Full-Color and Thermally Stable KSrPO$_4$:Ln (Ln = Eu, Tb, Sm) Phosphors for White-Light-Emitting Diodes

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The novel phosphors of KSrPO$_4$ doped with Eu$^{2+}$, Tb$^{3+}$, and Sm$^{3+}$ were synthesized by solid-state reaction, and their luminescence properties were investigated. The phosphors show pure three-basal-color (red-green-blue) luminescence in the CIE1931 chromaticity diagram, and it was observed that the concentration quenching was dependent on the different dopant contents. This series of phosphate-based phosphors shows higher thermally stable luminescence, which was found to be better than commercially available Y$_2$Al$_2$O$_4$:Ce$^{3+}$ phosphor at temperatures higher than 200°C. Considering the situation of high color-rendering index and chemical stability, we have demonstrated that KSrPO$_4$:Ln (Ln = Eu, Tb, Sm) are potentially useful new scintillation materials for white-light-emitting diodes.

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Experimental

In recent years there has been a gradual transition from traditional energy to alternative energy because of the advancement of eco-awareness in the world. Solid-state lighting which uses light-emitting diodes (LEDs) for illumination has attracted significant attention. Compared to conventional incandescent and fluorescent lamps, LED-based white light sources are superior in higher luminous efficiency, long operating lifetime (about 100,000 h), reliability, and environmental friendly characteristics.1-3 Yttrium aluminum garnet (Y$_2$Al$_2$O$_4$:Ce$^{3+}$) doped with cerium (Ce$^{3+}$) was known to be an outstanding phosphor material under highly efficient blue InGaN LED excitation. However, the present strategy suffers drawbacks such as lack of color rendition of a wavelength-emitting phosphor, narrow visible range, and color degradation attributed to material instability of commercial phosphors at high temperature. In this regard, Eu$^{2+}$-activated orthophosphates were studied by Poort et al.4 almost 10 years ago, and they were analyzed for thermal stability. Additionally, thermal quenching and activation energy were determined with the heating apparatus (THMS-600).

Results and Discussion

XRD. — X-ray patterns of the same KSrPO$_4$ host prepared by using maximum efficiency activator conditions of (a) Ln = Eu$^{2+}$, x = 0.005; (b) Ln = Tb$^{3+}$, x = 0.07; and (c) Ln = Sm$^{3+}$, x = 0.01 are shown in Fig. 1. The diffraction peaks of these three products can be indexed as an orthorhombic structure in a $Pnma$ space group, which coincides well with literature value (JCPDF card no. 33–1045). Additionally, the result has confirmed that no impurities exist and high crystallinity can be obtained by the convenient solid-state reaction.

PL spectra. — Figure 2 indicates PL excitation (PLE) and emission (PL) spectra of KSr$_{1-x}$PO$_4$: Ln$_x$ involving (a) Ln = Eu$^{2+}$, (b) Ln = Tb$^{3+}$, and (c) Ln = Sm$^{3+}$ as a function of the different activator concentrations.

![Figure 1: XRD patterns of KSr$_{1-x}$PO$_4$: Ln$_x$ phosphors consisting of (a) Ln = Eu$^{2+}$, x = 0.005; (b) Ln = Tb$^{3+}$, x = 0.07; (c) Ln = Sm$^{3+}$, x = 0.01; and pure KSrPO$_4$ (JCPDS file no. 33–1045).](attachment:figure1.png)
In the case of trivalent terbium ($^5D_3 \rightarrow ^7F_j$), the cross-relaxation is a result of concentration quenching which exists in ion pairs. However, PLE spectra of KSrPO_4:Ln phosphors show different absorption. Hence, it is necessary to match the excitation of these phosphors with different chips having a different emission wavelength in order to generate white LEDs. Figure 2c shows the emission spectra of KSrPO_4:Sm (x = 0.003, 0.005, 0.010, 0.050, and 0.100) under excitation at 400 nm (inset). The Sm^{3+} ion has 4f$^6$ configuration and therefore is labeled as a Kramer ion due to its electronic states that are at least doubly degenerated for any crystal field perturbation. There are four prominent emission peaks at 562, 596, 643, and 710 nm, which are contributed from the intra-4f or-$^6H_{7/2}$ level in the orange-red region. The extreme emission intensity can be attributed to $^6G_{5/2} \rightarrow ^6H_{11/2}$ located at 596 nm. 7,10

Additionally, the concentration quenching of the luminescence is due to the energy transfer from one activator to another until all the energy is consumed. For this reason, it is necessary to obtain the critical distance ($R_c$) that is the critical separation between the donor (activator) and acceptor (quenching site). Hence, we have calculated the critical distance among the three activator ions (Ln = Eu$^{2+}$, Tb$^{3+}$, Sm$^{3+}$) for energy transfer by using the relation given by Blasse: 7

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

where $V$ is the volume of the unit cell, $x_c$ is the critical concentration of activator ion, and $Z$ is the number of formula units per unit cell. For KSrPO_4 host, using $Z = 4$, Eu$^{2+}$ ($x_c = 0.005$), Tb$^{3+}$ ($x_c = 0.07$), Sm$^{3+}$ ($x_c = 0.010$), and $V = 393.89 \text{ Å}^3$, the obtained $R_c$ value of Eu$^{2+}$, Tb$^{3+}$, and Sm$^{3+}$ was found to be 34, 14, and 27 Å, respectively.

Figure 3. (Color online) The CIE1931 chromaticity diagram of KSr$_{1-x}$PO$_4$:Ln phosphors with different dopant (Ln = Eu, Tb, Sm) ions.
The CIE chromaticity coordinates for KSr$_{1-x}$PO$_4$:Ln$_x$ (Ln = Eu$^{2+}$, Tb$^{3+}$, Sm$^{3+}$) are represented in Fig. 3. We have observed the CIE coordinates ($x$, $y$) of (0.587, 0.413), (0.288, 0.547), and (0.161, 0.024), corresponding to hues of red (Sm$^{3+}$; $x_c$ = 0.010), green (Tb$^{3+}$; $x_c$ = 0.070), and eventually blue (Eu$^{2+}$; $x_c$ = 0.005) emission, respectively. The characteristic index shows that the blue KSrPO$_4$:Eu$^{2+}$ phosphor has superior color saturation; however, the color saturation of trivalent terbium and samarium are not as good as europium.

**Thermal quenching.** Thermal quenching is one of the important technological parameters for phosphors used in white LEDs. The temperature-dependent luminescent properties were measured at temperatures in the range of 25–300°C, and the results are shown in Fig. 4. The decrease in the emission intensity and the behavior of full width at half maximum was obtained, which can be assigned to thermal quenching at the configurational coordinate diagram. The peak positions of KSrPO$_4$:Eu$^{2+}$ emission spectra (Fig. 4a) are slightly blueshifted with increasing temperature, which can be explained by thermally active phonon-assisted excitation from lower-energy sublevel to higher-energy sublevel in excited states, although the luminous spectra of KSrPO$_4$:Tb$^{3+}$ (Fig. 4b) or KSrPO$_4$:Sm$^{3+}$ (Fig. 4c) reveal nearly no change. The thermal quenching temperature, $T_{50}$, is defined as the temperature at which the emission intensity is 50% of its original value. All the samples have higher $T_{50}$ than a commercial YAG:Ce$^{3+}$, over 300°C, which demonstrates superior thermal stability as RGB luminescent materials for white LEDs as shown in the inset. In order to interpret the relationship of PL with temperature and to calculate the activation energy from thermal quenching, the Arrhenius equation was fitted to the thermal quenching data.

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

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 Boltzmann’s constant. The activation energy for thermal quenching was found to be 0.16, 0.20, and 0.16 eV for Eu$^{2+}$, Tb$^{3+}$, and Sm$^{3+}$, respectively as shown in Fig. 5.

**Conclusion**

In conclusion, the excellent RGB phosphors, KSr$_{1-x}$PO$_4$:Ln$_x$ (Ln = Eu$^{2+}$, Tb$^{3+}$, Sm$^{3+}$), exhibiting color saturation, were prepared by simple solid-state reaction. This series of phosphor possesses thermal and chemical stability better than commercial YAG:Ce$^{3+}$ phosphors. In addition, the phosphate phosphors are a potential candidate for white-LEDs.

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**References**