermal stability and chemical resistance. However, the electro-optical properties of the nanostructured vanadium oxide materials are degraded after long-term exposure to humid environments. Especially, the humidity reacts easily within the surface of vanadium materials, and then the properties are quenched due to the presence of –OH groups on the surface. Therefore, it is very important to form a passivation layer for the vanadium oxide materials to protect them from the effect of humid conditions.

In this work, we have focused on the synthesis of vanadium oxide based Y(V,P)O₄:Eu³⁺ nanophosphors due to their facile application into devices excited with UV lights of the wavelengths (254 and 365 nm) such as cold cathode luminescence lamps, plasma display panels and lighting electron devices. It is well known that nanoscale materials exhibit interesting electrical, optical, chemical and magnetic properties that are quite different from their bulk counterparts. In this sense, size controlled synthesis is of key importance because the optimization of material size may expand their areas of application. For example, the single crystal orthovanadates can be applied as a host crystal to solid state lasers and there is also possibility of some special applications in bio-imaging and biosensors by reducing the particle size.1,2) However, the electro-optical properties of the nanostructured vanadium oxide materials are degraded after long-term exposure to humid environments. Especially, the humidity reacts easily within the surface of vanadium materials, and then the properties are quenched due to the presence of –OH groups on the surface. Therefore, it is very important to form a passivation layer for the vanadium oxide materials to protect them from the effect of humid conditions.

2. Experimental procedure

2.1 Synthesis of Y(P,V)O₄:Eu³⁺ nanophosphors by using LPP method

A liquid phase precursor (LPP) method was used for the synthesis of 5g Yₓ(V₀.₄₄P₀.₅₆)O₄:Euₙₓ₋₁ (x = 0.855, 0.875, 0.90 and 0.965) nanophosphors with non-stoichiometric composition...
tion.\textsuperscript{13}) The raw materials vanadium oxide sulphate [VO(SO\textsubscript{4})\textsubscript{2}·nH\textsubscript{2}O, \(n\geq 99.9\%\)], phosphoric acid (H\textsubscript{3}PO\textsubscript{4}, 85\%), yttrium chloride (YCl\textsubscript{3}·6H\textsubscript{2}O, \(99.9\%\)) and europium chloride (EuCl\textsubscript{3}·6H\textsubscript{2}O, \(99.9\%\)) were dissolved in deionized water in the weight ratio of 50, 50, 50 and 30 wt\%, respectively. These starting solutions were mixed together in terms of the molar ratio of Y\textsubscript{2}(V\textsubscript{0.44}P\textsubscript{0.56})O\textsubscript{4}:Eu\textsubscript{0.1} (\(x = 0.855, 0.875, 0.90, 0.965\)) compositions. Then these four groups of mixed solutions were impregnated into cellulose pulps of identical weight. The impregnated precursors were dried at 80\(^\circ\)C in a dry oven, and calcined for 2h at 800\(^\circ\)C to remove the cellulose template. Subsequently, the calcined powders were heated for 2h from room temperature to 1100\(^\circ\)C at a heating rate of 200\(^\circ\)C h\textsuperscript{-1} in air to obtain the required nanophosphors.

### 2.2 Synthesis of Y(V,P)O\textsubscript{4}:Eu\textsuperscript{3+}@amorphous-K-VO\textsubscript{3} core/shell nanophosphors by KOH solution treatment

The core–shell nanophosphors were synthesized by using KOH solution treatment. The raw phosphor powders obtained at 1100\(^\circ\)C were dispersed in a 5% KOH solution for 24h at room temperature, and the treated phosphor powders were separated by centrifugation using deionized water for two times. Then the obtained wet phosphor powders were dried at 80\(^\circ\)C for 10h. The ratio of KOH solution and the raw phosphor powders taken for the solution treatment was 100 ml/g.

### 2.3 Characterization techniques

An inductively coupled plasma (ICP) emission spectroscopy (Perkin-Elmer Optima 5300 DV ICP-OES) was used for the elemental analysis of the obtained phosphor samples and the solution separated after KOH treatment. Powder X-ray diffractometer (XRD, Cu K\textalpha, 30 kV, 100 mA, Rigaku) was utilized for the evaluation of crystalline phases. The surface morphology and crystallinity of the samples were observed by field emission scanning electron microscopy (FE-SEM, XL-30, Philips) and high resolution transmission electron microscopy (HR-TEM, JEOL 3000 kV). The average particle size of the nanophosphors after KOH solution treatment was measured by BET surface area analysis. The zeta potential measurements were performed on the obtained Y(V,P)O\textsubscript{4}:Eu\textsuperscript{3+} phosphors using a Zetasizer Nano-ZS (Malvern Instruments, Malvern, UK).

The emission and excitation spectra of the obtained samples were measured using a photoluminescence spectrophotometer (PL, Drasa PRO 5300, Korea) with a xenon lamp (500 W). X-ray photoelectron spectra (XPS) were analysed with 5-channeltron detection system equipped with a Al K\textalpha radiation (1486.6 eV) X-ray, at a pass energy of 20 eV in ~3 × 10\textsuperscript{-10} Torr. All the characterization measurements were carried out at room temperature. Micrograin-sized commercial phosphor was used for the comparative studies.

### 3. Results

#### 3.1 Synthesis mechanism of Y(V,P)O\textsubscript{4}:Eu\textsuperscript{3+}@amorphous-K-VO\textsubscript{3} core/shell structures by alkali-metal solution

First, we synthesized four phosphor samples, Y\textsubscript{2}(V\textsubscript{0.44}P\textsubscript{0.56})O\textsubscript{4}:Eu\textsubscript{0.1} (\(x = 0.855, 0.875, 0.90, 0.965\)) depending on yttrium composition. The samples (\(x = 0.855, 0.875, 0.90, 0.965\)) were named as S1, S2, S3 and S4 according to their composition. The synthesis of Y(V,P)O\textsubscript{4}:Eu\textsuperscript{3+}@amorphous-K-VO\textsubscript{3} core/shell structures is based on the mechanism of vanadium oxide (V\textsubscript{2}O\textsubscript{5}) dissolving in alkali metal solutions. In this process, some of the impurities on the surface of vanadium contained compounds were removed and phosphor particles became smooth and larger after KOH solution treatment at room temperature. This interesting phenomenon appears to originate from Ostwald ripening effect, which is simply schematized in Fig. 1. This phenomenon occurs due to the fact that vanadium oxide was dissolved in water and alkali water, and transformed to vanadate ions (VO\textsubscript{4}\textsuperscript{3-}). Therefore the solution treatments are very suitable for the synthesis of vanadium based oxide phosphors by dissolving the unreactive vanadates. However, the effect of KOH solution treatment differs on the surface of the phosphor particle treated with water or ammonia water. When the Y(V,P)O\textsubscript{4}:Eu\textsuperscript{3+} particles were dispersed in KOH solution, the vanadate ions were dissociated from the particles and form a thin layer surrounding the phosphor particles (cores) with ionic interactions of K\textsuperscript{+} ions due to the negative potential at the surface of the particle.\textsuperscript{14) Subsequently the K\textsuperscript{+} ions were absorbed by this VO\textsubscript{4}\textsuperscript{3-} layer and form a new shell after the initial shell with electrostatic interactions as following:

\[
(Y, Eu)(V, P)O_4(x/1/2 V_2O_5) + xKOH \rightarrow (Y, Eu)(V, P)O_4@amorphous-xK-VO_3 ↓ + x/1/2 H_2O
\]

The excess vanadium oxide (\(xV_2O_5\)) existed as impurities on the surface of Y(V,P)O\textsubscript{4}:Eu\textsuperscript{3+} phosphor and they easily react with water or base solution. By KOH solution treatment, these two types of layers composed of K\textsuperscript{+} and VO\textsubscript{4}\textsuperscript{3-} are attached on the particle surface alternatively and finally formed a shell. As we can see from the HR-TEM images in Figs. 2(d) and 2(h), the shell layer was amorphous. But a weak recrystallization bonding
The bonding is relatively stable through electrostatic interactions. Furthermore, this simple phenomenon almost did not influence on the final composition of Y(V,P)O₄:Eu³⁺ phosphor according to ICP analyses for S₃ sample in Table 1, which suggested almost all the dissociated VO₄³⁻ ligands were adsorbed on the particle surface and so there was little elemental loss in the phosphor composition. On the other hand, the particle growth of the Y(V,P)O₄:Eu³⁺ nanocrystals in the KOH solution was also supposed to follow an Ostwald ripening process, in which the small particles are attached and redeposit on the large particles. As a result, the phosphor particle size was increased after the KOH treatment including the commercial Y(V,P)O₄:Eu³⁺ phosphor powders on body colour, crystal size and crystal structure.

**Table 1.** ICP analyses of Y₀.⁹₅(V₀.₄₄P₀.₅₆)O₄:Eu₀.₁ phosphor powder (sample S₃) powder before and after KOH solution treatment

| Atoms          | Y   | V   | P   | Eu  |
|---------------|-----|-----|-----|-----|
| Before treatment (mol) | 0.90 | 0.44 | 0.57 | 0.09 |
| After treatment (mol)    | 0.90 | 0.43 | 0.55 | 0.09 |

K-VO₃ shell obtained by KOH solution treatment might have contributed to the non-polarized surface of materials. These results showed that the obtained core–shell structures are very stable.

**Table 2.** Zeta potential analyses of Y₀.⁹₅(V₀.₄₄P₀.₅₆)O₄:Eu₀.₁ (x = 0.855; S₁, 0.875; S₂, 0.90; S₃ and 0.965; S₄) phosphor powders before and after KOH solution treatment

| Sample | Zeta [mV] | KOH treatment |
|--------|-----------|---------------|
| S₁     | −9.45     | −10.02        |
| S₂     | −9.45     | −10.02        |
| S₃     | −9.45     | −10.02        |
| S₄     | −9.45     | −10.02        |

**Figure 3** showed the FE-SEM images of all the samples including the commercial Y(V,P)O₄:Eu³⁺ phosphor powders. The synthesized phosphors were found to be both spherical- and rod-shaped particles with nanoscale size and uniform size distribution. The commercial phosphors showed rod-shaped particles with size 3–5 μm. After KOH solution treatment, a larger size and smoother surface were found in all the synthesized particles. The smooth surface shows that particle grow up by 20–50 nm due to agglomeration after KOH solution treatment. The results were similar to our previously reported work of Y(V,P)O₄:Eu³⁺ phosphors synthesized at 600–800°C. Similarly, the micro-grain-sized commercial particles showed a big smooth surface after the KOH solution treatment. The SEM observation of the Y₀.⁹₅(V₀.₄₄P₀.₅₆)O₄:Eu₀.₁ (x = 0.855, 0.875, 0.90 and 0.965) phosphor particles before solution treatment shows rod- and spherical-shaped particles with increasing x value. **Figure 4** shows the variation of mean particle size after the KOH solution treated phosphor samples. The mean particle size was found to be 472, 243, 161 and 106 nm for the untreated phosphors samples with x = 0.855, 0.875, 0.90 and 0.965, respectively. It was observed that the particle size increased after the KOH solution treatment for all the samples.

The crystal structure and crystalline quality of the obtained samples are analyzed by using XRD measurements. The XRD
patterns for all the samples are shown in Fig. 5(a). The XRD patterns of $Y(V,P)O_4:Eu^{3+}$ crystal is normally composed of the characteristic peaks of both YVO$_4$ and YPO$_4$ phases. The XRD patterns of all the phosphor samples matched well with the standard $Y(V,P)O_4:Eu^{3+}$ crystal. With the decrease of $Y^{3+}$ ions concentration, the intensity of their peaks was found to be increased. The position of the major peaks of the samples was shifted slightly. The (200) peak moved slightly towards small 2$\theta$ values with increasing yttrium concentration as shown in Fig. 5(b). In addition, XRD peaks of S4-2 sample were slightly shifted to larger 2$\theta$ values after KOH solution treatment. It might be because of the fact that the YVO$_4$ crystal phase of $Y(V,P)O_4$: Eu$^{3+}$ phosphor can be dissolved and induce some damages at the surface of nanoparticle by 5% KOH solution treatment. The $Y^{3+}$ ions concentration of $Y(V_0.44P_0.56)O_4:Eu^{3+}$ phosphor has also influenced on the unit cell volume as shown in Fig. 5(c). The unit cell volume increased from 302.71 to 303.78 $\text{Å}^3$ with increasing $Y^{3+}$ ions concentration. The XRD analysis of our phosphor samples showed that the composition and crystallinity of all the samples were not much changed by the KOH solution treatment, suggesting that the reaction didn’t occur inside the bulk of the powder.

### 3.3 Characterization and luminescence behaviour of $Y(V,P)O_4:Eu^{3+}$@amorphous-K-VO$_3$ core/shell composite phosphors

The chemical composition (ionic state of the elements) for the S1 sample were measured by XPS analysis as shown in Fig. 6(a). The ionic state of the elements was $V^{4+}$ (516.91 eV, 2$p_{3/2}$), $V^{5+}$ (517.6 eV, 2$p_{3/2}$), $P^{5+}$ (133.34 eV, 2$p_{3/2}$), $Y^{3+}$ (157.44 eV, 3$d_{3/2}$), and $Eu^{3+}$ (1134.15 eV, 3$d_{3/2}$) after 5% KOH solution treatment. There was not much difference in binding energy in comparison with the untreated sample except on $V^{4+}$, $K^+$. The binding energy curves of vanadium ions were found to overlap between $V^{4+}$ and $V^{5+}$ chemical compositions as shown in Fig. 6(b). The appearance of $V^{4+}$ and $K^+$ peaks indicates that the shell is consisted with K-VO$_3$ on the surface of $Y(V,P)O_4:Eu^{3+}$ crystal. Figure 6(c) showed the binding energy of metal oxide O 1$s$ (530.84 eV) and this indicates that metal hydroxyl group bond is formed. The removal of this hydroxyl group bond leads to the formation of K-VO$_3$ crystal before KOH solution treatment and a metal oxide bond (530.29 eV) was detected in surface of $Y(V,P)O_4:Eu^{3+}$ crystal. With the decrease of $Y^{3+}$ ions concentration, the intensity of their peaks was found to be increased. The position of the major peaks of the samples was shifted slightly. The (200) peak moved slightly towards small 2$\theta$ values with increasing yttrium concentration as shown in Fig. 5(b). In addition, XRD peaks of S4-2 sample were slightly shifted to larger 2$\theta$ values after KOH solution treatment. It might be because of the fact that the YVO$_4$ crystal phase of $Y(V,P)O_4$: Eu$^{3+}$ phosphor can be dissolved and induce some damages at the surface of nanoparticle by 5% KOH solution treatment. The $Y^{3+}$ ions concentration of $Y(V_0.44P_0.56)O_4:Eu^{3+}$ phosphor has also influenced on the unit cell volume as shown in Fig. 5(c). The unit cell volume increased from 302.71 to 303.78 $\text{Å}^3$ with increasing $Y^{3+}$ ions concentration. The XRD analysis of our phosphor samples showed that the composition and crystallinity of all the samples were not much changed by the KOH solution treatment, suggesting that the reaction didn’t occur inside the bulk of the powder.

Figure 7 showed that the excitation ($\lambda_{em} = 621 \text{nm}$) and emission spectrum ($\lambda_{exc} = 254 \text{nm}$) of $Y_2(V_0.44P_0.56)O_4:Eu_{0.1}$ ($x = 0.855$; S1, 0.875; S2, 0.90; S3 and 0.965; S4) samples before the KOH treatment in comparison with the commercial product. The excitation spectrum (inset of Fig. 7) showed a broad band from 225 to 350 nm and a few weak bands in the longer wavelength region. The broadband was assigned to charge transfer from the oxygen ligands to the central vanadium ions inside the VO$_4^{3-}$ ligands, and those weak bands peaking at 381, 395 and 400 nm were attributed to f-f transitions of Eu$^{3+}$ ions. It was reported that the multiphonon relaxation by VO$_4^{3-}$ ions is unable to bridge the gaps between the higher energy levels ($\Delta D_0$, $\Delta D_2$, $\Delta D_3$) and the groundstate $D_0$ level, resulting in weak emissions in these
levels. However, the excitation peak intensity of the commercial sample lies in a similar position as in our obtained phosphor samples, even though its particle size is one order of magnitude larger as shown in Fig. 4. The emission spectra consist of three peaks assigned to $^{5}D_{0} \rightarrow ^{7}F_{1}$ (magnetic dipole transition) $^{5}D_{0} \rightarrow ^{7}F_{2}$ and $^{5}D_{0} \rightarrow ^{7}F_{4}$ (forced electric dipole transitions). The absence of inversion symmetry at the Eu$^{3+}$ lattice site (D$_{2d}$ symmetry) results in a strong luminescence intensity at 621 nm through $^{5}D_{0} \rightarrow ^{7}F_{2}$ transitions. The integrated emission intensities of the $Y_{x}V_{0.44}P_{0.56}O_{4}:Eu^{3+}$ samples showed an increase in PL intensity with decreasing $Y^{3+}$ ions concentration. After the solution treatment, the luminescence peaks from the $^{5}D_{0} \rightarrow ^{7}F_{2}$ transition were enhanced by $\approx 31, \approx 28, \approx 9,$ and $\approx 10\%$ for the samples S1, S2, S3 and S4, respectively (Table 3). The improvement in the luminescence intensity after the KOH solution treatment can be explained by the following:

![Fig. 5.](image1)

(a) The XRD patterns of $Y_{0.855}V_{0.44}P_{0.56}O_{4}:Eu^{3+}$ ($x = 0.855, 0.875, 0.90$ and $0.965$) samples before and after 5% KOH solution treatment (b) (200) peak shift of the phosphors with the solution treatment (c) variation of crystal unit cell volume with $Y^{3+}$ ions concentration.

![Fig. 6.](image2)

XPS analysis of $Y_{0.855}V_{0.44}P_{0.56}O_{4}:Eu^{3+}$ (S1) phosphor before and after KOH solution treatment.
Table 3. The emission intensity of \( \text{Y}_0\text{P}_{0.56}\text{V}_{0.44}\text{O}_4\text{Eu}_{0.1} \) (\( x = 0.855, 0.875, 0.90 \) and 0.965) phosphor samples at 595 and 621 nm corresponding to \( ^5\text{D}_0\rightarrow^7\text{F}_1 \) and \( ^5\text{D}_0\rightarrow^7\text{F}_2 \) transitions. The calculated asymmetry ratios and increments in emission efficiency are also given.

| Sample | \( x \) | \( ^5\text{D}_0\rightarrow^7\text{F}_1 \) (595 nm) | \( ^5\text{D}_0\rightarrow^7\text{F}_2 \) (621 nm) | \( ^5\text{D}_0\rightarrow^7\text{F}_2/\text{D}_0\rightarrow^7\text{F}_1 \) | Efficiency increment |
|--------|------|----------------|----------------|----------------|------------------|
| S1-KOH | 0.855 | 1210           | 5112           | 4.22           | +31%             |
| S2-KOH | 0.875 | 1068           | 4249           | 3.98           | +28%             |
| S3-KOH | 0.90  | 1003           | 4014           | 4.00           | +9%              |
| S4-KOH | 0.965 | 1237           | 5018           | 4.06           | +10%             |
| COM    |      | 1519           | 5433           | 3.58           | -1.4%            |
| COM, KOH | 1495 | 5337           | 3.58           |                |                  |

4. Conclusions

A liquid phase precursor method was used to synthesize \( \text{Y(V,P)}_0\text{O}_4\text{Eu}_{0.1} \) (\( x = 0.855, 0.875, 0.90 \) and 0.965) nanophosphors. Then a simple and facile method of KOH solution treatment was employed to synthesize \( \text{Y(V,P)}_0\text{O}_4\text{Eu}^{3+}\)@amorphous-K-VO\(_3\) core/shell structured phosphors. The KOH solution treatment not only influenced the formation of core–shell structures and they also contributed to the control of size and shape and enhanced luminescence properties of the phosphor particles. A significant grain growth from 20 to 50 nm occurred at room temperature after 5% KOH solution treatment. An increase of 9–31% luminescence efficiency was also observed after the formation of the amorphous K–VO\(_3\) core–shell structure in the phosphor. The core/shell structure is believed to play a role of a passivation layer in preventing impregnated water and humidity into the nanophosphor materials. The luminescence properties of the phosphors treated with various solutions indicates that the treatment with the metal hydroxide (KOH) solution showed better efficiency when compared with the phosphor treated using other solutions. This interesting crystal growth mechanism and core–shell formation opens new possibilities to facilely synthesize highly stable \( \text{Y(V,P)}_0\text{O}_4\text{Eu}^{3+}\)@amorphous-K-VO\(_3\) core/shell phosphors with improved luminescence properties for display and lighting devices.

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