

Photoluminescence properties of $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ for plant habitat-conscious LEDs

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We have prepared a new phosphor Dy-substituted $\text{La}_2\text{W}_2\text{O}_9$. The $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ exhibited a yellow-white luminescence consisting of sharp emission peaks assigned to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$, and ${}^4F_{9/2} \rightarrow {}^6H_{9/2}$ transitions in Dy^{3+} ions, respectively. The maximum internal quantum efficiency was 21.3% at $x = 0.05$ under the 387 nm excitation light. The white LED was fabricated by using a UV LED at 385 nm and the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ ($x = 0.05$) phosphor (Dy-WLED). The plant cultivation experiments for *Chlorella* photosynthetic growth was carried out by using the Dy-WLED and a reference commercial white LED, and the reduction of the *Chlorella* growth was confirmed in the Dy-WLED.

Key words: Photoluminescence, $\text{La}_2\text{W}_2\text{O}_9$, Dy^{3+} , Plant habitat-conscious LEDs.

Introduction

In recent progress of lighting technologies, light-emitting diodes (LEDs) are surely a breakthrough as a new low emission light source because of their very long lifetime and high luminous efficacy compared with conventional lighting systems. White LEDs (WLEDs) for residential light applications are generally formed by excitation blue or near UV LEDs and yellow phosphors or red/green phosphors [1-4]. Many researches have extensively studied phosphors that emit brighter and more comfortable light for human eyes. Recently, negative effects for natural plant growth environment are pointed out to conventional outdoor lighting systems. Natural plant habitats, particularly at dark sites such as natural caves and forests, can be damaged because the increase in illumination intensity allows inhabitation of different species [5-7]. This is an unignorable issue for plant ecosystem protection for native species and the preservation of natural heritage.

Thus, artificial lighting systems must consider the protection of plant habitats, and lighting that does not affect plant growth must be developed. We have fabricated a plant habitat-conscious WLED to protect native ecosystems, and identified Dy^{3+} luminescence as suitable for this purpose [6, 7]. In this study, this effect has been confirmed in an illumination of a WLED using emission from new phosphors $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$. We report optical properties of Dy-phosphors $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ and plant cultivation tests using a WLED consisted of the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ and an excitation UV LED.

Experimental

Polycrystalline $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ phosphors were synthesized by a solid-state reaction. A mixture of reagent powders, La_2O_3 , WO_3 , and Dy_2O_3 , in an appropriate molar ratio was heated at 1000 °C for 3 hrs in air. The Dy substitution was carried out to the La sites. The products were confirmed to be a single phase of $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ by X-ray diffraction (XRD, SmartLab, Rigaku). The photoluminescence (PL) spectrum, internal quantum efficiency (IQE), IQE excitation spectrum, and luminescence color properties of the samples were evaluated with a C9920-02 spectrometer (Hamamatsu Photonics) equipped with a xenon lamp, a monochromator, a back-illuminated multichannel charge-coupled device (CCD) photodetector, and an integrating sphere. The IQE (%) was calculated by using $\text{IQE} = N_{\text{em}}/N_{\text{abs}} \times 100$, where N_{em} and N_{abs} are the number of emitted and absorbed photons, respectively.

A WLED containing the Dy-phosphor (Dy-WLED) was prepared by embedding the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ powder onto a power UV LED (NS385L-6SMG, Nitride Semiconductors) with silicone resin. A commercial WLED (C-WLED, NVSW119BT, Nichia) was used for comparison as a reference. The color properties, spectral irradiance and illuminance for all LEDs were studied by a multichannel spectrometer USB2000+ (Ocean Optics) with a light-collecting optical fiber.

The *Chlorella*-cultivation experiment with the Dy-WLED and the reference C-WLED was performed. The *Chlorella* cells were dispersed in a 0.1% HYPONeX (HYPONeX Japan Co., Ltd.) aqueous solution. The *Chlorella* dispersion (3 mL) was placed in a container covered with aluminum foil inside to guarantee the light spectra originated from only the LED, and then it was illuminated with an LED under the equivalent illuminance ($300 \text{ lm} \cdot \text{m}^{-2}$) condition at 27 °C. The weight of the

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Chlorella was measured after drying the solution overnight at 60 °C.

Results and Discussion

Fig. 1 shows the XRD 2θ scan of the $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ powder. All the diffraction peaks were indexed to a triclinic unit cell as similar with the unsubstituted $\text{La}_2\text{W}_2\text{O}_9$ with a a -form [8]. This α - $\text{La}_2\text{W}_2\text{O}_9$ is crystallized with the space group $P\bar{1}$ (No. 2), and the La sites are $2i$ without inversion center (C_1 point symmetry).

Fig. 2(a) shows a PL spectrum of $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ under excitation light at 385 nm. The $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ exhibited a yellowish white luminescence, and sharp emission peaks were observed at 480, 578, 662, and 750 nm that can be assigned to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{9/2}$ transitions in Dy^{3+} ions, respectively. The luminescence CIE color coordinates (CIE(x , y)) and correlated color temperature (CCT) excited at 385 nm were estimated to be (0.385, 0.415) and 4128 K, respectively. Among the luminescence transitions in the $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$, the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition was dominant. This would be caused by the low site symmetry of $2i$ site in $P\bar{1}$ space group without inversion center, where the Dy^{3+} habited. It has been reported that the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} is very sensitive against the crystal-field environment: this transition can be enhanced when the Dy^{3+} occupies at the sites with low site symmetry [9]. The excitation spectrum of IQE for the $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ is shown in Fig. 2(b). In this spectrum, four excitation bands were observed at 328, 352, 365, and 387 nm that can be assigned to ${}^6H_{15/2} \rightarrow {}^6P_{3/2}$, ${}^6H_{15/2} \rightarrow {}^6P_{7/2}$, ${}^6H_{15/2} \rightarrow {}^4D_{5/2}$

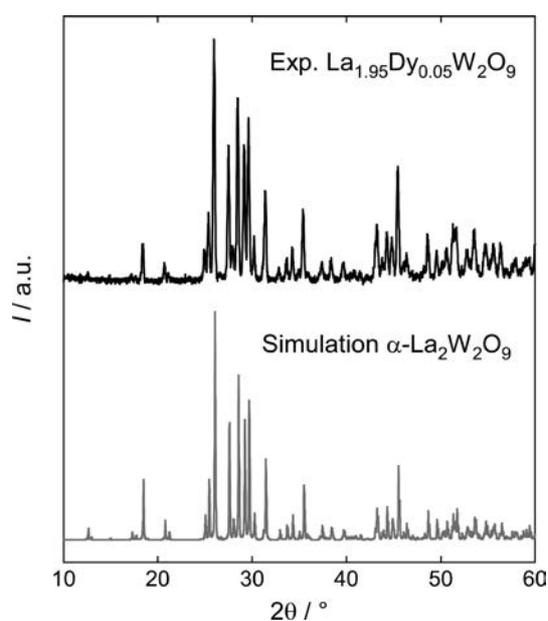


Fig. 1. XRD pattern of $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ and simulation pattern of α - $\text{La}_2\text{W}_2\text{O}_9$.

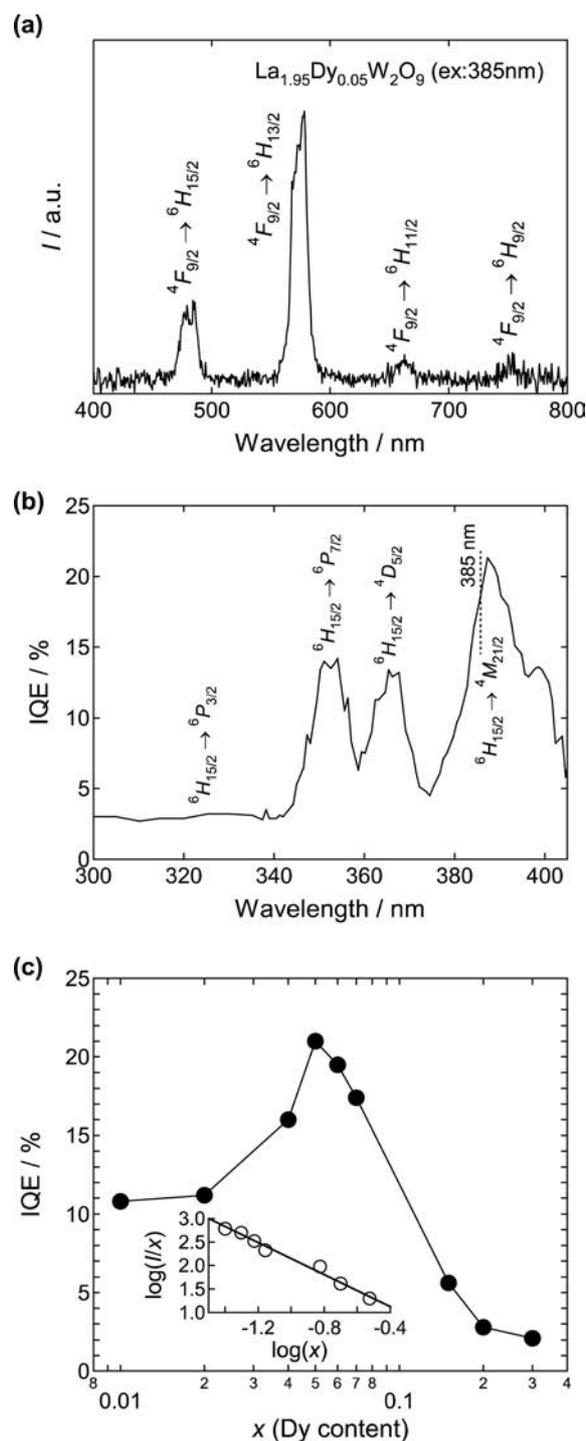


Fig. 2. (a) Photoluminescence spectrum of $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ excited at 385 nm. (b) IQE of $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ as a function of wavelength. (c) IQE for the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ as a function of concentration, x , under 385 nm excitation. The inset shows a plot of $\log(I/x)$ versus $\log(x)$ is shown for the luminescence integrated intensity of the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at around 578 nm in $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ under excitation at 385 nm. The line represents the fitting curve.

and ${}^6H_{15/2} \rightarrow {}^4M_{21/2}$ transitions in Dy^{3+} ions, respectively. The maximum IQE was reached to be 21.3% at 387 nm. The x dependence of IQE for the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ under the excitation at 385 nm had a maximum at $x = 0.05$, and

then it decreased down with the increasing x by the concentration quenching (Fig. 2c). Therefore, we identified the $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ as the optimum composition for the brightest luminescence for the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$. From the concentration quenching behavior, the critical distance (R_C), which describes the distance between the activator and the quenching site for most efficient energy transfer, can be evaluated by using the Blasse equation [10]:

$$R_C = 2 \left(\frac{3V}{4\pi X_C N} \right)^{\frac{1}{3}} \quad (1)$$

where, V is the volume of the unit cell, X_C is the critical concentration of Dy^{3+} , and N is the number of substitution sites for the dopant in the unit cell. For the $\alpha\text{-La}_2\text{W}_2\text{O}_9$ host, $V = 347.73 \text{ \AA}^3$ [9], $X_C = 0.05$ at the maximum IQE and $N = 4$, and consequently, the R_C is calculated to be 7.46 \AA . The exchange interaction generally restricts the critical distance to around 5 \AA when it is dominated by an energy transfer [11]. The R_C value was relatively large; therefore, the multipolar interaction was the dominant mechanism for the concentration quenching in the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ phosphors. In the plot of $\log(I/x)$ versus $\log(x)$ for the integrated luminescence intensity of the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at around 578 nm in $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ under excitation at 385 nm , the luminescence intensity (I) and the mole fraction of Dy^{3+} (x) at a sufficient dopant level are expressed as follows according to Dexter's law for evaluating multipolar energy transfer [12],

$$\log\left(\frac{1}{x}\right) = c - \left(\frac{\theta}{3}\right) \log(x) \quad (2)$$

where c is a constant. $\theta = 6, 8$ and 10 correspond to electric dipole-dipole ($d-d$), electric dipole-electric quadrupole ($d-q$), and electric quadrupole-electric quadrupole ($q-q$) interactions, respectively [13]. The q value was calculated as 5.11 , which is close to 6 , indicating that the concentration quenching in this material was the $d-d$ interaction.

The fabricated Dy-WLED containing the $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ powder showed white light mainly consisting of three sharp emissions (Fig. 3): violet/blue emission which was the excess light from the excitation UV LED, and green-blue and yellow-orange luminescences from the $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ phosphor corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} ions. The CIE color coordinates and CCT were CIE (0.355, 0.371) and 4720 K , respectively. We used the C-WLED as a reference that had a different type of spectrum as shown in Fig. 3. The commercial C-WLED emitted light over almost the entire wavelength range of visible light because of the wide luminescence band of the phosphors in addition to the blue light from the excitation LEDs. We compared effects of these different emission spectra on the *Chlorella* cultivation test corresponding to the photosynthesis under continuous LED illumination.

The *Chlorella* cultivation test using the Dy-WLED

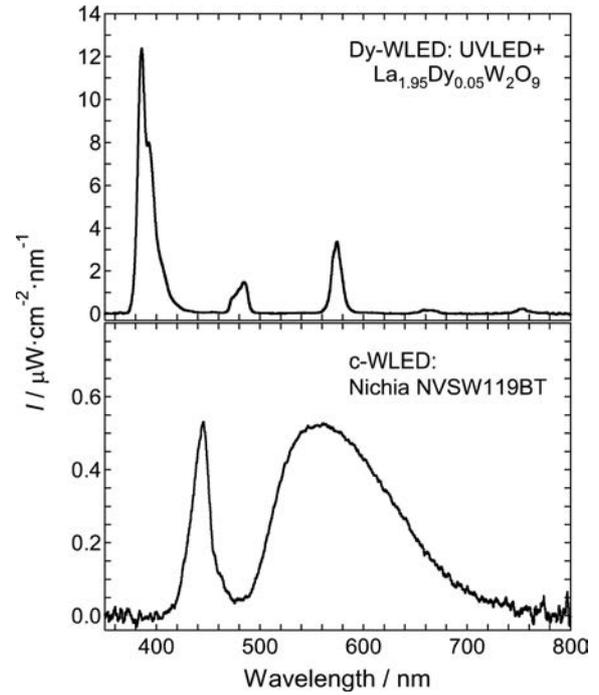


Fig. 3. Emission spectral irradiance for Dy-WLED using the $\text{La}_{1.95}\text{Dy}_{0.05}\text{W}_2\text{O}_9$ phosphor and commercial C-WLEDs (Nichia NVSW119BT) at $300 \text{ lm} \cdot \text{m}^{-2}$.

and C-WLED was carried out. The WLEDs illuminated to 3 mL *Chlorella* dispersion in cultivation cells for 15 days at equivalent illuminance $300 \text{ lm} \cdot \text{m}^{-2}$. The dried residue for grown *Chlorella* after 15 days was weighed: 810 mg for the Dy-WLED and 1258 mg for the C-WLED. The weight of the sample illuminated by the Dy-WLED was 36% less than the reference. The origin of reduced photosynthesis in the Dy-WLED has been explained as following reasons [6]: low correlation between the LED illumination and photosynthetic action spectra and especially reducing the Emerson effect [14], which is a synergetic effect of illuminated multi-wavelength bands, by decreasing red light illumination. Therefore, we have introduced following two indicators C_{PS} and I_{red} :

$$C_{PS} = \int_{350 \text{ nm}}^{800 \text{ nm}} PS(x) \cdot I(x) dx \quad (3)$$

$$I_{red} = \int_{600 \text{ nm}}^{800 \text{ nm}} I(x) dx \quad (4)$$

where x is the wavelength, $PS(x)$ is a typical photosynthetic action spectrum (Fig. 4(a)) [15], and $I(x)$ is the LED emission spectra. The C_{PS} and I_{red} were integrated from near-UV to near-IR wavelength ($350\text{--}800 \text{ nm}$), and from red to near-IR wavelength ($600\text{--}800 \text{ nm}$), respectively. The integrated intensities of the each WLED for the C_{PS} and I_{red} are shown in Fig. 4b. The residue weight had large relation especially to the I_{red} .

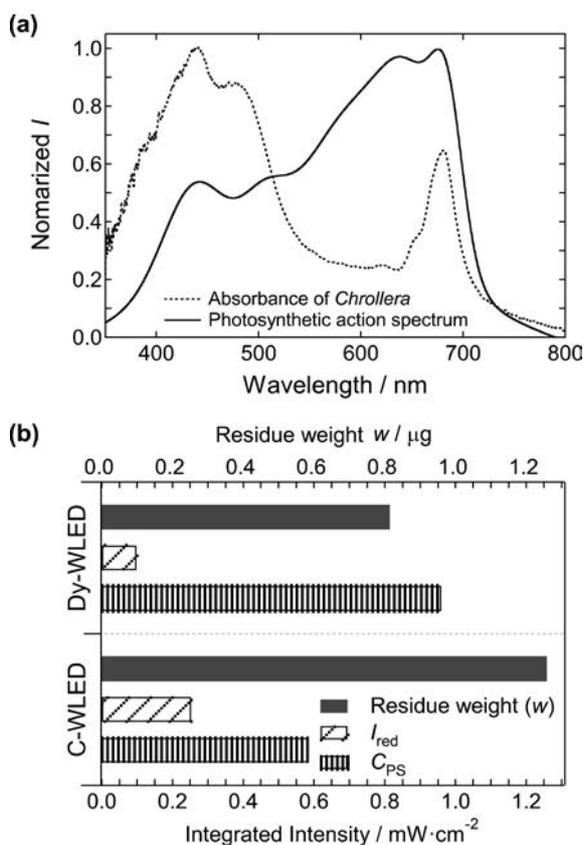


Fig. 4. (a) Absorbance spectrum of *Chlorella* and photosynthetic action spectrum [15, 16]. (b) Dried *Chlorella* residue weight after 15 days (w), C_{PS} and I_{red} of the Dy-WLED and C-WLED.

Therefore, our speculation that the reducing I_{red} is very dominant to suppress photosynthesis was strongly supported by these results. However, the data previously taken under similar experimental conditions by using the other Dy-based WLEDs showed larger reduction, e.g., 68% and 47% reductions in the Dy-WLEDs using the $\text{K}_2\text{Y}_{0.97}\text{Dy}_{0.03}(\text{WO}_4)(\text{PO}_4)$ [6] and $\text{Ca}_8\text{MgY}_{0.85}\text{La}_{0.10}\text{Dy}_{0.05}(\text{PO}_4)_7$ [7] phosphors, respectively. The reason why the Dy-WLED prepared in this study showed only 36% reduction of residue weight than the C-WLED would be a cause of the large excess near UV light from the excitation UV LED. Whereas the I_{red} of Dy-WLED was 61% lower than that of the C-WLED, the C_{PS} of Dy-WLED was 60% higher than that of C-WLED due to large excess excitation light from the UV LED (Fig. 3). (In the previous reports [6, 7], we used a UV-cut filter to reduce the excess UV light.) Light from near UV to blue wavelength range also has a relatively large correlation to the photosynthetic action spectrum and fundamental chlorophyll *a* and *b* absorptions (Fig. 4(a)) [16]. Therefore, a treatment of excess excitation light

would be also very important factor to further reduce the photosynthesis effect.

Conclusions

We have prepared the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ phosphor. The $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ exhibited a yellow-white luminescence consisting of sharp emission peaks at 480, 578, 662, and 750 nm that can be assigned to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$, and ${}^4F_{9/2} \rightarrow {}^6H_{9/2}$ transitions in Dy^{3+} ions, respectively. The maximum IQE was 21.3% at $x = 0.05$ under the 387 nm excitation light. Concentration quenching occurred at $x > 0.05$. The R_C value was 7.46 Å, and the *d-d* interaction was the dominant mechanism for the concentration quenching. The WLED was fabricated from a UV LED emitting at 385 nm and the $\text{La}_{2-x}\text{Dy}_x\text{W}_2\text{O}_9$ ($x = 0.05$) phosphor, and the CIE color coordinates and CCT were CIE (0.355, 0.371) and 4720 K, respectively. The plant cultivation experiments for *Chlorella* photosynthetic growth was carried out by using the Dy-WLED and reference C-WLED, and the reduction of the *Chlorella* growth as confirmed in the Dy-WLED.

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