An integrated first principles and experimental investigation of the relationship between structural rigidity and quantum efficiency in phosphors for solid state lighting

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ABSTRACT

In this paper, we outline an integrated approach for exploring novel near-UV excited phosphors. To test the hypothesis of whether high host structural rigidity results in phosphors with high quantum efficiency (Φ), we calculated the Debye temperatures (Θ) for 27 host materials using density functional theory calculations. We identified Eu^{2+} -activated $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ and $\text{CaMg}(\text{SiO}_3)_2$ as having a relatively high $\Theta = 601$ K and 665 K, respectively, and predicted excitation energies of 3.18 eV (337 nm) and 3.29 eV (377 nm), respectively, both of which are in good agreement with the results of photoluminescence spectroscopy. However, the measured Φ for these two phosphors was $< 30\%$, which indicates that Θ alone is not a sufficient condition for a high Φ . This work demonstrates the potential of combined first-principles calculations and experiments in the discovery and design of novel near-UV excited phosphors.

Keywords: First-principles calculation, density functional theory, near-UV phosphors, Eu^{2+} activation, Debye temperature, quantum efficiency

INTRODUCTION

White-light sources based on light-emitting diodes (w-LEDs) have attracted intense interest for next generation solid-state lighting technologies due to their longer lifetime, superior efficiency, and low operating temperatures compared with traditional incandescent bulb and fluorescent lamp technologies [1-3]. The common approach to create white-emitting LEDs is to combine a blue-emitting (450 nm) InGaN LED with a yellow-emitting phosphor [4, 5]. The drawbacks of this method are a non-uniform light output and a low color rendering index (CRI) value. An alternative, more attractive approach is to combine a near UV-LED (nUV-LED, 370-410 nm) with blue, green, and red phosphors to produce high-efficiency w-LEDs. A high CRI value can be achieved by optimization of phosphor blends and, ultimately, a higher extraction efficiency can be obtained due to a smaller current drop at high driving currents, compared to the blue-emitting LEDs [6-8].

Traditional trial-and-error approaches in the discovery of new blue-, green- and red-emitting phosphors for nUV-LED phosphors are time consuming and costly. Recently, new methodologies, such as mineral-inspired prototype evolution [9, 10] and single-particle-diagnosis [11] have been proposed for the discovery of new phosphors. Although these methods have achieved significant progress for developing new phosphors, in essence, they still focus on the exploration case-by-case.

An alternative approach is to use easily computable or measurable descriptors as a means to screen for various desired properties for phosphors, such as an appropriate excitation wavelength (370-410 nm), a high quantum efficiency ($> 80\%$), good thermal quenching behavior ($< 20\%$ decrease in emission intensity from room temperature to 150°C), and chemical stability (e.g. moisture stability). For example, the narrow-band descriptor combined with band gap and phase stability was recently proposed to discover promising narrow-band red-emitting phosphors for high-power LEDs in a high throughput approach

[12]. Based on the analysis of over 1000 rare-earth activated compositions, Dorenbos [13, 14] proposed that the excitation energy, $E_a(\text{Re}, \text{A})$ can be predicted from the following empirical relationship:

$$E_a(\text{Re}, \text{A}) = E_F(\text{Re}) - D(\text{A}) \quad (1)$$

where $E_F(\text{Re})$ and $D(\text{A})$ are the rare earth (Re) free ion energy and crystal field depression in host A, respectively. However, $D(\text{A})$ is difficult to calculate. It is usually tabulated and strongly related to the crystal structure of the host, therefore it is not easy to use Eqn. (1) for new host materials without knowledge of $D(\text{A})$.

More recently, the *ab initio* calculated Debye temperature (Θ) of host materials was proposed to have a positive relationship with the experimental photoluminescence (PL) quantum efficiency (Φ). For Ce^{3+} -activated phosphors, a $\Theta \geq 500$ K was suggested for $\Phi \geq 80\%$ [15]. For example, the calculated Θ for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) is 726 K with Φ measured to be 90% [15]. These preliminary results suggest that host materials with a high Θ may yield high Φ with an appropriate host band gap. However, there have been relatively few efforts utilizing a combined first-principles and experimental approach for the discovery of new phosphors.

In this work, 27 host materials were selected based on the criterion that Ce^{3+} - or Eu^{2+} -doping results in an absorption wavelength in the near-UV light range (370-410 nm). These host materials were found from potential phosphor compositions in the literature [13, 14, 16-18]. The Θ of these 27 hosts were calculated using density functional theory (DFT) calculations. Two potential candidates, $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4:\text{Eu}^{2+}$ and $\text{CaMg}(\text{SiO}_3)_2:\text{Eu}^{2+}$ having higher Θ were identified, and their excitation energies were calculated. Then, powders were synthesized. The $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ phosphor was prepared by the sol-gel/Pechini method and the $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ phosphor was prepared by the co-precipitation method. Subsequently, the PL properties were analyzed to compare to the first-principles predictions.

METHODS

Computational methods

All first-principles calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP) [19, 20]. The Perdew–Berke–Ernzerhoff (PBE) [21] exchange–correlation functional was used. More specific calculation parameters can be found in references [22, 23].

The Debye temperature, Θ , was calculated using the quasi-harmonic model given by [15]

$$\Theta = \frac{\hbar}{k_B} (6\pi^2 V^{\frac{1}{3}} n)^{\frac{1}{3}} f(\nu) \sqrt{\frac{B}{M}} \quad (2)$$

where V , n , $f(\nu)$, B and M are the unit cell volume, the number of atoms in the unit cell, a scaling function in terms of Poisson's ratio ν , the bulk modulus and the molar mass, respectively; $\hbar$ and k_B refer to the Plank constant and the Boltzmann constant, respectively. The elastic moduli were calculated by employing the Voigt-Reuss-Hill (VRH) approximation based on the computed elastic tensor [24]. Previous research indicated that an effective Hubbard U of 2.5 eV can reproduce the experimental $E(\text{VBM}-4f)$ for Eu^{2+} -activated oxides, [25] and the band width of the $\text{Eu}^{2+} 4f$ bands are not very sensitive to the U value used [12]. We here adopted $U = 2.5$ eV for the evaluation of orbital-projected density of states (DOS) with the PBE functional. The band structures of hosts were calculated using the modified Becke-Johnson localized-density functional (MBJLDA), which has been shown to yield more accurate band gap values for insulators compared to the standard generalized gradient approximation (GGA), but at a much lower computational cost compared to hybrid density functionals [26].

According to experimental findings on the absolute location of lanthanide (Ce^{3+} and Eu^{2+}) energy levels, the $4f$ and $5d$ energy levels generally lie in the band gap, with the $5d$ level closer to the conduction band minimum [27, 28]. This PL mechanism ($4f^{n-1}5d^1 \rightarrow 4f^n$ transition) for Ce^{3+} and Eu^{2+} activated phosphors is described in Figure 1 [27, 28]. The excitation energy (E_{ex}) is proposed from the following equation:

$$E_{ex} \approx E_g(\text{host, band gap}) - E(\text{VBM-}4f). \quad (3)$$

where E_g (host, band gap) is the band gap of the host material and $E(\text{VBM-}4f)$ is the energy gap between the valence band maximum (VBM) and $4f$ level. It is noted that there are some errors in the estimate of the excitation energy on the order of ~ 1 eV due to the neglect of the gap between the ground state $\text{Eu}5d$ level and the CBM. Dorenbos [29] found that the excited $\text{Eu } 5d$ level is generally located within about 1.0 eV below the conduction band minimum (CBM). Also, the Stokes shift usually lies in the range of 0.64 eV $\sim$ 1.22 eV. Nevertheless, the relative trend is reasonable. The Fermi energy in Eu^{2+} -activated systems refers to the highest occupied $4f$ orbital and is set to zero in the DOS plot.

Synthesis of phosphors

Reagents

All chemicals were used without further purification and included tetraethyl orthosilicate (TEOS, 99.9%, Sigma Aldrich), nitric acid (69.3%, Fisher Scientific), Eu_2O_3 (99.99%, Alfa Aesar), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.3%, Fisher Scientific), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.0%, Macron Fine Chemicals), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Macron Fine Chemicals), ethylene glycol ($\text{C}_2\text{H}_6\text{OH}$, Fisher Scientific), polyethylene glycol (PEG, $\text{C}_2\text{H}_4\text{O} \cdot n\text{H}_2\text{O}$, molecular weight = 20,000 g/mole, Sigma Aldrich), and ammonium hydroxide (28~30%, BDH Aristar Plus).

Preparation of $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$

The sol-gel/Pechini process was used to synthesize $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ powders. The 4 at.% Eu^{2+} concentration was chosen because it has been reported to have the highest PL emission intensity [16]. First, tetraethyl orthosilicate (2.23 mL) was added to ethanol (20 mL) with several drops of nitric acid and stirred for 30 min. Next, Eu_2O_3 was added in a dilute nitric acid solution to form a solution of aqueous $\text{Eu}(\text{NO}_3)_3$. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in deionized water. After these solutions became transparent, silica sol and the $\text{Eu}(\text{NO}_3)_3$ solution were poured to the $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ solution with stirring. Next, citric acid (4.2 g) and ethylene glycol (2.23 mL) were added to the mixed solution (metal: citric acid: ethylene glycol = 1:1:2), which acts as a chelating agent for the metal ions. Polyethylene glycol (2.5 g) was introduced in the mixture, which was used as a crosslinking agent. After stirring the solution for 30 minutes to ensure uniformity, precipitation occurred by adding drops of ammonium hydroxide until the pH reached 4. After completing the preparation, the mixture was continuously stirred at 80°C overnight to form a gel. The white colored product was preheated to remove organic materials at 350°C for 1 hour, and then annealed at 1100°C or 1350°C for 3 h, or 1400°C for 10 h in air. All samples were finally calcined at 1100°C for 4 h under a slight reducing condition (mixture of 5% H_2 and 95% N_2).

Preparation of $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$

$\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$ powders were synthesized by a co-precipitation technique that was modified from a previous reported method [30]. TEOS (2.23 mL) was added into ethanol (20 mL) with HNO_3 (5 mL) and stirred for 30 minutes to hydrolyze TEOS. The desired amount of Eu_2O_3 ($x = 0.02, 0.06, 0.1$, and 0.2) was introduced in a dilute nitric acid solution to form a solution of aqueous $\text{Eu}(\text{NO}_3)_3$. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 30 mL of deionized water. After the europium solution and the magnesium and calcium solution became transparent, the silica sol and europium solution were poured into the magnesium and

calcium solution and the mixture was stirred for 1 hour. Ammonium hydroxide was added dropwise into the solution until the pH was 10 to create a white precipitate. The precipitate solution was stirred for 8 h at room temperature. Next, the precipitate was centrifuged and washed with deionized water three times. The products obtained by centrifugation were dried at 100°C for 12 hours. Then a post-annealing step was performed at 1100°C for 2 h under air and then at 1100°C for 4 h under 5% H₂ / 95% N₂ to change Eu³⁺ to Eu²⁺.

Characterization

The crystallite phases and crystallite sizes of the annealed powders were determined by X-ray diffraction (XRD, Bruker D2 Phaser) using CuK α radiation and a step size of 0.014° over the 2 θ range of 20 to 80 degrees. The analysis was performed using the Diffrac.Eva plus program. Lattice parameters and crystallite sizes were calculated using the approach of Rietveld refinement by the TOPAS 4.2 software (Bruker), which averages the lattice constants associated with each XRD peak across the entire spectrum. The size and morphology of the particles were analyzed by a field emission scanning electron microscope (FESEM, XL30, Philips) at 10 keV. Samples were coated with iridium at 85 μ A for 10 s before FESEM imaging. Absolute quantum efficiency (Φ) measurements were performed using an integrating sphere system, with sodium salicylate ($\Phi = 44\%$) as a reference standard. Photoluminescence emission and excitation spectra were acquired with a fluorescence spectrophotometer (Hitachi F-7000) using $\lambda = 350$ nm excitation wavelength (pulse = 0.025 sec). This excitation wavelength was chosen as it produced the highest PL emission intensity. The thermal quenching analysis (25°C ~ 150 °C) was performed using a custom designed device that consist of a heater, thermocouple, and the spectrophotometer.

RESULTS AND DISCUSSION

Screening of rigid structures and predicting the excitation energy

High structural rigidity confines accessible phonon modes that result in non-radiative recombination. As mentioned previously, Θ was recently proposed as a descriptor of structural rigidity [15]. The higher Θ , the fewer lattice vibration modes can be accessed and thus the more rigid is a crystal structure. The calculated Θ of the 27 host candidates are summarized in Table 1. Six host candidates (in bold) have $\Theta > 500$ K, implying a strong rigidity of the crystal structure and correspondingly, a possible high Φ .

Among these six candidates, only the three silicate host materials Mg_2SiO_4 , $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$, and $\text{CaMg}(\text{SiO}_3)_2$, were considered further because of their high chemical stability, good thermal quenching properties [31], and facile synthesis methodologies. Since, in Mg_2SiO_4 the radius of Mg^{2+} (< 0.07 nm) is too small to be replaced by Eu^{2+} (~ 0.130 nm), $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\cdot\text{Eu}^{2+}$ and $\text{CaMg}(\text{SiO}_3)_2\cdot\text{Eu}^{2+}$ were selected further. In this case, Eu^{2+} can replace Ca^{2+} in the crystal structure due to similar ionic radii (0.118 nm and 0.123 nm for 9-coordinated and 10-coordinated Ca^{2+} , respectively; 0.130 nm and 0.135 nm for 9-coordinated and 10-coordinated Eu^{2+} , respectively) [32].

Figures 2a and 2b show the calculated band structures of $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ and $\text{CaMg}(\text{SiO}_3)_2$. Both hosts have direct ($\Gamma \rightarrow \Gamma$ transition) band gaps ($E_g = 6.86$ eV for $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ and $E_g = 7.08$ eV for $\text{CaMg}(\text{SiO}_3)_2$). Figures 3a and 3b show the calculated orbital projected DOS. The energies between 4f (located at Fermi energy level of 0) and VBM for $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\cdot\text{Eu}^{2+}$ and $\text{CaMg}(\text{SiO}_3)_2\cdot\text{Eu}^{2+}$ are 3.18 eV and 3.79 eV, respectively. The excitation energies can be estimated from Eqn. (3) by subtracting the calculated 4f-VBM gap (3.18 eV for $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\cdot\text{Eu}^{2+}$ and 2.79 eV for $\text{CaMg}(\text{SiO}_3)_2\cdot\text{Eu}^{2+}$) from E_g , which gives $E_{ex} = 3.68$ eV (337 nm) for $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\cdot\text{Eu}^{2+}$ and 3.29 eV (377 nm) for $\text{CaMg}(\text{SiO}_3)_2\cdot\text{Eu}^{2+}$.

Crystal structure, X-ray diffraction, and scanning electron microscopy of the synthesized phosphors

Figures 4a and 4b show the structures of $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\text{:Eu}^{2+}$ and $\text{CaMg}(\text{SiO}_3)_2\text{:Eu}^{2+}$ drawn by VESTA (Visualization for Electronic and STructural Analysis) [33]. In Figure 4a, $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ (mineral bredigite) has an orthorhombic structure with a space group $Pnn2$ where Ca^{2+} has three different crystallographic sites with coordination numbers 12, 10, and 9 [34]. As illustrated in Figure 4b, $\text{CaMg}(\text{SiO}_3)_2$ (mineral diopside) has a monoclinic structure with space group $C2/c$. The lattice parameters of $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ and $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ were calculated using TOPAS and the computed lattice constants are $a = 0.6742$ nm, $b = 1.0887$ nm, $c = 1.8339$ nm for $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ and $a = 0.9743$ nm, $b = 0.8879$ nm, $c = 0.5230$ nm for $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$, which are consistent with previous reports for $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ [34] and $\text{CaMg}(\text{SiO}_3)_2$ [35].

XRD patterns of the $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ powders for different calcination times and temperatures are shown in Figure 5a. The diffraction peaks were indexed by the standard data from PDF card 00-036-0399 ($\text{Ca}_7\text{MgSi}_4\text{O}_{14}$). A pattern for post-synthesis annealing at 1100°C , shows impurity peaks around $2\theta = 27, 29$ and 30° , which correspond to CaSiO_5 . However, these peaks disappear after annealing over 1350°C . No other diffraction peaks, other than those corresponding to $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$, are observed at both 1350°C and 1400°C . The crystallite sizes were determined by the TOPAS program and were ~ 54 nm, ~ 67 nm, and ~ 70 nm, for post-synthesis annealing at 1100°C for 3 h, 1350°C for 3 h, and 1400°C for 10 h, respectively. These results are in a good agreement with previous studies demonstrating that crystallites grow with an increase of the post-synthesis annealing temperature and time [36, 37].

Figure 5b shows XRD patterns of the $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$ ($x = 0.02, 0.06, 0.1$, and 0.2) powders. It is observed that, when the activator concentrations are 0.02 and 0.06, the peaks in the XRD patterns are consistent with the standard PDF card 01-070-3482 ($\text{CaMgSi}_2\text{O}_6$), indicating the successful synthesis of a pure phase of $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$. The crystallite sizes

from the TOPAS program were found to be ~16 nm, ~13 nm, ~17 nm, and ~10 nm for $x = 0.02, 0.06, 0.1, \text{ and } 0.2$, respectively, indicating that crystallite sizes did not significantly change with x in the current range of activator concentrations due to similarity of ionic radii of Ca^{2+} and Eu^{2+} .

Figure 6a shows SEM images of the phosphors after post-synthesis annealing at 1350°C for 3 h. The particles show agglomeration and form aggregates due to the high temperature during post-synthesis annealing. The morphology of the phosphors after post-synthesis annealing at 1400°C for 10 h is shown in Figure 6b. The particles are more agglomerated than those in Figure 6a. Figure 6c-f show the SEM images of $\text{Ca}_{1-x}\text{Eu}_x\text{Mg}(\text{SiO}_3)_2$ ($x = 0.02, 0.06, 0.1, \text{ and } 0.2$). It should be noted that the morphology of $\text{Ca}_{1-x}\text{Eu}_x\text{Mg}(\text{SiO}_3)_2$ is not altered when x increases.

Photoluminescence spectra, color calculator data and quantum efficiency of synthesized phosphors

Figure 7a shows the PL excitation (PLE, monitored at 511 nm) and PL emission (excitation wavelength, $E_{\text{ex}} = 350 \text{ nm}$) spectra for $(\text{Ca}_{0.06}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$. The PLE spectra show broadband absorption in the near UV region from 200 to 450 nm, with a maximum at ~350 nm, which arises from the allowed transition of Eu^{2+} . The experimental λ_{ex} (~350 nm) is very similar to the calculated λ_{ex} (337 nm), confirming the validity of our approach to discover new phosphor compositions. The PL emission spectrum consists of a broad band centered at 511 nm, which is attributed to the allowed $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} . The Φ of $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ with the post-synthesis annealing conditions of 1100°C for 3 h under air, 1350°C for 3 h under air, and 1400°C for 10 h under air, were ~19%, ~30%, and 11%, respectively. Generally, Φ is increased with increase of annealing temperature because of the increase of crystallite sizes [37]. In this work, although the crystallite sizes of the powders calcined at 1400°C for 10 h is slightly larger than the powders calcined at 1100°C

for 3 h and 1350°C for 3 h, the Φ from the 1400°C powders is significantly smaller than that of the 1100°C and 1350°C powders. This reduction of Φ can be attributed to aggregation of the phosphors particles. As shown in Figure 6a and b, the powders calcined at 1400°C form more aggregated structure compared to the powders calcined at 1350°C. Hong *et al.* [38] and Lenggoro *et al.* [39] reported that highly aggregated phosphor powders showed a reduction in emission intensity, which is related to Φ . Aggregated powders can possibly have an influence on the reabsorption and light scattering, which results in a reduction of Φ [40]. Thus, non-aggregated powders play an important role for the obtainment of a high Φ .

Previously reported Φ for $(\text{Ca}_{1-x}\text{Eu}_x)_7\text{Mg}(\text{SiO}_4)_4$, 18% for $x = 0.04$ ($\lambda_{\text{ex}} = 350$ nm) [16] and ~23% for $x = 0.02$ ($\lambda_{\text{ex}} = 400$ nm) [17]), synthesized by solid state reaction at 1350°C for 3 h in N_2/H_2 at 1100~1400°C for 4 h in N_2/H_2 , respectively, were similar to the present results. However, a high Φ (~64%) for $(\text{Ca}_{1-x}\text{Eu}_x)_7\text{Mg}(\text{SiO}_4)_4$ was previously found for an unusually low activator concentration, $x = 0.001$ ($\lambda_{\text{ex}} = 365$ nm) [41]. These powders were formed by a solid-state reaction at 1250°C for 6 h in N_2/H_2 . Since both the synthesis methodology and post-synthesis calcination, affect the crystallite sizes, the differences between values of Φ for the present work and for previous reports can be attributed to differences in synthesis method, post-processing temperature, and dopant concentration.

Figure 7b shows the PL excitation (PLE, monitored at 458 nm) and PL emission (excitation wavelength, $E_{\text{ex}} = 350$ nm) for $\text{CaMg}(\text{SiO}_3)_2:\text{Eu}^{2+}$. A broad excitation spectrum is observed from 200 nm to 400 nm, with a maximum at 350 nm, which is a result of the allowed transition of Eu^{2+} . This value is also close to our calculated excitation wavelength of 377 nm. The PL emission shows a spectrum maximum at 458 nm, which is attributed to the parity-allowed $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} . Solid lines in Figure 7b refer to the emission monitored at 350 nm for various concentrations of Eu^{2+} ($x = 0.02, 0.06, 0.1$, and 0.2) in $\text{CaMg}(\text{SiO}_3)_2$. The emission intensity increases until $x = 0.06$ and then decreases due to the

concentration quenching effect. The Φ was $\sim 5\%$ when $x = 0.06$ for $\lambda_{\text{ex}} = 350$ nm, which is the highest quantum efficiency among $x = 0.02, 0.06, 0.1$, and 0.2 . This Φ is similar to the previously reported value for this material of $\sim 9.1\%$ [42].

Our results indicate that high structural rigidity, as quantified by high Θ , is not a sufficient condition for high Φ . Both silicates studied in this work have high Θ , but relatively low Φ . For compounds that have similar band gaps and chemistries, Θ indeed seems to be correlated with Φ . For example, the calculated Θ 's of $\text{X1-Y}_2\text{SiO}_5$ (GGA band gap, 4.73 eV) and $\text{X2-Y}_2\text{SiO}_5$ (GGA band gap, 4.77 eV) are 491 K and 512 K (Table 1) and the Φ 's are $\sim 36\%$ and $\sim 45\%$, respectively, showing that as Θ increases, Φ also increases [43]. However, Φ is also strongly affected by the host band gap. Furthermore, it has been demonstrated that a host with low Θ yields high Φ when it is activated with Eu^{2+} . For instance, the computed Θ 's for Ba_2SiO_4 , $\alpha\text{-Sr}_2\text{SiO}_4$ and $\beta\text{-Sr}_2\text{SiO}_4$ are 307 K, 360 K and 428 K, respectively, each of which is smaller than the suggested 500 K, whereas the experimentally measured Φ for Eu^{2+} -activated Ba_2SiO_4 and Sr_2SiO_4 are $> 85\%$ [37, 44]. These findings suggest that although calculated Θ may be a starting point, caution should be given to the reliability of Θ as a descriptor of Φ . Therefore, more efforts need to be devoted to explore more accurate descriptors to screen for phosphors with high Φ .

For $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\text{:Eu}^{2+}$, the color represented by the x, y color coordinates (0.25, 0.49) is located in the green region of the diagram on the Commission International de l'Eclairage (CIE) diagram. According to the National Television System Committee (NTSC) RGB colors, the values of good green-emitting phosphors are 0.21 and 0.71 [45]. The color coordinates previously reported (0.20, 0.47) were for powders produced by a solid state reaction with $x = 0.001$ and $\lambda_{\text{ex}} = 365$ nm [41]. The discrepancy in these coordinates with the present results can be explained by the difference in x and λ_{ex} . It was previously shown [41] that the coordinates were dependent on both λ_{ex} and x (activator concentration), attributed to

the three different Eu^{2+} sites. Emission wavelengths were found to be 455 nm ($\text{Eu}(1)^{2+}$), 504 nm ($\text{Eu}(2)^{2+}$), and 540 nm ($\text{Eu}(3)^{2+}$). Eu^{2+} will enter in the $\text{Eu}(1)^{2+}$ sites preferentially for small concentrations of Eu^{2+} , which will increase the emission intensity from the $\text{Eu}(1)^{2+}$ sites (455 nm). When the activator concentration increases, Eu^{2+} preferentially occupies $\text{Eu}(2)^{2+}$ and $\text{Eu}(3)^{2+}$ sites, which will decrease the emission from the $\text{Eu}(1)^{2+}$ sites. It should be noted that these three emission spectra overlap and display one broad emission peak from 450 nm to 600 nm. Thus, the width of emission spectra would change, depending on x and λ_{ex} .

Despite the slight difference in values of the color coordinates in this work, the obtained values were in the green color range, indicating that $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4:\text{Eu}^{2+}$ is a potential green-emitting phosphor for use in nUV LEDs.

The x , y color coordinates of $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ were 0.14 and 0.05, located in the blue region on the CIE diagram and the color coordinates of all samples (x ranging from 0.02 to 0.2) are similar. These values are similar to those defined by NTSC CIE for blue color (0.14, 0.08), indicating that $\text{CaMg}(\text{SiO}_3)_2:\text{Eu}^{2+}$ could be utilized as a blue-emitting phosphor for nUV LEDs.

Concentration quenching of $\text{CaMg}(\text{SiO}_3)_2:\text{Eu}^{2+}$

The concentration quenching behavior was analyzed using the emission intensity change as a function of x . Blasse reported that the critical transfer distance (R_c) was defined as: [46]:

$$R_c = 2 \left(\frac{3V}{4\pi x_c N} \right)^{1/3} \quad (4)$$

where x_c is the critical dopant concentration when the emission intensity shows the maximum value, V is the volume of the unit cell, and N is the number of cations in the unit cell. R_c in $\text{CaMg}(\text{SiO}_3)_2$ was calculated to be ~1.5 nm by taking the values of V , x_c , and N as 0.438 nm³,

0.06, and 4, respectively, from experimental and analytical evaluations. The interaction type was proposed by Dexter [47] when $x > x_c$ [48, 49]:

$$\log\left(\frac{I}{x}\right) \propto -\frac{\theta}{3} \log(x) \quad (5)$$

where I is the emission intensity and θ is a function of electric multipolar character.

There are three types of concentration quenching mechanisms that result from electrostatic multipolar interaction: dipole-dipole ($d-d$), dipole-quadrupole ($d-q$), and quadrupole-quadrupole ($q-q$) interactions, corresponding to $\theta = 6, 8$, and 10 , respectively. The type of interaction can be estimated by plotting $(\log(I/x))$ as a function of $(\log x)$. For $\text{CaMg}(\text{SiO}_3)_2:\text{Eu}^{2+}$ with $x = 0.06, 0.1$, and 0.2 , the concentration quenching mechanism under 350 nm excitation was found to be $d-q$ interaction ($\theta \sim 8$), as shown in Figure 8. These findings are in contradiction with the previously reported ($d-d$) quenching mechanism for the same material for value of $x_c = 0.01$, with an excitation wavelength of 147 nm [50], possibly due to the difference in the excitation wavelength that could affect the emission intensity.

Thermal quenching process of $\text{Ca}_{0.96}\text{Eu}_{0.04}\text{Mg}(\text{SiO}_4)_4$ and $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$

The thermal-quenching process of both phosphors was measured as the decrease of emission intensity as a function of temperature (from 25°C to 150°C). The data was then plotted using the following equation to describe thermal quenching of luminescence intensity $I(T)$ with temperature T [29]:

$$I(T) = \frac{I_0}{1 + \frac{\Gamma_0}{\Gamma_v} \exp\left(-\frac{\Delta E}{kT}\right)} \quad (6)$$

where I_0 is the initial intensity at 25°C , ΔE is the energy barrier for thermal quenching, k is the Boltzmann's constant, Γ_0 is the attempt rate for thermal quenching at $T = \infty$, and Γ_v is the radiative decay rate of the $5d$ state of Eu^{2+} . Here we adopted the Γ_0 and Γ_v with values of $3 \times$

10^{13} Hz and 1.1×10^6 Hz, respectively, in line with estimations in the literature [29]. Figure 9a and b show the PL emission intensity as a function of temperature from 25°C to 150°C, demonstrating that there is a significant quenching of the luminescence over this temperature range. Figure 9c shows a plot of the relative intensity as a function of temperature for both phosphors. Γ_0/Γ_∞ is 2.7×10^7 . The values for average ΔE were obtained in each temperature. ΔE were 0.56 ± 0.03 eV for $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ and 0.52 ± 0.02 eV for $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$. Note that there are many factors that influence the measured intensity than just thermal quenching alone (e.g. synthesis conditions, particle crystallinity). These factors will also affect the measured curve and subsequently the fitted thermal activation barrier. But we believe the relative trend for both cases is reasonable. These ΔE values were in good agreement with the range of calculated values of similar calcium compounds (0.2-0.6 eV) [29]. In general, the larger the thermal activation energy, the better Φ obtained for Eu^{2+} -activated phosphors. Although the predicted Θ for $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ (601K) is smaller than $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ (665K), the Φ of $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ (30%) is relative higher than $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ (5%), which can be attributed to its larger thermal activation energy.

A simplified relationship between the energy barrier and the quenching temperature $T_{0.5}$ (the temperature at which the emission intensity declined to 50% of the low temperature value) was developed by Dorenbos [29] from Eqn. (6):

$$\Delta E = \frac{T_{0.5}}{680} (\text{eV}) \quad (7)$$

From this equation, the obtained $T_{0.5}$ for $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ and $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ are 381 K and 354 K, respectively. These low thermal quenching temperatures suggest that Φ 's of $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ and $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ can be severely degraded, even at room temperature.

Other models of thermal quenching exist. For instance, the thermal ionization model [29] suggests that thermal quenching stability is related to the energy gap between the excited Eu 5d level and CBM. However, first principles determination of excited states is challenging, though a few recent works have explored this relationship using advanced techniques [51]. For high-throughput screening, a more efficient approximation needs to be developed. For example, the band gap can sometimes be used as a proxy [12, 52]; the larger the band gap of the host, the more likely that there is a larger gap between the excited 5d level and the CBM (though the exact relationship depends on the magnitude of the Stokes shift). The investigation of these other first principles descriptors will be the subject of future work.

CONCLUSIONS

An integrated approach of exploring new phosphors for near-UV (nUV) excitation by combining experiments and calculations is outlined. The descriptors of Debye temperature (Θ) and excitation energy were combined to screen plausible phosphors that are predicted to have high quantum efficiency (Φ) and can be employed in near-UV emitting LEDs. From the calculation of 27 host materials, $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ and $\text{CaMg}(\text{SiO}_3)_2$ were selected because predicted Θ for $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ and $\text{CaMg}(\text{SiO}_3)_2$ were found to be 601 K and 665 K, respectively, which are expected to have high Φ ($> 80\%$). The predicted and experimental excitation energies are similar. The measured values of Φ are lower than the expected values, based on high Θ . The main peak in the photoluminescence emission spectra under excitation of 350 nm is 511 nm for $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$, with chromaticity coordinates of (0.25, 0.49), and 458 nm for $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$ with chromaticity coordinates of (0.14, 0.05). The concentration self-quenching mechanism for $\text{CaMg}(\text{SiO}_3)_2:\text{Eu}^{2+}$ under 350 nm is the $d-q$ interaction. The thermal quenching temperatures ($T_{0.5}$) are 381 K and 354 K for $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ and $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$, respectively, indicating poor thermal stability. Despite having a high Θ , a low Φ is found for the two candidates. Conversely, other

screened hosts (e.g. $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$) have low computed Θ , but are known to have a high Φ . Therefore, the use of high Θ as an indicator for high quantum efficiency should be treated with caution when screening host candidates. It is desirable to develop more well-defined criteria for the screening of host candidates for high Φ phosphors. The approach developed in this work can be leveraged for the discovery of additional nUV excited phosphors.

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LIST OF TABLE AND FIGURE CAPTIONS

Table 1. Calculated Debye temperature (Θ) of 27 identified host for Ce^{3+} or Eu^{2+} activation. The compositions in bold have $\Theta > 500\text{K}$. The excitation energy (E_{ex}) and emission energy (E_{em}) were selected from [13, 14, 16-18, 37, 44].

Figure 1. Schematic diagram of $4f \rightarrow 5d$ transition in Ce^{3+} or Eu^{2+} activated phosphors. E_g , E_{ex} and $E_{4f\text{-VBM}}$ denote the band gap of host material, excitation energy, and $4f\text{-VBM}$ energy gap, respectively.

Figure 2. The band structure of the host material $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ (a) and $\text{CaMgSi}_2\text{O}_6$ (b), where it has a direct $\Gamma \rightarrow \Gamma$ transition band gap of 6.86 eV and 7.08 eV, respectively.

Figure 3. The orbital-projected density of state (DOS) of $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\text{:Eu}^{2+}$ (a), and $\text{CaMgSi}_2\text{O}_6\text{:Eu}^{2+}$ (b), where the $4f\text{-VBM}$ energy gap is 3.18 eV and 3.79 eV, respectively. The Fermi level is set to 0.

Figure 4. Unit cell representation of the crystal structure of (a) $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\text{:Eu}^{2+}$ (b) $\text{CaMgSi}_2\text{O}_6\text{:Eu}^{2+}$ drawn with VESTA [33]. $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ has an orthorhombic structure with space group $Pnn2$ with lattice constants $a = 0.6742\text{ nm}$, $b = 1.0887\text{ nm}$, $c = 1.8339\text{ nm}$. $\text{CaMg}(\text{SiO}_3)_4$ has a monoclinic structure with space group $C2/c$ with lattice constants $a = 0.9743\text{ nm}$, $b = 0.8879\text{ nm}$, $c = 0.5230\text{ nm}$. Both lattice parameters are calculated using TOPAS.

Figure 5. X-ray diffraction patterns: (a) $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ prepared by the sol-gel/Pechini method with post-synthesis annealing conditions of 1100°C or 1350°C for 3 h or 1400°C for 10 h. (b) $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$ ($x = 0.02, 0.06, 0.1$, and 0.2) prepared by the co-precipitation method with post-synthesis annealing condition of 1100°C for 2 h.

Figure 6. Scanning electron micrographs of the powders. $\text{Ca}_{0.96}\text{Eu}_{0.04}\text{Mg}(\text{SiO}_4)_4$ after post-synthesis annealing at: (a) 1350°C for 3 h and (b) 1400°C for 10 h. $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$ with post-synthesis annealing condition of 1100°C for 2 h: (c) $x = 0.02$ (d) $x = 0.06$, (e) $x = 0.10$ and (f) $x = 0.20$.

Figure 7. (a) Photoluminescence excitation (dashed line monitored at 511 nm) and emission (solid line, $\lambda_{ex} = 350\text{ nm}$) spectra of $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$. Blue lines = post-synthesis annealing at 1350°C for 3 h and the red lines = post-synthesis annealing at 1400°C for 10 h. Both powders were subsequently heated to 1100°C for 4 h in a reducing atmosphere. (b) Photoluminescence excitation (dashed line monitored at 458 nm) and emission (solid line, $\lambda_{ex} = 350\text{ nm}$) spectra of $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$, $x = 0.02, 0.06, 0.1$, and 0.2 . Post-synthesis annealing condition was 1100°C for 2 h. The inset photographs are the phosphor powders excited with 365 nm. Φ = quantum efficiency.

Figure 8. The relationship between the $\log(I/x)$ and $\log(x)$ of $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$. I = emission intensity, and x = concentration of Eu^{2+} ($x = 0.06, 0.1$, and 0.2).

Figure 9. The emission intensity (I) of the photoluminescence spectra as a function of temperature for **(a)** $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$, **(b)** $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$. **(c)** Plot of the relative intensity as a function of temperature from the data in (a) and (b). ΔE = activation energy and Γ_0 is the attempt rate for thermal quenching at $T = \infty$, and Γ_v is the radiative decay rate of the 5d state of Eu^{2+} .

Table 1. Calculated Debye temperature (Θ) of 27 identified host for Ce^{3+} or Eu^{2+} activation. The compositions in bold have $\Theta > 500\text{K}$. The excitation energy (E_{ex}) and emission energy (E_{em}) were selected from [13, 14, 16-18, 37, 44].

Host material	E_{ex} (nm)	E_{em} (nm)	Θ (K)
$\text{Mg}_2\text{SiO}_4:\text{Ce}^{3+}$	373	432	734
$\text{X1-YSiO}_2\text{N}:\text{Ce}^{3+}$	-	-	695
$\text{CaMg}(\text{SiO}_3)_2:\text{Eu}^{2+}$	365	450	665
$\text{Mg}_3\text{F}_3\text{BO}_3:\text{Ce}^{3+}$	399	474	615
$\text{X2-YSiO}_2\text{N}:\text{Ce}^{3+}$	370	405	606
$\text{Ca}_7\text{Mg}(\text{SiO}_4)_4:\text{Eu}^{2+}$	350	505-520	601
$\text{X2-Y}_2\text{SiO}_5:\text{Ce}^{3+}$	381	480	512
$\text{X1-Y}_2\text{SiO}_5:\text{Ce}^{3+}$	365	430	491
$\text{SrY}_2\text{O}_4:\text{Ce}^{3+}$	397	560	465
$\text{La}_2\text{Be}_2\text{O}_5:\text{Ce}^{3+}$	365	445	464
$\beta\text{-Sr}_2\text{SiO}_4$	310	~543	428
LuBO_3 (vaterite) : Ce^{3+}	365	388	423
$\text{Ba}_3\text{Mg}(\text{SiO}_4)_2:\text{Eu}^{2+}$	410	438	422
$\text{X2-Lu}_2\text{SiO}_5:\text{Ce}^{3+}$	376	462	416
$\text{X1-Sr}_2\text{SiO}_4:\text{Eu}^{2+}$	390	490	410
$\text{NaF}:\text{Ce}^{3+}$	390	472	387
$\text{CaAl}_2\text{S}_4:\text{Ce}^{3+}$	396	440	373
$\alpha\text{-Sr}_2\text{SiO}_4$	310	573	360
$\text{Sr}_2\text{SiCl}_2\text{O}_3:\text{Eu}^{2+}$	410	490	349
$\text{SrAl}_2\text{S}_4:\text{Ce}^{3+}$	397	462	338
$\text{BaAl}_2\text{S}_4:\text{Ce}^{3+}$	384	444	331
$\text{ThO}_2:\text{Ce}^{3+}$	408	-	319
Ba_2SiO_4	360	512	307
$\text{Ba}_2\text{YB}_2\text{O}_{62}\text{Cl}:\text{Ce}^{3+}$	370	466	300
$\text{Ba}_2\text{LuB}_2\text{O}_6\text{Cl}:\text{Ce}^{3+}$	370	466	294
$\text{La}_3\text{Si}_2\text{S}_8\text{I}:\text{Ce}^{3+}$	370	446	262
$\text{LaOI}:\text{Ce}^{3+}$	385	435	161

Figure 1. Schematic diagram of $4f \rightarrow 5d$ transition in Ce^{3+} or Eu^{2+} activated phosphors. E_g , E_{ex} and E_{4f-VBM} denote the band gap of host material, excitation energy, and $4f$ -VBM energy gap, respectively.

(a)

(b)

Figure 2. The band structure of the host material $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ (a) and $\text{CaMgSi}_2\text{O}_6$ (b), where it has a direct $\Gamma \rightarrow \Gamma$ transition band gap of 6.86 eV and 7.08 eV, respectively.

(a)

(b)

Figure 3. The orbital-projected density of state (DOS) of $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4\text{:Eu}^{2+}$ (a), and $\text{CaMgSi}_2\text{O}_6\text{:Eu}^{2+}$ (b), where the 4f-VMB energy gap is 3.18 eV and 3.79 eV, respectively. The Fermi level is set to 0.

(a)

(b)

Figure 4. Unit cell representation of the crystal structure of (a) $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4:\text{Eu}^{2+}$ (b) $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$ drawn with VESTA [33]. $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ has an orthorhombic structure with space group $Pnn2$ with lattice constants $a = 0.6742$ nm, $b = 1.0887$ nm, $c = 1.8339$ nm. $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ has a monoclinic structure with space group $C2/c$ with lattice constants $a = 0.9743$ nm, $b = 0.8879$ nm, $c = 0.5230$ nm. Both sets of lattice parameters were calculated using TOPAS.

(a)

(b)

Figure 5. X-ray diffraction patterns: (a) $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$ prepared by the sol-gel/Pechini method with post-synthesis annealing conditions of 1100°C or 1350°C for 3 h or 1400°C for 10 h. (b) $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$ ($x = 0.02, 0.06, 0.1, \text{ and } 0.2$) prepared by the co-precipitation method with post-synthesis annealing condition of 1100°C for 2 h.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 6. Scanning electron micrographs of the powders. $\text{Ca}_{0.96}\text{Eu}_{0.04}\text{Mg}(\text{SiO}_4)_4$ after post-synthesis annealing at: (a) 1350°C for 3 h and (b) 1400°C for 10 h. $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$ with post-synthesis annealing condition of 1100°C for 2 h: (c) $x = 0.02$ (d) $x = 0.06$, (e) $x = 0.10$ and (f) $x = 0.20$.

(a)

(b)

Figure 7. (a) Photoluminescence excitation (dashed line monitored at 511 nm) and emission (solid line, $\lambda_{\text{ex}} = 350$ nm) spectra of $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)$. Blue lines = post-synthesis annealing at 1350°C for 3 h and the red lines = post-synthesis annealing at 1400°C for 10 h. Both powders were subsequently heated to 1100°C for 4 h in a reducing atmosphere. (b) Photoluminescence excitation (dashed line monitored at 458 nm) and emission (solid line, $\lambda_{\text{ex}} = 350$ nm) spectra of $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$, $x = 0.02, 0.06, 0.1$, and 0.2 . Post-synthesis annealing condition was 1100°C for 2 h. The inset photographs are the phosphor powders excited with 365 nm. Φ = quantum efficiency.

Figure 8. The relationship between the $\log(I/x)$ and $\log(x)$ of $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$. I = emission intensity, and x = concentration of Eu^{2+} ($x = 0.06, 0.1$, and 0.2).

Figure 9. The emission intensity (I) of the photoluminescence spectra as a function of temperature for **(a)** $(\text{Ca}_{0.96}\text{Eu}_{0.04})_7\text{Mg}(\text{SiO}_4)_4$, **(b)** $\text{Ca}_{0.94}\text{Eu}_{0.06}\text{Mg}(\text{SiO}_3)_2$. **(c)** Plot of the relative intensity as a function of temperature from the data in (a) and (b). ΔE = activation energy and Γ_0 is the attempt rate for thermal quenching at $T = \infty$, and Γ_v is the radiative decay rate of the 5d state of Eu^{2+} .