On the origin of fine structure in the photoluminescence spectra of the \( \beta \)-sialon:Eu\(^{2+} \) green phosphor

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Abstract
The photoluminescence (PL) and PL excitation (PLE) spectra of \( \text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z} \) (\( \beta \)-sialon):Eu\(^{2+} \) phosphors with small \( z \) values (\( z = 0.025–0.24 \)) were studied at room temperature and 6 K. The PL and PLE spectra exhibit fine structure with the PL lines being as sharp as 45–55 nm even at room temperature; this fine structure was enhanced by decreasing the \( z \) value. These results can be used for expanding the color gamut of liquid crystal displays, particularly in the blue–green region. From low-temperature measurements, the fine PLE structure was ascribed to discrete energy levels of \( \text{^7F}_j \) states. The 4f\(^6\)5d excited states of Eu\(^{2+} \) are considered to be localized near the 4f orbital. This is because the bonding of Eu\(^{2+} \) with surrounding atoms is ionic rather than covalent. Lattice phonon absorptions were also observed in the PLE spectrum, revealing that the optically active Eu\(^{2+} \) ions are located in the \( \beta \)-sialon crystal. The PL spectrum of the sample with the smallest \( z \) value (0.025) consists of a sharp zero-phonon line and lattice phonon replicas, which results in a sharp and asymmetric spectral shape.

Keywords: phosphor, sialon, photoluminescence, LED, LCD

1. Introduction

White light-emitting diodes (LEDs) are replacing cold-cathode fluorescent lamps as the backlight of liquid crystal displays (LCDs). For example, white LEDs using a yellow cerium-doped yttrium aluminum garnet (YAG:Ce) as a phosphor are already used as backlights for small LCDs like cell phone displays [1]. Although this type of LED has a high luminous efficiency, its emission spectrum is reduced in the red and blue–green regions. An alternative is to use LEDs with emission matching red, green and blue (RGB) LCD filters. For this purpose, white LEDs utilizing red and green phosphors have been designed and are penetrating the market. In these LEDs, the emission spectrum of the green phosphor is extremely important because it is located in between blue and red filters. Si\(_{6-z}\)Al\(_z\)O\(_z\)N\(_{8-z} \) (\( \beta \)-sialon):Eu\(^{2+} \) is one of the most suitable green phosphors [2] and has a sufficiently narrow emission peak at around 535 nm [3, 4]. With regard to most oxide or oxynitride phosphors utilizing Eu\(^{2+} \) 5d–4f transitions, the narrow line-width of \( \sim 55 \) nm (1800 cm\(^{-1}\)) observed in \( \beta \)-sialon is quite unusual. For example, Ba\(_2\)SiO\(_4\) : Eu\(^{2+} \) and Sr-sialon:Eu\(^{2+} \) green phosphors have the line-width of 66 nm (2500 cm\(^{-1}\)), and the line-width in Ca\(_\alpha\) sialon:Eu\(^{2+} \) (yellow) and CaAlSiN\(_3\) : Eu\(^{2+} \) (red) phosphors is 90 nm (2600 and 2200 cm\(^{-1}\), respectively) [5–8]. Also unique is the asymmetric shape of the emission spectrum in \( \beta \)-sialon, with
a steeper rise at the high-energy side than at the low-energy side. Moreover, the spectra contain a fine structure with some shoulders and notches, which can be enhanced by decreasing the \( z \) value [11].

To clarify the origin of these features, we have studied PL and PLE spectra of \( \beta \)-sialon at room temperature and at 6 K focusing on samples with small \( z \) values. Although much effort has been devoted to the crystal structure of \( \beta \)-sialon [3, 9, 10], the Eu coordination structure remains unsolved due to the small Eu concentration. It is difficult to characterize the Eu sites by common structural analysis techniques, but they can be directly probed by luminescence measurements.

2. Experimental details

The \( z \) value of \( \beta \)-sialon was controlled by changing the atomic ratio of Si and Al. The sample with \( z = 0.24 \) was obtained using \( \alpha \)-Si\(_3\)N\(_4\) as a Si source as reported in [3, 4]. To reduce the oxygen content, high-purity (4N) Si powder (Shin-Etsu Chemical Co. Ltd, Japan) was used as the Si source for the samples with \( z = 0.025, 0.050 \) and 0.075. AlN (Type F, Tokuyama Corp., Japan) and Eu\(_2\)O\(_3\) (Shin-Etsu Chemical Co. Ltd, Japan) were selected as Al and Eu sources, respectively. The Eu concentration was fixed at 0.1 at.\%.

The powder mixtures were fired in a nitrogen atmosphere in two steps using a gas-pressure sintering furnace (Fujidempa Kogyo Co. Ltd, Osaka, Japan) as reported elsewhere [11]. The chemical compositions of these samples were measured using an inductively-coupled plasma (ICP) method and an oxygen–nitrogen analyzer (TC-436, LECO). Crystalline phases were identified by x-ray diffraction (XRD, Smart Lab, Rigaku) using Cu K\(_{\alpha1}\) radiation. The photoluminescence (PL) and PL excitation (PLE) spectra of the phosphors were recorded using two fluorescence spectrophotometers: MODEL F-4500 (Hitachi) at room temperature and MODEL Fluoro Max-3 (Horiba) at 6 K. Time-resolved PL was measured using a fluorescence lifetime measurement system (Hamamatsu C4780). The samples were excited by 70 ps pulses from a GaInN laser operating at \( \lambda = 440 \) nm.

3. Results and discussion

3.1. Room-temperature measurements

Figure 1 shows the XRD pattern of the sample with \( z = 0.025 \). Only the \( \beta \)-sialon phase is present with no trace of crystalline Si at \( 2\theta = 28.5^\circ \), indicating that the Si source was completely nitridized during the synthesis. The same observation was made for all the samples.

Figure 2 shows room-temperature PL and PLE spectra for samples with various \( z \) values. The PL spectra were measured by exciting at the PL maximum and the PLE spectra were recorded for the PL peak. At \( z < 0.075 \), \( \beta \)-sialon:Eu exhibits fine structure in both PL and PLE spectra, which is particularly prominent for \( z = 0.025 \). Such sharp peaks are hardly seen at room temperature for Eu\(^{2+}\) 5d–4f electronic transitions in nitride and oxynitride phosphors. With decreasing \( z \) value, the PL maximum shifts to the short wavelengths, but the superimposed sharp peaks keep their positions as indicated by the vertical lines in figure 2; meanwhile, the overall line-width of the emission spectrum becomes smaller. The fine structure is also seen in PLE spectra, but only at its long-wavelength side.

Figure 3 shows typical PL decay curves. All the samples had a lifetime of \( \sim 1 \) \( \mu \)s, which is typical for Eu\(^{2+}\) ions. This result confirms that the green PL emission of \( \beta \)-sialon originates from 5d–4f allowed transitions, although the spectrum has a fine structure uncommon for the previous reports on oxide or oxynitride phosphors.

Figure 4 shows the Commission International de l’Eclairage (CIE) chromaticity coordinates for the same samples as in figure 2. With decreasing \( z \) value, the coordinates \((x, y)\) move from (0.322, 0.642) to (0.276, 0.665) owing to the decreasing overall line-width of the emission spectrum. As a result, the blue–green color gamut can be extended beyond the triangle of the sRGB standard. This property favors the \( \beta \)-sialon phosphors with the small \( z \) values for the backlight applications.

3.2. Low-temperature measurements

To understand the origin of the PL and PLE features, we performed low-temperature measurements. Sharp PLE line

![Figure 1. XRD pattern of \( \beta \)-sialon:Eu with \( z = 0.025 \).](image1)

![Figure 2. Room-temperature PL and PLE spectra of \( \beta \)-sialon:Eu with various \( z \) values.](image2)
Figure 3. PL decay curves of β-sialon:Eu with \( z = 0.24 \) (solid triangles) and \( z = 0.050 \) (open circles).

Figure 4. Chromaticity coordinates of β-sialon:Eu phosphors with \( z = 0.025–0.24 \).

Figure 5. Low-temperature PLE spectra (510 and 523 nm emission) of β-sialon:Eu with \( z = 0.025 \). The \( ^7F_1 \) energies of Eu\(^{3+} \) (top) and shifts corresponding to the IR modes of β-Si\(_3\)N\(_4 \) (middle) are indicated by the vertical bars.

Figure 6 shows the PL spectrum measured at 6 K for the sample with \( z = 0.025 \) under 450 nm excitation. The major peak at 510 nm (19 610 cm\(^{-1} \)) can be assigned to a level separations of Eu\(^{3+} \). Some features of these bands can also be seen in the room-temperature spectra shown in figure 2. While the \( ^7F_1 \)-related energy structure is rarely observed in Eu\(^{2+} \) oxide or nitride phosphors, similar PLE spectra were reported in some ionic crystals, and the \( ^7F_1 \) structure was clearly observed in the lowest d excitation band [13–16]. For example, Ryan et al. reported a similar spectrum for Eu\(^{2+} \) in BaMg\((SO_4)_2\) [14]. This similarity suggests that the crystal field around Eu\(^{2+} \) in β-sialon is so weak that the lowest s level is high enough to exhibit the 4f-electronic structure. This result contradicts the general assumption that the covalency and nephelauxetic effect are strong for nitride and oxynitride materials. However, from the characteristic PLE spectrum, we conclude that the bonding of Eu\(^{2+} \) in β-sialon with the surrounding atoms is ionic rather than covalent, and the Eu\(^{2+} \) excited state (4f\(^6\)5d\(^2\)) is localized near the 4f orbital. The separation of less than 100 cm\(^{-1} \) between the sharp peaks in some groups can be ascribed to the Stark splitting of the 4f levels by the crystal field. In each group, broad minor peaks on the high-energy side accompany the sharp major peaks. We assign these minor peaks to phonon absorptions, by analogy with the results reported for MgF\(_2\):Eu\(^{2+} \) [13]. Although the phonon modes of β-sialon are still unclear, those of β-Si\(_3\)N\(_4 \) are known [17], and the crystal structure of β-sialon with low concentrations of aluminum and oxygen is quite similar to that of β-Si\(_3\)N\(_4 \). The phonon spectrum of β-Si\(_3\)N\(_4 \) consists of 11 Raman-active modes and six infrared (IR)-active modes. These six IR modes are indicated by short vertical bars for the major peaks assigned to the \( ^7F_0 \rightarrow ^7F_J \) transitions in figure 5 [17]. There is a good agreement in the line pattern for the \( ^7F_6 \) energy group, although the energy positions are complicated by the Stark splitting of the major peaks. In other energy groups, the broad minor peaks on the high-energy side overlap with other major peaks. However, the overall pattern of these minor peaks fits well to phonon absorptions.

The spectra were measured for the 510 and 523 nm emissions, which correspond to the first and second major PL peaks, respectively. A PL spectrum for this sample is shown in figure 6 and is discussed below. The fine structure is similar in both PLE spectra of figure 5, except for an additional sharp excitation peak at 510 nm observed for the 523 nm emission. We assign the 510 nm emission to the zero-phonon transition from the lowest excited state. To interpret the complex PLE spectra, we decomposed them into seven groups and added the lowest 4f energy level separations of Eu\(^{3+} \) reported for EuCl\(_3\) (long vertical bars in the top part of figure 5) [12]. Note that these groups are not equidistantly spaced and that their centers fit well to the energy structure of Eu\(^{3+} \).
Figure 6. Low-temperature PL spectrum of β-sialon:Eu with $z = 0.025$. Shifts corresponding to the Raman and IR modes for β-Si$_3$N$_4$ are indicated by the vertical solid and dashed bars, respectively.

zero-phonon transition because of its intensity, sharpness and coincidence with the lowest excitation peak in figure 5. The peaks at 523 nm (19120 cm$^{-1}$) and 533 nm (18760 cm$^{-1}$) correspond to two major peaks observed for samples with various $z$ values at room temperature (figure 2). A number of additional peaks, which are not resolved at room temperature, are observed at 6 K. Such peaks are unusual for phosphors with Eu$^{2+}$ 5d–4f transitions even at low temperature. Although they were observed for 4f–4f transitions [18–20], for Eu$^{2+}$ 5d–4f transitions they were only reported for halide ionic crystals [13, 21] and ascribed to phonon-assisted transitions. The reported phonon shifts by both modes [16] indicated in figure 6 agree well with our measured spectrum. We can conclude that the PL spectrum consists of a sharp zero-phonon line at 510 nm and lattice phonon replicas. These features result in the sharp and asymmetric PL line shape at room temperature.

We analyze the variation of low-temperature (6 K) PL and PLE spectra with $z$ value for samples with $z = 0.025$ and 0.24 (figures 7(a) and (b)). The PLE spectra were measured for various emission wavelengths as indicated in the PL spectrum. In the case of $z = 0.025$, the shape and position of PLE features are almost independent of the monitored wavelength (a–d), indicating that all the emission peaks originate from the same Eu$^{2+}$ excited state. In contrast, for $z = 0.24$, the PLE spectra shift to lower energies and broaden when the monitored energy is decreased from e to i; meanwhile, the energy intervals between major peaks are similar to those in figure 7(a). This shift and broadening suggest that the emission spectrum is composed of a group of mutually shifted zero-phonon lines and their associated phonon replicas. The formation of such a group can be ascribed to the enhancement of the variety of atomic configurations around Eu atoms due to the increase of Al or O concentration. However, sharp PL lines are still observed even for $z = 0.24$, at the same positions as in samples with low $z$. This is evident even at room temperature as shown in figure 2.

Figure 7. Low-temperature PLE spectra of β-sialon:Eu with $z = 0.025$ (a) and $z = 0.24$ (b) for various energies indicated in the PL spectrum.

4. Conclusions

β-sialon:Eu$^{2+}$ phosphors exhibit a distinct fine structure in the PLE and PL spectra, which becomes more prominent at lower $z$ values. Results of low-temperature measurements suggest that this structure originates from the $^7F_J$ states and the lattice phonon in the Eu$^{2+}$ f–d transition. This feature distinguishes β-sialon from other nitride and oxynitride phosphors. Our measurements provide new information on the atomic site of Eu dopant. Coupling to crystal lattice phonons was observed in PLE and PL spectra, suggesting that PL-active Eu$^{2+}$ ions are located at specific sites in the β-sialon structure rather than at defects or grain boundaries. Although Eu atoms were observed in the β-sialon hexagonal channel by electron microscopy [3, 9], there was no evidence that they emit green luminescence. As the PLE fine structure is associated with the $^7F_1$ level and lattice phonons, it is plausible that the luminescent Eu$^{2+}$ ions occupy specific sites with large neighbor spacing and are ionically bonded with neighboring O and Al atoms, which substitute N and Si atoms for charge balance. These sites are likely located in the hexagonal channel or another unique position in the β-sialon structure and should be characterized by x-ray absorption fine structure (XAFS) measurements.
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