Thermally stable luminescence of KSrPO₄:Eu²⁺ phosphor for white light UV light-emitting diodes

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(Received 24 January 2007; accepted 10 March 2007; published online 10 April 2007)

A novel blue phosphor based on phosphate host matrix, KSrPO₄ doped with Eu²⁺, was prepared by solid state reaction. The phosphor invariably emits blue luminescence with a peak wavelength at 424 nm under ultraviolet excitation at 360 nm. Eu²⁺-doped KSrPO₄ phosphors show higher thermally stable luminescence which was found to be better than commercially available Y₃Al₅O₁₂:Ce³⁺ phosphor at temperature higher than 225 °C. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721846]

There is an increasing demand for white light based light emitting diodes (LEDs) as a potential replacement for the incandescent and fluorescent light sources because of their long lifetime, higher energy efficiency, and environmental friendly characteristics.¹–³ The present strategy to produce white light utilizes combination of blue LED with yellow luminescence from Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) phosphor materials.⁴ However, this strategy faces serious problems of thermal quenching, poor color rendition, and narrow visible range. As an alternative, a novel approach has been suggested which utilizes vacuum or near UV excitation to generate white LED.⁵ The choice of the phosphor in the UV LED for white light depends on its high quantum efficiency and ability to withstand high temperatures generated during the LED action without compromising the luminescence. The commercially available YAG:Ce phosphor also faces problems in white LED due to reduced thermal stability. Therefore, it is necessary to develop novel phosphor materials exhibiting higher thermal stability or small thermal quenching for white LED. In this regard, thermally stable Eu³⁺ activated oxynitride phosphors have been reported for white light-emitting diodes.⁶

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.⁷–⁹ However, there are no reports on the efficient phosphors with thermally stable blue emissions for white light LEDs based on KSrPO₄ host matrix. In this letter, we demonstrate thermally stable luminescence from novel KSrPO₄ doped with Eu²⁺ blue phosphor. The thermal stability of luminescence of KSrPO₄:Eu²⁺ was found to be better than commercially available YAG:Ce phosphor at temperatures higher than 225 °C. We report here the synthesis and photoluminescence properties of KSrPO₄:Eu phosphor.

KₓSr₁₋ₓPO₄:Euₓ (x=0.001, 0.003, 0.005, 0.007, and 0.01) phosphors were synthesized by solid-state reaction using KH₂PO₄, SrCO₃, and Eu₂O₃ as raw materials. The molar ratio of K: Sr: PO₄: 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 °C for 3 h followed by sintering in reductive atmosphere at 1300 °C for 3 h in a 5% H₂/95% N₂ gas mixture. The samples were then characterized by x-ray diffraction (XRD), photoluminescence (PL), and thermal quenching measurements.

The crystal structure and phase purity of the synthesized samples were identified by XRD analysis using X’Pert PRO advanced automatic diffractometer with Cu Ka radiation operated at 45 kV and 40 mA. The XRD patterns of KₓSr₁₋ₓPO₄:Euₓ synthesized in the present study are shown in Fig. 1. The XRD patterns agree well with pure KSrPO₄ (Ref. 9) and indicate single phase formation. KSrPO₄ crystallizes in orthorhombic structure and has a space group of Pnma with lattice constants of a ~ 7.35 Å, b ~ 5.56 Å, and c ~ 9.64 Å.

The excitation (photoluminescence excitation; PLE) and emission (PL) spectra of KₓSr₁₋ₓPO₄:Euₓ for different concentrations of doped Eu⁺ were measured by using a FluoroMax-3 and FluoroMax-P. Figure 2 shows excitation (λₑₓ=424 nm) of the KₓSr₁₋ₓPO₄:Euₓ (x=0.001, 0.003, 0.005, 0.007, and 0.01) for different Eu⁺ contents, respect-

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FIG. 1. XRD patterns of KₓSr₁₋ₓPO₄:Euₓ.
The excitation spectra show a broad peak from 300 to 400 nm, which can be attributed to $4f$-$5d$ transition of Eu$^{2+}$ ions. It suggests that the KSr$_{1-x}$PO$_4$:Eu$_x$ phosphors can be effectively excited by UV LEDs (360–400 nm). Figure 3 shows the emission spectra of KSr$_{1-x}$PO$_4$:Eu$_x$ for different Eu$^{2+}$ contents using 360 nm excitation at room temperature. The phosphors invariably emit blue luminescence with a peak wavelength predominating at 424 nm. The peak position for all compositions did not shift much indicating that the crystal structure of KSrPO$_4$ remains unchanged by substitution of divalent strontium by Eu$^{2+}$ ions.

The Commission Internationale de l’Éclairage (CIE) chromaticity point of the KSr$_{1-x}$PO$_4$:Eu$_x$ with $x=0.005$ is shown in the upper inset of Fig. 3. As the concentration of Eu$^{2+}$ is increased, the CIE coordinate $(x,y)$ did not change from the value (0.161, 0.0238) observed for $x=0.005$. The emission intensity of Eu$^{2+}$ doped KSrPO$_4$ phosphors as a function of the Eu$^{2+}$ concentration is also shown in the lower inset of Fig. 3. The emission intensity increases with Eu$^{2+}$ content from $x$ value of 0.001 to a maximum critical value without any concentration quenching effect. The highest emission intensity was observed for the Eu$^{2+}$ content of $x=0.005$, which is about 70% higher than that for $x=0.001$ and 0.01. However, beyond the critical concentration intensity decreased gradually as Eu$^{2+}$ content increased thereafter. The decrease in the emission intensity occurs as a result of nonradiative energy transfer between Eu$^{2+}$ ions due to electric multipole-multipole interactions, which are distance dependent according to Dexter’s theory. Since the fluorescence mechanism of Eu$^{2+}$ in KSrPO$_4$ host is $4f$-$5d$ allowed electric-dipole transition, multipole-multipole interactions are the probable cause of nonradiative energy transfer ruling out the possibility of exchange interaction for energy transfer. As the concentration of Eu$^{2+}$ ions increases, the distance between the Eu$^{2+}$ ions becomes smaller which favors the nonradiative pathway by energy transfer among Eu$^{2+}$ ions. Hence we have calculated the critical distance between the Eu$^{2+}$ ions for energy transfer by using the relation given by Lammers et al.,

$$R_c = 2 \left( \frac{3V}{4\pi x Z} \right)^{1/3},$$

where $V$ is the volume of the unit cell, $x$ is the critical concentration of activator ion, $Z$ is the number of formula units per unit cell. For KSrPO$_4$ host, using $Z=4$, $x=0.005$, and $V=393.89$ Å$^3$, the obtained $R_c$ value is 34 Å. The larger value of $R_c$ can be thought as stiffness of host matrix due to phosphate tetrahedral network and spectral overlap between the absorption and emission bands.

Figure 4 shows fluorescence decay curve of 424 nm emission for KSr$_{1-x}$PO$_4$:Eu$_x$ with $x=0.005$. It is well known that the decay behavior can be expressed as

$$I = I_0 \exp(-t/\tau),$$

where $I$ and $I_0$ are the luminescence intensities at time 0 and $t$, respectively, and $\tau$ is the luminescence lifetime. Using this equation, the lifetime of the excited states in KSrPO$_4$ for different Eu$^{2+}$ contents was calculated. The values of lifetime were found to be 514, 503, 494, 478, and 444 ns for $x$ values of 0.001, 0.003, 0.005, 0.007, and 0.01, respectively. The lifetime values decrease monotonically with an increase in the dopant ion in the host matrix as shown in the inset of Fig. 4. The decrease in the lifetime can be attributed to energy transfer among Eu$^{2+}$ ions nonradiately at higher concentration of Eu$^{2+}$ ions in the KSrPO$_4$ host matrix.

Another important property exhibited by the KSr$_{1-x}$PO$_4$:Eu$_x$ phosphors is the smaller thermal quenching. Figure 5 in the inset shows the thermal quenching of luminescence intensity, which is important for practical application.
nescence spectra of KSr$_{0.995}$PO$_4$:Eu$_{0.005}$ at different temperatures from room temperature to 300 °C. The relative peak intensity (excitation at 360 nm and monitored at 424 nm) of KSr$_{0.995}$PO$_4$:Eu$_{0.005}$ decreased marginally with temperature. It reached 10% of initial value at 150 °C and then 20% at 300 °C, as shown in Fig. 5. The thermal stability of KSr$_{0.995}$PO$_4$:Eu$_{0.005}$ was higher than the thermal stability of commercially available YAG:Ce phosphor (excitation at 460 nm and monitored at 550 nm), as shown in the Fig. 5. The small decrease in the emission intensity even at higher temperature above 225 °C indicates smaller thermal quenching of KSrPO$_4$ phosphors. Moreover, KSrPO$_4$ doped Eu$^{2+}$ blue phosphors can be effectively used for white light UV LEDs without causing the degradation of intensity due to increase in temperature.

In summary, we have synthesized successfully novel blue phosphors KSr$_{1-x}$PO$_4$:Eu$_x$, and investigated its luminescent properties in an effort for development of potential applications in white light UV LED. The phosphor showed good thermal luminescence stability better than commercially available YAG phosphor at temperatures above 250 °C. Eventually, the KSrPO$_4$:Eu$^{2+}$ phosphors possess the higher thermal luminescence efficiencies and chemical stability which will be crucial for its potential application in white light-emitting diodes.

The authors would like to thank for the financial supports from the National Science Council of Taiwan (Contract Nos. NSC 95-2112-M-003-125 and NSC 95-2113-M-002-009), the Economic Affair (Contract No. 95-EC-17-A-07-S1-043), Taiwan, and the Epistar Corporation (Hsinchu, Taiwan).

9 JCPDF No. 33-1045 (2002).