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Exploration of metaphosphate glasses dispersed with Eu-doped SiAlON for white LED applications

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ABSTRACT

Ca-α-SiAlON:Eu^{2+} oxynitride phosphors are typical luminescent materials with a high thermal tolerance. A series of metaphosphate glass samples (50MO–50P_2O_5; mol%, M = Zn, Ca, and Ba) were prepared in order to investigate their ability to disperse Ca-α-SiAlON:Eu^{2+} phosphor powders. The glass structures of all of the samples were formed using Q^2 species and composed in long chain networks by investigation of the NMR and Raman spectra. In the glass samples, SiAlON was dispersed until reaching 5 or 6 mass%. The color due to irradiation by a blue LED (wavelength of 450 nm) depended on the glass composition, concentration of SiAlON, and thickness of the composite. Regarding the glass formation and quantum efficiency, the BaP glass with between 3 and 4 mass% SiAlON composite was determined to be the most suitable for use as a host material for white LEDs.

1. Introduction

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, Eu^{2+}-doped Ca-α-SiAlON (Ca-α-SiAlON:Eu^{2+}) emits yellow light when irradiated by blue light [1] and was used to produce a white light-emitting diode (LED): the powder was embedded in an organic resin and irradiated by a blue LED [2]. The heat generated by high-power blue LEDs causes the deterioration of this resin, thereby shortening the lifetime of such devices. With respect to thermal stability, glass matrices are the more suitable option for dispersing the phosphor powder, provided that the glass melting temperature is sufficiently low that the phosphor is not degraded during the dispersion.

Our group explored various types of low-melting glass to disperse SiAlON without degradation [3,4]. Recently, we reported that zinc phosphate glasses are good candidates for dispersing SiAlON [4]. Phosphate glasses are known to be applicable as optical glasses [5,6] and sealing glasses [7,8] because of their low melting temperature. In particular, zinc phosphate glasses have a glass transition temperature, T_g, of less than 500 °C [9]. Among these glasses, the glass comprising 60 mol% ZnO and 3 mass% SiAlON exhibited the best performance with respect to glass formation and quantum efficiency [4]. We found that the refractive index of the glass greatly influenced the suitability of the host material; the glasses with a high refractive index were more suitable. However, phosphate glasses with a high refractive index have not yet been sufficiently explored.

The refractive index can be controlled according to the types of cations. In this study, we focus on metaphosphate glasses, in which cations are known to modify the PO_4 tetrahedra and form long chain structures containing different cations as the host glass to disperse SiAlON for a white LED. Glass and Ca-α-SiAlON:Eu^{2+} phosphor composites were prepared by melting, and the photoluminescence spectra were then measured, allowing the exploration of suitable glass structures for use in white LEDs. The glass structures were investigated using Raman and nuclear magnetic resonance (NMR) spectroscopy, and the refractive indices of the structures were measured. From the data, their effect on the optical properties is also discussed.

2. Experimental

2.1. Sample preparation

A series of phosphate glass structures, 50MO–50P_2O_5 (mol%; M = Zn, Ca, and Ba), was prepared by melting appropriate amounts of $M(PO_3)_2$ in a silica crucible at 1200 °C for 15 min and then quenching on a carbon plate. A Ca-α-SiAlON:Eu^{2+} phosphor powder was prepared by gas-pressure sintering [10] resulting in angular particles with an average size of approximately 10 μm [3]. Further details can be found in reference [1]. The phosphate glass was crushed and mixed with the Ca-α-SiAlON:Eu^{2+} powders

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in concentrations of 1–6 mass% for the crushed glasses. The mixtures were re-melted in silica crucibles at 1200 °C for 10 min and then quenched on a steel plate to obtain glasses dispersed with SiAlON. The final glass-phosphor composites were polished to thicknesses of 1, 2, and 3 mm.

The exact composition of each glass was determined by inductively coupled plasma spectrometry (ICP) after dissolving the glass powders in an aqueous solution of HCl and HF at 105 °C. The T_g of the glass powders was measured by differential thermal analysis at a heating rate of 10 °C/min (TG-DTA2000SR; Brucker AXS) with α-Al_2O_3 powders as the reference.

2.2. Structural characterization

The glass structures were investigated using NMR and Raman spectroscopy. ^{31}P magic angle spinning (MAS) NMR spectra—with or without cross polarization (CP)—were collected using a spectrometer (JEOL ECA500) with a 3.2-mm double-tuned broadband probe at a frequency of 202.4 MHz. The spectra were obtained using a spinning frequency of 20 kHz, a 1.75-μs π/4-pulse, and a 40-s recycle delay and by averaging over 128 measurements. The chemical shift of ^{31}P was recorded with respect to the external phosphoric acid (δ = 0 ppm). The CP process discriminates against ^{31}P nuclei far away from protons, and in this study, the CP contact time (ct) was set as 1 and 5 ms.

Raman spectra were collected for the surface of the polished bulk glasses using a Raman spectrometer (Spectrum GX2000R, PerkinElmer) together with a Nd:YAG (λ = 1064 nm) laser operating at 1000 mW.

2.3. Optical measurements

Photoluminescence (PL) spectra were measured using a multichannel photo detector (MCPD-7000, Otsuka Electronics) with a Xe-lamp as an exited source. The 1, 2, and 3-mm-thick polished glass-phosphor composites were irradiated by blue light of wavelength 450 nm, and the PL spectra transmitted through a 5-mmφ hole situated on the opposite side of the light source were measured. Using the PL spectra, color coordinates of the CIE-1931 chromaticity diagram were obtained to determine how close to white light the samples were.

The quantum efficiency (QE) was estimated according to the PL spectra emitted upward from the glass surface of 3-mm-thick samples irradiated by blue light of wavelength 450 nm and collected for 220–800 nm by an integrated sphere. The samples were deposited onto a layer of $BaSO_4$ powder set at the bottom of the integrated sphere in order to reflect the scattering emission into the integrated sphere. The QE was calculated using the following equation:

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

where $E(\lambda)/h\nu$ is the number of photons in the excitation spectrum, and $P(\lambda)/h\nu$ is the number of photons in the emission spectrum. Further details of this calculation are given in Ref. [11].

The refractive index of the surface of the polished bulk glasses without SiAlON was measured as 633 nm using a prism coupler (Metricon 2010).

3. Results

The sample names and analyzed composition of the glasses are presented in Table 1, along with the T_g and refractive index. All of the glasses were transparent without devitrification. The data in Table 1 indicate that P_2O_5 was partially evaporated during the melting and SiO_2 slightly contained from the crucible. Among the samples, CaP exhibited the highest T_g, and ZnP exhibited the lowest. The refractive indices were in the following order: ZnP < CaP < BaP. Considering the electric field strength of the cations, which can be calculated as Z/r^2 (Z: number of valence electrons and r: ionic radius [12]), Zn^{2+}: 3.6, Ca^{2+}: 2.0, and Ba^{2+}: 1.1. The refractive index increased as the electric field strength decreased, indicating that the electrons on the oxygen atoms were localized.

Table 1
Sample names and analyzed compositions (mol%) of the glasses with their corresponding T_g and refractive index values.

Sample name	Analyzed composition			T_g (°C)	n@633 nm
	MO	P_2O_5	SiO_2		
ZnP	51.5	48.1	0.4	425	1.5191
CaP	52.1	46.9	1.0	540	1.5497
BaP	53.3	45.6	1.1	479	1.5956

Fig. 1 shows the normalized ^{31}P MAS/DD (^{1}H Dipolar Decoupling) NMR spectra, without CP, of the glass-phosphor composites comprising 1 mass% SiAlON. Isotropic chemical shifts are labeled with Q^i values, where i represents the number of bridging oxygen atoms per phosphate tetrahedron. The remaining peaks can be attributed to spinning sidebands that arise from the anisotropies of the Q^2 species, as detailed in reference [9]. The isotropic peaks were decomposed by Gaussian fits, and the resulting chemical shifts and area ratios are summarized in Table 2. The peak shifted to a lower magnetic field in the order of ZnP, CaP, and BaP, indicating that the P–O bond became more ionic in that order. The peak area ratio of Q^2 is larger than 90%, which indicates that PO_4 long chain networks were formed in the glass and that the glass structures hardly depended on the type of cation.

The CP MAS spectra of the glasses with 1 mass% SiAlON with act of 1 and 5 ms of the glass-phosphor composites with 1 mass% SiAlON, shown alongside the MAS/DD spectra in Fig. 2(a)–(c), represent the signal due to P coupled with protons. The CP MAS spectra where ct = 1 ms indicate the signals from P coupled with protons that are closer than observed for ct = 5 ms, and the MAS/DD spectra indicate the signals from all of the P atoms obtained by setting the recycle delay time to allow the relaxation of the ^{31}P. As shown in Fig. 2, the intensity of the CP MAS spectra was on the order of 5 times weaker for ZnP and 20 times weaker for CaP and BaP compared with the MAS/DD spectra. The intensity of the Q^2 peak of the CP MAS spectra increased relative to the Q^1 peak, together with an increase in ct, and it increased further for the MAS/DD spectra, indicating that more protons exist around the Q^1 species than the Q^2 species. This suggests that the protons might bond to terminated oxygen to form P–OH. For ZnP, the intensity of the CP MAS spectrum was the highest among the samples, which indicates that the number of available protons was the largest. The NMR spectra of the BaP composite with 3 mass% SiAlON are shown in Fig. 2(d), and the chemical shift and area ratio of the Q^1 and Q^2 peaks are presented in Table 2. Comparing the data of BaP with 1 mass% SiAlON, the Q^1 peak increased with increasing SiAlON concentration. The increase of Q^1 species with increasing SiAlON concentration was observed in the other glass systems. This indicates that the SiAlON contributes slightly to the formation of Q^1 species by separating the P–O–P bonds in Q^2 spices that form the glass network; however, the structure is hardly changed by the addition of the SiAlON.

The Raman spectra of the 50MO–50P_2O_5 (mol%) glasses (normalized by the highest peak in each spectrum) are shown in Fig. 3. The high and sharp peaks near 1150–1200 cm^{-1} and low and broad peaks near 1250 cm^{-1} correspond to the symmetric ($\nu(PO_2)_{sym}$) and asymmetric ($\nu(PO_2)_{asym}$) stretching modes of the two non-bridging oxygen atoms bonded to the phosphorous atom