Fabrication of TiO$_2$–SiO$_2$ glasses containing Ca-α-SiAlON:Eu$^{2+}$ phosphor using the sol–gel process

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We prepared titanosilicate glasses by the sol–gel method and studied its ability to disperse Ca-α-SiAlON:Eu$^{2+}$ phosphor, which is a typical yellow phosphor and applicable for white light-emitting diodes (LEDs). xTiO$_2$–(100–x)SiO$_2$ glasses dispersed with SiAlON powders were obtained by sintering at 900°C with x ranging from 10 to 30; the glasses changed to black after sintering at 1000°C. Diffuse reflectance spectra suggested that the colorization was caused by the formation of Ti$^{3+}$ ions in the samples. The local structures of Ti and Eu were measured by X-ray absorption fine structure spectroscopy. Ti K-edge spectra showed that the local structure of Ti was 5-coordinated in the glass where x = 10 and 6-coordinated in the glass where x = 30. Eu L$_{3}$-edge spectra indicated that both Eu$^{2+}$ and Eu$^{3+}$ were present and the ratio of Eu$^{2+}$ to Eu$^{3+}$ depended on the heating temperature. The reduction atmosphere might affect the colorization of the glasses sintered at 1000°C. The quantum efficiencies (QE) of the glasses sintered at 900°C were estimated and that of the glass with x = 10 was the highest among of the samples, higher than that of the SiAlON powders. It is suggested from the measurement of refractive index and XRD patterns that the improvement in QE is caused by the decrease in the light scattering at the interface between the phosphor and the glasses due to differences in refractive indices and the formation of crystals.

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1. Introduction

Nitrides and oxynitrides doped with rare-earth ions have been studied for use as luminescent materials because of their non-toxicity, thermal stability, and interesting luminescent properties. In particular, they are applicable for light-emitting diodes (LEDs), in which phosphor powders imbedded in the organic resin are irradiated by blue or ultraviolet LED as a light source.1) However, it has recently been reported that with an increase in the power of the source LED, the resulting heat generation lets the resin to deteriorate and the LED lifetime to shorten. Thus, in terms of thermal stability, glass5–7 or glass–ceramic6,7 matrices are more suitable as packaging materials for dispersing phosphors than organic resins.

Among glass or glass–ceramics, our group has reported that borate and tellurite glasses are good candidates for dispersing Ca-α-SiAlON doped with Eu$^{2+}$ ions (Ca-α-SiAlON:Eu$^{2+}$), which is a phosphor that emits yellow light under blue light irradiation9) and can be applied in pseudo-white LEDs.9 The 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 deterioration of the phosphor upon heating. In this process, a few glasses exhibited homogeneously dispersed phosphors without deterioration, but the phosphors reacted easily with most of the prepared glasses during the remelting.

On the other hand, glasses can be obtained by the sol–gel method, in which metal alkoxides are hydrolyzed and condensed in a solution.9) In the case of the sol–gel method, a phosphor can be added to the sol during the reaction, which is generally carried out at approximately room temperature. Recently, silica glass dispersed with SiAlON was successfully obtained by controlling the drying process via the sol–gel method.5) The chromaticity of the silica glass could be controlled by the SiAlON concentration and glass thickness, and white light was most closely achieved when the glass was irradiated by a light with a wavelength of 450 nm. The sol–gel method thus shows the potential to produce glass with dispersed phosphors without deterioration. However, the efficiency of silica glasses was lower than those of the borate and tellurite glasses. There are two possible reasons for this: one is the differences in the refractive indices between the phosphor and the glasses. The refractive index of silica glass is about 1.45, which is lower than those of borate and tellurite glasses.

The refractive indices of the phosphors range from 1.855 to 1.897, depending on the composition, and the difference in the refractive indices between the silica glass and phosphors is the largest of all the glasses. The efficiency of the silica glass dispersed with phosphors was lower than those of the borate and tellurite glasses because of the significant light scattering at the interfaces. Another reason is the presence of pores in the silica glass. Generally, many pores are generated during the sol–gel process, and some of those pores might remain depending on the sintering temperature. The pores also might cause light scattering at the interface. Thus, it is important to increase the refractive index and reduce the number of pores.10)

To increase the refractive index, it is useful to add oxides such as TiO$_2$11) and SnO$_2$12) to the silica glasses. Among them, TiO$_2$ has a high refractive index and titanosilicate glasses could serve effectively as a matrix dispersed with SiAlON.

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In this study, TiO₂ is added to silica glass to increase the refractive index of the glass matrix, and titanosilicate glasses dispersed with SiAlON were fabricated at different sintering temperatures. The effect of the addition of TiO₂ and the sintering temperatures on the optical properties was investigated using X-ray absorption fine structure spectroscopy (XANES) and diffuse reflectance spectra.

2. Experimental procedure

Titanosilicate was prepared using tetramethoxysilane (TMOS, Junsei Chemical Co., Ltd.), titanium isopropoxide [Ti(OPr)₃, Kojundo Chemical Laboratory Co., Ltd.], and titanium chloride (TiCl₄, Wako Pure Chemical Industries, Ltd.). The molar ratio of Si(OC₂H₅)₄:Ti(OPr)₃:TiCl₄ was set to (100 − x):0.7:x:0.3 to obtain xTiO₂−(100 − x)SiO₂ (mol %) glasses. The source materials were stirred in a capped PFA bottle, and methanol, HCl solution (pH = 1), and propylene carbonate (PC, Kanoto Chemical Co., Inc.) were added. The molar ratio of (Si+Ti):methanol:HCl:PC was set to 1:2.8:5:3. After stirring for 1 h, Ca-α-SiAlON:Eu⁺+ phosphor, which was prepared by gas-pressure sintering, was added to the sol. The Ca-α-SiAlON:Eu⁺+ phosphor is described in detail in the paper of Xie et al.8) The phosphor particles were angular, with an average size of about 10 μm. The concentration of SiAlON was set to 5 mass % relative to the TiO₂−SiO₂ glass. The sol was rotated at 60 rpm and 30°C on a mix rotor (VMRC-5, AS ONE Corp.) until the sol was gelled. The wet gels were dried in the same bottles, which were covered with aluminum foil, from 25 to 120°C at a rate of 1.3°C·h⁻¹ in an electric oven, resulting in dried gels. The produced dry gels were sintered at 900 and 1000°C, denoted as 9S9, 10S9, 9S10, and 10S10, respectively. These powders, prepared dried gels, and sintered samples were diluted by mixing with BN (Kojundo Chemical Laboratory Co., Ltd.) and pelletized by pressing for the measurement.

The Ti K-edge spectra were measured in the energy range 4459.5–6064.65 eV. The background was subtracted by fitting the spectral lower absorption edge (pre-edge) region from 4902.4 to 4952.4 eV. The spectra were then normalized for atomic absorption based on the average absorption coefficient of the spectral post-edge region from 5132.4 to 5482.4 eV. Eu L₃-edge spectra were measured in the narrow energy range 6850–7050.5 eV because the fluorescence mode needs more time to collect spectra than the transmittance mode. The background was subtracted by the fitting of the spectral pre-edge region from 6880 to 6945 eV.

3. Results and discussion

We attempted to prepare titanosilicate gels, xTiO₂−(100 − x)SiO₂ (mol %), without phosphors in preliminary experiments. Dried gels were obtained in the range from x = 10 to 50, but gelation did not occur when x was more than 60 mol %. Among the resulting samples, the x = 40 and 50 dried gels were broken into many small pieces. Thus, the dried gels of x = 10, 20, and 30 were sintered at 1000°C. The glasses were obtained, although there were cracks in the bulk samples. Images of the sintered samples of x = 10 and 30 are shown in Fig. 1. The x = 10 sintered sample is transparent without colorization, although cracks are partially formed at the top. The x = 30 sintered sample is transparent with a brownish color and is broken in small pieces. In the following sections, we focus on the samples of x = 10 and 30 to disperse SiAlON.

Figure 2 shows images of the x = 10 and 30 dried gels and those same samples sintered at 900 and 1000°C. The x = 10 dried gel, denoted as 1D, was successfully obtained without cracks and it shrank isotropically without cracks by sintering at 900°C, denoted as 1S9. The color of the 1S9 sample was yellow and similar to 1D. However, the x = 10 sample sintered at 1000°C, denoted as 1S10, was broken in small pieces and the color changed to black, although the phosphors emitted slightly yellow light under UV irradiation. The x = 30 dried gel, denoted as 3D, was cracked in a few pieces but the gel was yellow, which indicates that the phosphor was homogeneously dispersed in the gel. After sintering at 900°C, the x = 30 sample, denoted as 3S9, was broken again in many pieces but the sample color was yellow, the same as 1S9 without deterioration. The color of the x = 30 sample sintered at 1000°C, denoted as 3S10, also changed to black, retaining the fluorescence.

![Fig. 1. Images of nondoped xTiO₂−(100 − x)SiO₂ samples: (a) x = 10 and (b) x = 30, sintered at 1000°C.](image-url)

![Fig. 2.](image-url)
The crystallinity of the sintered samples was investigated by XRD. Figure 4 shows the XRD patterns of the sintered samples. All spectra show a broad peak in the range from 10 to 30°, which is called a halo peak. The peak decreases with an increase in the amount of TiO₂. The halo peak indicates that the samples are primarily amorphous, and thus, these sintered samples are characterized as glasses. In Fig. 4(a), there are several sharp peaks, which are assigned to α-SiAlON (JCPDS #033-0261) and are marked by open circles. In Figs. 4(b)–4(d), there are two kinds of peaks, which are assigned to α-SiAlON and anatase (JCPDS #070-7348) and are marked by closed circles. The intensity of the anatase peaks increases with increasing sintering temperature from 900 to 1000°C and with increasing concentration of TiO₂.

Figure 6(a) shows XANES Ti K-edge spectra at the pre-edge region. The intensity and energy of the spectra are known to depend on the coordination structure of Ti. The height and energy of the highest pre-edge peaks are summarized in Table 1. The edge energy of Ti₂O₃ is significantly lower than that of the other samples, and the pre-edge peak is not clear. This suggests that most of the Ti in the samples is Ti⁴⁺ and that Ti⁵⁺ is poorly contained. From Table 1, 1S9, 1S10, and 1NS10 (a non-SiAlON-doped x = 10 glass sintered at 1000°C) are composed of [TiO₄] units, whereas 1D and 3S9 are composed of [TiO₆] units. Figure 5(b) shows the spectra of 1S9, 1S10, and 1NS10 and of [TiO₆] powders: Sr₂TiSi₂O₈, K₂Ti₆O₁₆, and Na₂Ti₄O₉. It is apparent from the figure that the spectra of the samples are similar to each other. In particular, the spectrum of 1S10 is as same as that of 1NS10. This means that the local structure of Ti did not depend on whether SiAlON was doped or not. The peak intensities of the samples at around 4967 eV are between those of Sr₂TiSi₂O₈ and K₂Ti₆O₁₆ or Na₂Ti₄O₉. This indicates that the Ti of the x = 10 glasses is 5-coordinated. The coordination number of the Ti in the gel glass heated at 400°C was reported to be 5 and [TiO₅] pyramids formed. The spectra show that similar [TiO₅] structures formed during the sintering and remained in the glasses after calcination at 1000°C. The peak height of 1S10 is somewhat higher than that of 1S9. In Fig. 5(c), the spectra of 1D, 3S9, and a few [TiO₆] samples are shown. The spectrum of 1D is similar to that of FeTiO₃. These results for the x = 10 samples indicate that the TiO₆ units change to TiO₅ units by calcination and that the TiO₅ units increased with increasing calcination temperature. The spectrum of 3S9 is similar to that of anatase or rutile. The x = 30 glass contained more anatase than did the x = 10 glass, indicating that the pre-edge spectrum was affected by the existence of anatase.

Figure 6 shows the XANES Eu LIII-edge spectra of the x = 10 samples, the SiAlON powder, and the reference samples EuCl₂ and Eu₂O₃. The height was normalized in a narrow region because the spectra assigned to Eu L₃-edge and L₂-edge absorptions appeared at the higher energy. Thus, a comparison of the height is difficult; however, the relative ratio of the two peaks at around 6974 and 6982 eV can be compared. The peaks are in the same positions as those of EuCl₂ and Eu₂O₃, respectively, and are assigned to Eu³⁺ and Eu²⁺ ions. From Fig. 6, the SiAlON pow-
der contained both Eu²⁺ and Eu³⁺ ions, and the ratio is known to affect the PL properties. The ratio of Eu²⁺ to Eu³⁺ of our samples is higher than that of the SiAlON powder, whereas that of 1D is the same as that of 1S9 but lower than that of 1S10. This means that the Eu³⁺ ions in the SiAlON powders were partially reduced by the sol–gel process and that the reduction proceeded by sintering at 1000°C.

![Figure 5](image)

**Figure 5.** Ti K-edge XANES spectra of prepared TiO₂–SiO₂ glasses: 1D, 1S9, 1S10, 3S10, and 1NS10, and commercial powders: rutile, anatase, CaTiO₃, FeTiO₃, Sr₂TiSi₂O₈, K₂Ti₄O₉, Na₂Ti₃O₇, and Ti₂O₃. (a) all spectra, (b) spectra of 1S9, 1S10, 1NS10, and [TiO₅] samples, and (c) spectra of 1D, 3S10, and a few [TiO₆] samples.

![Table 1](image)

**Table 1.** Normalized height and energy position of Ti K-edge pre-edge peaks

| Sample | Energy (eV) | Height |
|--------|------------|--------|
| Sr₂TiSi₂O₈ | 4968.4 | 0.54 |
| K₂Ti₃O₇ | 4968.8 | 0.28 |
| Na₂Ti₅O₇ | 4968.8 | 0.28 |
| anatase | 4969.8 | 0.14 |
| rutile | 4969.1 | 0.15 |
| FeTiO₃ | 4968.4 | 0.22 |
| CaTiO₃ | 4974.0 | 0.17 |
| 1S9 | 4967.7 | 0.40 |
| 1S10 | 4967.7 | 0.43 |
| 1NS10 | 4967.7 | 0.44 |
| 1D | 4968.4 | 0.21 |
| 3S10 | 4969.5 | 0.16 |

der contained both Eu²⁺ and Eu³⁺ ions, and the ratio is known to affect the PL properties. The ratio of Eu²⁺ to Eu³⁺ of our samples is higher than that of the SiAlON powder, whereas that of 1D is the same as that of 1S9 but lower than that of 1S10. This means that the Eu³⁺ ions in the SiAlON powders were partially reduced by the sol–gel process and that the reduction proceeded by sintering at 1000°C. α-SiAlON has a cage structure, and the Eu ions are incorporated in the α-SiAlON lattice. In the source materials, TiCl₄ was contained, and the Cl⁻ ions caused Eu³⁺ ions to reduce partially during the sol–gel reaction; the Eu ions hardly changed when subjected to temperatures from 120 to 900°C, although the coordination number of Ti changed from 5 to 6. The Eu³⁺ changed additionally to Eu²⁺, but the Ti coordination number did not change as the sintering temperature increased from 900 to 1000°C. The QE of the glasses sintered at 900°C is plotted in Fig. 8. The QE value of the SiAlON powders was measured from the surface of the powders packed in a box by the same method of the bulk samples and is shown as a dotted line. The QE value of silica glass dispersed with 5 mass% SiAlON was measured and plotted at x = 0 mol% as a reference. The QE value of the titanosilicate glasses is larger than that of the source powders and silica glasses. This indicates that the QE was improved by the
packing in the glasses. One reason for this may be differences in the refractive indices between the phosphors and the packaging materials. The difference in refractive index causes significant light scattering at the interfaces between the phosphor powders and the packaging material. The refractive indices of the glasses are higher than those of air or the silica glass. The refractive index of the $x = 10$ glass was 1.482, which is lower than the calculated value, 1.53, referred to as Appen's equation, because the glass might contain some bubbles and TiO$_2$ sources might partially evaporate; however, the refractive index of the $x = 10$ glass is higher than that of silica glass, which is 1.45. The refractive index of SiAlON ranges from 1.855 to 1.897, depending on the composition. Thus, the QE of the titanosilicate glasses increased by the addition of TiO$_2$. However, the QE of the $x = 30$ glass, the refractive index of which must be higher than that of $x = 10$, although it could not be measured, was smaller than that of $x = 10$. In regards to the formation of anatase crystals, which collapsed into small pieces and resulted in colorization of the glass, as shown in Fig. 1, the crystals or many cracks in the samples might cause the scattering of the light, and the color of the packaging material may have affected the optical properties.

4. Conclusions

We investigated the ability of titanosilicate glass to disperse Ca-cr-SiAlON:Eu$^{3+}$ phosphor via the sol–gel method, aiming at white-LED applications. TiO$_2$ containing 10 and 30 mol % silica gel and glass were obtained. SiAlON was well dispersed in the glass sintered at 900°C without phosphor deterioration. However, the glasses turned black upon sintering at 1000°C. On the basis of the diffuse reflectance spectra, this change in color is thought to originate from the formation of Ti$^{4+}$. From the XANES spectra of the Ti K-edge, it was found that a 5-coordinated Ti was formed by sintering in 10 mol % TiO$_2$ glass and a 6-coordinated Ti is formed with 30 mol % TiO$_2$ glass. The Eu L$_{III}$-edge spectra showed that the ratio of Eu$^{2+}$ to Eu$^{3+}$ increased with the sol–gel process and with sintering at 1000°C. This suggests that the gels might be sintered in a reduction atmosphere, resulting in the partial color change of Ti to a black-colored glass. The quantum efficiency of the titanosilicate glass was higher than those of both the original powder and the silica glass because of the decrease in the difference in the refractive indices of the phosphors and glasses. Control of the refractive index of the packaging materials such as glasses is thus clarified to be important for obtaining improved optical properties.

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