Novel Phosphors for UV Excitable White Light Emitting Diodes

Ru-Shi Liu[1,*], **Chun-Che Lin**[1], **Yu-Sheng Tang**[2] and **Shu-Fen Hu**[3,*]

[1]Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
TEL:+886-2-3366-1169, e-mail: rsliu@ntu.edu.tw
[2]Institute of Electro-optical Science and Technology, National Taiwan Normal University, Taipei 116, Taiwan
[3]Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan

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Abstract

$KSrPO_4$ and $Sr_3(Al_2O_5)Cl_2$ phosphors doped with Eu^{2+} emit a blue and orange-yellow luminescence under ultraviolet (UV) excitation at ~ 400 nm, respectivel, which can be used for making white light emitting diodes.

1. Introduction

The first white LEDs developed by Nichia utilized blue LED such as InGaN in combination with a yellow phosphor such as YAG:Ce^{3+}.[1] However due to the limitation such as thermal quenching, low stability and narrow visible range of this phosphor, a novel approach has been suggested which utilizes vacuum or near UV (360-410 nm) excitation instead of blue LED in combination with red, green and blue phosphors to generate white LED. [2] Generally, the phosphors used in the UV LED for white light should possess high quantum efficiency, absorption under long wavelength UV radiation and ability to withstand high temperatures generated during the LED action without compromising the luminescence.

Among the various host families such as oxides and sulfides, the phosphate based compounds have shown excellent luminescent properties. Recently, phosphate compounds have emerged as an important family of luminescent materials because of excellent thermal stability and the tetrahedral rigid three dimensional matrix of phosphate is thought to be ideal for charge stabilization. [3,4] Eu^{2+}-activated $KSrPO_4$ phosphors emitting strong blue light under UV-light irradiation with excellent thermal stabilities have been reported. [5] Halophosphate-based phosphors have been widely applied in fluorescent lamps.[6] Because of their broad excitation band from vacuum ultraviolet (VUV) to ultraviolet (UV) and high luminescence. Here we demonstrate the synthesis and characterization of $KSrPO_4$ and $Sr_3(Al_2O_5)Cl_2$ phosphors that have been doped with Eu^{2+} ions as a potential phosphor using in packaging the warm white light for LEDs.

2. Experimental

$KSr_{1-x}PO_4:Eu_x$ (x = 0.001, 0.003, 0.005, 0.007 and 0.01) phosphors were synthesized by solid-state reaction with KH_2PO_4, $SrCO_3$, and Eu_2O_3 as raw materials. The molar ratio of K:Sr:PO_4:Eu was kept at 1:1-x:1:x, respectively. Stoichiometric homogeneous mixtures of highly pure raw materials were obtained by thorough grinding. In order to avoid the inclusion of carbonate impurities, the mixture was first calcined in air at 600 ℃ for 3 h followed by sintering in reductive atmosphere at 1300 ℃ for 3 h in a 5% H_2/95% N_2 gas mixture. $Sr_{3-x}(Al_2O_5)Cl_2:Eu_x$ (x = 0.05, 0.1, 0.15 and 0.2) phosphors were synthesized by solid-state reaction using $SrCl_2 \cdot 6H_2O$, $SrCO_3$, Al_2O_3, and Eu_2O_3 as raw materials. The molar ratio of Sr:Al:Cl:Eu was kept at 3-x:2:2:x, respectively. Stoichiometric homogeneous mixtures of highly pure raw materials were obtained by thorough grinding and then sintering in reductive atmosphere at 1300 ℃ for 3 h in a 5% H_2/95% N_2 gas mixture. The crystal structure and phase purity of the synthesized samples were identified by X-ray diffraction (XRD) analysis using an X'Pert PRO advanced automatic diffractometer with Cu Kα radiation operated at 45 kV and 40 mA. The photoluminescence (PL) of the samples was measured using a FluoroMax-3 & FluoroMax-P. Thermal quenching and activation energy were studied using a heating apparatus (THMS-600) in combination with PL equipment.

3. Results and discussion

XRD patterns of $KSr_{1-x}PO_4:Eu_x$ (x = 0.001, 0.003, 0.005, 0.007, 0.01) and $Sr_{3-x}(Al_2O_5)Cl_2:Eu_x$ (x = 0.05, 0.1, 0.15 and 0.2) series phosphors match those of pure $KSrPO_4$ (JCPDF 33-1045) and $Sr_3(Al_2O_5)Cl_2$ (JCPDF 80-0564), indicating the formation of a single phase. Figure 1 shows experimental, calculated, and difference results of the XRD refinement of $KSr_{0.995}PO_4:Eu_{0.005}$ at room temperature, obtained using GSAS program. $KSr_{0.995}PO_4:Eu_{0.005}$ crystallizes as an orthorhombic structure with a space group of *Pnma* and lattice constants of a = 7.34728(13) Å, b = 5.55126(11) Å, c = 9.61510(19) Å and v (cell volume) = 392.168(13) $Å^3$. All of the observed peaks satisfy the reflection condition, $\chi^2 = 2.03$, $R_p = 5.06\%$ and $R_{wp} = 7.32\%$. The inset of Fig. 1 is the SEM image of this phosphor, presenting the mean particle size is around 10 um.

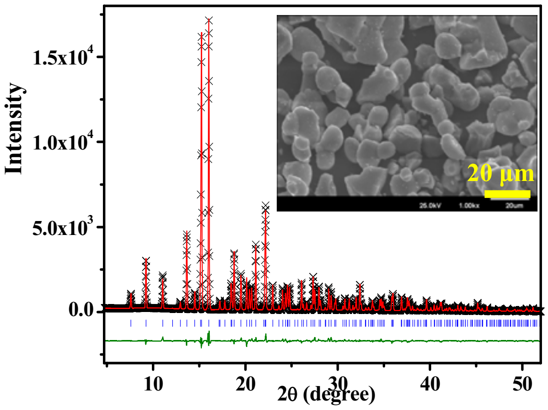

Fig. 1. XRD refinement of $KSr_{0.995}PO_4:Eu_{0.005}$. The inset is the SEM image.

The excitation (PLE) and emission (PL) spectra of $KSr_{0.995}PO_4:Eu_{0.005}$ and $Sr_{2.85}(Al_2O_5)Cl_2:Eu_{0.15}$ were measured. As shown in Fig. 2, the former ($KSr_{0.995}PO_4:Eu_{0.005}$) excitation spectra shows a broad peak between 300 and 400 nm, which can be attributed to 4*f* - 5*d* transition of Eu^{2+} ions. It suggests that can be effectively excited by UV LED's (360-400 nm) with blue luminescence with a peak wavelength predominating at 424 nm; the latter [$Sr_{2.85}(Al_2O_5)Cl_2:Eu_{0.15}$] presented the similar excitation spectra between 300 and 450 nm, and excited not only by UV LED, but Near UV LED. It invariably emit orange-yellow luminescence with a peak wavelength of 620 nm.

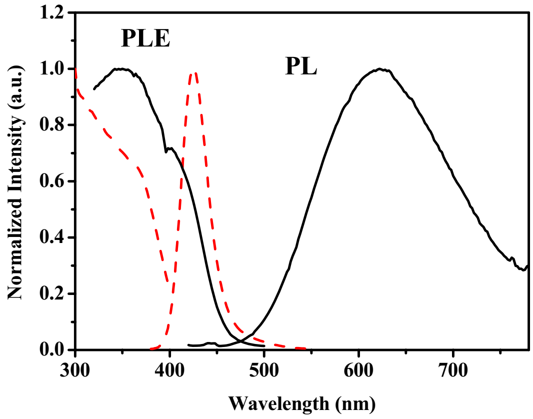

Fig. 2. Excitation and Emission spectra of $KSr_{0.995}PO_4:Eu_{0.005}$ and $Sr_{2.85}(Al_2O_5)Cl_2:Eu_{0.15}$.

Figure 3 presents variation of the relative intensity of the luminescence spectra of $KSr_{0.995}PO_4:Eu_{0.005}$ and $Sr_{2.85}(Al_2O_5)Cl_2:Eu_{0.15}$ at various temperatures from 100 K to room temperature. The former reached 10 % of its initial value at 300 K and the later reached 10 % of its initial value at 200 K and 20 % at 250 K; the thermal quenching temperature (T_{50}) was found to be 875 K and 365 K, respectively, that the temperature at the emission intensity was 50% of its initial value.

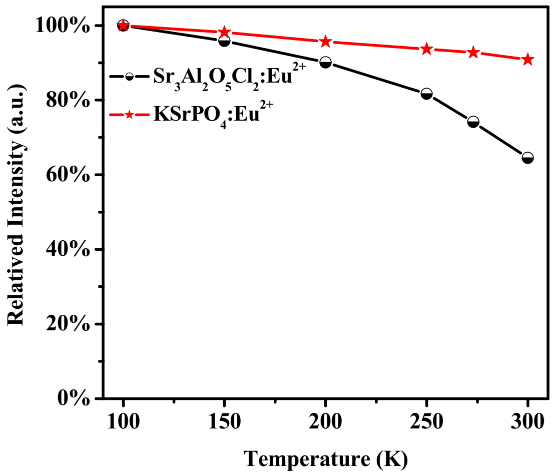

Fig. 3. Temperature dependent emission intensity of $KSrPO_4:Eu^{2+}$ and $Sr_3(Al_2O_5)Cl_2:Eu^{2+}$

To understand the thermal quenching behavior at various temperatures, the thermal quenching data were fitted using the Arrhenius equation.[5, 7]

$$I(T) \approx \frac{I_0}{1 + c\exp\left(\frac{-E}{kT}\right)} \qquad (1)$$

Where I_0 is the initial intensity, I(T) is the intensity at a given temperature T; c is a constant; E is the activation energy for thermal quenching, and k is Boltzman's constant. Figure 4 shows of ln[(I0/I)-1] vs 1/(kT), and the activation energy (E), which fitted all of the data closely, is 0.31 eV for $KSr_{1-x}PO_4:Eu_x$ and 0.14 eV for $Sr_{3-x}(Al_2O_5)Cl_2:Eu_x$.

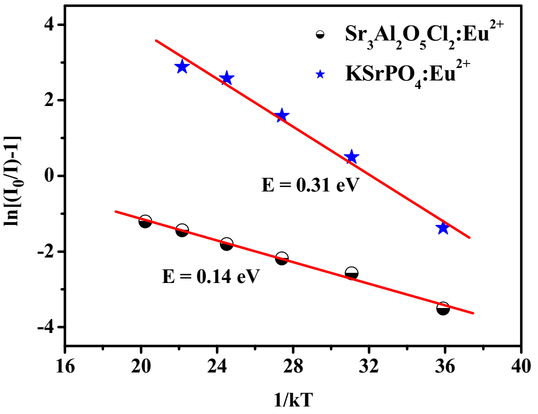

Fig. 4. Plots the log(xEu^{2+}) vs log[I/xEu^{2+}] of $KSrPO_4:Eu^{2+}$ and $Sr_3(Al_2O_5)Cl_2:Eu^{2+}$

The packaging of the light LEDs was performed by using $KSr_{0.995}PO_4:Eu_{0.005}$ and $Sr_{2.85}(Al_2O_5)Cl_2:Eu_{0.15}$ phosphor and a NUV chip with 400 nm emission. The optical properties of LEDs were measured with 20 mA forward-bias current at room temperature. The CIE points of this alignment did not fall into the pure white light region. Accordingly, the green emission phosphor, the silicate doped with Eu ion, should be added to perform the true white light. Fig. 5 shows the electroluminescence (EL) with various drive current from 20 to 60 mA, and the emission spectra unchanged under the experimental conditions. The inset of the Fig. 5 shows the photo of packaging result with driven current 20 mA. Table I summarized the optical properties of this white LED.[8]

Table I. The CIE chromaticity points, domain wavelength, color temperature and the color rendering index at different drive currents.

Drive current (mA)	x	y	CCT (K)	CRI
20	0.3592	0.3614	4539	85
30	0.3576	0.3610	4591	85
40	0.3558	0.3600	4645	85
50	0.3538	0.3595	4714	85
60	0.3525	0.3589	4758	85

It should be noted that the CIE coordinate are almost the same, and the color temperature is about 4600 K. The color rendering index (CRI) is 85 and it shows the high stability of EL.

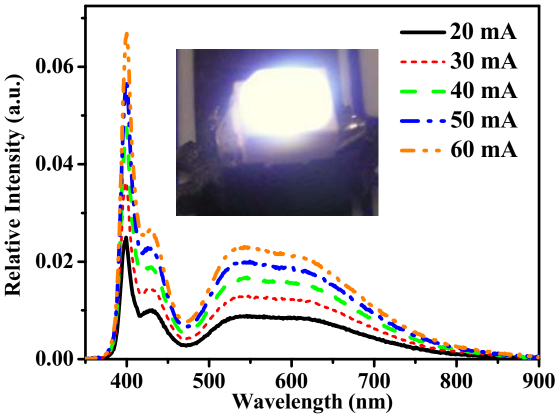

Fig. 5. Electroluminescence with various drive current from 20 to 60 mA of the $KSr_{0.995}PO_4:Eu_{0.005}$ and $Sr_{2.85}(Al_2O_5)Cl_2:Eu_{0.15}$ phosphor with NUV 400 nm chip.

Fig. 6 shows the the Commission Internationale de l'Éclairage (CIE) chromaticity points of electroluminescence (EL) with various driving current. It indicats the gradually blue-shift of the chromaticity points with the driving current increased from 20 mA to 60 mA.

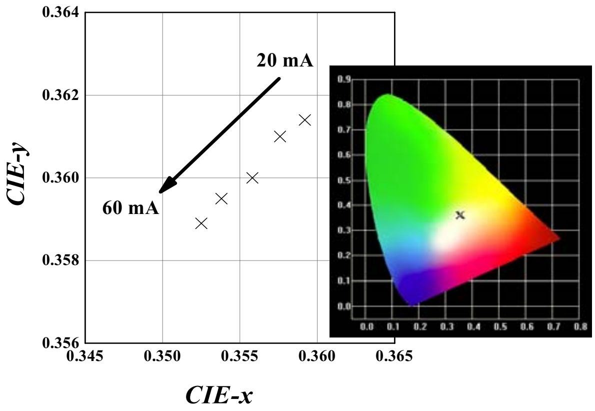

Fig. 6. CIE chromaticity points of electroluminescence (EL) with various driving current.

4. Summary

We have successfully synthesized a blue phosphor $KSrPO_4$:Eu and $Sr_3(Al_2O_5)Cl_2$:Eu by solid state reaction, and packaged these phosphors to generate the warm white light with CCT is about 4600 K and CRI is 85. The luminescent properties of the phosphors were investigated in making an effort for development of potential applications in illumination and light-emitting diode devices.

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