

Photoluminescence of $YVO_4:Eu^{3+}$ Prepared by Li_2CO_3 Addition

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ABSTRACT

Deep red color emitting $YVO_4:Eu^{3+}$ phosphors were investigated in an attempt to achieve promising performances in cold cathode fluorescent lamp (CCFL) applications. For this purpose, several additives such as LiF, $LiCO_3$ and HBO_3 were introduced in the processing. While two of the additives were ineffective, the inclusion of $LiCO_3$ during the solid state synthesis of $YVO_4:Eu^{3+}$ phosphors was proven to enhance photoluminescent intensity and the color chromaticity. Unlike the commercially available $Y(V,P)O_4:Eu^{3+}$ red phosphor for use in PDP applications, pure $YVO_4:Eu^{3+}$ excluding phosphorous was shown to be favorable for CCFL applications, improving color chromaticity at 254 nm excitations.

Key words: Phosphor, Photoluminescence, Energy transfer, Color chromaticity

1. Introduction

Phosphors with better color chromaticity have attracted a great deal of attention since the display industry has recently put more emphasis on color purity issues than on luminance.¹⁻⁶⁾ This is an obvious trend currently prevailing in most commercially available flat panel displays, such as liquid crystal displays (LCD) and plasma display panels (PDP). The search for phosphors that give deeper red colors has been of particular concern because all of the commercially available red phosphors are unable to meet the customers' demands in terms of realizing actual red color on the screen. In this regard, the development of red phosphors, the CIE chromaticity x value of which exceeds 0.66 without losing luminance, should be of primary concern from a practical point of view. In fact, all of the commercially available red phosphors are lacking in their chromaticity properties. This has hampered the realization of actual red color and the enlargement of the color gamut in all types of flat panel displays such as PDP and LCD. In this regard, commercially available $Y(V,P)O_4:Eu^{3+}$ phosphors have been spotlighted for their outstanding color chromaticity, which has expanded CIE x value to 0.67; recently the $Y(V,P)O_4:Eu^{3+}$ phosphor began to be applied to PDPs as a constituent in a mixture with existing red phosphors, so that this mixture can give rise to a wider color gamut and improved red colors.¹⁻⁶⁾

Even though the $Y(V,P)O_4:Eu^{3+}$ phosphors play a significant role in improving the color chromaticity in PDP applications, the luminance of these phosphors is not compatible

with that of other red phosphors such as $(Y,Gd)BO_4:Eu^{3+}$, $Y_2O_3:Eu^{3+}$, $Y_2O_2S:Eu^{3+}$ etc. In addition, the luminance and color chromaticity of $Y(V,P)O_4:Eu^{3+}$ phosphors still needs more improvement to apply these phosphors to cold cathode fluorescent lamps (CCFL) for LCD back light units (BLU). To achieve an improvement in terms of both luminance and chromaticity, we introduced Li-containing additives in the processing of $YVO_4:Eu^{3+}$ phosphors to enhance the photoluminescent intensity and the color chromaticity up to a level higher than the commercially available $Y(V,P)O_4:Eu^{3+}$ phosphor under a CCFL excitation environment. The inclusion of Li_2CO_3 during the solid state synthesis of $YVO_4:Eu^{3+}$ red phosphors was proven to be favorable for high luminescent intensity and good color chromaticity because Li_2CO_3 acts as an efficient fluxing agent.

2. Experimental Procedures

The conventional solid state reaction method was adopted for the synthesis of $YVO_4:Eu^{3+}$ phosphors. Y_2O_3 , V_2O_5 , and Eu_2O_3 powders were blended and ground in an agate mortar. H_3BO_3 , LiF, or Li_2CO_3 are also included as a starting material. The ground starting materials were fired through a two step process including intermediate pulverization at 850~1100°C. The fired phosphors were reground and leached. The photoluminescence spectrum and x-ray diffraction pattern of the final phosphors were examined.

3. Results and Discussions

Among such additives as LiF, Li_2CO_3 and H_3BO_3 , only Li_2CO_3 played a positive role in enhancing the PL intensity and color chromaticity of $YVO_4:Eu^{3+}$, while the other compounds never worked. Fig. 1 shows the effect of Li_2CO_3 content on the PL intensity of $YVO_4:Eu^{3+}$. The center area of

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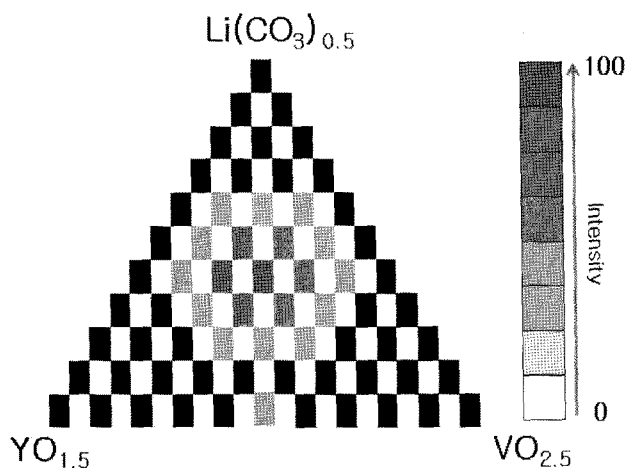


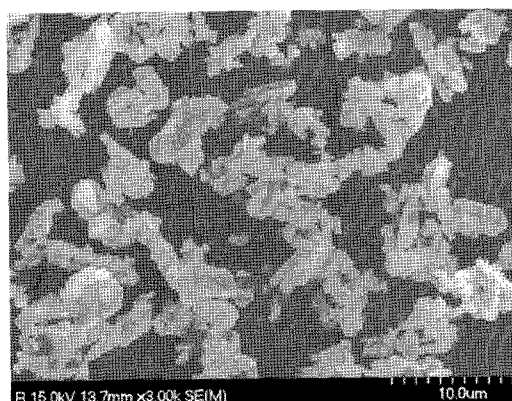
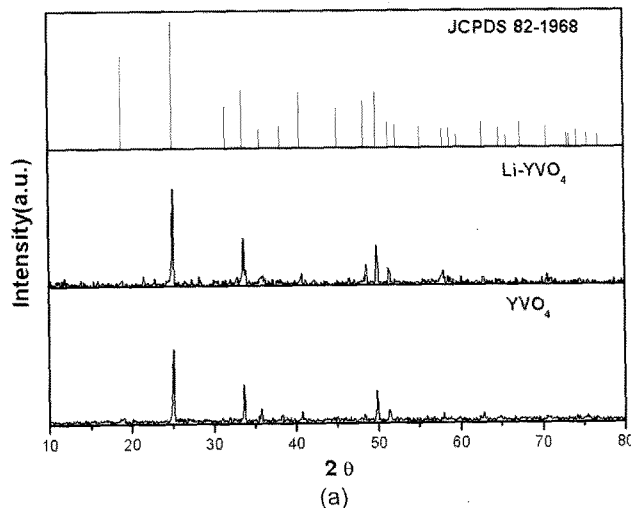
Fig. 1. $\text{Y}_2\text{O}_3\text{-V}_2\text{O}_5\text{-LiCO}_3$ ternary map in terms of PL intensity.

the ternary composition map shows a high PL intensity in comparison to the Li-absent $\text{YVO}_4:\text{Eu}^{3+}$, which was marked by the bottom line ($\text{Y}_2\text{O}_3\text{-V}_2\text{O}_5$ binary line) of the ternary composition map. Even though the compound appearing in Fig. 1 did not contain Li in the structure, it is obvious that the LiCO_3 addition led to PL intensity enhancement.

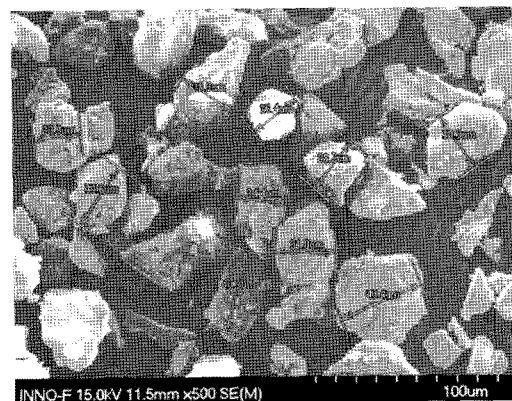
In spite of the addition of a considerable amount of Li_2CO_3 , as much as the addition of Y_2O_3 and V_2O_5 , no Li-containing phase was detected in the XRD measurement. Most of the Li_2CO_3 might have been volatilized during the high temperature process. Also, from the fact that no evidence was detected in the XRD measurement, it is not likely that Li^+ ion doping was accommodated in the YVO_4 host structure. Fig. 2(a) shows the exact coincidence in XRD peak location between Li_2CO_3 -involved and -excluded samples, which could be indicative of the absence of Li^+ ions in the structure. The only conspicuous difference between Li_2CO_3 -involved and -excluded $\text{YVO}_4:\text{Eu}^{3+}$ samples was the XRD peak intensity, not the peak shift. The Li_2CO_3 addition gave rise to higher XRD peak intensity, corresponding to better crystallinity, which led to an increase in PL intensity.

Another distinction between Li_2CO_3 -involved and -excluded $\text{YVO}_4:\text{Eu}^{3+}$ samples was found in the powder size and surface morphology. Fig. 2(b) and (c) shows that the powder size of the Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ sample was around several tens of micrometers, with rougher surfaces, that were larger than the Li_2CO_3 -excluded sample. This implies that the Li_2CO_3 addition facilitated the sintering process and thereby gave rise to larger crystallites with better crystallinity.

The concentration quenching behavior of activators in host is one of the most practically important issues in phosphor research.⁷⁾ In this regard, we calculated the exact value of the critical interaction distance from the concentration quenching data of Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ phosphors. Fig. 3 shows a typical concentration quenching behavior: the peak Eu^{3+} concentration was determined to be 6.3 mol %. The corresponding critical distance is estimated using the



(b)



(c)

Fig. 2. (a) XRD patterns of LiCO_3 -involved and -excluded $\text{YVO}_4:\text{Eu}^{3+}$ samples along with standard data, and SEM micrographs of LiCO_3 (b) -involved and (c) -excluded $\text{YVO}_4:\text{Eu}^{3+}$ samples.

well-known Blasse's approach.⁸⁾ For the present case in which the energy transfer (cross-relaxation) occurs from one Eu^{3+} ion to another, it is possible to obtain the critical distance (R_c) from the concentration quenching data. R_c is, in fact, the critical separation between donor (activator ion) and acceptor (quenching site), at which the non-radiative

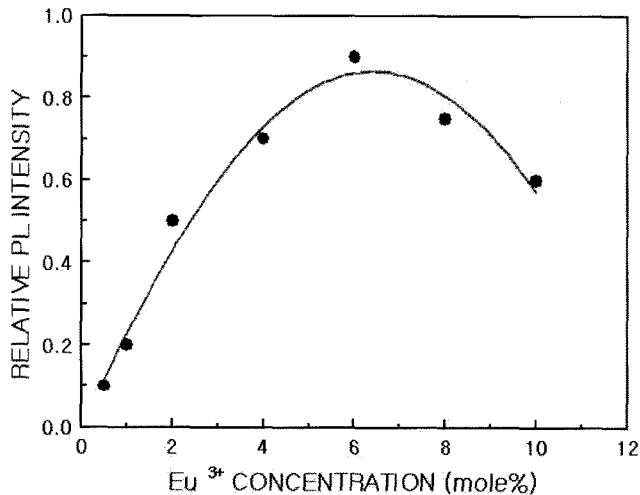


Fig. 3. PL intensity versus Eu^{3+} concentration for LiCO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ sample.

rate equals that of the isolated single ion relaxation. It can thus be assumed that for the critical concentration the average shortest distance between nearest activator (Eu^{3+}) ions is equal to the critical distance R_c . The R_c value based on the dipole-dipole interaction scheme can be practically calculated using the following equation.

$$R_c = 2 \left(\frac{3V}{4\pi x_c N} \right)^{1/3} \quad (1)$$

Where x_c is the critical concentration, N the number of Y^{3+} ions in the YVO_4 unit cell (Eu^{3+} ions are assumed to be introduced solely into Y^{3+} sites) and V the volume of the unit cell (in this case, $318.68 \times 10^{-30} \text{ m}^3$). Using Eqn. (1), the critical distance is determined to be 13 \AA . This value is within a plausible range in comparison to other Eu^{3+} doped phosphors.⁹⁾

Fig. 4 shows the emission spectrum of our Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ sample along with that of a commercially available $\text{Y(V,P)O}_4:\text{Eu}^{3+}$ phosphor provided by Samsung SDI Ltd. Co., which is currently being used for PDP applications. The Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ phosphor exhibited higher emission peak intensity than the commercially available product. In addition, the CIE color chromaticity x value was slightly higher, as was presented in Fig. 4. It is worthwhile to note that the Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ phosphor has the higher CIE x value. The color chromaticity of Eu^{3+} doped phosphors is closely related to the distribution of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transition peaks, the so-called branch ratio. The forced electric dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) should be activated while the magnetic dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) must be deactivated in order to enhance the CIE x value. In this regard, the LiCO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ phosphor was more favorable in terms of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ peak ratio than the commercially available $\text{Y(V,P)O}_4:\text{Eu}^{3+}$ phosphor was, as evidenced in Fig. 4. The higher PL intensity and better color chromaticity of our Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ phosphor must be due to the absence of phosphorous, which was

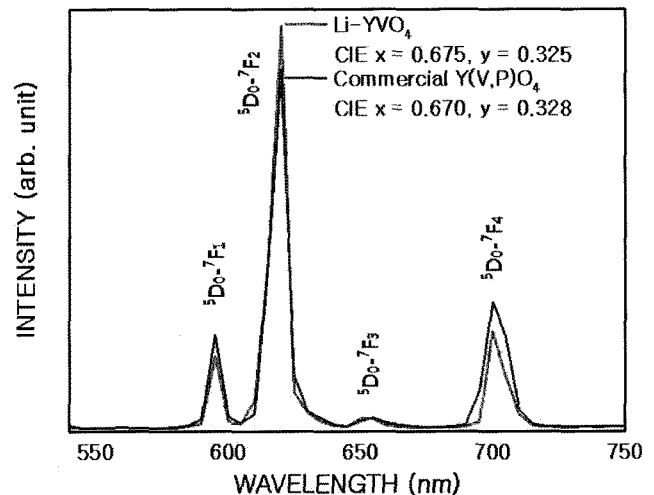


Fig. 4. Emission spectrum of LiCO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ sample, in comparison to a commercially available $\text{Y(V,P)O}_4:\text{Eu}^{3+}$ sample.

included in the commercially available $\text{Y(V,P)O}_4:\text{Eu}^{3+}$ phosphor for the sake of enhancing the PL intensity at vacuum ultra violet excitations.¹⁰⁾ The Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ phosphor was found to be more advantageous at 254 nm excitations for the CCFL application than the commercially available $\text{Y(V,P)O}_4:\text{Eu}^{3+}$ phosphor was.

4. Conclusion

In summary, the inclusion of Li_2CO_3 during the solid state synthesis of $\text{YVO}_4:\text{Eu}^{3+}$ red phosphors was proven to be favorable for high luminescent intensity as well as for good color chromaticity, whereas some other fluxing agents, such as LiF and H_3BO_3 , did not have any effect. Even though a considerable amount of Li_2CO_3 was incorporated, neither the formation of Li-containing phases nor Li^+ ion doping in the host took place. A fluxing effect, as evidenced by the coarsening of the powder accompanying improved crystallinity, was responsible for the enhanced PL properties. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ peak ratio of Li_2CO_3 -involved $\text{YVO}_4:\text{Eu}^{3+}$ phosphors was improved in comparison to a commercially available $\text{Y(V,P)O}_4:\text{Eu}^{3+}$ phosphor, which led to better color chromaticity.

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