FULL PAPER

Phosphors of $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ with $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structureNaoyoshi NUNOTANI¹, Marina TAIRA¹ and Nobuhito IMANAKA^{1,†}¹Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2–1 Yamadaoka, Suita, Osaka 565–0871, Japan

Green-emitting phosphors of $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ with a $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure were synthesized via a solid-state reaction technique. Their crystal structures and photoluminescence properties were investigated. Crystal structural analyses of $\text{Rb}_3\text{LaSi}_2\text{O}_7$ and $\text{Rb}_3\text{TbSi}_2\text{O}_7$ were carried out for the first time and revealed that the rare-earth sites (La or Tb) were separated by the RbO_6 and SiO_4 units. According to photoluminescence spectroscopy of $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ monitored at 249 and 481 nm, the highest emission intensity was obtained for the $\text{Rb}_3\text{TbSi}_2\text{O}_7$ phosphor under the 481-nm excitation, which indicates that the satisfactory separation of the Tb^{3+} ions suppressed the concentration quenching. The intensity of $\text{Rb}_3\text{TbSi}_2\text{O}_7$ was 32 % in comparison to that of the commercial green-emitting $(\text{La}_{0.52}\text{Ce}_{0.31}\text{Tb}_{0.17})\text{PO}_4$ phosphor.

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Key-words : Phosphor, $\text{Rb}_3\text{LaSi}_2\text{O}_7$, $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure, Terbium ion, Structural analysis

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1. Introduction

Trivalent rare-earth ions are well-known candidates for luminescent centers owing to their specific 4f intrashell transition, because the 4f electrons are shielded from the surroundings by the filled outer 5s and 5p orbitals. Therefore, rare-earth ion-doped phosphors have been studied for various luminescence applications. Among the rare-earth ions, Tb^{3+} has been commonly regarded as a green-emitting center because of the efficient emission originating from the $^5\text{D}_4\text{--}^7\text{F}_5$ transition (approximately 550 nm).¹⁾

The photoluminescence properties are dependent on the host material. The separation between the activators is effective to obtain a high emission intensity. The photo-emission intensity is enhanced by increasing the concentration of the activator. However, an excess amount of the activator causes a decrease in the intensity due to concentration quenching, often induced as the migration of excitation energy between the activators can result in non-radiative deactivation due to quenching centers.^{2),3)} As such an energy migration is caused by the reduction in the mean distance between the activators, the concentration quenching is expected to be suppressed by a host lattice in which the activators are separated from each other. Among the candidates for a host material, silicate systems are promising owing to their high thermal and chemical stabilities.^{4),5)} In our previous study, we focused on $\text{K}_3\text{GdSi}_2\text{O}_7$ with a $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure, in which two Gd^{3+} sites in the GdO_6 prism and GdO_6 octahedron are effectively

separated by the KO_6 and SiO_4 units.⁶⁾ By introducing Eu^{3+} ions as red-emission centers, the concentration quenching was suppressed up to $\text{K}_3\text{Gd}_{0.1}\text{Eu}_{0.9}\text{Si}_2\text{O}_7$; i.e., the optimal Eu^{3+} doping amount was 90 %.

The aim of this study was to develop a host material of $\text{Rb}_3\text{LaSi}_2\text{O}_7$ with a $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure, which contains the large-ionic-size Rb^+ (0.166 nm, coordination number $[\text{CN}] = 6$)⁷⁾ and La^{3+} (0.117 nm, $\text{CN} = 6$)⁷⁾ instead of K^+ (0.152 nm, $\text{CN} = 6$)⁷⁾ and Gd^{3+} (0.108 nm, $\text{CN} = 6$)⁷⁾ respectively, to further increase the distance between activators. To the best of our knowledge, the $\text{Rb}_3\text{RESi}_2\text{O}_7$ (RE: rare earth) series with a $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure has not been reported. Although $\text{Rb}_3\text{YSi}_2\text{O}_7\text{:Tb}^{3+}$ has been studied,⁸⁾ it has a $\text{K}_3\text{LuSi}_2\text{O}_7$ -type crystal structure. Therefore, in this study, we prepared $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ solids as novel phosphors and investigated their crystal structures and photoluminescence properties.

2. Experimental procedures

$\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ solids were synthesized using a solid-state reaction process. Rb_2CO_3 (Wako), La_2O_3 (Shin-Etsu), Tb_4O_7 (Shin-Etsu), and SiO_2 (Wako) were weighed in a $\text{Rb}:\text{La}:\text{Tb}:\text{Si}$ ratio of $5.4:(1-x):x:2$ and mixed thoroughly using an agate mortar and pestle. The mixture was calcined in a tube furnace at 1000 °C for 9 h under an air flow. For the Tb-doped samples, the obtained powders were heated at 800 °C for 3 h under a reducing gas flow (2 vol % H_2 –98 vol % Ar).

An X-ray powder diffraction (XRD) measurement (SmartLab, Rigaku) was carried out using a continuous-scanning method in the 2θ range of 10–70° with $\text{Cu-K}\alpha$ radiation (40 kV, 30 mA). The lattice parameters were calculated using the XRD peak angles and refined by mixing $\alpha\text{-Al}_2\text{O}_3$ as an internal standard. For $\text{Rb}_3\text{LaSi}_2\text{O}_7$ and

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$\text{Rb}_3\text{TbSi}_2\text{O}_7$, Rietveld analyses were carried out using RIETAN-FP,⁹⁾ where the XRD data (MultiFlex, Rigaku) were recorded via a step-scanning method in the 2θ range of 10 – 150° using $\text{Cu-K}\alpha$ radiation (40 kV , 40 mA). Crystal structure schematics were drawn using the VESTA program.¹⁰⁾ Photoluminescence excitation and emission spectra were recorded at room temperature using a spectrofluorophotometer (RF-5300PC, Shimadzu) with a xenon lamp as the light source. The excitation spectra were obtained for an emission wavelength (λ_{em}) of 549 nm , while the emission spectra were recorded at excitation wavelengths (λ_{ex}) of 249 and 481 nm .

3. Results and discussion

3.1 Crystal structure

Considering the lack of reports on the $\text{Rb}_3\text{RESi}_2\text{O}_7$ series with the $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure, Rietveld analyses were carried out using the XRD patterns of $\text{Rb}_3\text{LaSi}_2\text{O}_7$ and $\text{Rb}_3\text{TbSi}_2\text{O}_7$. **Figure 1(a)** presents the results of the Rietveld refinement for the $\text{Rb}_3\text{LaSi}_2\text{O}_7$ solid. $\text{Rb}_3\text{LaSi}_2\text{O}_7$ has a single-phase hexagonal $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure with a space group of $P6_3/mcm$; the structural parameters are summarized in Table S1. A similar result was obtained for the $\text{Rb}_3\text{TbSi}_2\text{O}_7$ solid (Fig. S1 and Table S1). The crystal structure of $\text{Rb}_3\text{MSi}_2\text{O}_7$ ($M = \text{La}, \text{Tb}$) is shown in Fig. 1(b). As expected, M^{3+} ions exist in the MO_6 triangular prism and MO_6 octahedron, which are separated by RbO_6 and SiO_4 units. The M – M length was calculated using the VESTA program.¹⁰⁾ The distances between the first-, second-, and third-nearest-neighbor M^{3+} ions are denoted as $d_{1\text{st}}$, $d_{2\text{nd}}$, and $d_{3\text{rd}}$, respectively [Fig. 1(b)]. For the $\text{Rb}_3\text{LaSi}_2\text{O}_7$ sample, $d_{1\text{st}}$, $d_{2\text{nd}}$, and $d_{3\text{rd}}$ were 0.592 , 0.698 , and 0.738 nm , respectively. The values for $\text{Rb}_3\text{TbSi}_2\text{O}_7$ are

$d_{1\text{st}} = 0.578\text{ nm}$, $d_{2\text{nd}} = 0.682\text{ nm}$, and $d_{3\text{rd}} = 0.722\text{ nm}$; i.e., each distance is reduced upon the replacement of La^{3+} (0.117 nm , $\text{CN} = 6$)⁷⁾ with the smaller-ionic-size Tb^{3+} (0.106 nm , $\text{CN} = 6$)⁷⁾.

The XRD patterns of $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ are shown in **Fig. 2**. All peaks were indexed to a single-phase $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure; no impurity phases were observed. **Table 1** lists the lattice volumes calculated by the XRD peak angles. With the increase in Tb^{3+} content (x), the lattice volume monotonously decreased. This phenomenon indicates the partial replacement of the La^{3+} (0.117 nm , $\text{CN} = 6$)⁷⁾ site for the smaller-ionic-size Tb^{3+} (0.106 nm , $\text{CN} = 6$)⁷⁾ neither the introduction of Tb^{3+} into the aliovalent Rb^+ (0.166 nm , $\text{CN} = 6$)⁷⁾ nor Si^{4+} (0.040 nm , $\text{CN} = 4$)⁷⁾ site having remarkably different ionic-size compared to the Tb^{3+} ion. The lattice shrinkage suggests a continuous reduction in the distance between two rare-earth ion sites, which is supported by the Rietveld refinement results of $\text{Rb}_3\text{LaSi}_2\text{O}_7$ and $\text{Rb}_3\text{TbSi}_2\text{O}_7$. Table 1 also lists the full width at half maximum (FWHM) of the 224 diffraction line. The FWHM increased with the Tb^{3+} content (x) up to $x = 0.5$. The largest FWHM was observed for the sample with $x = 0.5$, where the $\text{La}:\text{Tb}$ molar ratio was $1:1$. This indicates that the crystal lattice of the $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure was distorted by the introduction of Tb^{3+} with a different ionic size from that of La^{3+} . For $x > 0.5$, the FWHM decreased, which indicates relaxation of the lattice distortion.

Fig. 1. (a) Result of the Rietveld refinement of $\text{Rb}_3\text{LaSi}_2\text{O}_7$ and (b) crystal structure of $\text{Rb}_3\text{MSi}_2\text{O}_7$ ($M = \text{La}, \text{Tb}$). The black arrows indicate $d_{1\text{st}}$, $d_{2\text{nd}}$, and $d_{3\text{rd}}$.

Fig. 2. XRD patterns of the $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ solids.

Table 1. Lattice volume and FWHM of the 224 diffraction line for the $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ solids

Sample	Lattice volume/ nm^3	FWHM/deg.
$x = 0$	1.353	0.107
$x = 0.1$	1.343	0.144
$x = 0.3$	1.321	0.238
$x = 0.5$	1.302	0.304
$x = 0.7$	1.286	0.285
$x = 0.9$	1.271	0.170
$x = 1$	1.263	0.127

Fig. 3. Photoluminescence (a) excitation ($\lambda_{\text{em}} = 549$ nm) and emission (b) ($\lambda_{\text{ex}} = 481$ nm), (c) ($\lambda_{\text{ex}} = 249$ nm) spectra of the $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ phosphors ($0.1 \leq x \leq 1$).

3.2 Photoluminescence

Figure 3(a) shows photoluminescence excitation spectra obtained by monitoring the emission at 549 nm for the $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ solids. Several broad bands were observed between 230 and 290 nm, corresponding to the $4f^8-4f^75d^1$ transitions of the Tb^{3+} ion. The excitation $4f^75d^1$ states of the Tb^{3+} ion have low-spin 7D_J and high-spin 9D_J states, while the $4f^8$ ground state is the 7F_6 energy level.^{11)–13)} Thus, the spin-allowed transitions of $^7F_6-^7D_J$ might generate bands at 249 and 265 nm, while the spin-forbidden transitions of $^7F_6-^9D_J$ led to a band at 280 nm.^{13),14)} The splitting of the $4f^8-4f^75d^1$ transition is also considered to be affected by the two different sites for Tb^{3+} in the structure, the triangular prismatic site and octahedral site.¹⁵⁾ In the range over 290 nm, several bands assigned to the f–f transitions of Tb^{3+} were observed.^{16)–18)} The dominant band at 481 nm corresponds to the $^7F_6-^5D_4$ transition. High intensities were obtained for the bands at 249 nm ($4f^8-4f^75d^1$) and 481 nm ($^7F_6-^5D_4$). Figures 3(b) and 3(c) show the emission spectra under excitations at 481 and 249 nm, respectively. The bands are indexed to the transitions of $^5D_4-^7F_J$ ($J = 6, 5, 4$, and 3).^{17)–20)} The main bands derived from $^5D_4-^7F_6$ and $^5D_4-^7F_5$ were clearly split because of the crystal field splitting¹⁹⁾ and/or emission from two different Tb^{3+} sites in the structure.¹⁷⁾ The highest intensity was obtained for the green emission attributed to the $^5D_4-^7F_5$ transition under excitations at 481 and 249 nm.

The relative emission intensities were estimated by comparing the integrated area of the green emission band for the $^5D_4-^7F_5$ transition to that of a commercial ($\text{La}_{0.52}\text{Ce}_{0.31}\text{Tb}_{0.17}$) PO_4 phosphor ($\lambda_{\text{ex}} = 290$ nm) in order to investigate the concentration quenching. Figure 4 shows the compositional dependence of the relative emission intensity for excitations at 481 and 249 nm. In the case of the 481-nm excitation, the relative emission intensity monotonously

Fig. 4. Compositional dependencies of the relative emission intensity of $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ under the excitations at λ_{ex} of 481 and 249 nm.

increased with the Tb^{3+} content (x) up to $x = 1$, which implies that concentration quenching did not occur. The lattice shrinkage (Table 1) had an unfavorable effect as well as the excess Tb^{3+} doping, because they reduce the mean distance between two Tb^{3+} ions, which accelerates the energy migration. In addition, the lattice distortion (Table 1) generally acts as a quenching center to trap the excitation energy.^{21),22)} Nevertheless, a continuous enhancement in the emission intensity was obtained, which indicates that the satisfactory separation of the Tb^{3+} ions in the $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure suppressed the concentration quenching. Consequently, the $\text{Rb}_3\text{TbSi}_2\text{O}_7$ phosphor exhibited the highest emission intensity of 32 % in comparison to that of the commercial phosphor under the 481-nm excitation.

In the case of the 249-nm excitation (Fig. 4), the relative emission intensity increased with x in the range of $x \leq 0.5$,

while the lattice was shrunk and distorted (Table 1). Similar to the 481-nm excitation case, the effective separation of the Tb^{3+} ions affected the enhancement in the emission intensity. The relative emission intensities under the 249-nm excitation were higher than those under the 481-nm excitation in the range of $x \leq 0.5$, because the high-energy light (short-wavelength light) might pump a large number of electrons from the ground state ($^7\text{F}_6$) to the excited state (5d). In contrast, in the range of $x > 0.5$, the relative emission intensity ($\lambda_{\text{ex}} = 249 \text{ nm}$) decreased with the increase in x ; i.e., the opposite trend was observed for the 481-nm excitation ($^7\text{F}_6 \rightarrow ^5\text{D}_4$) case. Some of the excited electrons in the 5d levels of Tb^{3+} relax to the $^5\text{D}_3$ level, which leads to the cross-relaxation process between two Tb^{3+} ions [$\text{Tb}^{3+} (^5\text{D}_3) + \text{Tb}^{3+} (^7\text{F}_6) \rightarrow \text{Tb}^{3+} (^5\text{D}_4) + \text{Tb}^{3+} (^7\text{F}_0)$].^{12),18),19)} This resonant energy transfer might accelerate the concentration quenching for $x > 0.5$ ($\lambda_{\text{ex}} = 249 \text{ nm}$). Accordingly, the $\text{Rb}_3\text{La}_{0.5}\text{Tb}_{0.5}\text{Si}_2\text{O}_7$ phosphor exhibited the highest emission intensity of 20 % under the 249-nm excitation. Concentration quenching was not observed even after the introduction of a high amount of Tb^{3+} ions [$x = 1$ ($\lambda_{\text{ex}} = 481 \text{ nm}$) and $x = 0.5$ ($\lambda_{\text{ex}} = 249 \text{ nm}$)], which suggests that $\text{Rb}_3\text{LaSi}_2\text{O}_7$ with the $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure is suitable as the host material for a phosphor to suppress the concentration quenching. The highest emission intensity was obtained for the $\text{Rb}_3\text{TbSi}_2\text{O}_7$ phosphor under the 481-nm excitation, where the relative intensity was 32 % in comparison to that of the commercial green-emitting phosphor.

As for the emission under the 249-nm excitation, the concentration quenching mechanism was investigated. The critical energy transfer distance (R_c) was estimated using the equation as follows:²³⁾

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

where V , x_c , and N are the lattice volume, the critical concentration, and the number of the dopant sites, respectively. Here, it is accepted that the nonradiative energy transfer is caused by the exchange interaction and the multipolar interaction in the case of $R_c < 0.5 \text{ nm}$ and $R_c > 0.5 \text{ nm}$, respectively.^{17),24)–26)} In the $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ series under the 249-nm excitation ($V = 1.302 \text{ nm}^3$, $x_c = 0.5$, and $N = 6$), the R_c value was estimated to be 0.93 nm, which was larger than 0.5 nm; that is, the multipolar interactions mainly induced the concentration quenching process. According to Van Uitert,²⁷⁾ the type of the multipolar interaction can be evaluated using the following equation:

$$\frac{I}{x} = \frac{K}{1 + \beta(x)^{Q/3}}$$

$$\log\left(\frac{I}{x}\right) = -\frac{Q}{3}\log(x) + \log\left(\frac{K}{\beta}\right)$$

where I is the emission intensity, x is the Tb^{3+} concentration, K and β are constants in the same excitation condition for the given host crystal, and Q is an indication of multipolar interaction. Dipole–dipole, dipole–quadrupole,

and quadrupole–quadrupole interactions correspond to $Q = 6, 8$, and 10 , respectively. In the range over the critical concentration ($x > 0.5$), the relationship between $\log(I/x)$ and $\log(x)$ was linear and the slope ($-Q/3$) was -1.89 (Fig. S2); i.e., $Q \approx 6$. Therefore, the concentration quenching of Tb^{3+} was predominantly caused by dipole–dipole interaction.

4. Conclusion

Novel phosphors of $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ with a $\text{K}_3\text{NdSi}_2\text{O}_7$ -type structure were prepared via a solid-state reaction process. The crystal structures of $\text{Rb}_3\text{LaSi}_2\text{O}_7$ and $\text{Rb}_3\text{TbSi}_2\text{O}_7$ were determined using Rietveld analyses for the first time. The La^{3+} or Tb^{3+} ions existed in two different sites, triangular prismatic and octahedral sites, separated by the RbO_6 and SiO_4 units. For the $\text{Rb}_3\text{La}_{1-x}\text{Tb}_x\text{Si}_2\text{O}_7$ solids, the lattice volume decreased with the increase in Tb^{3+} . Lattice distortion was observed in the region of coexistence of La^{3+} and Tb^{3+} . In the excitation spectra, the phosphors exhibited high-intensity bands at 249 and 481 nm, assigned to the $4\text{f}^8\text{--}4\text{f}^75\text{d}^1$ and $^7\text{F}_6\text{--}^5\text{D}_4$ transitions, respectively. Under the excitation at 481 nm, the emission intensity monotonically increased with the Tb^{3+} ion content up to $x = 1$, irrespective of the lattice shrinkage and lattice distortion. In the case of the 249-nm excitation, an improvement in the emission intensity was observed for $x \leq 0.5$, while the intensity decreased for $x > 0.5$. For both cases ($\lambda_{\text{ex}} = 481$ and 249 nm), the concentration quenching was effectively suppressed, which indicates that the Tb^{3+} ions were satisfactorily separated from each other. The highest emission intensity was obtained for the $\text{Rb}_3\text{TbSi}_2\text{O}_7$ phosphor under the 481-nm excitation [32 % compared to that of the commercial ($\text{La}_{0.52}\text{Ce}_{0.31}\text{Tb}_{0.17}$)- PO_4 phosphor ($\lambda_{\text{ex}} = 290 \text{ nm}$)].

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