Fabrication of sodium borosilicate glass and Eu-doped SiAlON composites for white LED

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The oxynitride phosphor Ca- α -SiAlON:Eu²⁺ has a high thermal tolerance. A series of sodium borosilicate glasses [$x\text{Na}_2\text{O}-(60-x)\text{B}_2\text{O}_3-40\text{SiO}_2$, mol %, $x=2-40$] was prepared to investigate their ability to host the Ca- α -SiAlON:Eu²⁺ phosphor powder. The glass-SiAlON phosphor composites, which can emit yellow light when irradiated with blue light (wavelength = 450 nm), were successfully fabricated when the re-melting temperature was 1000 or 1100°C. The chromaticity of the composites, which was estimated from photoluminescence spectra, changed from blue to yellow with increasing SiAlON concentration and sample thickness. This indicates that white light could be generated by controlling the SiAlON concentration and sample thickness. In particular, the 3-mm-thick $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass with a 2 mass % of phosphor generated near-white light. The quantum efficiency of the composites increased with increasing SiAlON concentration and reached a similar value to that of the phosphor powder, and increased as the Na₂O concentration of the glass decreased.

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Rare-earth-doped nitrides and oxynitrides have been studied for use as luminescent materials because of their non-toxic, thermal, and luminescent properties. For example, Eu²⁺-doped Ca- α -SiAlON (Ca- α -SiAlON:Eu²⁺) emits yellow light when irradiated with blue light,¹⁾ and it has been used to produce white light-emitting diodes (LEDs) by embedding the powder in an organic resin and irradiating it with a blue LED.²⁾ However, the heat generated by the high-power blue LED resulted in the deterioration of the resin, and thus, shortened the lifetime of the device. In terms of thermal stability, glass is far more suitable host material for phosphor powders, and because of this, researchers have paid much attention to fabricating glass-phosphor composites.³⁾⁻⁶⁾

Generally, glasses are prepared at temperatures higher than 1000°C; the melting point of the glass is high enough to degrade many kinds of phosphors. However, the high thermal stability of nitride and oxynitride phosphors is well known. Therefore, our group has explored various types of glasses to host SiAlON without degradation.⁴⁾⁻⁶⁾ We have found that alkali zinc borate glasses with low alkali contents produce well-dispersed phosphor-glass composites. In addition, we found that the presence of small amounts of non-bridging oxygens (NBOs) in the glass improved the dispersion of the phosphor.⁴⁾ Recently, our group reported that phosphate glasses, which are used as optical^{7),8)} and sealing glasses,^{9),10)} are good candidates for creating composites with SiAlON^{5),6)} because of their low melting point. We found that $60\text{ZnO}-40\text{P}_2\text{O}_5$ (mol %) and $50\text{BaO}-50\text{P}_2\text{O}_5$ (mol %) glasses are suitable for fabricating glass-phosphor composites for white LEDs.^{5),6)} On the other hand, borate and phosphate glasses are known to be unstable in humid conditions, whereas silica glasses are far more stable under such conditions. However, the dispersion of phosphors in silica-based glasses has rarely been reported because of their high melting point.

Borosilicate glasses are used in optical^{11),12)} and sealing applications.^{13),14)} They are also used for the sequestration of radioactive waste.¹⁵⁾ A large amount of structural data has been gathered for sodium borosilicate glasses. In sodium borosilicate glasses, two major composition-dependent structural changes are known: the disintegration of six-membered boroxol rings into non-ring BO₃ units and the dissociation of BO₄ species into symmetric BO₃ units with three B-O-B linkages and NBOs.

In this study, sodium borosilicate glasses were investigated as a host material for a SiAlON phosphor, which could be used to fabricate white LEDs. The glass and Ca- α -SiAlON:Eu²⁺ phosphor composites were prepared by melting, and the photoluminescence spectra of the composites were measured to determine their feasibility for use in white LEDs.

A series of sodium borosilicate glasses with the composition $x\text{Na}_2\text{O}-(60-x)\text{B}_2\text{O}_3-40\text{SiO}_2$ (mol %, $x=2-40$) was prepared by melting various mixtures of NaCO₃, H₃BO₃, and SiO₂ in a platinum crucible at 1200°C for 1 h and then quenching the samples on a carbon plate. A Ca- α -SiAlON:Eu²⁺ phosphor powder was prepared by gas-pressure sintering,¹⁶⁾ resulting in angular particles with an average size of approximately 10 μm .⁴⁾ Further details on the synthesis of the phosphor can be found in the literature.¹⁾ The obtained glasses, which were crushed and the particles screened to be under 2 mm in size, were mixed with various concentrations of the Ca- α -SiAlON:Eu²⁺ powder (1 to 6 mass % of the crushed glasses). The mixtures were re-melted in platinum crucibles for 10 min in air and then quenched on a carbon plate to obtain the glass-phosphor composites. The glass-phosphor composites were then polished to thicknesses of 1, 2, and 3 mm.

Photoluminescence (PL) spectra of the composites were measured with a multichannel photodetector (MCPD-7000, Otsuka Electronics Co., Ltd., Osaka) using a Xe lamp as the excitation source. The 1-, 2-, and 3-mm-thick polished glass-phosphor composites were irradiated with blue light (wavelength = 450 nm), and the resulting PL, which was transmitted through a

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Fig. 1. Photographs of the $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites with various concentrations of SiAlON. The scale bars represent 10 mm.

5-mm-diameter hole situated on the opposite side of the light source, was measured. From the PL spectra, the color coordinates, as defined by the CIE-1931 chromaticity diagrams, were obtained to determine how well the light emitted by the samples corresponded to white light.

The quantum efficiency (QE) of the samples was estimated from the PL spectra emitted upward from the surface of the 3-mm-thick samples irradiated with the blue light and collected by an integrated sphere (collection range = 220 to 800 nm). The samples were surrounded with BaSO_4 powder and placed at the bottom of the integrated sphere to reflect the scattered emissions onto the integrated sphere. The QE was calculated with the following equation:

$$\text{QE} = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda E(\lambda) d\lambda} \quad (1)$$

where $\lambda E(\lambda)/hc$ is the number of photons in the excitation spectrum, and $\lambda P(\lambda)/hc$ is the number of photons in the emission spectrum. Further details of this calculation can be found in the literature.¹⁷⁾ The absorption spectra of the polished composites were measured with a UV-VIS spectrometer (SolidSpec3700, Shimadzu Co., Kyoto).

The fabricated glasses were transparent after quenching. Using these glasses, the glass-phosphor composites obtained when the re-melting temperature was 1000°C or 1100°C were yellow, but the SiAlON was degraded by re-melting at 1200°C and produced white composites.

Figure 1 shows photos of the $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites re-melted at 1000°C with different SiAlON concentrations. The size of these composites decreased with increasing SiAlON concentration because of the increasing viscosity of the melts. In addition, the color of the composites deepens slightly with increasing SiAlON concentration.

Figure 2 shows an optical microscope image of the $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composite re-melted at 1000°C with a SiAlON concentration of 1 mass %. The SiAlON powder is indicated by the brighter regions in the image. The powder appears to have partially melted onto the surface. This indicates the surface of the SiAlON powder has reacted with the glass matrix. The increasing viscosity of the melts with increasing SiAlON concentration might be caused by the reaction between the glass matrix and SiAlON powder. However, the shapes of the powder showed no dependence on the glass composition or SiAlON concentration.

The PL spectra of the 2-mm-thick $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites with different SiAlON concentrations are shown in **Fig. 3(a-1)**, while the absorption spectra of the 1-mm-thick $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites are shown in **Fig. 3(b)**. The fluorescence (FL) spectra were

Fig. 2. An optical microscope image of the $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composite re-melted at 1000°C with a SiAlON concentration of 1 mass %.

Fig. 3. (a-1) Photoluminescence spectra of the 2-mm-thick $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites with different SiAlON concentrations. (a-2) The expanded PL spectra of (a-1) at approximately 450 nm. (b) Absorption spectra of the 1-mm-thick $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites with different SiAlON concentrations.

measured over 500 to 750 nm, and the emission peak position for all samples is constant at approximately 590 nm, which corresponds to the emission peak of pure SiAlON powder. As can be seen, the FL intensity is dependent on the SiAlON concentration. As the phosphor concentration increases from 1 to 3 mass %, the FL intensity increases, but then it decreases for phosphor concentrations greater than 3 mass % because of the increased volume of the phosphors. In addition, the SiAlON concentra-

Fig. 4. Chromaticity diagrams of the (a) 3- and (b) 2-mm-thick $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites with different SiAlON concentrations.

Fig. 5. External quantum efficiency of the $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites: (a) re-melted at 1000°C (blue circles) and 1100°C (red circles), as a function of SiAlON concentration, and (b) re-melted at 1000°C with a SiAlON concentration of 1 mass % as a function of Na_2O concentration.

tion required for the maximum FL intensity is dependent on the sample thickness and re-melting temperature. However, the increasing and then decreasing FL intensity with increasing SiAlON concentration was observed for all composites fabricated. In Fig. 3(a-1), the peaks at 450 nm correspond to the blue light source, which are expanded in Fig. 3(a-2), with the peak intensity representing the amount of light transmitted by the samples. As the SiAlON concentration increases, the amount of blue light transmitted by the sample decreases. This is caused by the increasing absorption and multiple scattering processes with increasing SiAlON concentration, as evidenced by Fig. 3(b).

The chromaticity, which was estimated from the PL spectra, can be used to estimate suitable conditions for obtaining white light. **Figures 4(a) and 4(b)** show the chromaticity diagrams of the 3- and 2-mm-thick $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composite re-melted at 1000°C with different SiAlON concentrations, respectively. The chromaticity was found to be minimally dependent on the re-melting temperature (either 1000°C or 1100°C). The colors shown on the chromaticity diagram are known to agree with the colors perceived by human eyes, and the position of white light is indicated by the “+” symbol. As can be seen in Figs. 4(a) and 4(b), the chromaticity shifts from blue to yellow with increasing SiAlON concentration when the sample thickness and the kinds of glasses were same. The observed shift

is caused by the changes in the transmittance of the blue excitation light and FL intensity, as shown in Fig. 3. In Fig. 4(a), the chromaticity of the 3-mm-thick composite with a SiAlON concentration of 2 mass % is close to white light. The chromaticity diagram in Fig. 4(b) suggests that for the 2-mm-thick composite, a SiAlON concentration of 2 to 3 mass %, perhaps 2.5 mass %, is needed for near-white light. It was also found that the chromaticity shifted from blue to yellow with increasing sample thickness for each glass tested. Thus, by controlling the phosphor concentration and thickness of the samples, each composite could emit white light.

The external QE of the $10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites as a function of the SiAlON concentration is shown in **Fig. 5(a)**. As the SiAlON concentration increases, the QE increases, reaching a maximum at a SiAlON concentration of 5 mass % for the samples re-melted at 1000°C and 1100°C . The QEs of the 5 mass % samples are approximately 0.5, which is similar to that of the SiAlON powder, and thus, indicates that most of the SiAlON powder was dispersed throughout the glass without degradation. Figure 5(b) shows the QE of $x\text{Na}_2\text{O}-(60-x)\text{B}_2\text{O}_3-40\text{SiO}_2$ glass-phosphor composites re-melted at 1000°C with a SiAlON concentration of 1 mass % as a function of the Na_2O concentration, x . The QE increases as x increases from 2 to 4 mol %, and then gradually decreases with increasing

x , reaching almost 0 at 20 mol %. In addition, the yellow color of the composites decreased with increasing x . In particular, the yellow color was hardly visible when $x = 30$ and it vanished when $x = 40$. This suggests that the addition of Na_2O significantly affects the QE, and that a glass without Na_2O might be a better host material for SiAlON. However, fabricating a glass without Na_2O was too difficult because of the high viscosity of the melt; Na_2O plays an important role in reducing the viscosity of the melt through the formation of NBOs or 4-coordinated borons. Thus, we conclude that $x = 4$ is the optimum glass composition at this stage.

The structure of alkali borosilicate glasses is often discussed as functions of the molar ratios $R = \text{Na}_2\text{O}/\text{B}_2\text{O}_3$ and $K = \text{SiO}_2/\text{B}_2\text{O}_3$. Using the molar ratios, Yun and Bray,¹⁸⁾ and Dell et al.¹⁹⁾ have developed structural models based on a large number of ^{11}B NMR measurements. For $R \leq 0.5$, the Na^+ ions are primarily attached to the borate network, and the ternary glasses are similar to binary sodium borate glasses diluted with SiO_2 . For $R > 0.5$, the additional Na_2O forms $[\text{BSi}_4\text{O}_{10}]^{-1}$ units,¹⁸⁾ which are found in reedmergnerite ($\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 6\text{SiO}_2$). In particular, for $R_{\text{MAX}} = 1/2 + K/16 \leq R \leq R_{\text{D1}} = 1/2 + K/4$, all additional Na_2O is employed in forming NBOs on the silica tetrahedral. For $R_{\text{D1}} \leq R \leq R_{\text{D3}} = 2 + K$, the fraction $(K + K/4)/(2 + K)$ of the additional Na_2O destroys the reedmergnerite groups and forms pyroborate units and silica tetrahedrals with two NBOs per Si atom, whereas the fraction $(2 - K/4)/(2 + K)$ of the additional Na_2O destroys the diborate groups and forms additional pyroborate units. In this study, $R \leq 0.5$ for all glasses, except when $x = 30$ and 40. For $x = 30$ and 40, $R_{\text{D1}} \leq R \leq R_{\text{D3}}$, and thus, many NBOs exist in these glasses. The surface of the SiAlON powder might react more with the glass matrix than that in the composites with lower Na_2O concentrations, but we could not find a difference between the surfaces with microscope observation. The Eu^{2+} ions in the SiAlON phosphors might be affected by the presence of NBOs because the NBOs have a high electron density. The changes to the surface of the SiAlON powder and Eu^{2+} ions might cause the degradation of this phosphor. In the case of zinc borate glass, the formation of NBOs through the addition of alkaline oxides improved the dispersion of the SiAlON powder.⁴⁾ However, in this study, the dispersion of the SiAlON powder was hardly affected, as judged with human eyes, whether NBOs were present or not. At this stage, the relationship between the glass structure and dispersion of phosphor powder is not clear and will be discussed in the near future based on the structural data of the glass. For the glasses with $x < 30$, the number of NBOs was minimal and the 4-coordinated borons were mainly formed by the addition of Na_2O . The 4-coordinated borons have less influence than the NBOs on the SiAlON, and the degradation of the phosphor was decreased because of the lower electron density of the 4-coordinated borons. As shown in Fig. 5(b), the QE decreases with increasing Na_2O concentration. In this study, the number of 4-coordinated borons increases with increasing Na_2O concentration. Thus, the electron density of the oxygens increases, and this causes in the QE to decrease. Moreover, the influence of the 4-coordinated borons is explained by the following equilibrium equation:

At high temperatures, the equilibrium favors the right side.²⁰⁾ Therefore, more NBOs are formed during the re-melting process as the number of 4-coordinated borons increases, resulting in the

degradation of the SiAlON phosphor and the decreasing QE with increasing Na_2O concentration.

In summary, the potential of sodium borosilicate glasses as a matrix for the dispersion of $\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$ phosphor powder to produce white LEDs was investigated. It was found that SiAlON could be dispersed in $x\text{Na}_2\text{O}-(60-x)\text{B}_2\text{O}_3-40\text{SiO}_2$ glasses. The chromaticity of the composites became yellow because of the decreasing transmission of blue light and increasing yellow fluorescence intensity of the composites with increasing SiAlON concentration. In addition, the chromaticity of the composites could be adjusted to produce near-white light by optimizing the SiAlON concentration and thickness of the composites. The QE increased as the SiAlON concentration increased to 5 mass % for re-melting temperatures of 1000 and 1100°C. The QE increased with decreasing x , with $x = 4$ the best matrix for the dispersion of the SiAlON powder. With further studies to optimize the SiAlON concentration and thickness of the composites, the composites prepared with the $x = 4$ glass could become suitable for white LEDs with high QE.

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