Syntheses of Rare-Earth Silicon Oxynitrides and Their Luminescence Properties

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Synthesis conditions of melilite-type rare-earth silicon oxynitrides ($RE_2Si_3O_3N_4$; RE = La, Ce, Nd, Sm, Gd, Dy, Er and Yb) were examined using Si_3N_4 and rare-earth oxides as starting materials. The stoichiometric compounds could be synthesized by the solid-state reaction of equimolar RE_2O_3 (RE=Nd, Sm, Gd, Dy and Er) with Si_3N_4 at 1700°C for 2 h in N_2 atmosphere. When near-ultraviolet light was irradiated to these compounds, only $Gd_2Si_3O_3N_4$ emitted yellow light without activator. The excitation and emission behaviors of $Gd_2Si_3O_3N_4$ were further examined by doping the activator (RE'^{3+}; RE'= Ce, Sm, Tb, Dy and Er). Orange-colored light was emitted by doping Sm^{3+} to $Gd_2Si_3O_3N_4$; the relative emission intensity of $Gd_{1.98}Sm_{0.02}Si_3O_3N_4$ achieved 1.8 (reference: $CaWO_4$). When Tb^{3+} was doped to $Gd_2Si_3O_3N_4$, the emission band of $Gd_{2-2x}Tb_{2x}Si_3O_3N_4$ was centered at 545 nm where the green-colored light was emitted; the maximum emission intensity achieved 3.5 (refernce:$CaWO_4$) at x=0.06.
Key words: Rare-earth silicon oxynitrides, Solid-state reaction, Phosphor, Luminescence properties

1. INTRODUCTION

Rare-earth doped phosphors, which are used in modern fluorescent lamps, convert ultraviolet radiation of 254 and 185 nm by a mercury gas discharge into visible light. Examples of such phosphors are (Ce, Tb, Gd)MgB_5O_{10}, (Ce, Tb)$MgAl_{11}O_{19}$, (La, Ce, Tb) PO_4, (Ba, Eu)$MgAl_{10}O_{17}$ and (Y, Eu)$_2O_3$[1]~[3]. As a new type of lighting for general illumination, white-light LEDs are promising devices in order to replace the conventional lamps, because they have numerous advantages over conventional lamps, such as longer life time, energy saving, minituarization and mercury-free.

Oxynitrides doped with rare-earth ions are the candidates of such phosphor materials. Previously, van Krevel and coworkers[4]~[5] investigated the luminescence properties of Y-Si-O-N compounds and M-Si-Al-O-N compounds (M=Metal). On the other hand, Xie et al.[6], as well as van Krevel et al.[5], investigated the luminescence properties of Ca-α-sialon. For Eu-doped α-sialon samples are yellow-green colored, they can be efficiently excited by visible light in the range of 400 to 450 nm. However, information about the luminescence properties of rare-earth silicon oxynitrides is scarce until now.

On the basis of such background, the present research describes the syntheses of various melilite-type rare-earth silicon oxynitride compounds ($RE_2Si_3O_3N_4$; RE=rare-earth element), and their luminescence properties.

2. EXPERIMENTAL

2.1 Starting materials

All of the starting materials were reagent grades and commercially available. The starting α-silicon nitride (α-Si_3N_4; SN-E10) was obtained from Ube Industries (Ube, Japan); the oxygen content was 1.30 mass%. The rare-earth oxides used in this research were lanthanum oxide (La_2O_3; calcined at 1300°C for 1 h before use), cerium oxide (CeO_2), neodymium oxide (Nd_2O_3), samarium oxide (Sm_2O_3), gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), erbium oxide (Er_2O_3) and ytterbium oxide (Yb_2O_3).

2.2 Syntheses of silicon oxynitrides

The starting materials of α-Si_3N_4 and rare-earth oxide were weighed stoichiometrically (Si/RE=1.5), and then mixed with 0.1-7 mol% of activator in the presence of acetone. The resulting mixture was pressed uniaxially at 50 MPa and then cold-isostatically at 100 MPa to form a compact with a diameter of 14 mm and a thickness of 2 mm. The compact was heated at a temperature between 1300 and 1700°C for 2 h in

N_2 atmosphere. After heating, the compact was ground using an alumina mortar and pestle.

2.3 Evaluations

The crystalline phases of resulting powder were examined using an X-ray diffractometer (RINT2100V/P, Rigaku, Tokyo) with CuKα radiation at 40 kV and 40 mA. The amounts of elements in the resulting powder were determined using an energy-dispersive X-ray microanalyzer (EDX; EMAX 5770, Horiba, Kyoto) and an N/O analyzer (TC436, St. Joseph, MI, USA). Emission and excitation spectra were recorded with a spectrometer equipped with a Xe flash lamp (F-4500, Hitachi, Tokyo).

3. RESULTS AND DISCUSSION

3.1 Syntheses of silicon oxynitrides

The effect of temperature on the crystalline phases due to the reaction of rare-earth oxides with Si_3N_4 was examined by fixing the heating time to be 2 h. Typical results (RE=Gd) are shown in **Fig. 1**. The objective $Gd_2Si_3O_3N_4$ started to be formed by heating the mixture of Gd_2O_3 and Si_3N_4 at 1600°C for 2 h. When the mixture was heated at 1650°C for 2 h, $Gd_4Si_2O_7N_2$ (J-phase) was formed additionally. The single phase of $Gd_2Si_3O_3N_4$ was obtained by firing the mixture at 1700°C for 2 h.

The analytical results on this single phase measured by EDX and N/O analyzer were: Gd, 15.36 mol%; Si, 22.98 mol%; O, 24.79 mol%; and N, 34.05 mol%. The Si/Gd ratio was found to be 1.496 (theoretical, 1.500), whereas the O/N ratio was 0.728 (theoretical, 0.750). Thus the stoichiometric $Gd_2Si_3O_3N_4$ is found to be obtained through the solid-state reaction.

Syntheses of other rare-earth silicon oxynitrides were also conducted under the same conditions as those for pure $Gd_2Si_3O_3N_4$. Typical XRD patterns of the silicon oxynitrides successfully synthesized by the solid-state reactions are shown in **Fig. 2**. Note that the XRD patterns are referenced using the XRD pattern of $Y_2Si_3O_3N_4$ as an iso-structure, because some JCPDS cards of these compounds are not available until now. These XRD patterns were in accordance with the pattern of $Y_2Si_3O_3N_4$. The quantitative analysis indicated that the amounts of these elements were almost in accordance with the theoretical values. Then we concluded that the silicon oxynitrides are synthesized when REs in $RE_2Si_3O_3N_4$ are Nd, Sm, Gd, Dy and Er.

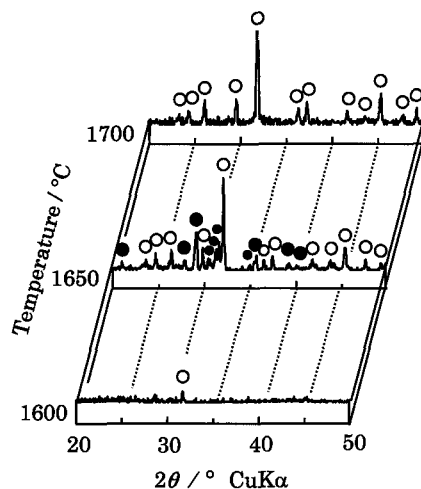On the other hand, when REs in $RE_2Si_3O_3N_4$ were La, Ce or Yb, no single phase of

Fig. 1 XRD patterns of the powders obtained by heating Gd_2O_3 with Si_3N_4 for 2 h in N_2 atmosphere.

O: $Gd_2Si_3O_3N_4$ ●: $Gd_4Si_2O_7N_2$

melilite-type rare-earth silicon oxynitride was obtained. The crystalline phases detected by XRD were $LaSiO_2N$ (RE=La) and $CeSiO_2N$ (RE=Ce; K-phase) after heating the mixture of Si_3N_4 with La_2O_3 or CeO_2 at 1450°C for 2 h. Similar results have been obtained by Mitomo *et al.*[7], who reported that no $La_2Si_3O_3N_4$ and $Ce_2Si_3O_3N_4$ could be synthesized, due to the largest ionic radii of all rare earth ions.

When RE in $RE_2Si_3O_3N_4$ was Yb, $Yb_4Si_2O_7N_2$ was formed, together with unknown phases. No formation of the single phase may be ascribed to the mixed valances of Yb^{2+} and Yb^{3+}. The present results reveal that the ionic radius is essential in order to synthesize stoichiometric melilite-type silicon oxynitrides. For example, the ionic radius of Yb^{3+} is 0.0985 nm and the smallest ionic
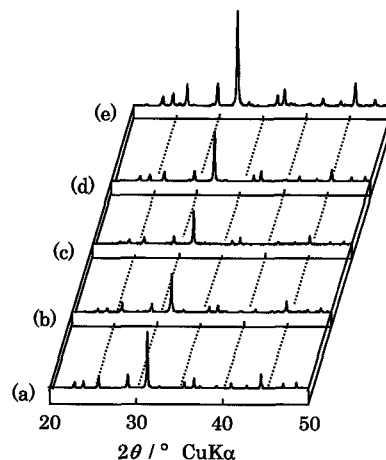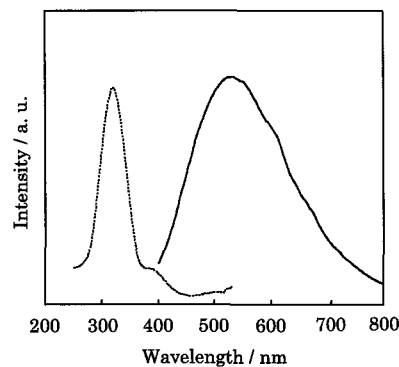

Fig. 2 XRD patterns of the powders obtained by heating RE_2O_3 (RE: (a) Nd, (b) Sm, (c) Gd, (d) Dy and (e) Er) with Si_3N_4 at 1700°C for 2 h in N_2 atmosphere.

radius after Lu^{3+} in the lanthanoid series. This idea is further supported by Hirosaki *et al.*[8], who found that no single phase of $Lu_2Si_3O_3N_4$ with the smallest ionic radius (Lu^{3+}, 0.0977 nm) among ions in the lanthanoid series could be synthesized.

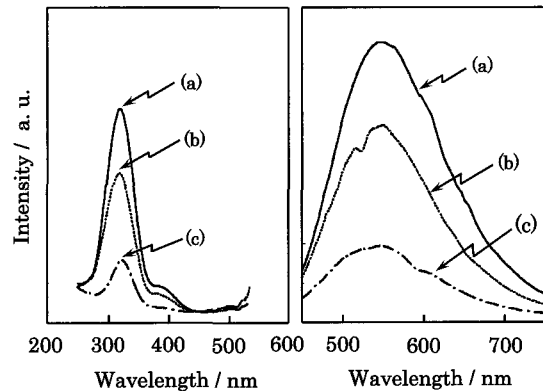## 3.2 Luminescence properties of $Gd_2Si_3O_3N_4$ with and without activator

As shown in Section 3.1, we successfully synthesized the rare-earth silicon oxynitrides, *i.e.*, $RE_2Si_3O_3N_4$ with RE = Nd, Sm, Gd, Dy and Er. When the near-ultraviolet light was irradiated to these compounds, only $Gd_2Si_3O_3N_4$ emitted the yellow light with no activator. The excitation and emission spectra of $Gd_2Si_3O_3N_4$ are shown in **Fig. 3**. The excitation and emission bands of $Gd_2Si_3O_3N_4$ were centered at 321 and 547 nm, respectively. The luminescence properties of $Gd_2Si_3O_3N_4$ were further examined by doping the activator (RE'^{3+}; RE'= Ce, Sm, Tb, Dy and Er). Typical excitation and emission spectra of $Gd_{1.98}Er_{0.02}Si_3O_3N_4$ and $Gd_{1.98}Nd_{0.02}Si_3O_3N_4$ are shown in **Fig. 4**. No peak shifts of the excitation and emission bands were observed, regardless of the doping of Er^{3+} and Nd^{3+} to the $Gd_2Si_3O_3N_4$; moreover, the excitation and emission peak intensities were reduced by doping Er^{3+} and Nd^{3+} to the $Gd_2Si_3O_3N_4$. No peak shift of the excitation bands suggest that the energy does not sufficiently transfer to the activator ions and, therefore, $Gd_2Si_3O_3N_4$ alone may emit the light. Moreover, no clear emissions due to the Er^{3+} and Nd^{3+} occur in both cases; the former is attributed to the overlapping of Er^{3+} and $Gd_2Si_3O_3N_4$ emission bands, whereas the latter is ascribed to the emission of Nd^{3+} in the infrared range.

Typical cases where the activators act as emission centers are shown in **Fig. 5**. The excitation spectrum of $Gd_{1.98}Sm_{0.02}Si_3O_3N_4$ possessed (i) the broad band centered at 300 nm

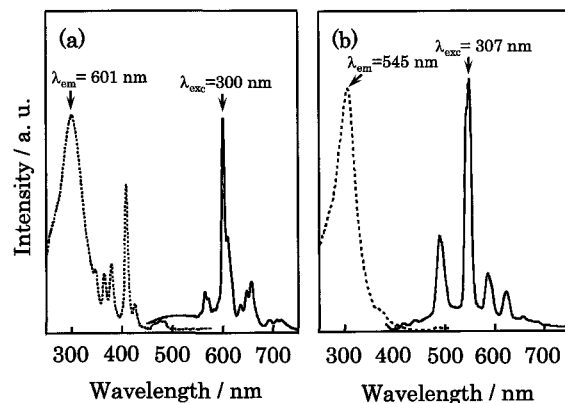**Fig. 4**   Excitation (left) and emission (right) spectra of (a) $Gd_2Si_3O_3N_4$, (b) $Gd_{1.98}Er_{0.02}Si_3O_3N_4$ and (c) $Gd_{1.98}Nd_{0.02}Si_3O_3N_4$ obtained by heating Gd_2O_3, RE_2O_3 and Si_3N_4 at 1700°C for 2 h in N_2 atmosphere.

and (ii) the lines centered at 364, 378 and 408 nm. On the other hand, the emission lines were centered at 564, 601 and 656 nm. The excitation band centered at 300 nm is attributed to the absorption of the host lattice ($Gd_2Si_3O_3N_4$), whereas other three lines centered at 364, 378 and 408 nm may be ascribed to 4f → 4f excitation of Sm^{3+}. The emission lines centered at 564, 601 and 656 nm are assigned to $^4G_{5/2}$ → $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ transitions, respectively. The emission color was orange and became more reddish with increasing Sm^{3+} content.

The excitation spectrum of $Gd_{1.88}Tb_{0.12}Si_3O_3N_4$ possessed a strong band centered at 307 nm, whereas the emission spectrum possessed four lines centered at 490, 545, 586 and 622 nm. Although $Gd_{1.88}Tb_{0.12}Si_3O_3N_4$ showed a broad emission band due to host lattice, this emission was

Fig. 3 Excitation (λ_{em}=547 nm) and emission (λ_{exc}=321 nm) spectra of the $Gd_2Si_3O_3N_4$ obtained by heating Gd_2O_3 with Si_3N_4 at 1700°C for 2 h in N_2 atmosphere.


Fig. 5 Excitation (dotted line) and emission (solid line) spectra of (a) $Gd_{1.98}Sm_{0.02}Si_3O_3N_4$ and (b) $Gd_{1.88}Tb_{0.12}Si_3O_3N_4$ obtained by heating the Gd_2O_3, Rare-earth oxide (RE=Sm or Tb) and Si_3N_4 at 1700°C for 2 h in N_2 atmosphere.

reduced with increasing Tb^{3+} content. The emission color was observed to be vivid green. The emission lines centered at 490, 545, 586 and 622 nm are attributed to $4f \rightarrow 4f$ transition of Tb^{3+}.

3.3 Emission intensities

Since the emission intensities of $Gd_{2-2x}Sm_{2x}Si_3O_3N_4$ and $Gd_{2-2x}Tb_{2x}Si_3O_3N_4$ were much higher than those of other rare-earth doped $Gd_2Si_3O_3N_4$, relative emission intensities of these compounds are examined, using $CaWO_4$ as a reference (emission wavelength: 422 nm). Results are shown in **Fig. 6**, as a function of the amount of activator. The relative emission intensity of $Gd_{2-2x}Sm_{2x}Si_3O_3N_4$ increased with increasing x and attained maximum (1.8) at x=0.01; the relative intensity was reduced on further increase in x. On the other hand, the relative emission intensity of $Gd_{2-2x}Tb_{2x}Si_3O_3N_4$ was enhanced with increasing x and attained maximum (3.5) at x=0.06. The doping of Sm^{3+} and Tb^{3+} to the $Gd_2Si_3O_3N_4$ may be effective for obtaining orange and vivid green phosphors, respectively. The excellent emission of $Gd_{2-2x}Tb_{2x}Si_3O_3N_4$ is attributed to the efficient energy transfer through Tb^{3+} doping. Taking the practical use of this compound into consideration, however, we will continue a further effort to enhance the relative emission intensity. Regardless of the similarity between ionic radii (0.1040 nm for Tb^{3+} and 0.1027 nm for Dy^{3+}), it is noted that the relative emission intensity of $Gd_{2-2x}Tb_{2x}Si_3O_3N_4$ was much higher than the case of Dy^{3+} doping. Since the emission spectra of $Gd_{2-2x}Dy_{2x}Si_3O_3N_4$
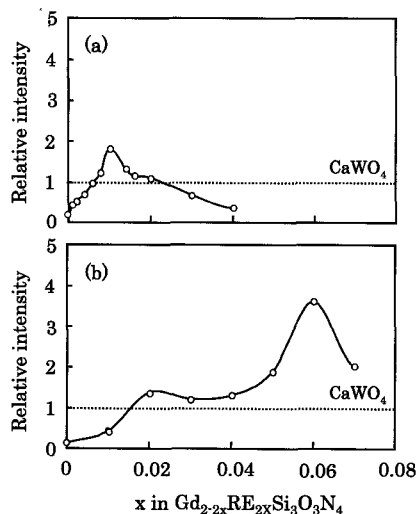
included the bands due to the host lattice, the energy does not seem to sufficiently transfer to the activator ions (Dy^{3+}). Thus the present light-emitting phenomenon may be attributed not only to the ionic radius but also to other factors. We continue the further investigation in order to clarify such light emitting mechanism.

4. CONCLUSION

Syntheses of rare-earth silicon oxynitrides ($RE_2Si_3O_3N_4$ (melilite structure); RE = La, Ce, Nd, Sm, Gd, Dy, Er and Yb) were examined using Si_3N_4 and rare-earth oxides as starting materials. The following results were obtained:

(i) The rare-earth silicon oxynitrides $RE_2Si_3O_3N_4$ could be synthesized by the solid-state reaction of equimolar RE_2O_3 (RE=Nd, Sm, Gd, Dy and Er) with Si_3N_4 at 1700°C for 2 h in N_2 atmosphere.

(ii) When the near-ultraviolet light was irradiated to the rare-earth silicon oxynitrides, only $Gd_2Si_3O_3N_4$ emitted yellow light without any activator. The orange-colored light was emitted by doping Sm^{3+} to the $Gd_2Si_3O_3N_4$; the relative intensity of $Gd_{1.98}Sm_{0.02}Si_3O_3N_4$ achieved 1.8 (reference: $CaWO_4$). When Tb^{3+} was doped to the $Gd_2Si_3O_3N_4$, the emission band of $Gd_{2-2x}Tb_{2x}Si_3O_3N_4$ was centered at 545 nm where the green-colored light was emitted; the maximum emission intensity achieved 3.5 (reference: $CaWO_4$) at x=0.06.

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Fig. 6 Relative emission intensities of (a) $Gd_{2-2x}Sm_{2x}Si_3O_3N_4$ (λ_{exc}=300 nm) (b) $Gd_{2-2x}Tb_{2x}Si_3O_3N_4$ (λ_{exc}=307 nm) obtained by heating the Gd_2O_3, RE_2O_3 (RE=Sm or Tb) and Si_3N_4 at 1700°C for 2 h in N_2 atmosphere.