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Short communication

Enhancement of fluorescence by Ce^{3+} doping in green-emitting $Ca_{15}(PO_4)_2(SiO_4)_6:Eu^{2+}$ phosphor for UV-based w-LEDs

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Abstract

$Ca_{15}(PO_4)_2(SiO_4)_6:Eu^{2+},Ce^{3+}$ phosphor was synthesized by a solid-state reaction. Doping of Ce^{3+} into the Ca^{2+} site of the $Ca_{15}(PO_4)_2(SiO_4)_6:Eu^{2+}$ phosphor enhanced the Eu^{2+} emission greatly, as observed by measuring the photoluminescence properties and the quantum efficiency levels. The mechanism of the enhancement of the Eu^{2+} emission by Ce^{3+} doping was investigated by comparing the normalized photoluminescence (PL) spectra with the normalized photoluminescence excitation (PLE) spectra and analyzing the absorbance and the fluorescence lifetime of the $Ca_{15}(PO_4)_2(SiO_4)_6:Eu^{2+},Ce^{3+}$ phosphors. Furthermore, the thermoluminescence properties were measured to confirm the thermal stability of the synthesized phosphor when exposed to the high junction temperature of recent high-power LED chips, showing a thermal activation energy barrier of 0.213 eV.

Keywords: A. Powders: solid state reaction; C. Optical properties; D. Silicate; E. Functional applications

1. Introduction

White light-emitting diodes (w-LEDs) have been considered as a next-generation light source due to their many advantages, such as their low power consumption, long lifetime, and environmental friendliness [1]. W-LEDs are generally fabricated by a combination of a blue LED chip and the bright commercial yellow phosphor $YAG:Ce^{3+}$ [2]. However, these w-LEDs have problems, such as their low color rendering index (CRI) and changes in the color depending on the input current due to the mixing of two colors [3]. An alternative method of fabricating w-LEDs involves combining UV LEDs with tri-color phosphors [1], such as red-emitting $Y_2O_2S:Eu^{3+}$ [4], green-emitting $ZnS:Cu^+,Al^{3+}$, and blue-emitting $ZnS:Ag^+$ phosphors due to their excellent color rendering indexes, high color tolerance levels, and high conversion efficiency for conversion into visible light [5].

Due to their high luminescence properties and physical/chemical stability, rare-earth-ion-doped alkaline earth-silicate phosphors, such as $CaMgSi_2O_6:Eu^{2+}$ and $M_2SiO_4:Eu^{2+}$ (M = Ca, Sr, Ba) are plausible candidates for w-LEDs [6,7]. Therefore, we recently reported a novel green-emitting $Ca_{15}(PO_4)_2(SiO_4)_6:Eu^{2+}$ phosphor for applications in n-UV based w-LEDs [8]. It is excited well by an InGaN-based near-ultraviolet (n-UV) LED chip. Furthermore, there have been many reports about phosphors in which the luminescence intensity of the Eu^{2+} emission is enhanced by Ce^{3+} doping with SrCaSiO4:Eu^{2+},Ce^{3+} [9], $Ca_9Y(PO_4)_7:Eu^{2+},Ce^{3+}$ [10], $BaAl_{12}O_{19}:Eu^{2+},Ce^{3+}$ [11], and $Li_2SrSiO_4:Eu^{2+},Ce^{3+}$ [12].

In this work, the $Ca_{15}(PO_4)_2(SiO_4)_6:Eu^{2+},Ce^{3+}$ phosphor was synthesized by a solid-state reaction, after which a significant enhancement in the Eu^{2+} emission was found by investigating its luminescent properties. The mechanism of enhancement of the Eu^{2+} emission by Ce^{3+} doping was carefully investigated by comparing the normalized photoluminescence (PL) with the

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normalized photoluminescence excitation (PLE) spectra and analyzing the absorbance and the fluorescence lifetime of the synthesized phosphors. Through these analyses, the mechanism of enhancement of the Eu^{2+} emission by Ce^{3+} doping into the Ca^{2+} site was determined to be the energy transfer from Ce^{3+} to Eu^{2+}. Furthermore, the thermal stability of the $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+},Ce^{3+} phosphor was investigated by thermoluminescence measurements, as the high junction temperature of recent high-power LED chips has led to a large amount of heat generated in these chips [13].

2. Experimental

2.1. Preparation of the $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+}, Ce^{3+} phosphor

Powder samples of $Ca_{15(0.995\text{-}x)}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$, $x$$Ce^{3+}$ (x=0, 0.00125, 0.0025, 0.00375, 0.005, 0.0075, 0.01) and $Ca_{14.9625}(PO_4)_2(SiO_4)_6$:0.0025$Ce^{3+}$ are prepared by a conventional solid-state reaction method. To synthesize $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+},Ce^{3+}, the reaction materials $CaCO_3$ (Kojundo, 99.99%), $(NH_4)_2HPO_4$ (Junsei, 99%), SiO_2 (Kojundo, 99.9%), Eu_2O_3 (Kojundo, 99.9%) and CeO_2 (Kojundo, 99.9%) are used. Stoichiometric amounts of raw materials are mixed by ball milling using ZrO_2 balls and ethanol for 24 h and are dried on hot plates. The mixture is then ground well and pre-heat-treated in an alumina crucible at 600 °C for 8 h in air. The obtained powder is thoroughly re-ground and then placed in an alumina crucible and heated at 1300 °C for 8 h in a reducing atmosphere (5% H_2/balance N_2) at a flow rate of 500 mL/min. After these procedures, yellow–green powder samples of $Ca_{15(0.995\text{-}x)}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,$x$$Ce^{3+}$ (x=0, 0.00125, 0.0025, 0.00375, 0.005, 0.0075, 0.01) and a white powder sample of $Ca_{14.9625}(PO_4)_2(SiO_4)_6$:0.0025$Ce^{3+}$ are obtained.

2.2. Characterizations

X-ray measurements of the synthesized samples are identified using an X-Ray Diffractometer (D8-advance, Bruker Miller Co.). The photoluminescence (PL) and the photoluminescence excitation (PLE) in the UV–vis region at room temperature were measured using a fluorescence spectrometer (LS-55, PerkinElmer). The absorbance, internal quantum efficiency and external quantum efficiency are measured using a Quantum Efficiency Measurement System (QE-1100, Otsuka Electronics Co.). The fluorescence decay curves were measured using the TRPL streak-scope system of the streak scope (C4334, Hamamatsu) at the Korea Basic Science Institute of KBSI in the Gwangju Center in Korea.

3. Results and discussion

To investigate the effect of Ce^{3+} doping on the Eu25, 0.00375,$^{2+}$ emission, a series of $Ca_{15(0.995\text{-}x)}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,$x$$Ce^{3+}$ phosphors (x=0, 0.00125, 0.00 0.005, 0.0075, 0.01) were synthesized by a solid-state reaction. Because the optimum doping concentration of Eu^{2+} in the $Ca_{15}(PO_4)_2(SiO_4)_6$ host was found to be 0.005 [8], the Eu^{2+} ion concentration was fixed at 0.005. The XRD patterns of the synthesized $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+},Ce^{3+} phosphors are shown in Fig. 1. The XRD patterns of the $Ca_{15(0.995\text{-}x)}$-$(PO_4)_2(SiO_4)_6$:0.005Eu^{2+},$x$$Ce^{3+}$ phosphors (x=0, 0.00125, 0.0025, 0.00375, 0.005, 0.0075, and 0.01) are well matched to that of the standard $Ca_{15}(PO_4)_2(SiO_4)_6$ sample (ICDD 04-011-0264). Because the ionic radii of Ce^{3+} (0.107, 0.1143, and 0.125 nm for the coordination number 7, 8, and 10 respectively [14]) and Ca^{2+} (0.106, 0.112, and 0.123 nm for the coordination number 7, 8, and 10 respectively [14]) with the same coordination number possible in the $Ca_{15}(PO_4)_2(SiO_4)_6$ structure [15] are similar, Ce^{3+} is expected to occupy the Ca^{2+} site preferably [16].

Fig. 2 demonstrates the PL spectra of the series of $Ca_{15(0.995\text{-}x)}$-$(PO_4)_2(SiO_4)_6$:0.005Eu^{2+},$x$$Ce^{3+}$ phosphors (x=0, 0.00125, 0.0025, 0.00375, 0.005, 0.0075, and 0.01) relative to the intensity of the $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ phosphor. The inset shows the peak intensity of the emission band versus x. The emission intensity at 490 nm of Eu^{2+} is enhanced by Ce^{3+} doping, which increased until the concentration of Ce^{3+} reached 0.0025. With a 0.0025 Ce^{3+} doping of the $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ phosphor, the peak intensity of the Eu^{2+} emission is greatly enhanced by 60%.

The absorbance, internal quantum efficiency (IQE) and external quantum efficiency (EQE) of the $Ca_{15(0.995\text{-}x)}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,$x$$Ce^{3+}$ (x=0, 0.00125, 0.0025, 0.00375, 0.005, 0.0075, and 0.01) phosphors measured at an excitation wavelength of 330 nm are shown in Table 1. With an increase in the Ce^{3+} doping concentration, the EQE is greatly increased by 67% at a Ce^{3+} concentration of 0.0025. In this case, both the absorbance and the IQE are increased by Ce^{3+} doping. The increase in the absorbance with the increased Ce^{3+} concentration indicates that the Ce^{3+} ions doped into the phosphor absorb additional photons, facilitating the energy transfer from Ce^{3+} to Eu^{2+}. As there are many phosphors whose emissions are enhanced by the energy transfer from Ce^{3+} to Eu^{2+} [17], this

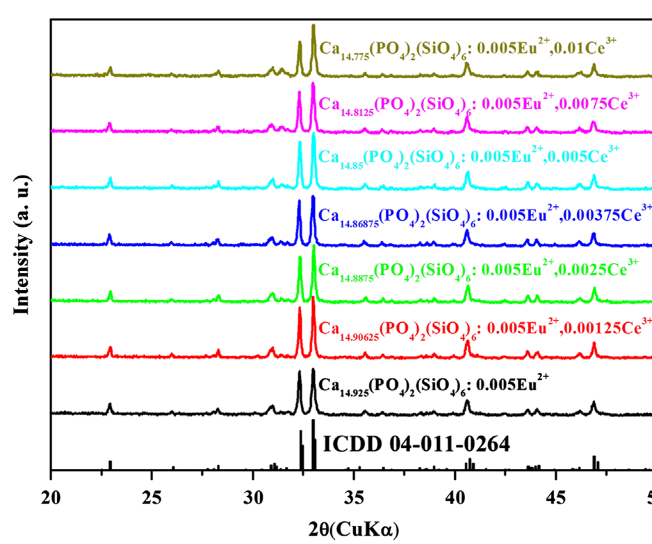

Fig. 1. XRD patterns of $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+},Ce^{3+} powders obtained after calcination at 1300 °C for 8 h in a reducing atmosphere.

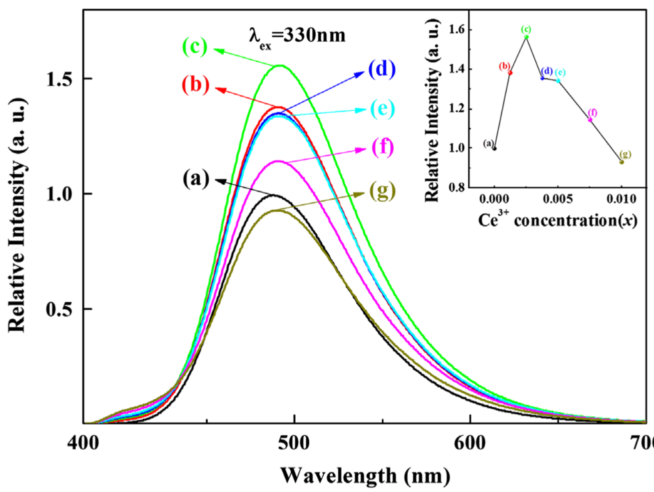

Fig. 2. PL spectra of the series of $Ca_{15(0.995\text{-}x)}(PO_4)_2(SiO_4)_6$:0.005 Eu^{2+},xCe^{3+} phosphors ($x=0$, 0.00125, 0.0025, 0.00375, 0.005, 0.0075, and 0.01. (a), (b), (c), (d), (e), (f), and (g), respectively). The inset shows the peak intensity of the emission band versus x.

Table 1
Absorbance and quantum efficiencies of the $Ca_{15(0.995\text{-}x)}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$, xCe^{3+} ($x=0$, 0.00125, 0.0025, 0.00375, 0.005, 0.0075, and 0.01) phosphors.

x	Absorbance (%)	IQE (%)	EQE (%)
0	64.1	33.6	21.5
0.00125	66.8	46.7	31.2
0.0025	70.9	50.7	36.0
0.00375	70.7	43.6	30.8
0.005	70.3	43.8	30.8
0.0075	72.6	37.1	26.9
0.01	77.3	29.5	22.8

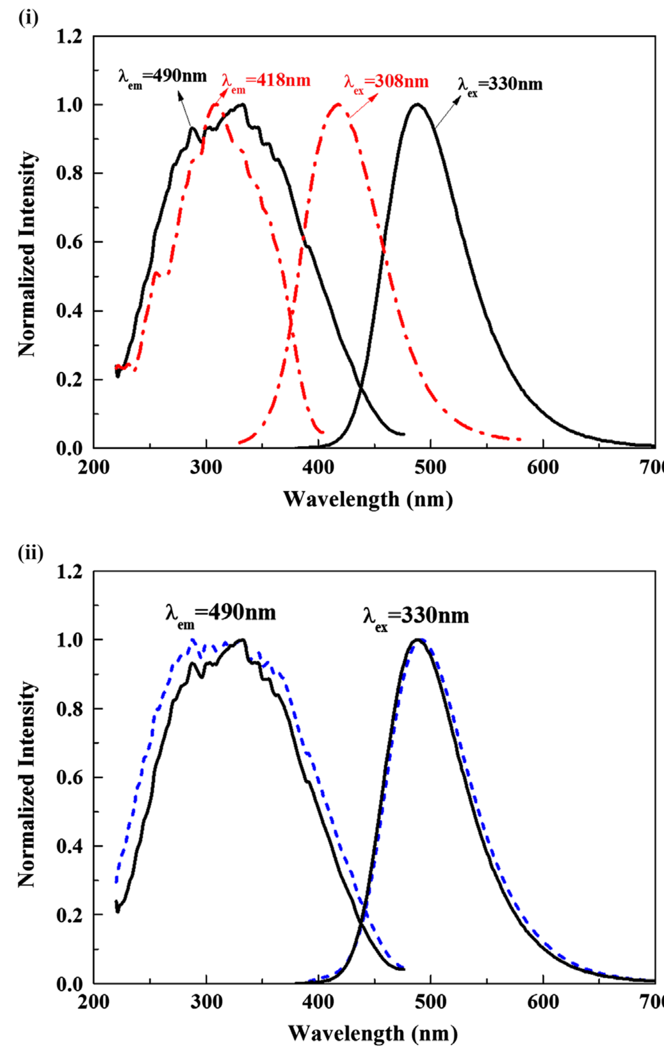

Fig. 3. (i) Normalized PL and PLE spectra of the $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ phosphor (black solid lines) and the $Ca_{14.9625}(PO_4)_2(SiO_4)_6$:0.0025$Ce^{3+}$ phosphor (red dot-dashed lines). (ii) Normalized PL and PLE spectra of the $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ phosphor (black solid lines) and the $Ca_{14.8875}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,0.0025$Ce^{3+}$ phosphor (blue short dashed lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

energy transfer from Ce^{3+} to Eu^{2+} may be the cause of the enhanced Eu^{2+} emission. The IQE increases with an increase in the Ce^{3+} concentration until it reaches 0.0025. There should be a mechanism for the increase of IQE, though this requires further research to be found.

In order to find additional factors that affect the energy transfer from Ce^{3+} to Eu^{2+}, the normalized PL and PLE spectra of the $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ phosphor and the $Ca_{14.9625}(PO_4)_2(SiO_4)_6$:0.0025$Ce^{3+}$ phosphor at an optimum doping concentration are presented in Fig. 3(i). The excitation spectrum of the Ce^{3+}-doped phosphor is extended from 220 to 410 nm, with a maximum at 308 nm, showing a narrower band compared to that of the Eu^{2+}-doped phosphor, which is extended to 470 nm and peaks at 330 nm. Under an excitation wave-length of 308 nm, the emission spectrum of the Ce^{3+} doped phosphor exhibits an asymmetric blue band with a maximum at 418 nm, which was shorter than the 490 nm value of the of Eu^{2+}-doped phosphor under an excitation wave-length of 330 nm. According to research by Liu, the spectral overlap of PLE and PL of phosphors co-doped by Eu^{2+} and Ce^{3+} indicates an energy transfer from a sensitizer to an activator [3,9]. As shown in Fig. 3(i), there is considerable spectral overlap of the PL spectrum of the Ce^{3+}-doped phosphor and the PLE spectrum of Eu^{2+}-doped phosphor, indicating that there may be an energy transfer from Ce^{3+} to Eu^{2+} [3,9]. The PLE spectrum of the $Ca_{15(0.9925)}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,0.0025$Ce^{3+}$ phosphor exhibits stronger excitation at all measured wave-length than that of the $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ phosphor. Furthermore, there is much stronger excitation around 308 nm than 330 nm as shown in the Fig. 3(ii), which is due to the absorption of Ce^{3+} ions.

In Fig. 4, the fluorescence decay curves of the 490 nm emission of Eu^{2+} of the $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ and $Ca_{14.8875}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,0.0025$Ce^{3+}$ phosphors are shown. The decay curve can be expressed by the equation,

$$I = I_0 e^{-(t/\tau)}$$

where I and I_0 are the luminescence intensities at time t and 0, respectively, and where τ is the fluorescence lifetime as described by Blasse and Grabmarier [18]. Using this single

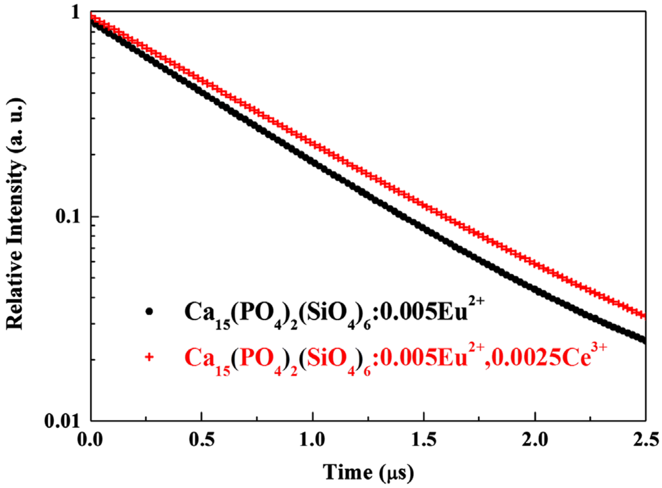

Fig. 4. The fluorescence decay curves of the 490 nm emission of Eu^{2+} of $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005 Eu^{2+} (black line) and $Ca_{14.8875}(PO_4)_2(SiO_4)_6$:0.005 Eu^{2+},0.0025Ce^{3+} (red line) phosphors under 374 nm excitation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

exponential equation to fit the decay curves, the fluorescence lifetime of the Eu^{2+} emission in the $Ca_{14.925}(PO_4)_2(SiO_4)_6$: 0.005$Eu^{2+}$ and $Ca_{15(0.995-x)}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,0.0025$Ce^{3+}$ are obtained as 0.616 μs and 0.682 μs, respectively. The increase of the fluorescence lifetime of the Eu^{2+} emission after Ce^{3+} doping also indicates that there may be an energy transfer from Ce^{3+} to Eu^{2+} [9]. Therefore, the mechanism of the enhancement of the Eu^{2+} emission by Ce^{3+} doping into the Ca^{2+} site is shown to be the energy transfer from Ce^{3+} to Eu^{2+}, as confirmed by the increased absorbance, the spectral overlap of the Ce^{3+} emission with Eu^{2+} excitation, and the increased decay time of the Eu^{2+} emission.

In Fig. 5, the thermoluminescence of the $Ca_{14.8875}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,0.0025$Ce^{3+}$ phosphor measured within a temperature range from room temperature to 160 °C is presented. In order to calculate the activation energy barrier of thermal quenching, the measured data are fitted using the Arrhenius equation [19]

$$I(T)\approx\frac{I_0}{1+c\exp(-(E_a/kT))}$$

Here, $I(T)$ is the emission intensity at the given temperature T, I_0 is the initial emission intensity, c is a constant to be fitted, E_a is the activation energy barrier of thermal quenching, and k is Boltzmann's constant. The thermal activation energy barrier is calculated by fitting the $\ln[(I_0/I)-1]$ versus $1/kT$ curve linearly and subtracting the slope. The calculated thermal activation energy is 0.213 eV.

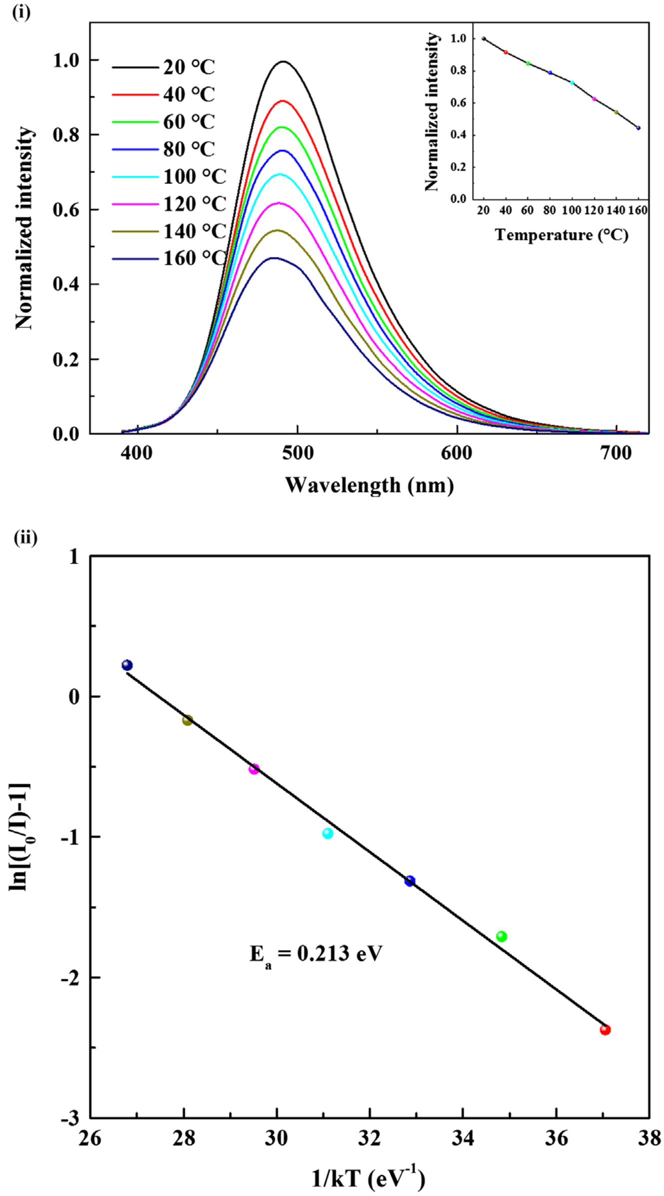

Fig. 5. (i) The TL emission spectra of the $Ca_{14.8875}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$, 0.0025$Ce^{3+}$ phosphor. The inset shows the temperature-dependency of the $Ca_{14.8875}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,0.0025$Ce^{3+}$ phosphor. (ii) Plots of fitted activation energy for thermal quenching.

4. Conclusion

The $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+},Ce^{3+} phosphor was synthesized by a solid-state reaction. Doping of Ce^{3+} into the Ca^{2+} site of the $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+} phosphor enhanced the Eu^{2+} emission greatly. The enhancement of the Eu^{2+} emission is maximized with a doping of 0.0025 Ce^{3+} into the Ca^{2+} site with a great enhancement of the external quantum efficiency of 67%. In this case, both the absorbance and the IQE are increased. The PL spectrum of Ce^{3+} and the PLE spectrum of Eu^{2+} revealed significant overlap. The absorbance of the $Ca_{15}(PO_4)_2(SiO_4)_6$:Eu^{2+},Ce^{3+} phosphor is increased by Ce^{3+} doping. In addition, the fluorescence lifetimes of the Eu^{2+} emission in both $Ca_{14.925}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$ and $Ca_{14.8875}(PO_4)_2(SiO_4)_6$:0.005$Eu^{2+}$,0.0025$Ce^{3+}$ were found to be 0.616 μs and 0.682 μs, respectively. Therefore, the mechanism of enhancement of the Eu^{2+} emission by Ce^{3+} doping into the Ca^{2+} site is shown to be the energy transfer from Ce^{3+} to Eu^{2+}, as confirmed by the spectral overlap of the Ce^{3+} emission with Eu^{2+} excitation, the increased absorbance and the increased decay time of the Eu^{2+} emission. Furthermore, the thermal activation energy barrier was calculated to be 0.213 eV.

Acknowledgments

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