Global warming is worsening on account of the consumption of fossil fuels, which produce CO₂ gas,¹ and the fact that a large amount of energy is required for illumination, including both industrial and residential lighting. Accordingly, white light-emitting diodes (WLEDs) represent a potential next-generation illumination source, as they have very favorable properties, such as high energy efficiency, low power consumption, reliability, and environmental protection.²³ Phosphors are important materials in lighting and have been extensively investigated.³ The most universal WLED employs a 450–470 nm blue-emitting chip that is coated with a yellow phosphor, Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) and CaSiAlN₃:Eu²⁺. The thermal stability of these phosphors, depending weakly on the composition and the activator concentration, remains high over a wide range of temperatures (25–300°C). When a mixture of YAG:Ce and CaSiAlN₃:Eu²⁺ was coated on a blue LED, the resultant white LED had a high luminous efficiency of ηₜ = 68 lm/W, a high color rendering index of Ra = 93, and a color temperature of Tc = 3007 K (at 50 mA). Additionally, the color coordinates, Ra and Tc, of the white LED tend to remain constant against an appreciable variation in applied current.

Results and Discussion

Figure 1 presents the XRD patterns of the powdered phosphors Y₃₋ₓAlₓO₁₂:Ceₓ⁻⁺ (x = 0.01) (top) and Ca₀.₉₈SiAlN₃:Euₓ⁺ (bottom). The crystal structures of all the samples were similar to those in the database. YAG:Ce has a cubic lattice with a space group of Pm₃n. La-doped YAG:Ce was excited using a blue LED, and the WLED thus fabricated by associating an InGaN-based blue LED chip with highly luminescent phosphors, Y₃₋ₓAlₓO₁₂:Ceₓ⁻⁺ (YAG:Ce) and CaSiAlN₃:Eu²⁺. The thermal stability of these phosphors, depending weakly on the composition and the activator concentration, remains high over a wide range of temperatures (25–300°C). When a mixture of YAG:Ce and CaSiAlN₃:Eu²⁺ was coated on a blue LED, the resultant white LED had a high luminous efficiency of ηₜ = 68 lm/W, a high color rendering index of Ra = 93, and a color temperature of Tc = 3007 K (at 50 mA). Additionally, the color coordinates, Ra and Tc, of the white LED tend to remain constant against an appreciable variation in applied current.

In this study, oxide- and nitride-based highly luminescent phosphors, such as yellow-emitting YAG:Ce and red-emitting CaSiAlN₃:Eu²⁺, respectively, are adopted. A mixture of YAG:Ce and CaSiAlN₃:Eu²⁺ was excited using a blue LED, and the WLED thus produced comprised a high luminous efficiency, high color rendering index, and Commission International de’l’Eclairage (CIE) chromaticity coordinates that did not vary with applied current. The thermal stability of the phosphors was explored herein.

Experimental

First, a polycrystalline sample of Y₃₋ₓAlₓO₁₂:Ceₓ (x = 0.01) was synthesized by a solid-state reaction using raw precursors, such as Y(NO₃)₃·6H₂O, Al(NO₃)₃·9H₂O, and Ce(NO₃)₃·6H₂O. The mixture was first calcined at 1000°C in air for 24 h. Subsequently, the calcined light-yellow powder was ground again and sintered in air at 1500°C for 24 h to yield a highly crystalline material. The crystalized powder was then milled and annealed in a reducing atmosphere (5% H₂ in N₂) at 1500°C for 12 h to reduce Ce⁴⁺ to Ce³⁺. Nitrite-based precursors, including EuN, Ca₃N₂, AlN, and Si₃N₄, were weighted by the stoichiometric molar ratio in a glove box that was filled with N₂. The mixture was charged in a boron nitride crucible and then fired in 1 MPa N₂ at 1600°C for 2 h and at 1800°C for 2 h. The fired Ca₁₋ₓSi₃Al₅O₁₂Euₓ (x = 0.02) was crushed, sieved, and prepared for measurements to be made. Finally, the two phosphors were mixed with epoxy and coated onto InGaN-based blue LEDs.

The phase purity of the synthesized samples was identified by X-ray powder diffraction (XRD) analysis using an X’Pert PRO advanced automatic diffractometer with Cu Kα radiation of 45 kV and 40 mA. The photoluminescence (PL) spectra were obtained using a FluoroMax-3 and a FluoroMax-P spectrophotometer at room temperature. Thermal quenching was conducted using a heating apparatus (THMS-600) with PL equipment. Scanning electron microscopy (SEM) micrographs of the products were captured using a field-emission-scanning electron microscope (JSM-6700F, JEOL). The electro-optical characteristics and current stability of the WLED were measured using an Everfine PMS-50 spectra system.

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lattice constants $a = b = c$, as determined by Menzer in 1928.\textsuperscript{11} The unit cell is composed of a single $Y$, which occupies the 24(c) site, with a dodecahedral (distorted cubic) lattice and a coordination number of 8. Al ions have two sites in the lattice: octahedral (space group $Pm3m$), the Al and Si atoms in the crystal were distributed randomly among the 8b sites. The tetrahedra of SiN$_4$ and AlN$_4$ form a six-member ring by sharing corners with the Ca$^{2+}$ ions, which occupies the 24d site, respectively. The particles show some aggregation with diameters of the aggregates between 5 and 10 $\mu$m. Further optimization of the reaction conditions and flux yielded particles of controllable diameters and a narrower size distribution.

EDX measurements revealed that the formation of all samples herein were Y, Al, O, Ce, Ca, and Si.

Figure 3 shows the normalized photoluminescence excitation and PL spectra of various phosphors. All of the PL spectra were obtained under excitation by a 460 nm blue LED at room temperature. The YAG:Ce phosphor emits a yellow light that peaked at $\sim 565$ nm via the transition from $4f^55d^1$ to $4f^4$ of cerium ions (Ce$^{3+}$). The broad emission band of the red-emitting CaSiAlN$_3$:Eu$^{3+}$ sample is assigned to the allowed $4f^55d^1$ to $4f^2$ transition of Eu$^{3+}$ ions from 550 to 750 nm. Because the emission spectra of the yellow phosphor YAG:Ce are short of the red part, a high color rendering index WLED can be produced by adding the available red-emitting phosphor CaSiAlN$_3$:Eu$^{3+}$. Figure 4 plots the relationship between the emission intensity and environmental temperature of (a) Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ and (b) CaSiAlN$_3$:Eu$^{3+}$, measured under a 460 nm excitation. The emission intensity of Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ declines as the temperature increased because the nonradioactive transition from the excited states to the ground state increased, as shown in the configurationally coordinate diagram; this effect is called the thermal quenching effect.\textsuperscript{16} As a result, the emission peaks of YAG:Ce$^{3+}$ were redshifted from 560 to 570 nm, which phenomenon is explained with reference to the Varshni equation for temperature dependence.\textsuperscript{17}
The emission band of CaSiAlN₃:Eu²⁺ is blueshifted, as presented in Fig. 5. In this study, the luminescence intensity decreases by 45% as the temperature increases from 25 to 300°C, as displayed in Fig. 5. The temperature-dependent relative emission intensity of Y₃Al₅O₁₂:Ce³⁺ and CaSiAlN₃:Eu²⁺ is shown in Fig. 6. Two samples have a thermal quenching temperature, defined as the temperature at which the emission intensity is 50% of its original value. Two samples have a thermal quenching temperature, defined as the temperature at which the emission intensity is 50% of its original value. Two samples have a thermal quenching temperature, defined as the temperature at which the emission intensity is 50% of its original value.

The thermal quenching temperature, \( T_q \), is defined as the temperature at which the emission intensity is 50% of the blue line in Fig. 4c. The thermal quenching temperature, \( T_q \), is defined as the temperature at which the emission intensity is 50% of its original value. Two samples have a \( T_q \) of over 300°C, suggesting their superior thermal stability as luminescent materials for use in WLEDs, as shown in Fig. 5. To calculate the activation energy of thermal quenching, the Arrhenius equation was fitted to the thermal quenching data. The thermal quenching temperature, \( T_q \), is defined as the temperature at which the emission intensity is 50% of its original value. Two samples have a \( T_q \) of over 300°C, suggesting their superior thermal stability as luminescent materials for use in WLEDs, as shown in Fig. 5. To calculate the activation energy of thermal quenching, the Arrhenius equation was fitted to the thermal quenching data. The thermal quenching temperature, \( T_q \), is defined as the temperature at which the emission intensity is 50% of its original value. Two samples have a \( T_q \) of over 300°C, suggesting their superior thermal stability as luminescent materials for use in WLEDs, as shown in Fig. 5. To calculate the activation energy of thermal quenching, the Arrhenius equation was fitted to the thermal quenching data.

\[
I(T) = \frac{I_o}{1 + c \exp\left(\frac{-E}{kT}\right)}
\]

where \( I_o \) denotes the initial intensity of the emission at room temperature, \( I(T) \) is the intensity at temperature \( T \), \( c \) is a constant, \( E \) is the activation energy for thermal quenching, and \( k \) is Boltzmann’s constant. The activation energies for thermal quenching were 0.25 and 0.21 eV for Y₃Al₅O₁₂:Ce³⁺ and CaSiAlN₃:Eu²⁺, respectively.

Figure 6 shows the emission spectra of the Y₃Al₅O₁₂:Ce³⁺ and CaSiAlN₃:Eu²⁺-based WLED under forward bias currents of 50, 150, 250, 350, 450, 550, 650, 750, 850, and 950 mA. At 50 mA, the optical properties of WLED were a high luminous efficiency of 68 lm/W, a high color rendering index \( Ra = 93 \), and a color temperature \( T_C = 3007 \) K. The total spectral flux of the blue, yellow, and red bands of the pc WLEDs increased with the applied current from 50 to 950 mA. Our luminous efficiency (68 lm/W) is significantly increased with a comparable color rendering (\( Ra = 93 \)) by using only a blue LED pumped for one oxide (YAG) and one nitride (CaSiAlN₃) phosphor as compared to the results of Kimura et al. in which they used a blue LED to pump three oxynitride phosphors.

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### Table I. Optical properties of various WLEDs at applied currents from 50 to 950 mA.

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>( \eta_l ) (lm/W)</th>
<th>CIE-x</th>
<th>CIE-y</th>
<th>( T_C ) (K)</th>
<th>Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>68</td>
<td>0.4305</td>
<td>0.3949</td>
<td>3007</td>
<td>93</td>
</tr>
<tr>
<td>150</td>
<td>59</td>
<td>0.4292</td>
<td>0.3922</td>
<td>2997</td>
<td>93</td>
</tr>
<tr>
<td>250</td>
<td>52</td>
<td>0.4281</td>
<td>0.3896</td>
<td>2991</td>
<td>93</td>
</tr>
<tr>
<td>350</td>
<td>46</td>
<td>0.4274</td>
<td>0.3875</td>
<td>2988</td>
<td>92</td>
</tr>
<tr>
<td>450</td>
<td>44</td>
<td>0.4263</td>
<td>0.3856</td>
<td>2983</td>
<td>92</td>
</tr>
<tr>
<td>550</td>
<td>41</td>
<td>0.4256</td>
<td>0.3835</td>
<td>2952</td>
<td>92</td>
</tr>
<tr>
<td>650</td>
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<td>0.3816</td>
<td>2978</td>
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<td>0.3800</td>
<td>2978</td>
<td>92</td>
</tr>
<tr>
<td>850</td>
<td>34</td>
<td>0.4220</td>
<td>0.3776</td>
<td>2979</td>
<td>91</td>
</tr>
<tr>
<td>950</td>
<td>30</td>
<td>0.4212</td>
<td>0.3762</td>
<td>2980</td>
<td>91</td>
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</table>

<table>
<thead>
<tr>
<th>Current differential</th>
<th>( \eta_{\text{diff}} )</th>
<th>CIE-x differential</th>
<th>CIE-y differential</th>
<th>( T_C ) differential</th>
<th>Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>50–950</td>
<td>–38</td>
<td>–0.0093</td>
<td>–0.0187</td>
<td>–27</td>
<td>–2</td>
</tr>
</tbody>
</table>
the luminous efficiency properties of the pc WLEDs. As the applied current was increased, changed, as displayed in Fig. 7. The results demonstrate the high effect.20,21 Therefore, the CIE color coordinates of WLED barely color rendering index Ra = 93, and a color temperature $T_C = 3007$ K (at 50 mA). Additionally, its color coordinates, Ra and $T_C$, were stable against an increase in applied current.

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