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Reaction of europium-doped α-SiAlON phosphors with sodium borosilicate glass matrices

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ABSTRACT

The quantum efficiency of composites containing Europium(II)-doped Ca-α-SiAlON phosphors and sodium borosilicate glasses has been reported to decrease with an increase in the Na_2O concentration in the glass matrix. To understand the reason for the dependence of this degradation on the glass composition, the reaction between the SiAlON powder and the glass matrix was investigated using a variety of techniques. SEM images of the areas around SiAlON powders showed the formation of a new layer between the SiAlON particles and the glass matrix. EDX images showed that the number of silicon and aluminium atoms decreased while that of boron atoms increased in the new layer. Raman spectra of the composites showed the formation of B—N bonds. New layers between the SiAlON phosphor and the glasses were formed owing to exchange between silicon or aluminium and boron; this resulted in the degradation of the composites.

1. Introduction

Organic polymers and silicone resins have been used as a medium for dispersing phosphors, allowing the realization of white light-emitting diodes (LEDs) in which these phosphors are irradiated by a blue LED [1,2]. However, the heat generated by the high-power blue LED causes the resin to deteriorate, shortening the lifetime of such devices. In terms of the thermal stability, glass is more suitable than resin as a host material in which to disperse the phosphor powders, and researchers have already succeeded in fabricating glass–phosphor composites [3–9]. Glass–phosphor composites are made by either sintering [3–5] or melting a mixture of a glass powder and phosphor [6–9]. In both processes, the mixtures are heated to temperatures exceeding 500 °C depending on the type of glass. During the heating, interfacial layers occasionally form between the phosphor and the glass, resulting in the degradation of the phosphor. Thus, a detailed understanding of the reaction between the phosphor powder and the glass matrix is important, as it allows for a suitable choice of glass matrix in which to disperse the phosphor powder.

Europium(II)-doped Ca-α-SiAlON (referred to as SiAlON, below) is a phosphor with a high thermal stability that emits yellow light when irradiated with blue light [10]. Our group has investigated various types of glass that allow us to disperse SiAlON phosphors without any degradation [6–9]. In sodium borosilicate glasses, $x\mathrm{Na_2O}$–$(60-x)\mathrm{B_2O_3}$–$40\mathrm{SiO_2}$ (x = 2–40 mol%), the stability of the SiAlON phosphors depends on the glass composition, with an increase in the sodium concentration decreasing the quantum efficiency of the phosphor. Glass for which x = 4 mol% produced a composite with the highest quantum efficiency [8], and scanning electron microscopy (SEM) images revealed that the phosphors barely reacted with the sodium borosilicate glasses [9]. Generally, the structures of sodium borosilicate glasses have been investigated using Raman spectroscopy [11,12] and nuclear magnetic resonance (NMR) spectroscopy [13–16]. It is known that the coordination number of boron changes from 3 to 4, and non-bridging oxygens are formed when the Na_2O concentration is increased. However, the dependence of the reaction of the phosphors in the glass matrices on the glass composition has not yet been sufficiently considered.

In the present study, we examined the reaction between sodium borosilicate glasses and a SiAlON phosphor based on the glass structures. The structures of the host glasses were determined using Raman and NMR spectroscopy. The reaction between the glass matrices and the phosphors was studied using cathodoluminescence (CL) and energy-dispersive X-ray (EDX) measurements; scanning electron microscopy was used to study the areas around the phosphor particles in the glass composites. Based on the obtained results, we discuss the dependence of the degradation of the phosphors on the composition of the glass composites.

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2. Materials and methods

2.1. Sample preparation

Sodium borosilicate glasses with a composition of xNa$_2$O–(60 − x) B$_2$O$_3$–40SiO$_2$ (x = 2–30 mol%) were prepared by melting appropriate amounts of special-grade reagents: NaCO$_3$ (Kanto Chemical Co., Inc.), H$_3$BO$_3$ (Kanto Chemical Co., Inc.), and SiO$_2$ (Junsei Chemical Co., Ltd.) in a platinum crucible at 1200 °C for 1 h and then quenching the samples on a carbon plate. The Ca-α-SiAlON:Eu^{2+} phosphor powder was prepared by gas-pressure sintering [17] according to the protocol described in Xie et al. [10]. The obtained mother glasses, which were crushed and screened to yield particles less than 2 mm in size, were mixed with 1-mass% Ca–α–SiAlON:Eu^{2+} powder. The mixtures were then re-melted at 1000 °C in a platinum crucible for 10 min in air and then quenched on a carbon plate to produce the glass–phosphor composites.

2.2. Characterization

The exact composition of each mother glass was determined by inductively coupled plasma spectrometry (ICP) after dissolving the mother glass powders in an aqueous solution of H$_2$SO$_4$ and HF at 100 °C. The structures of the mother glasses were investigated using NMR and Raman spectroscopy. ^{11}B magic angle spinning (MAS) NMR spectra were collected using a spectrometer (JEOL ECA500) with a 3.2-mm double-tuned broadband probe at a frequency of 160.4 MHz. The spectra were obtained using a spinning frequency of 21 kHz, a 1.75-μs π/4-pulse, and a 40-s recycle delay and by averaging over 128 measurements. The chemical shift of 11 B was recorded with respect to the external reference H$_3$BO$_3$ (δ = 19.5 ppm).

Raman spectra were collected from the surface of the polished bulk glasses and glass–phosphor composites by using a Raman spectrometer (Spectrum GX2000R, PerkinElmer, Inc., Waltham, MA, USA) with a Nd:YAG (λ = 1064 nm) laser operating at 1000 mW.

The photoluminescence spectra of the polished SiAlON-glass composites and SiAlON powder were measured using an F-7100 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) to determine the degree of dissolution of Eu ions into the glass matrix from the SiAlON.

The surfaces of the polished SiAlON–glass composites were etched using an Ar-ion cross-section polisher (SM-09010, JEOL, Tokyo, Japan) to perform cross-sectional CL and EDX analyses. CL measurements were conducted using a field-emission scanning electron microscope (FE-SEM: S-4300, Hitachi, Tokyo, Japan) equipped with a CL system (MP32S/M, Horiba, Kyoto, Japan). The accelerating voltage and beam current were fixed to 5 kV and 100 pA, respectively. The elemental compositions of the samples were estimated by an EDX analysis (E-max, Horiba) using an FE-SEM (S-4800, Hitachi). To avoid the build-up of an electrical charge on the samples, they were coated with a 10-nm carbon film and then covered with a copper grid. All the measurements were performed at room temperature.

3. Results

3.1. Mother glasses

All the mother glasses except for x = 2 were transparent. The x = 2 mother glass was a little opaque due to the phase separation. Table 1 lists the estimated compositions of the mother glasses, xNa$_2$O–(60 − x) B$_2$O$_3$–40SiO$_2$ (mol%). Generally, the structures of the borosilicate glasses are reported in terms of K (mol% SiO$_2$/mol% B$_2$O$_3$) and R (mol % Na$_2$O/mol% B$_2$O$_3$). The values of K and R, calculated from the glass compositions, are listed in Table 1. It is known that Na$^+$ ions are attracted by the borate network and the glass structure is similar to that of binary sodium borate glass when R is 0.5 or less. In all the glasses except for x = 30, the Na$^+$ ions appear to form tetragonal 4-coordinated boron (BO$_4$ groups that are known as $^{[4]}$B).

Table 1
Estimated glass compositions, xNa$_2$O–(60–x)B$_2$O$_3$–40SiO$_2$ (mol%).

x	Estimated composition (mol%)			K	R
	Na$_2$O	B$_2$O$_3$	SiO$_2$		
2	2.0	57.8	40.2	0.70	0.03
4	4.2	56.1	39.7	0.71	0.07
6	6.0	53.3	40.7	0.77	0.11
8	8.1	51.7	40.2	0.78	0.16
10	10.2	49.3	40.5	0.82	0.21
15	15.2	45.3	39.5	0.87	0.34
20	19.8	39.4	40.9	1.04	0.50
30	29.6	30.6	39.8	1.30	0.97

The Raman spectra of the mother glasses without SiAlON are presented in Fig. 1. In these spectra, the broad peak around 500 cm^{-1} is assigned to Si—O—Si bonding. There is hardly any shift in the position of the peak with a change in the Na$_2$O concentration, except for x = 30. The two peaks around 800 and 770 cm^{-1} are assigned to a boroxol ring composed of trigonal 3-coordinated boron (BO$_3$ groups known as $^{[3]}$B) and boroxol with $^{[4]}$B, respectively [11]. The two peaks are expanded in Fig. 1b. The intensity of the peak at 800 cm^{-1} decreases and that at 770 cm^{-1} increases with the Na$_2$O concentration. These changes in the Raman spectra suggest that Na ions exist near $^{[4]}$B and do not form bonds with the non-bridging oxygen in the silica network when the R values are 0.5 or less; this is similar to the previously-reported results [13]. At x = 30, these three peaks almost disappear, and a new peak appears at 1060 cm^{-1}, which is assigned to Si—O— stretching [12]. The Na ions interact with the non-bridging oxygen in the silica network. In the high-frequency range from 1200 cm^{-1} to 1600 cm^{-1}, a broad peak is observed in all the spectra. This can be attributed to the B—O— stretching in chain-type metaborate groups. In particular, the peak can be deconvoluted to the three Gaussian bands centred at 1320, 1410, and 1480 cm^{-1} [18,19]. The peak did not deconvolute in the present study. However, the band at 1320 cm^{-1} decreased as x increased. The band at 1320 cm^{-1} is assigned to loose BO$_3$ units, and the decrease means that the $^{[3]}$B in the rings decreases with an increase in x. The band at 1410 cm^{-1}, which is assigned to $^{[4]}$B in the metaborate groups is not clear at x = 2–10, but the band can be clearly observed at x = 15 and 20. This means that large metaborate groups are formed at x = 15 and 20.

Fig. 2 shows the ^{11}B MAS NMR spectra of the mother glasses. The sharp peak at around 0 ppm and broad peaks between 20 and 5 ppm are assigned to $^{[4]}$B and $^{[3]}$B, respectively [15,16]. The peak intensity of $^{[4]}$B increased and that of $^{[3]}$B decreased with an increase in the Na$_2$O concentration. Detailed structural information was obtained from the ^{11}B 3QMAS spectra. The two-dimensional spectrum of the x = 2 glass is shown as one example in Fig. 3a. For the 3QMAS peaks, the areas are assigned to $^{[3]}$B in rings or non-rings and $^{[4]}$B, as shown in Fig. 3a. The spectra projected along both saxis represents the projection, without second-order broadening. Thus, the projections for each glass are plotted in Fig. 3b. The region for a lower magnetic field is assigned to $^{[3]}$B, and the peak around 0 ppm is assigned to $^{[4]}$B [15,16]. The spectra assigned to $^{[3]}$B have two peaks, and the peaks around 22 ppm and 17 ppm are assigned to $^{[3]}$B in the boroxol rings and non-ring sites. In $^{[3]}$B, the number of non-ring sites decreased with an increase in the Na$_2$O concentration, and no non-ring sites were observed at x = 20 and 30. In the x = 2–10 glasses, the band of $^{[4]}$B exhibits a shoulder at around 2 ppm, suggesting that the $^{[4]}$B exists with different chemical states of more than two. The shoulder at 2 ppm almost disappears, and a new peak appears at high magnetic fields when x = 20 and 30, although the assignment of the peak is difficult because of the small peak width. The chemical shift of $^{[4]}$B is known to occur at high magnetic fields when the number of Si bonds with $^{[4]}$B increases. Considering the