Paper

Improvement in Luminescent Characteristics by Al Codoping in $\text{Ba}_2\text{SiS}_4\text{:Ce}$ Blue Phosphor for White LEDs

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ABSTRACT

$\text{Ba}_2\text{SiS}_4\text{:Ce}$ has been proposed as a novel blue phosphor for white LED application. It has been found that photoluminescent characteristics are improved by Al-codoping, which realizes a high doping of Ce^{3+} luminescent centers. The relative PL luminance of 145% has been achieved compared to the commercial BAM under 405-nm-excitation. The internal quantum efficiency is about 36 %. The PL intensity at 150°C maintains about 80% of that at room temperature. It has been also confirmed that $\text{Ba}_2\text{SiS}_4\text{:Ce}$ is chemically stable enough for applying to white LEDs.

KEYWORDS: white LEDs, blue phosphor, $\text{Ba}_2\text{SiS}_4\text{:Ce}$

1. Introduction

Recently, the development of phosphor materials for white LED application has been intensively attempted¹⁾²⁾. $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ (BAM) and $\text{Sr}_5(\text{PO}_4)_3\text{Cl:Eu}$ have attracted the attention as promising blue phosphors. Generally, sulfide phosphors have an advantage that they can be produced at lower temperature compared to nitride and oxide phosphors. CaS:Eu is the promising red phosphor for blue-LED-excitation, however it is chemically unstable. Alkaline earth thiosilicates have been reported to be relatively stable in sulfides³⁾. It has been recently reported that Eu-activated Ca_2SiS_4 shows an efficient red luminescence⁴⁾. We pay attention to $\text{Ba}_2\text{SiS}_4\text{:Ce}$ as a novel blue phosphor for white LED application. $\text{Ba}_2\text{SiS}_4\text{:Ce}$ shows a broad emission spectrum over an entire blue wavelength range, and has a relatively strong excitation band due to Ce^{3+} luminescent centers in a near-UV wavelength range⁵⁾. However, a luminous efficiency has not reached the practical level. In this paper, luminescent characteristics of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ phosphors are attempted to improve by codoping Al as a charge compensator, which is expected to promote the activation of Ce^{3+} centers. The feasibility of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ for white LEDs application has been confirmed.

2. Experimental

$\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder samples were prepared by solid-state reaction. BaS , Ce_2S_3 , Si , S and Al_2S_3 were used as source materials. The mixture of these powders was fired at 1,100 °C for 4 hour in Ar

atmosphere. The molar fraction $x = \text{Al}/(\text{Si}+\text{Al})$ was varied from 0 to 0.2, since Al is expected to substitute for Si. To investigate the crystallinity of phosphor samples, X-ray diffraction (XRD) measurements were performed. Photoluminescence (PL) measurements were carried out under UV excitation using a monochromatic light from D₂ lamp.

3. Results and discussion

Figure 1 shows XRD patterns of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder samples for $x = 0, 0.05, 0.10, 0.20$. The concentration of Ce was 1 mol% for all samples. The XRD pattern of Ba_2SiS_4 obtained from the inorganic crystal structure database (ICSD) is also shown as a reference. All diffraction peaks are identified as diffraction peaks due to the orthorhombic structure of Ba_2SiS_4 for all samples. No peak due to other impurity phases is observed. The full width at half maximum (FWHM) of the strongest peak at around 22° is decreased by codoping Al. The result implies that a formation of defects is suppressed by codoping Al.

Figure 2 shows PL spectra of the $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder samples for $x = 0, 0.05, 0.10, 0.20$. The PL spectra show a broad band in the spectral range of 400-550 nm due to the $5d-4f(^2F_J)(J=5/2, 7/2)$ transition in Ce^{3+} luminescent centers. The spectral figuration is almost the same for all samples. Corresponding Commission Internationale de l'Eclairage (CIE) color coordinates (x, y) are (0.14, 0.09). The PL intensity is increased with increasing x , and reaches maximum at $x = 0.1$. Figure 3 shows PL excitation (PLE) spectra of the same samples. The

Figure 1 XRD patterns of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder samples for $x = 0, 0.05, 0.10, 0.20$. The XRD pattern of Ba_2SiS_4 obtained from ICSD is also shown as a reference.

PLE measurement was carried out by monitoring a luminescence at 435 nm. The PLE spectra locate in the wavelength region from 270 to 420 nm. The PLE band above 340 nm is due to the transition from 4f to lower 5d level in Ce^{3+} centers, and that below 340 nm is thought to be due to the band-to-band excitation of the Ba_2SiS_4 host and/or the transition from 4f to higher 5d level. The PLE spectral figuration is not changed by varying the Al content. By increasing x , PLE intensity increases and reaches maximum at $x=0.1$. These results imply that the Al codoping enhances the Ce activation without formation of the defects in the host lattice.

To further improve the luminescent characteristics, the proper Ce concentration was investigated.

Figure 4 shows the Ce-concentration dependences of the PL peak wavelength and the PL peak intensity for the Al-codoped ($x=0.1$) powder samples. The excitation wavelength is 405 nm. The PL peak shifts to longer wavelength from 436 to 447 nm with increasing the Ce concentration. The PL intensity increases with increasing the Ce concentration, and reaches the maximum at 2 mol%. The fact indicates

Figure 2 PL spectra of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder samples for $x = 0, 0.05, 0.10, 0.20$. The excitation wavelength is 405 nm.

Figure 3 PL excitation spectra of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder samples for $x = 0, 0.05, 0.10, 0.20$.

that the high doping of Ce centers can be achieved by Al codoping.

Table 1 summarizes the relative PL luminance respect to the commercial BAM (Kasei Optonix, Ltd., LP-B4) under 380 nm- and 405 nm- excitation for Al-codoped $\text{Ba}_2\text{SiS}_4\text{:Ce}$ samples. The CIE color coordinates (x, y) are also shown in Table 1. It should be noted that the relative luminance of the sample ($x=0.1$, Ce:4 mol%) under 405 nm-excitation is about 145 %. The internal quantum efficiency of the same sample is about 36 %.

The feasibility of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ for white LED application was studied. Figure 5 shows temperature dependences of PL intensity of the typical $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder sample. The measurement was performed under 405-nm-excitation. The PL intensity at 150°C

Figure 4 Ce-concentration dependences of the PL peak wavelength and the PL peak intensity for the Al-codoped ($x=0.1$) $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder samples

Table 1 Relative PL luminance respect to the commercial BAM for Al-codoped $\text{Ba}_2\text{SiS}_4\text{:Ce}$ samples under 380 nm- and 405 nm- excitation
The CIE color coordinates (x, y) are also shown.

Ce Concentration (mol%)	Relative Luminance (%)		CIE (x, y)
	$\lambda_{\text{ex}}(\text{nm})$ 380	$\lambda_{\text{ex}}(\text{nm})$ 405	
0.5	43	37	(0.14, 0.08)
1	69	81	(0.14, 0.09)
2	95	137	(0.14, 0.11)
4	97	145	(0.14, 0.13)

maintains about 80% of that at room temperature. The accelerated degradation test was also performed at 85°C and 85%-humidity in air. As shown in Fig. 6, after 200 h, the PL intensity of $\text{Ba}_2\text{SiS}_4\text{:Ce}$ maintains 90% respect to the initial level, despite that of $\text{Y}_2\text{O}_3\text{:Eu}$ decreases to 60%. Taking these results into account, $\text{Ba}_2\text{SiS}_4\text{:Ce}$ is chemically stable enough for applying to white LEDs.

3. Summary

$\text{Ba}_2\text{SiS}_4\text{:Ce}$ phosphor has been proposed as a novel blue phosphor for white LED application. The PL intensity is improved by Al-codoping, which realizes a high doping of Ce centers. The relative PL luminance of 145% has been achieved compared to the commercial BAM under 405-nm-excitation. The internal quantum efficiency is about 36 %. The PL intensity at 150°C maintains about 80% of that at room temperature. It has been also confirmed that $\text{Ba}_2\text{SiS}_4\text{:Ce}$ is chemically stable enough for applying to white LEDs.

Figure 5 Temperature dependences of PL intensity of the typical $\text{Ba}_2\text{SiS}_4\text{:Ce}$ powder sample
The excitation wavelength is 405 nm

Figure 6 Results of the accelerated degradation test performed at 85°C and 85%-humidity in air for $\text{Ba}_2\text{SiS}_4\text{:Ce}$ and $\text{Y}_2\text{O}_3\text{:Eu}$ phosphor samples

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