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$\label{eq:content} \begin{array}{l} Effect \ of \ Li \ Content \ on \ The \ Microstructure \ and \\ Photoluminescence \ of \ (Y_{0.5}Gd_{0.5})_{0.94\text{-}x}(V_{0.25}P_{0.75})_{04}\text{:}Eu_{0.06}\text{,}Li_x \\ phosphors \end{array}$

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ABSTRACT

 $(Y_{0.5}Gd_{0.5})_{0.94\cdot x}(V_{0.25}P_{0.75})O_4:Eu_{0.06},Li_x (0 \le x \le 0.02)$ red emitting phosphor powder were synthesized via the solution combustion process and the luminescent intensity under vacuum ultraviolet VUV (147 nm) excitation was investigated by co-doping Li⁺ content, Y/Gd molar ration. According to the X-ray diffraction (XRD) results $(Y_{0.5}Gd_{0.5})_{0.94\cdot x}(V_{0.25}P_{0.75})O_4:Eu_{0.06},Li_x$ phosphors had the tetragonal structure. Photoluminescence (PL) results have shown strongest red emission at 620 nm, which originated from the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu³⁺ ion, for the $(Y_{0.5}Gd_{0.5})_{0.925}(V_{0.25}P_{0.75})O_4:Eu_{0.06},Li_{0.015}$ phosphor. The addition of Li⁺ was greatly improved the photoluminescence properties of $(Y_{0.5}Gd_{0.5})_{0.94}(V_{0.25}P_{0.75})O_4:Eu_{0.06}$ phosphors due to an effective energy transfer between Eu³⁺ ion and Li⁺ ion.

I. INTRODUCTION

Rare-earth activated phosphors have attracted great interest for application to flat panel displays (FPDs) such as plasma display panels (PDPs) and field emission displays (FEDs). Recently, plasma display panels (PDPs) are widely used as flat-panel information-display devices. The three-primary-color based phosphors applied in PDPs are excited by a vacuum ultraviolet (VUV) ray, which is normally generated by the discharge of Ne-Xe gas, to produce the visible light [1]. Lanthanum orthophosphates (LnPO₄: Ln = Y, La, or Gd) are potential phosphors for applications in PDPs because of the high absorption in VUV radiation [2-13]. The lanthanide ions such as Tb³⁺, Eu³⁺, and Pr³⁺ in the orthophosphates offer a high quantum yield of visible luminescence [14]. One major problem with the ions is effective excitation of their high-energy states. The other problem is the fact that activator ions often cannot be excited directly to their bands by available radiation sources. To solve these problems, one effective way is to introduce a sensitizer, e.g., Gd³⁺, which can be excited directly by a radiation source and provides effective

energy transfer to activator ions. The transfer efficiency and luminescence characteristics are influenced by the nature and concentration of activator and sensitizer. In this work, in order to improve photoluminescence (PL) characteristics, we investigated the microstructure and PL properties of $(Y_{0.5}Gd_{0.5})_{0.94-x}Li_x(V_{0.25}P_{0.75})O_4:Eu_{0.06}$ phosphors, fabricated by the solution combustion method, considering the Li⁺ content.

These submicron-sized particles were well dispersed and of uniform morphology. Both luminescence enhancement and quenching effects by the Li^+ co-dopant was observed. The effect of Li^+ co-doping concentrations on the luminescence of $(Y_{0.5}Gd_{0.5})_{0.94}$. ${}_x\text{Li}_x(V_{0.25}P_{0.75})O_4$:Eu_{0.06} was investigated in detail.

II. EXPERIMENTAL

 $(Y_{0.5}Gd_{0.5})_{0.94-x}Li_x(V_{0.25}P_{0.75})O_4$:Eu_{0.06} (*x*=0, 0.005, 0.01, 0.015, and 0.02) powders were synthesized via the solution combustion process, using citric acid $(C_3H_4(OH)(COOH)_3)$ as combustion fuel and its corresponding metal nitrates as oxidizers. The solution

combustion process was effective in synthesizing oxide nanopowders. Y_2O_3 , Gd_2O_3 , and Eu_2O_3 were separately dissolved by HNO₃ to form the Y^{3+} , Gd^{3+} , and Eu^{3+} nitrates. The appropriate amount of $(NH_4)_2HPO_4$, NH_4VO_3 and citric acid was dissolved in deionized water.

The Li^+ nitrate was added into a mixture of the Y^{3+} , Gd^{3+} and Eu³⁺ nitrates and the solution of (NH₄)₂HPO₄ and NH₄VO₃. Subsequently, the obtained solutions were heated slowly on a hot plate until excess free water evaporated to form a highly viscous gel precursor. On further heating, the precursor spontaneously ignited to produce voluminous powder. The powders formed from this process were annealed at 1000 °C for 4 h in air. The crystal structure of the synthesized and annealed $(Y_{0.5}Gd_{0.5})_{0.94-x}Li_x(V_{0.25}P_{0.75})O_4:Eu_{0.06}$ powders was analyzed with an X-ray diffractometer (XRD; Rigaku RINT2000). The morphological characteristics of the powders were investigated with a field emission scanning electron microscope (FE-SEM; Hitachi S4700).

The photoluminescence spectra of the powders were obtained with a spectro-fluorophotometer (PSI) equipped with a D_2 flash lamp. The emission spectra were obtained in the VUV region of 147 nm.

III. RESULTS AND DISCUSSION

XRD pattern and surface morphology of $(Y_{0.5}Gd_{0.5})_{0.94-x}(V_{0.25}P_{0.75})O_4$: Eu_{0.06}, Li_x ($0 \le x \le 0.02$):



Figure 1. XRD patterns (left) and FE-SEM images(right) of the $(Y_{0.5}Gd_{0.5})_{0.94}$ $_xLi_xEu_{0.06}(V_{0.25}P_{0.75})O_4$ with x = (a) 0, (b) 0.01, (c) 0.015, (d) 0.02, and (e) 0.025 phosphors.

Figure 1 (left) shows the XRD pattern of $(Y_{0.5}Gd_{0.5})_{0.94-x}(V_{0.25}P_{0.75})O_4:Eu_{0.06}Li_x$ (0 $\leq x \leq 0.02$) phosphors. $Y_{0.5}Gd_{0.5})_{0.94-x}Li_x(V_{0.25}P_{0.75})O_4:Eu_{0.06}$

phosphors crystallized in the tetragonal structure, belonging to the space group I4 $_1$ /amd [17]. No impurity or unreacted compound peaks were detected. This indicates that the Li⁺ ion had no significant influence on the crystal structure of the host material [17]. The XRD pattern matches well with the JCPDS file no. 17-0260. Morphologies examined by FE-SEM images (fig.1 right) of the $(Y_{0.5}Gd_{0.5})_{0.94-x}(V_{0.25}P_{0.75})O_4:Eu_{0.06},Li_x (0 \le x \le 0.02)$ powder. We prepared phosphor high-quality $(Y_{0.5}Gd_{0.5})_{0.94-x}Li_x(V_{0.25}P_{0.75})O_4:Eu_{0.06}$ phosphor powders, i.e., spherical and regular morphologies as well as smooth surfaces. The size of the annealed phosphor powders increased with an increase in the Li⁺ content. In spite of the annealing treatment, the powders showed high-quality characteristics.

Photoluminescence properties of $(Y_{0.5}Gd_{0.5})_{0.94}$. $_{x}(V_{0.25}P_{0.75})O_{4}:Eu_{0.06},Li_{x} (0 \le x \le 0.02):$



Figure 2. VUV emission spectra of the $(Y_{0.5}Gd_{0.5})_{0.94}$. $_xLi_xEu_{0.06}(V_{0.25}P_{0.75})O_4$ with x = (a) 0, (b) 0.01, (c) 0.015, (d) 0.02, and (e) 0.025 phosphors ($\lambda_{ex} = 147$ nm).



Figure 3. Plot for the emission intensity per Li sensitizer ions as a function of Li concentration

It is known that the luminescence property of phosphor is strongly affected by the concentration of the activator and the luminescence of activator can be improved by the incorporation of suitable sensitizer. Figure 2 shows the emission spectra of the $(Y_{0.5}Gd_{0.5})_{0.94}$ $_{x}Li_{x}Eu_{0.06}(V_{0.25}P_{0.75})O_{4}$ with x = (a) 0, (b) 0.01, (c) 0.015, (d) 0.02, and (e) 0.025 phosphors under an excitation 147 nm. The spectra consist of three strong and sharp peaks at 594, 615 - 620, and 697 - 704 nm. These peaks are assigned to the transitions from the excited ${}^{5}D_{0}$ to ${}^{7}F_{1}$ (i = 1, 2, and 4) of Eu³⁺ activator [18]. The doped Li⁺ leads to a significant increase in the emission intensity.(Y_{0.5}Gd_{0.5})_{0.925}Li_{0.015}(V_{0.25}P_{0.75})O₄:Eu_{0.06} phosphor shows the strongest emission intensity at 615 -620 The of nm. intensity $(Y_{0.5}Gd_{0.5})_{0.925}Li_{0.015}(V_{0.25}P_{0.75})O_4:Eu_{0.06}$ phosphor is stronger than that of $(Y_{0.5}Gd_{0.5})_{0.94}(V_{0.25}P_{0.75})O_4:Eu_{0.06}$ phosphor by 122%. The luminescence enhancement of $(Y_{0.5}Gd_{0.5})_{0.94-x}Li_xEu_{0.06}(V_{0.25}P_{0.75})O_4$ is occurred due to the effective energy transfer from Li⁺ ion to Eu³⁺ under an excitation of 147 nm. When the concentration of Li^+ ion was more than 0.02 mol%, the luminescence decreased again. This phenomenon is same as the concentration quenching occurred in case of activator. So, for explaining which type of interaction is involved in intensity enhancement we use the Dexter theory. Dexter has given the following equation between emission intensity (I) and sensitizer concentration(x) [19-21].

$$\frac{I}{x} = \frac{K}{1 + \beta x^{Q/3}} - - - - - (1)$$

Where K and β are constants for the interaction is an electric multipolar character which is 3,6,8 and 10 for the exchange interaction, dipole–dipole, dipole– quadrupole, and quadrupole– quadrupole interactions, respectively. Assuming that $\beta x^{Q/3} >>1$ equation (1) can be simply rearranged as follows,

$$\ln\left[\frac{I}{x}\right] = A - \frac{Q}{3}\ln x \left[A = \ln K - \ln \beta\right] - - - (2)$$

Considering these equations we had calculated and plotted In (1/x) Vs In(x) for Li (as shown in Figure 3) .From this plot we had calculated the slope of the respective curve. From Figure 3 the slope of curves is - 1.64. From this obtained value of slope we had calculated Q value which is found to be ≈ 5 ,which means that dipole-dipole interaction(Q=6) as well as the exchange interaction (Q=3) is involved in luminescence quenching.

IV. CONCLUSION

We prepared high-quality $(Y_{0.5}Gd_{0.5})_{0.94}$ $_{x}Li_{x}(V_{0.25}P_{0.75})O_{4}:Eu_{0.06}$ (0 $\leq x \leq 0.02$) phosphor powders, i.e., spherical and regular morphologies as well as smooth surfaces. The $(Y_{0.5}Gd_{0.5})_{0.94}$ $_{x}Li_{x}(V_{0.25}P_{0.75})O_{4}:Eu_{0.06}$ phosphors showed a strong red emission at 615 - 620 nm, which originated from the ${}^{5}D_{0}$ \rightarrow ⁷F₂ transition of Eu³⁺ ion. The incorporation of Li⁺ was highly effective to improve the PL properties of The $(Y_{0.5}Gd_{0.5})_{0.94}(V_{0.25}P_{0.75})O_4:Eu_{0.06}$ phosphors. exchange and dipole-dipole interaction between Eu³⁺ ion and Li⁺ ion was mainly responsible for the enhancement in intensity. This fine red phosphor $(Y_{0.5}Gd_{0.5})_{0.94-}$ $_{x}Li_{x}(V_{0.25}P_{0.75})O_{4}:Eu_{0.06} (0 \le x \le 0.02)$ particles would be a good candidate of red emitting phosphor for the plasma display panels.

V. REFERENCES

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