

# Development of a Novel Green-Emitting Phosphate Phosphor $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$

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## ABSTRACT

In this study, fluorescence characteristics were evaluated by synthesizing  $\text{Eu}^{2+}$  doped samples for phosphates of various compositions. The study led to a green light emitting  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$ , which is rare for a phosphate phosphor.  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  had an excitation band between 250 and 450 nm and emitted green light, reaching an emission maximum at 520 nm. As this result suggests that excitation by a near-ultraviolet LED is possible,  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  could be useful as a phosphor for white LEDs.

**Keywords:** Phosphate Phosphor;  $\text{Eu}^{2+}$ -Activation; Green Emission

## 1. Introduction

White LEDs have been drawing attention in recent years owing to their useful properties, including energy conservation, compact size, and long life. The currently widely popular two-wavelength type white LEDs comprising the blue LED (InGaN) and yellow phosphor  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  (YAG: $\text{Ce}^{3+}$ ) have imperfections such as poor color-rendering properties and highly correlated color temperature, as they lack green and red components. In order to express white light that is close to natural light, the emissions of the green and red color components must be compensated. The solutions include construction of a three-wavelength type white LED consisting of a near-ultraviolet LED and red, green and blue phosphors. In order to realize the three-wavelength type white LED, we need to overcome a significant challenge of developing a novel phosphor that can be excited by a near-ultraviolet LED.

As fluorescence characteristics of phosphors strongly depend on activators and host crystals, their selection is very important. Because  $\text{Eu}^{2+}$  shows a wide range of emission based on  $4f^65d^1-4f^7$  transition, and its excitation/emission characteristics vary significantly depending on the type of the host crystal, it has widely been used as an activator. Oxides, oxynitrides, and nitrides that contain silicon or aluminum have been actively studied as  $\text{Eu}^{2+}$ -activated phosphors in the past. However, there are

relatively few reports of  $\text{Eu}^{2+}$ -activated phosphors for phosphates. Generally, phosphates are physically and chemically very stable, adjusting their particle size is simple and the conditions for their firing temperatures are relatively mild [1,2], so they could be useful as a host crystal of phosphors. The difficulty that phosphate phosphors have in emitting light at long wavelengths has been recognized because many  $\text{Eu}^{2+}$ -activated phosphate phosphors, such as  $\text{KSrPO}_4:\text{Eu}^{2+}$  [3,4],  $\text{LiCaPO}_4:\text{Eu}^{2+}$  [5], and  $\text{Ca}_2\text{Sr}(\text{PO}_4)_2:\text{Eu}^{2+}$  [6] emit purple and blue light. However, recently there have been reports of yellow glowing phosphate phosphors ( $\text{Sr}_8\text{MgGd}(\text{PO}_4)_7:\text{Eu}^{2+}$  [7],  $\text{Sr}_8\text{MgLn}(\text{PO}_4)_7:\text{Eu}^{2+}$  (Ln = Y, La) [8] and  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}$  [9]) and a red glowing phosphor ( $\text{Ca}_4(\text{PO}_4)_2\text{O}:\text{Eu}^{2+}$  [10]). Phosphates can therefore be considered a material group with a potential to become hosts for phosphors that emit light at long wavelengths.

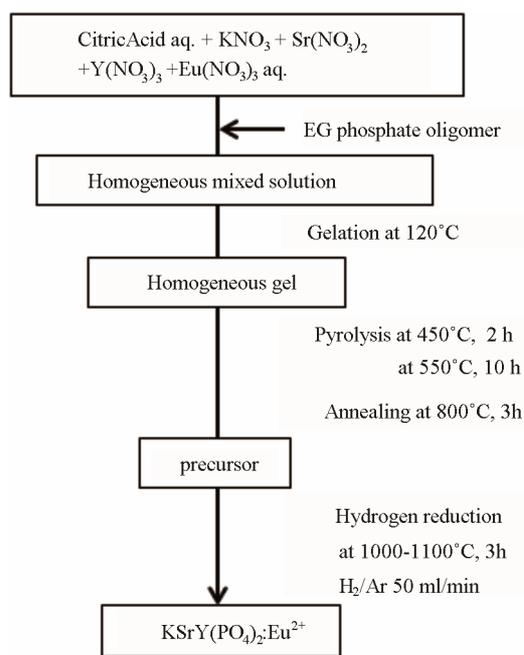
We conducted this study aiming to develop a novel  $\text{Eu}^{2+}$ -activated phosphate phosphor. In searching for a new phosphate phosphor, we picked up known phosphates from a database. Among these phosphates we further extracted phosphates whose  $\text{Eu}^{2+}$ -activated fluorescence characteristics had not been reported previously and created their library. For the phosphates in the library, we prepared  $\text{Eu}^{2+}$ -activated phosphor samples using a parallel solution synthesis method in combination with the amorphous metal complex (AMC) method [11] and using a solid-state reaction method to examine their fluorescence characteristics. A new phosphor,  $\text{KSrY}(\text{PO}_4)_2:$

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$\text{Eu}^{2+}$ , which emits green light, a rarity among phosphate phosphors, was discovered as a result, and the report is provided herein.

## 2. Experiments

$\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  was synthesized by using the amorphous metal complex (AMC) method and the solid state reaction (SSR) method. Based on the chemical compositional formula,  $\text{KSr}_{1-x}\text{Eu}_x\text{Y}(\text{PO}_4)_2$ , replacement of  $\text{Eu}^{2+}$  was performed at 0.5 - 10 atom% to  $\text{Sr}^{2+}$ . In this paper, unless otherwise specified, 1% displacement samples are used. The synthesis procedure using the AMC method is shown in **Figure 1**. The AMC method involved first mixing the aqueous solutions of citric acid and metallic nitrates according to the stoichiometric proportions and then heating them at  $80^\circ\text{C}$  to form metal complexes. Here, the ratio of citric acid:metal was set to 4:1. The ethylene glycol phosphate oligomer [12], which is a phosphorus source, was then added. This mixed solution was heated at  $120^\circ\text{C}$  to polymerize, and a gelatinous material was obtained. The obtained gelatinous material was heated at  $450^\circ\text{C}$  for 2 h, then heated at  $550^\circ\text{C}$  for 10 h in the atmosphere to perform heat decomposition, and then fired at  $800^\circ\text{C}$  for 3 h to obtain the precursor. The obtained precursor was then reduced by  $1000^\circ\text{C}$  to  $1100^\circ\text{C}$  for 3 h in  $\text{H}_2$  (4%)/Ar to obtain the final product. The synthesis procedure using the SSR method involved mixing  $\text{K}_2\text{CO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ , and  $\text{Eu}_2\text{O}_3$  according to the stoichiometric proportions, firing them at  $800^\circ\text{C}$  for 3 h in the atmosphere, and then reducing them in an atmos-



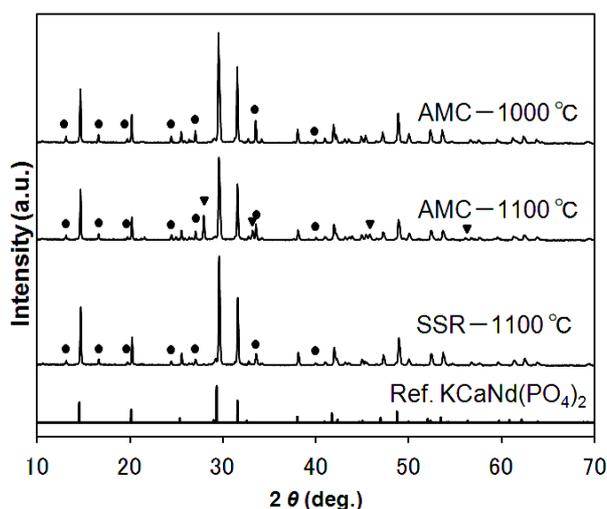
**Figure 1.** Flowchart of  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  synthesis by AMC method.

phere of  $\text{H}_2$  (4%)/Ar under various conditions. The obtained specimen was evaluated by a powder X-ray diffractometer measurement, an SEM-EDS measurement, and a fluorescence spectrum measurement.

## 3. Results and Discussion

### 3.1. Comparison of SSR Method and AMC Method

The diffraction patterns of the specimen synthesized by the AMC and the SSR methods are shown in **Figure 2**. The triangle and circle in the figure indicate the diffraction peaks of impurity phase,  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ , and of the unknown phase, respectively. The standard diffraction pattern of  $\text{KCaNd}(\text{PO}_4)_2$  [13], which has the same structure type as  $\text{KSrY}(\text{PO}_4)_2$ , is also shown in the same figure. All the samples contained some unknown phases, but  $\text{KSrY}(\text{PO}_4)_2$ , which was the target substance, was formed as the main phase. Among the samples synthesized with the AMC, those reduced at  $1000^\circ\text{C}$  did not show impurity-origin peaks other than unknown phases, but reduction at  $1100^\circ\text{C}$  newly formed impurity phases of  $\text{Sr}_3(\text{PO}_4)_2$  and  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ . This points to the fact that the  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$  phase, which does not include any K, was formed, as K having highly volatile nature volatilized with the rise in temperature. On the other hand, for the case of the SSR method, no  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ , which is an impurity, was formed even when the reduction was performed at  $1100^\circ\text{C}$ , and a practically single phase  $\text{KSrY}(\text{PO}_4)_2$  was obtained. This indicates that K tends to be less likely to volatilize with the SSR method. This is probable because the precursors prepared by the AMC were formed with particulates with a larger specific surface area, resulting in more significant volatilization of K.



**Figure 2.** XRD patterns of the samples prepared by AMC and SSR methods. Symbols indicate diffraction peaks from impurities; circles: unknown phase, triangles:  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ .

### 3.2. The Excitation and Emission Characteristics of $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$

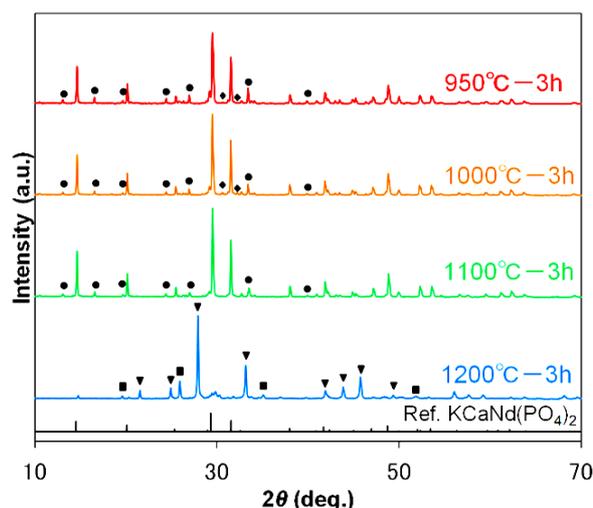
The results obtained from the fluorescence spectrum measurement taken from the specimens synthesized with the AMC method as well as the SSR method are shown in **Figure 3**. Spectra with similar shapes were obtained for all specimens.  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  had an excitation band between 250 and 450 nm and emitted green light, reaching an emission maximum at 520 nm. Many previously reported  $\text{Eu}^{2+}$ -activated phosphate phosphors, such as  $\text{KSrPO}_4:\text{Eu}^{2+}$ ,  $\text{LiCaPO}_4:\text{Eu}^{2+}$  and  $\text{Ca}_2\text{Sr}(\text{PO}_4)_2:\text{Eu}^{2+}$  emit blue light by ultraviolet excitation. The fact that  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  was discovered by this study to emit green light can be considered to be a very interesting outcome for a phosphate phosphor. The specimens synthesized by the AMC method and reduced at  $1100^\circ\text{C}$  indicated more intense light emissions than those processed at  $1000^\circ\text{C}$ . The specimens synthesized by the SSR method and reduced at  $1100^\circ\text{C}$  indicated a light emission intensity that was approximately 1.7 times that of the specimens synthesized with the AMC method. The reason for higher brightness in the SSR samples could be the influence of volatilization of K. Defects could have been formed in the crystals in the samples synthesized by the AMC method due to more volatilization of K, resulting in the reduction of their emission intensity.

### 3.3. Optimization of Firing Conditions

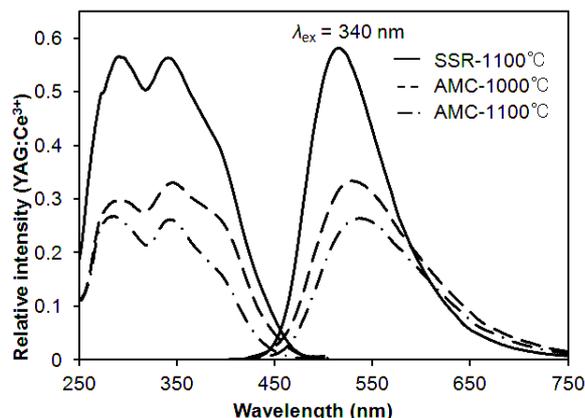
As mentioned above, the SSR sample showed higher emission intensities than the AMC samples. Accordingly, we studied the synthesis conditions of the SSR method in detail. **Figure 4** shows the diffraction pattern of  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  synthesized with a firing time of 3 h and by changing the temperature from  $950^\circ\text{C}$  to  $1200^\circ\text{C}$ . When synthesized at  $950^\circ\text{C}$  and  $1000^\circ\text{C}$ , there was some  $\text{KSrPO}_4$  as well as unknown phases, even though the main phase was  $\text{KSrY}(\text{PO}_4)_2$ . On the other hand, in the

samples synthesized at  $1100^\circ\text{C}$ , the  $\text{KSrPO}_4$  phase disappeared with the volatilization of K, and  $\text{KSrY}(\text{PO}_4)_2$  was obtained almost as a single phase with a small amount of unknown phases. Further increase in the treatment temperature to  $1200^\circ\text{C}$  resulted in a mixed phase of  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$  and  $\text{YPO}_4$  and the disappearance of the  $\text{KSrY}(\text{PO}_4)_2$  phase. At higher temperatures,  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$  and  $\text{YPO}_4$ , which do not contain K, were probably formed because of the significant loss of K through volatilization. Thus, firing at high temperatures was not suitable for the synthesis of  $\text{KSrY}(\text{PO}_4)_2$ . These results indicate that  $\text{KSrY}(\text{PO}_4)_2$  of the highest phase purity can be obtained by heat treatment at  $1100^\circ\text{C}$ .

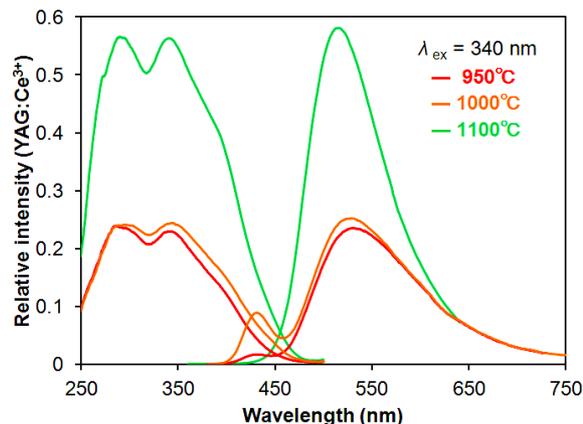
The excitation and emission spectra of these samples (excluding those synthesized at  $1200^\circ\text{C}$  containing almost no  $\text{KSrY}(\text{PO}_4)_2$ ) are shown in **Figure 5**. The samples containing a  $\text{KSrPO}_4$  phase synthesized at 950 and



**Figure 4.** XRD patterns of samples various temperatures. Symbols indicate diffraction peaks from impurities; circles: unknown phase, triangles:  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ , diamonds:  $\text{KSrPO}_4$ , squares:  $\text{YPO}_4$ .



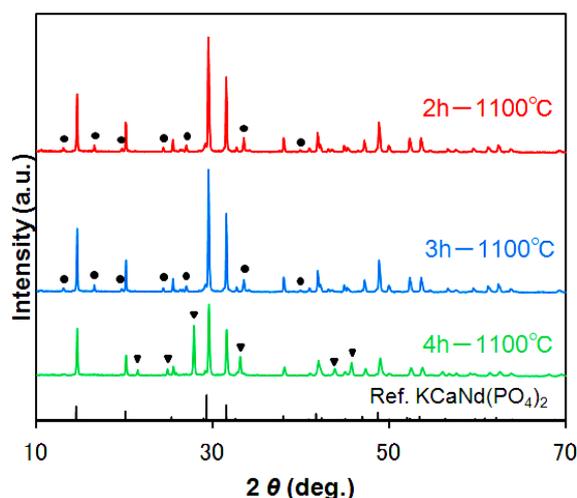
**Figure 3.** PL spectra of the samples prepared by AMC and SSR methods.



**Figure 5.** PL spectra of samples synthesized at various temperatures.

1000°C had an emission derived from  $\text{KSrPO}_4:\text{Eu}^{2+}$  near 430 nm as well as an emission peak derived from  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  near 520 nm. The emission intensity of the  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  origin near 520 nm of these samples was remarkably lower compared with that synthesized at 1100°C. Even we excited these samples at 230 nm, sharp luminescence originating from  $\text{Eu}^{3+}$  was not observed. These results suggest that all Eu turned into  $\text{Eu}^{2+}$  with the reduction at 950 and 1000°C. During synthesis at low temperatures, Eu does not spread easily, leading to poor dispersion of Eu in the  $\text{KSrY}(\text{PO}_4)_2$  host, resulting in the local quenching due to energy transfer among Eu ions. On the other hand, the heat treatment at 1100°C increased the dispersion of  $\text{Eu}^{2+}$  and reduced local quenching, resulting in a higher emission intensity. It was demonstrated that reduction at 1100°C was suitable for the synthesis of samples with higher emission intensities. Next, the firing temperature was set to 1100°C and samples were synthesized using various lengths of firing time.

The diffraction patterns of the samples and their excitation and emission spectra are shown in **Figures 6 and 7**, respectively. Even with a short firing time of 2 h,  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  of relatively high phase purity was obtained with formation of a small amount of unknown phases (marked with circles). On the other hand, firing for 4 h formed no unknown phases, but the diffraction intensity of the  $\text{KSrY}(\text{PO}_4)_2$  phase considerably decreased, instead of which a  $\text{Sr}_3\text{Y}(\text{PO}_4)_3$  phase (marked with triangles) was formed. The samples with 2 and 3 h of firing time had excitation and emission spectra of a similar profile. The samples with 3 h of firing time glowed brighter than the samples with 2 h of firing time. On the other hand, the emission maximum wavelength of the sample synthesized with 4 h of firing time blue shifted to 510 nm. This is because the emission of  $\text{Sr}_3\text{Y}(\text{PO}_4)_3:\text{Eu}^{2+}$



**Figure 6.** XRD patterns of samples synthesized at 1100°C for different times.

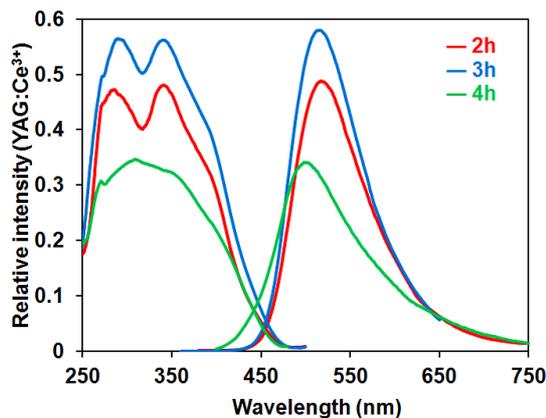
(emission maximum wavelength: 490 nm) contained as an impurity phase is mixed up, in addition to the emission from  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$ . These results demonstrate that the synthesis condition to obtain a  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  with high emission intensity is firing at 1100°C for 3 h.

### 3.4. Optimization of $\text{Eu}^{2+}$ Concentration

In general, the light-emitting characteristics of the  $\text{Eu}^{2+}$ -activated phosphors are strongly dependent on the concentration of  $\text{Eu}^{2+}$ . An investigation was therefore conducted on the  $\text{Eu}^{2+}$  concentration dependence on photoluminescence properties of  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  phosphors. The samples were synthesized by the SSR method, firing at 1100°C for 3 h. The results of the X-ray diffraction confirmed that the targeted phase was obtained practically in a single phase, with no dependence on the  $\text{Eu}^{2+}$  concentration. The excitation and emission spectra of 0.5% - 10% of the  $\text{Eu}^{2+}$ -activated  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  are shown in **Figure 8**. The wavelength of the emitted light was 520 nm when the  $\text{Eu}^{2+}$  concentration was 0.5 and 1%, but shifted to 525 nm for 4 to 10%. A review of the excitation spectrum revealed that the relative intensity of the shoulder peaks at 394 nm was greater when the  $\text{Eu}^{2+}$  concentration was 4% or more.  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  exhibited maximum light emissions when the  $\text{Eu}^{2+}$  concentration was 1%, whereas the light emission intensity decreased uniformly when the  $\text{Eu}^{2+}$  concentration was further increased. The light emission intensity of  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  (1%) at the present point in time is 58% for the  $\text{YAG}:\text{Ce}^{3+}$  (P46) phosphor available on the market, while the internal quantum efficiency and absorption rate at 340 nm were 30% and 73%, respectively.

### 3.5. Thermal Quenching Properties

When applying phosphors for white LEDs, it is essential that the temperature dependence of the fluorescence cha-

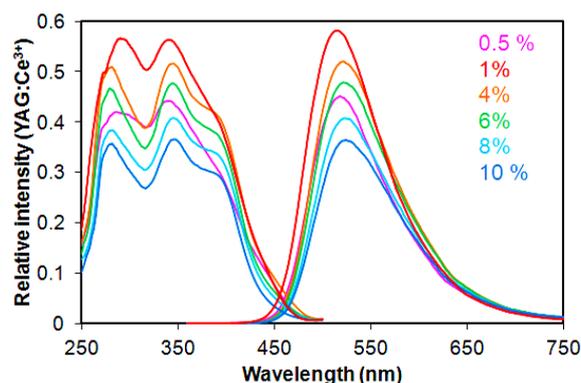


**Figure 7.** PL spectra of the samples synthesized at 1100°C for different times.

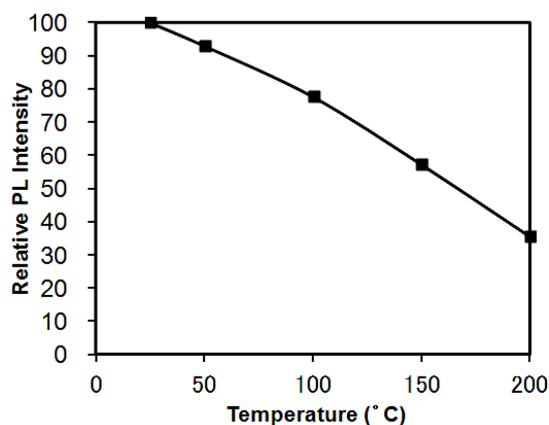
characteristics is investigated, as temperature fluctuations impact the output of light- and color-rendering properties. The results of the investigation on the fluctuation of light emission intensity from room temperature to 200°C for  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  (1%) are shown in **Figure 9**. The light emission intensity decreases as the temperature rises, reaching 57% at 150°C. Thermal quenching has been reported to be less likely to occur when the  $\text{PO}_4$  units inside the crystal structure of the phosphate phosphor share oxygen [14]. It can be speculated that because in  $\text{KSrY}(\text{PO}_4)_2$ , which has the same type of structure as  $\text{KCaNd}(\text{PO}_4)_2$ ,  $\text{PO}_4$  units exist in isolation [13], so its thermal quenching is relatively significant.

#### 4. Conclusion

$\text{Eu}^{2+}$ -activated  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  was discovered to be a new phosphor. The new phosphor,  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$ , has an excitation band between 250 and 450 nm and emits green light, reaching an emission maximum at 520 nm. The emission intensity of  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  samples depended strongly on the heat treatment temperature for their synthesis. The heat treatment at 1100°C was suitable for obtaining  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  with a high emis-



**Figure 8.** PL spectra of  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  with different  $\text{Eu}^{2+}$  concentration.



**Figure 9.** Thermal quenching of  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$ .

sion intensity. The optimum  $\text{Eu}^{2+}$  concentration for  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$  was 1%. As described above, we were successful in our development of a green light phosphor,  $\text{KSrY}(\text{PO}_4)_2:\text{Eu}^{2+}$ , which can be excited using near-ultraviolet LEDs.

#### 5. Acknowledgements

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