Fabrication of silica glass containing yellow oxynitride phosphor by the sol–gel process

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Abstract
We have prepared silica glass by the sol–gel method and studied its ability to disperse the Ca-α-SiAlON:Eu2+ phosphor for application in white light emitting diodes (LEDs). The emission color generated by irradiating doped glass with a blue LED at 450 nm depended on the concentration of SiAlON and the glass thickness, resulting in nearly white light. The luminescence efficiency of 1-mm-thick glass depended on the SiAlON concentration, and was highest at 4 wt% SiAlON.

Keywords: sol–gel process, silica glass, SiAlON, white LED

1. Introduction
Nitrides and oxynitrides doped with rare-earth ions have been studied for use as luminescent materials because of their nontoxicity, thermal stability and interesting luminescent properties. Among them, Ca-α-SiAlON doped with Eu2+ ions (Ca-α-SiAlON:Eu2+) emits yellow light under blue light irradiation [1] and can be applied in pseudowhite light-emitting diodes (LEDs). White LED was produced using a Ca-α-SiAlON:Eu2+ phosphor powder imbedded in the organic resin that covers a blue LED [2]. However, the heat generated by high-power blue LEDs results in resin degradation, thereby shortening the LED lifetime. In terms of thermal stability, glass matrices are more suitable for dispersing a phosphor, provided their melting temperature is low enough not to degrade the phosphor during the dispersion.

Our group has recently reported that borate and tellurite glasses are good candidates for dispersing SiAlON [3]. Such composites were prepared in two steps: first, glass was formed by melting a mixture of oxide powders. Then, the glass was crushed into cullets, mixed with the phosphor and remelted at low temperature in order to minimize the degradation of the phosphor upon heating. Alkali zinc borate glass with low alkali content dispersed the phosphor well. However, the phosphor gradually degraded with increasing the alkali oxide concentration above 2 mol%. In the case of tellurite glass, the phosphor easily reacted with the glass at the second step, degrading in the process. Degradation could be avoided for only two types of sodium zinc tellurite glass by controlling the melting temperature. After adjusting the SiAlON concentration and sample thickness, nearly white light could be obtained from these glasses upon irradiation with a blue LED. These results demonstrate that glass can serve as a matrix for luminescent materials, but its composition and melting conditions must be optimized.

Glass can be prepared by the sol–gel method, in which metal alkoxides are hydrolyzed and condensed in a solution [4]. A phosphor can be added to the sol during the reaction, which is generally carried out at around room temperature. Thus, the phosphor can be dispersed homogeneously without the degradation caused by reactions with the sol. The sol–gel process has the potential to produce glass with a phosphor dispersed in it, although large bulk samples are difficult to fabricate owing to the formation of cracks during the solvent evaporation. Sakka et al reported the preparation of centimeter-sized samples of silica glass from silicon alkoxides by the sol–gel process followed by sintering at 1050 °C, which is well below the melting temperature of the...
In this fabrication method, it was important to control the drying speed of the solvent [5, 6].

In this paper, we prepared silica glass containing Ca-α-SiAlON:Eu$^{2+}$ phosphor by the sol–gel process and investigated its white-light luminescence.

### 2. Experimental procedure

Silica glass was prepared using tetramethoxysilane (TMOS), dimethylformamide (DMF) and methanol as described in [5, 6]. The molar ratio of TMOS: DMF: methanol was set to 1:1:2. This sol was stirred for 15 min in a capped Teflon bottle (25 mm diameter and 68 mm height). After stirring, a mixture of distilled water and NH$_4$OH was added to the sol. The molar ratios of water and NH$_4$OH to TMOS were 12 and 5×10$^{-4}$, respectively. After stirring for 30 min, Ca-α-SiAlON:Eu$^{2+}$, which was prepared by gas-pressure sintering [7], was added to the sol. The Ca-α-SiAlON:Eu$^{2+}$ phosphor is described in detail in [1]. The phosphor particles were angular, with an average size of about 10 µm [3]. The concentration of the SiAlON was changed from 1 to 7 wt% relative to the silica glass. After stirring for 10–30 min, the viscosity of the sol increased markedly, and the stirring was stopped. Wet gels were aged in the same bottle covered with aluminum foil for 8 h at 35°C and dried at a temperature between 35 and 80°C for 48 h in an electric oven. Then, three pinholes of 1 mm diameter were created in the aluminum foil, and the gels were baked at 80°C for 120 h, then heated from 80 to 150°C and kept for 96 h at 150°C. The thus produced dry gels were sintered by heating them from room temperature to 1050°C at a rate of 20°C min$^{-1}$ and keeping at 1050°C for 2 h in a furnace, followed by natural cooling. Their apparent density was estimated from their weight and volume.

The distribution of the SiAlON powder in glass was observed under an optical microscope, and the microstructure of the samples was imaged with a scanning electron microscope (SEM, S-5000, Hitachi). The crystallinity was investigated by X-ray diffraction (XRD, RINT2200, Rigaku Co., Ltd.). The samples were crushed and the resultant powders were measured at room temperature, using CuKα radiation (40 kV, 40 mA), in the angular range of 5–70° with a step of 1° min$^{-1}$.

The glass samples were polished to a thickness of 1, 3 or 4 mm, and their photoluminescence (PL) spectra were measured with a multichannel photodetector (MCPD-7000, Otsuka Electronics). The glasses were irradiated by blue light at a wavelength of 450 nm, and the PL spectra and transmitted blue light were detected through a 5-mm-diameter aperture in the forward scattering geometry. From the PL spectra, the color coordinates of the CIE-1931 (CIE stands for the International Commission on Illumination) chromaticity diagram were obtained, and the conversion efficiency, $E$, was calculated as

$$E = \frac{N_{em}}{N_{ex} - N_{trans}}.$$  

(1)

Here, $N_{em}$ is the number of emitted photons integrated over the spectral range of 500–780 nm, and $N_{ex}$ and $N_{trans}$ represent the numbers of exciting photons and transmitted photons through the sample, respectively. The denominator is equal to the numbers of exciting photons that are absorbed, scattered, or reflected from the sample. This equation was used to compare the relative PL efficiency of the samples and does not rigorously represent the quantum efficiency.

### 3. Results and discussion

Figure 1 shows images of a dried gel and a sintered sample containing 5 wt% SiAlON (b).

Figure 1 shows images of a dried gel and a sintered sample containing 5 wt% SiAlON. All the samples were yellow, and the phosphor appeared to be homogeneously dispersed in them. The diameter and height of the dried gels were about 16 and 26 mm, respectively. Sintering resulted in isotropic shrinking of the dried gel cylinder to a diameter of 11 mm, a height of 18 mm and a volume of 70%, and small fragments were exfoliated as shown in figure 1(b). Glasses prepared by the sol–gel process are known to crack owing to the evaporation of a large amount of solvent. In this case, the cracks were easily formed, and some samples split into a few pieces upon drying at temperatures from 80 to 150°C that evaporated most of the solvent. The cracks did not form easily as the SiAlON concentration increased up to 5 wt%, and cracks formed easily up to 5 wt%. Spaces in the silica networks were formed by the evaporation of the solvents, which are also the main reason for the formation of cracks. Thus, the spaces were occupied partially by the added SiAlON powders and the cracks might not form easily as the SiAlON concentration increases up to 5 wt%. However, the spaces were widened owing to the SiAlON powders and loosened the glass networks when SiAlON was increased to more than 5 wt%, resulting in the easy formation of cracks.

Figure 2 shows an optical microscopy image of a sintered sample containing 4 wt% SiAlON. The dark spots correspond to SiAlON particles, which transformed from elongated to rounded shapes upon sintering, although most particles did not agglomerate. Similar images were observed for other SiAlON concentrations.

Figure 3 shows SEM images of a sintered sample containing 4 wt% SiAlON. The sample is mostly composed of SiO$_2$ particles smaller than 10 nm formed in the sol–gel process. SEM images revealed that the sintered samples had numerous small pores.
Figure 2. Optical microscopy image of the sintered sample containing 4 wt% SiAlON.

Figure 3. SEM image of the sintered sample containing 4 wt% SiAlON.

Figure 4. Density of the sintered samples (○) and shrinkage from the sol to the sintered sample (●) versus the SiAlON concentration.

Figure 5. XRD pattern of the sintered sample containing 5 wt% SiAlON. ● Ca-α-SiAlON.

Figure 7 shows PL spectra of 1-mm-thick silica glasses containing 1–7 wt% SiAlON. The blue excitation light was transmitted through all the samples and its intensity decreased with increasing SiAlON concentration. The inset magnifies the emission spectra revealing that the PL intensity increases with increasing SiAlON concentration up to 4 wt% and decreased above that level.

Figure 8 shows the CIE chromaticity diagram of 1-, 3- and 4-mm-thick silica glasses containing 1–7 wt% SiAlON, which was generated using the PL data. The color on the chromaticity diagram is known to agree with the color perceived by human eyes, and the white cross marked as W corresponds to white light. The figure reveals that the glass emission color changes along the line connecting the chromaticities of the light source (450 nm) and of the SiAlON (585 nm). The color shifted toward 450 nm with decreasing thickness and SiAlON concentration, and the chromaticity closest to white light was achieved for 1-mm-thick silica glasses containing 3 or 4 wt% SiAlON, and of absorption and scattering of light by the small pores shown in figure 3.
Figure 6. PL spectra of 1-, 3- and 4-mm-thick silica glasses containing 5 wt% SiAlON.

Figure 7. PL spectra of 1-mm-thick silica glasses containing 1–7 wt% SiAlON. The spectra are magnified in the inset.

Figure 8. CIE chromaticity diagram of 1, 3 and 4-mm thick silica glasses containing 1–7 wt% SiAlON. The cross corresponds to white light; closed diamonds: silica glasses with 1 wt% SiAlON; circles: 2 wt%; diamonds: 3 wt%; closed triangles: 4 wt%; triangles: 5 wt%; squares: 7 wt%.

Figure 9. PL efficiency of the SiAlON-containing silica glasses versus the SiAlON concentration. Closed circles: 1 mm, circles: 3 mm, closed diamonds: 4 mm thickness.

for 3-mm-thick glass with 1 wt% SiAlON. This result implies that SiAlON-containing glass can be used in white LEDs after optimization of its thickness and phosphor content.

Figure 9 shows the PL efficiency, $E$, of the 1-, 3- and 4-mm-thick silica glasses. The efficiency slightly decreases with the SiAlON concentration for 3- and 4-mm-thick samples, possibly due to the scattering by the SiAlON particles. Most of the blue excitation light was not transmitted through these samples (see figure 6), because the glass had many small pores. Thus, the emission light was stronger than the excitation light, and pseudowhite light could not be obtained. In the 1-mm-thick samples, the efficiency increases with increasing SiAlON concentration up to 4 wt%, and decreases at higher doping level, in agreement with the data of figure 7. In these samples, the transmittance of the excitation light decreased with the SiAlON concentration. Thus, the excitation light was used effectively to excite the phosphor at the SiAlON concentration of up to 4 wt%. However, because of light scattering and absorption, a portion of the blue light might not have reached the phosphor, and thus, the emission decreased at SiAlON concentrations above 4 wt%, although the microstructure of the samples was only weakly dependent on the SiAlON concentration.

On the other hand, the efficiency of the 1-mm-thick SiAlON-dispersed silica glass was about 2/3 times as low
as that of the glasses prepared by melting [3]. The refractive index is higher than 1.84 for tellurite glass, about 1.59 for borate glass, and only 1.45 for silica glass, and the refractive index of SiAlON ranges from 1.855 to 1.897 depending on the composition [10]. Thus, the difference in refractive index is the largest for SiAlON and silica glass; this difference must have caused significant light scattering at the interfaces, and the pores should have also contributed to the scattering. Thus, the silica glass was less efficient as the SiAlON matrix than other glasses, such as tellurite or borate glasses, and glasses with higher refractive indices, prepared by the sol–gel process, should have higher PL efficiency. The same argument applies to resins, which are used in packaging materials. The differences in the refractive index between SiAlON and resins is large, which should increase light scattering at the interface. Nevertheless, inorganic glasses are relatively stable to high light intensities and, therefore, are suitable for packaging materials in high-power LEDs, and the sol–gel process can yield glass with a homogeneously dispersed phosphor owing to the liquid process. We conclude that the sol–gel process is a promising technique of producing luminescent materials with dispersed phosphors; however, the refractive index of the glass matrix needs to be increased and optimized to match the phosphor.

4. Conclusions

We investigated the ability of silica glass to disperse Ca-\(\alpha\)-SiAlON:Eu\(^{2+}\) phosphor via the sol–gel method aiming at white LED applications. SiAlON was well dispersed in the glass at concentrations of 1–7 wt% without phosphor degradation. The luminescence efficiency and color generated by irradiating the resulting glass with a blue LED depended on the SiAlON concentration and the glass thickness. The highest efficiency was obtained for the glass containing 4 wt% SiAlON. Glasses prepared by the sol–gel method have the potential to disperse nitride and oxynitride phosphors at low temperatures.

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