

High thermal stable blue-emitting alkali silicate phosphor, Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$

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White LEDs based on near ultraviolet LED and red/green/blue phosphors have been attracted in terms of outstanding color rendering index. In particular, we focus on the blue emitting phosphors because the commercial $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ needs high temperature in order to be obtained. In this study, we succeeded in synthesizing Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ phosphors as a single phase by the conventional solid state reaction. Eu^{2+} -doped $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ phosphors showed the broad blue emission from 400–550 nm due to the 4f–5d allowed transition of Eu^{2+} under the ultraviolet light excitation. Moreover, the emission intensity of Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ phosphor at high temperature kept about 85% at 423 K, which indicated the thermal stability of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}:\text{Eu}^{2+}$ was extremely higher than that of other Eu^{2+} -activated silicate phosphors. Thus, Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ phosphor is able to become the novel luminescent material for White LED based on the near-ultraviolet LED.

Key words: silicate phosphor, good thermal stability, Eu^{2+} -activated phosphor, alkaline sites

Introduction

The solid-state lighting (SSL) has become considerably attentions since the development of white-emitting diodes (WLEDs) based on InGaN (the blue-emitting device) and YAG:Ce³⁺ (the yellow emission phosphor) because WLEDs have magnificent properties such as long lifetime, low energy consumption and lack of mercury, as compared with the conventional fluorescent lamp [1–5]. Hence, WLEDs has been regarded as the next generation illumination lump. However, the current WLEDs that composes of the blue LED and the yellow emitting phosphor materials are occur in poor color rendering index (CRI) owing to the lack of the red emission component [6–9]. Therefore, novel WLEDs are desired in order to develop this problem. Recently, several combinations of LED and phosphor materials have been proposed such as near-ultraviolet LED (NUV) + red/green/blue phosphor [10–12]. This assemblage of WLEDs can cover the visible light region (400–700 nm), which indicates that the value of CRI becomes higher than that of present WLEDs. Especially, Eu^{2+} and Ce³⁺ ions are frequently used due to an attractive luminescent properties, 4f–5d transition which can accomplish high emission efficiency. Moreover, they can change the luminescent properties depending on the crystal structure of the host lattice

[13]. For example, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ and $\text{CaAlSiN}_3:\text{Eu}^{2+}$, although they consist of the same emission ion, the emission color shows blue, green and red, respectively due to the 4f–5d allowed transition [14–16]. In this study, we focus on blue-emitting phosphor materials. In blue-emitting phosphors doped emission ions, Tm³⁺ and Eu^{2+} are often included [17–19]. However, the emission efficiency of Tm³⁺-activated phosphors is inferior to that of Eu^{2+} -doped blue emitting phosphors owing to the 4f–4f forbidden transition of Tm³⁺. In the previous work, it is well known that Eu^{2+} -activated $\text{BaMgAl}_{10}\text{O}_{17}$ (BAM:Eu²⁺) has the great emission efficiency [20]. On the other hand, the thermal stability of BAM:Eu²⁺ at high temperature is poor. In addition, the synthesis of BAM:Eu²⁺ is difficult due to the high temperature heating (1600 °C) for several hours [21, 22]. Thus, novel blue emitting phosphors which can be synthesized easily have been developed. In this paper, we concentrate on the Eu^{2+} -activated phosphors substituted into alkaline sites. Most of Eu^{2+} -activated phosphors can appear the luminescent properties by Eu^{2+} substituting into alkaline earth sites, Ca²⁺, Sr²⁺ and Ba²⁺ because the ionic radius and the charge state of alkaline earth elements are similar to Eu^{2+} . Nevertheless, Eu^{2+} -activated phosphors substituted alkaline sites such as Na⁺ and K⁺ have been reported recently (Ex. $\text{NaMgPO}_4:\text{Eu}^{2+}$, $\text{NaScSi}_2\text{O}_6:\text{Eu}^{2+}$, $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3:\text{Eu}^{2+}$ and $\text{NaAlSiO}_4:\text{Eu}^{2+}$) [23–28]. In these paper, Eu^{2+} ion is occupied for Na⁺ sites because the ionic radius of Eu^{2+} and Na⁺ are resemble. Even if the reports of Eu^{2+} -activated alkaline phosphors has a few, the luminescent properties are marvelous in terms of

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the thermal stability and efficient fluorescent attribute. In particular, Eu^{2+} -activated alkali lithosilicate phosphors such as $\text{Li}_3\text{NaSiO}_4\cdot\text{Eu}^{2+}$, $\text{KLi}_3\text{SiO}_4\cdot\text{Eu}^{2+}$, $\text{NaK}_7[\text{Li}_3\text{SiO}_4]_8\cdot\text{Eu}^{2+}$, $\text{RbNa}_3\text{Li}(\text{Li}_3\text{SiO}_4)_4\cdot\text{Eu}^{2+}$ and $\text{RbLi}(\text{Li}_3\text{SiO}_4)_2\cdot\text{Eu}^{2+}$ have been reported in this year [29–33]. Eu^{2+} -alkaline lithosilicate phosphors have special characteristics, such as the narrow band emission and high thermal stability due to high rigidity of their crystal structure and cuboidal alkaline sites [34]. Hence, Eu^{2+} -activated alkali phosphors have been attentions rapidly due to their glamorous luminescent properties. In this study, we select the alkali silicate $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ as a phosphor host crystal. $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ has Tuhualite crystal structure, which is one of the minerals [35]. However, Eu^{2+} -doped Tuhualite phosphor has not been reported yet. Hence, the luminescent characteristics of Eu^{2+} ions in Tuhualite structure is indeterminate. We prepared Eu^{2+} -doped $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ powder by the solid-state reaction. Moreover, we conducted the measurement of photoluminescence and thermal quenching properties. As a result, Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ shows the broad blue emission and higher thermal stability than that of Eu^{2+} -doped phosphors

Experimental

Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ phosphors were synthesized by the conventional solid-state reaction. Na_2CO_3 (Kanto Chemical Co., Inc., 99.0 %), MgO (Kanto Chemical Co., Inc., 99.99 %), SiO_2 (Kanto Chemical Co., Inc., 99.9 %) and Eu_2O_3 (Shin-etsu Chemical Co., Inc., 99.99 %) were mixed at stoichiometry ratio using an agate mortar with acetone. Then, the mixtures were calcined at 1273 K for 6 h in air in order to remove CO_2 and H_2O . Next, these mixtures were heated at 1273 K for 6 h in a reducing atmosphere (95 vol. % Ar,

5 vol. % H_2) for reduction from Eu^{3+} to Eu^{2+} using a tube furnace.

Characterization

Powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (MX-Labo, Mac Science Co., Ltd.) with monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.154056$ nm) under 25 mA and 40 kV. Photoluminescence (PL), photoluminescence excitation (PLE) spectra, and thermal stability were measured at room temperature using a spectrofluorometer (FP-6500/FP-6600, Jasco, Inc.) with a 150 W Xenon lamp.

Results and Discussion

XRD and Crystal structure

Fig. 1(a) shows the XRD patterns of $\text{Na}_{2(1-x)}\text{Mg}_2\text{Si}_6\text{O}_{15}\cdot 2x\text{Eu}^{2+}$ ($x = 0.005, 0.007, 0.01, 0.03, 0.05, 0.07, 0.1$). The simulation pattern of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ was calculated from Inorganic Crystal Structure Database (ICSD) number 2850. Consequently, the XRD patterns of all samples show the orthorhombic $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ simulation pattern perfectly without impurity phases. Moreover, the enlarged view (33° – 34°) of the XRD patterns of the $\text{Na}_{2(1-x)}\text{Mg}_2\text{Si}_6\text{O}_{15}\cdot 2x\text{Eu}^{2+}$ ($x = 0.005, 0.007, 0.01, 0.03, 0.05, 0.07, 0.1$) are shown in Fig. 1(b). The diffraction peaks of the majority of samples show a little shift to lower diffraction angles with increasing the concentration of the Eu^{2+} , which indicates that the Eu^{2+} succeeds in occupying the Na^+ sites in $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ because the ionic radius of Eu^{2+} is bigger than that of Na^+ . In contrast, when the concentration of Eu^{2+} exceeds 5 %, the diffraction angles around 33° occur in a shift to higher diffraction peaks, which indicates that some of Eu^{3+} ions occupy Na^+ sites. In general, the ionic radius of Na^+ is bigger than that of Eu^{3+} , therefore the

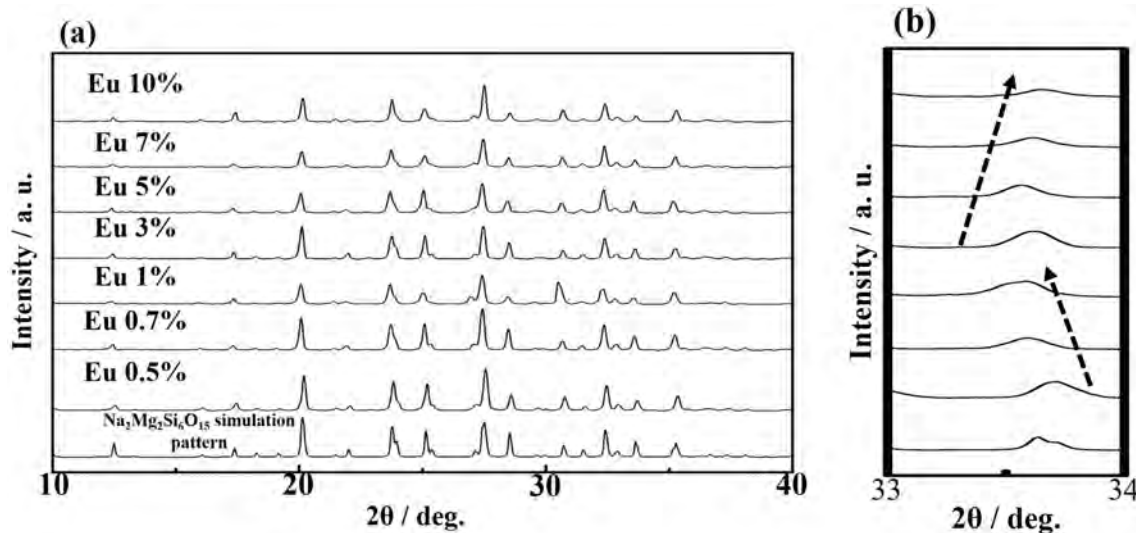


Fig. 1. (a) XRD patterns of the $\text{Na}_{2(1-x)}\text{Mg}_2\text{Si}_6\text{O}_{15}\cdot 2x\text{Eu}^{2+}$ ($x = 0.005, 0.007, 0.01, 0.03, 0.05, 0.07, 0.1$) and (b) the enlarged view (33° – 34°) of the XRD patterns of the $\text{Na}_{2(1-x)}\text{Mg}_2\text{Si}_6\text{O}_{15}\cdot 2x\text{Eu}^{2+}$ ($x = 0.005, 0.007, 0.01, 0.03, 0.05, 0.07, 0.1$).

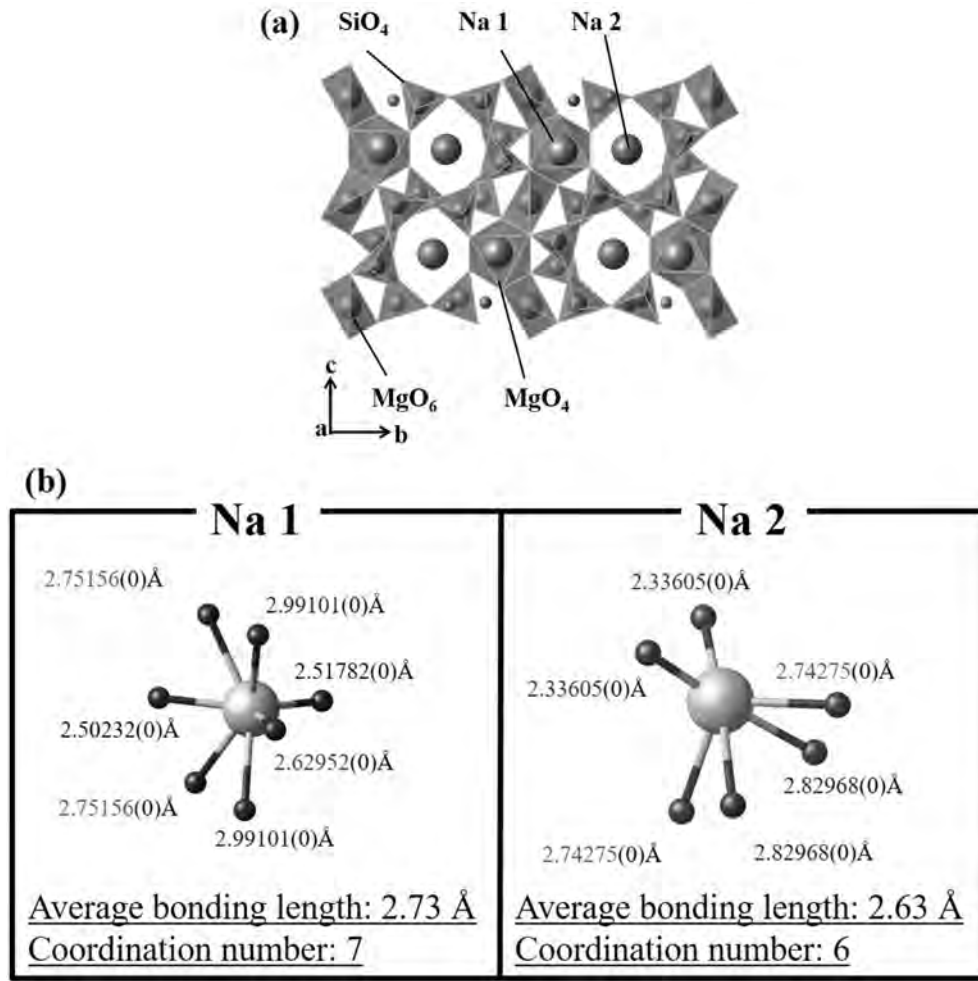


Fig. 2. (a) the crystal structure of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ (ICSD #2850) and (b) the two Na sites illustrated by VESTA program.

diffraction peak shift to higher angles is exhibited [36]. Next, we discuss the crystal structure of orthorhombic $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ in order to identify the substitutional sites of Eu^{2+} . Fig. 2(a) shows the crystal structure of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ illustrated by using VESTA program [37]. The lattice parameters is $a = 1.465$ nm, $b = 1.759$ nm and $c = 1.205$ nm for an orthorhombic system with a space group $Cmca$ (No. 64). This crystal structure includes two Na sites, NaO_6 and NaO_7 polyhedron as shown in Fig. 2(b). According to Shannon, the ionic radius of Eu^{2+} shows 0.117 nm (with a 6-fold coordination) and 0.120 nm (with a 7-fold coordination). Moreover, it reports that the ionic radius of Na^+ is 0.102 nm (with a 6-fold coordination) and 0.112 nm (with a 7-fold coordination), respectively [36]. Peng et al. and Pires et al. proposed that the acceptable percentage difference between the doped and substituted ions must not exceed $\pm 30\%$ [38, 39]. The acceptable percentage difference is calculated as following equation (1):

$$D_r = \frac{[R_m(\text{CN}) - R_d(\text{CN})]}{R_m(\text{CN})} \times 100 \quad (1)$$

where D_r is the ionic radius percentage difference, $R_m(\text{CN})$ means the radius of the host cation (CN means the coordination number) and $R_d(\text{CN})$ is the ionic radius of doped ion, respectively. Based on the equation (1), Table 1 shows the result of D_r values in $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ structure when Eu^{2+} ion is doping. The ionic radius of Eu^{2+} with a 4-fold coordination data have not been reported, hence we carry out the calculation about MgO_6 , and NaO_6 and NaO_7 . Table 1 indicates that Eu^{2+} ion occupies two Na^+ sites, especially NaO_7 sites. Although the charge of Mg^{2+} is the same as Eu^{2+} , it seems to be difficult for Eu^{2+} ion to substitute for MgO_6 sites because D_r values exceeds $\pm 30\%$.

Table 1. Calculate date of D_r in $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$.

Ions	Ionic radius [nm]	D_r [%]
Eu^{2+} (6-fold coordination)	0.117	-
Eu^{2+} (7-fold coordination)	0.120	-
Na^+ (6-fold coordination)	0.102	-14.706
Na^+ (7-fold coordination)	0.112	-7.143
Mg^{2+} (6-fold coordination)	0.072	-62.5

PL and PLE

Fig. 3(a) shows the emission and excitation spectra of $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$ monitored at 254 nm. All Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ phosphors show a broad emission band from 400 nm to 550 nm due to 4f-5d allowed transition of Eu^{2+} . From the previous section, Eu^{2+} -doped $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ can emit the blue emission at approximately 430 nm by Eu^{2+} occupying two Na sites. The charge imbalance should be occur because the substitution of Eu^{2+} into Na^+ sites is proceeded between different charge ions. However, previous reports suggests that Eu^{2+} -doped phosphor materials substituted in Na^+ sites generate a single vacancy explained the Kröger-Vink, as following equation (2):



where V'_{Na} is formed when Eu^{2+} is substituted for the Na sites. Hence, the charge balance in Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ is neutral [29]. Moreover, the dependence of the emission intensity on the concentration Eu^{2+} ion is shown in Fig. 3(b). It indicates that the optimal

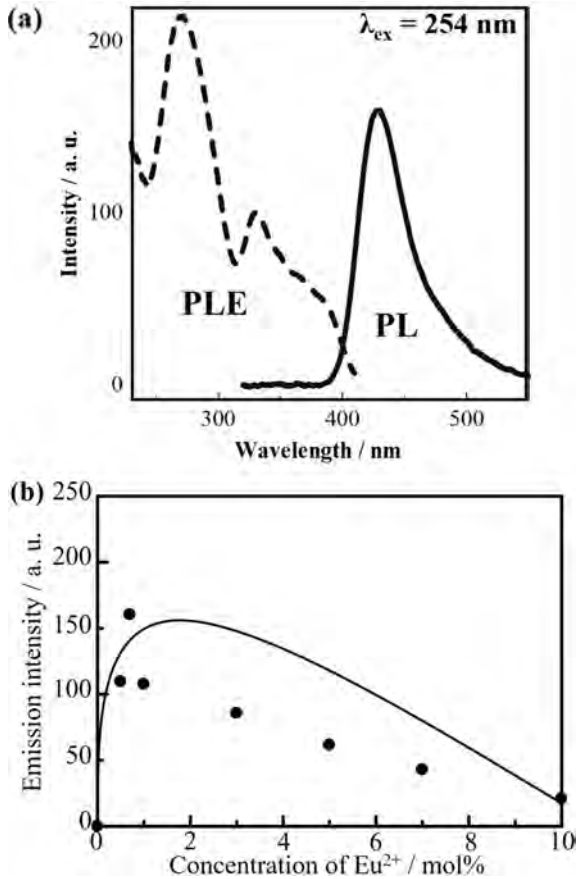


Fig. 3. (a) Excitation (dashed line) and emission (solid line) spectra of $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$. Photographs indicates the blue emitting $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$ and (b) the dependence of the emission peak ($\lambda_{\text{em}} = 430$ nm) intensities on the concentration of Eu^{2+} in the $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$.

concentration of Eu^{2+} in $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ is 0.7 mol% because the emission intensity of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}:\text{Eu}^{2+}$ decreases gradually owing to the energy transfer among Eu^{2+} ions as the concentration of the emission ion increases from 0.7%. Furthermore, the determination of the mechanism of the energy transfer among emission ions is suggested by Blasse, as in equation (3) [40-42]:

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

where R_c is the critical distance, V means the cell volume, x_c is the total concentration of doping ions and Z refers to the number of formula units per unit cell, respectively. In the case of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ structure, $V = 2.5427 \text{ nm}^3$, $x_c = 0.007$, $N = 8$, thus the critical distance R_c estimates 4.43 nm, which is extremely longer than that of the nearest distance between NaO_6 and NaO_7 sites (0.473 nm). It indicates that the energy transfer among Eu^{2+} ions in $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ occurs actively. Thus, the optimal concentration of Eu^{2+} in $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ structure is reasonable based on the calculation from the equation (3). Furthermore, the emission band of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}:\text{Eu}^{2+}$ is asymmetric shape because Eu^{2+} occupies two substitutional sites, NaO_6 and NaO_7 . Thus, we carried out the peak deconvolution of the emission spectrum. As a result, we succeeded in separating the emission band as two components (Fig. 4). According to Henderson et al., the relationship between the crystal field strength of cation sites and the average bond length for the surrounding sites is expressed by the equation (4):

$$Dq \propto \frac{1}{R^5} \quad (4)$$

where Dq means the crystal field strength and R is the

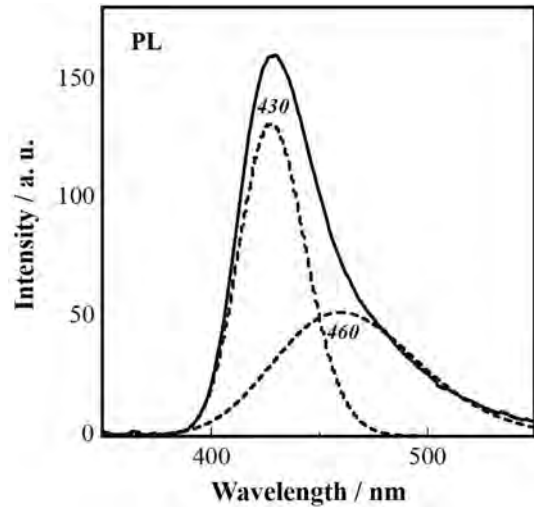


Fig. 4. The deconvolution of emission spectrum for $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$ (black solid line: observed data, red solid line: calculated data, black dashed line: components of calculate data).

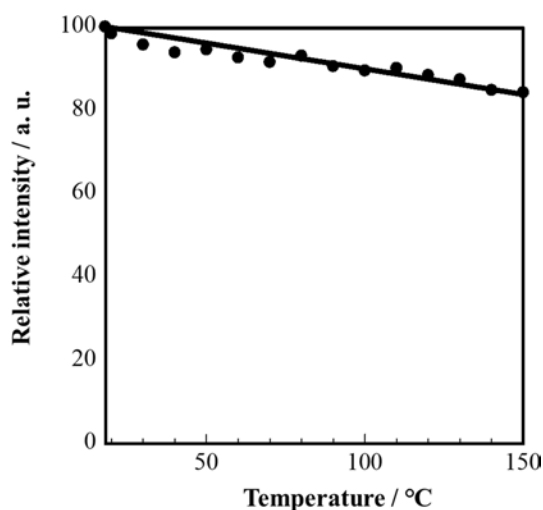


Fig. 5. Temperature dependence of relative intensity for $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$.

average bond distance of sites [43]. Based on this equation (4), the crystal field strength of NaO_6 is stronger than that of NaO_7 because the average bond length of NaO_6 (0.263 nm) is smaller than that of NaO_7 (0.273 nm) (Fig. 2(b)).

Thermal stability

It is quite important for phosphor materials to measure the thermal stability at high temperature because the temperature in most of luminescent devices rises when they are driven [44]. Therefore, the temperature dependence of relative intensities for $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$ is shown in Fig. 5 in order to evaluate the influence of the emission intensity in Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$. The higher the room temperature increases from room temperature, the more the emission intensity of Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ decreases due to the thermal quenching. However, compared with other Eu^{2+} -activated phosphors, such as $(\text{Ba},\text{Ca})_2\text{SiO}_4:\text{Eu}^{2+}$, $\text{NaAlSiO}_4:\text{Eu}^{2+}$ (Nepheline) and $\text{Li}_3\text{NaSiO}_4:\text{Eu}^{2+}$, the emission intensity of $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$ at 150 °C keeps about 85 % [29, 45-46]. It indicates that the thermal stability of $\text{Na}_{1.986}\text{Mg}_2\text{Si}_6\text{O}_{15}:0.014\text{Eu}^{2+}$ is considerably higher than that of other Eu^{2+} -activated silicate phosphors. Therefore, $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}:\text{Eu}^{2+}$ phosphor can be useful under the high temperature environment such as driving luminescent devices. According to our previous study, we revealed that the vacancies that generate when emission ions dope into alkaline sites act as an electron trap and assist the thermal stability at high temperature by release the electron from the trap levels to the emission level of Eu^{2+} [29]. In addition, Kim et al. and Wang et al. proposed that the emission intensities of $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3:\text{Eu}^{2+}$ exceed 100% above 100 °C because the sodium vacancy (V'_{Na}) locates between the valence band and conduction band, which means this vacancy behaves as the trap level [26, 27]. Moreover, although

the relationship between the thermal stability and the substitution of Eu^{2+} into alkaline sites have not been revealed completely, the thermal stability of Eu^{2+} -activated alkaline phosphors is quite marvelous, such as $\text{Li}_3\text{NaSiO}_4:\text{Eu}^{2+}$, $\text{NaMgPO}_4:\text{Eu}^{2+}$ (olivine), $\text{NaAlSiO}_4:\text{Eu}^{2+}$ (Nepheline), $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ and $\text{RbNa}_3(\text{Li}_3\text{SiO}_4)_4:\text{Eu}^{2+}$ [23, 29, 32, 47]. Thus, we must continue to study the mechanism of the thermal stability in phosphors substituted into alkaline sites.

Conclusion

Novel blue-emitting alkaline silicate phosphors, Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ have been obtained by the conventional solid-state reaction for the first time. Eu^{2+} -activated $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ phosphors exhibits the broad emission from 400 nm to 550 nm due to the 4f-5d allowed transition. Moreover, it indicates that Eu^{2+} ions occupy the NaO_6 and NaO_7 sites based on the calculation. The thermal stability of $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}:\text{Eu}^{2+}$ is extremely stronger than that of Eu^{2+} -activated phosphors. Thus, it indicates that novel $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}:\text{Eu}^{2+}$ phosphors have excellent luminescent properties for the luminescent properties.

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