

Synthesis and Luminescent Properties of Li Containing Nitride Phosphors

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ABSTRACT

Some Li containing nitride and oxynitride phosphors have been reported to show interesting properties. Li can occupy independent crystallographic sites and contribute to a variety of crystal structures. Here we show interesting Li containing nitride phosphors discovered by the single particle diagnosis approach.

1 INTRODUCTION

Some Li containing nitride and oxynitride phosphors have been reported to show interesting properties; i.e. narrow-band emission [1], supertetrahedron [2]. The ionic size of Li is between large constitution elements (i.e. Ba, Sr, Ca, La) and small constitution elements (Si, Al). Li can occupy independent crystallographic sites and contribute to a variety of crystal structures. Here we show two interesting Li containing nitride phosphors discovered by the single particle diagnosis approach [3].

Ba₂LiSi₇AlN₁₂:Eu²⁺ particle shows an emission spectrum with a peak at approximately 515 nm and a full width at half maximum (FWHM) of 61 nm [4]. Besides narrow-band emission, it shows high internal quantum efficiency (79% with 405 nm excitation) and a small degree of thermal quenching. Luminescence properties were measured for the discovered Ba₂LiSi₇AlN₁₂:Eu²⁺ particles by a micro-spectroscopy method. A single phase powder of Ba₂LiSi₇AlN₁₂:Eu²⁺ is not obtained from the nominal composition of Ba₂LiSi₇AlN₁₂:Eu²⁺. The Li component is easily evaporated in the high-temperature synthesis, and the composition of the product deviates from the target composition. In this presentation, the single phase powder of Ba₂LiSi₇AlN₁₂:Eu²⁺ was obtained by controlling the starting composition, annealing condition, reaction vessel and its luminescence properties were studied [5].

Another example is a BaSi₇N₁₀:Eu derived phosphor. The original BaSi₇N₁₀:Eu shows blue emission [6]. By introducing Li into the BaSi₇N₁₀:Eu structure, the emission spectra changed from blue to broad white.

2 EXPERIMENT

The starting materials of Ba₃N₂, EuN, Si₃N₄, AlN, and Li₃N were mixed in a designed molar ratio described in a glove box under a nitrogen atmosphere. They were placed in a boron nitride (BN) crucible or sealed in a molybdenum

(Mo) tube, and fired in a nitrogen atmosphere of 0.92 MPa at 1650 - 1900 °C for 0.5 - 4 h.

3 RESULTS and DISCUSSION

In the synthesis of Ba₂LiSi₇AlN₁₂:Eu²⁺, firstly, we changed the starting composition (excess Li amount) and annealing condition (annealing temperature and time). In the 1.75 times Li₃N composition and 1700°C/1h, the ratio of the Ba₂LiSi₇AlN₁₂:Eu²⁺ phase was 89% at maximum. In the next we changed Si/Al ratio. Both Si₃N₄ and AlN contain a small amount of oxygen impurities (c.a. 1 wt%). In the presence of oxygen contamination, the charge neutrality of the ideal composition Ba₂LiSi₇AlN₁₂:Eu²⁺ is not retained. In the Al rich composition, the charge neutrality is satisfied as Ba₂LiSi_{7-x}Al_{1+x}N_{12-x}O_x:Eu²⁺. On changing the Si/Al ratio from 7/1, the ratio of the Ba₂LiSi_{7-x}Al_{1+x}N_{12-x}O_x:Eu²⁺ phase increased and was highest as 95% at the Si/Al ratio of 6.5/1.5 (x = 0.5). Although the product was considerably close to a single phase, a small amount of impurity phases remained.

BN ceramics are porous compact materials and cannot completely seal the inner evaporative component. It is suitable to use a sealed system to control the Li content. We used a Mo tube and sealed the mixed starting materials. At the Si/Al ratio of 6.5/1.5, the excess Li amount was again optimized in the sealed Mo tube condition. In the 1.3 times Li₃N composition, a single phase of Ba₂LiSi_{6.5}Al_{1.5}N_{11.5}O_{0.5}:Eu²⁺ was obtained.

Excitation and emission spectra of Ba_{1.94}LiSi_{6.5}Al_{1.5}N_{11.5}O_{0.5}:Eu_{0.06} are shown in Fig. 1. The emission spectrum has a peak at approximately 508 nm with a FWHM of 68 nm. The value of 68 nm is larger than the value obtained from the single particle (61 nm). High uniformity is attained in the single crystal. On the other hand, compositional variation among particles (i.e., Al/Si and O/N ratio, Eu concentration) is expected in the powder sample. This will lead to a variety of coordination structures of Eu and broadening of the emission spectrum.

The temperature dependence of the peak intensity, and integrated intensity of Ba_{1.94}LiSi_{6.5}Al_{1.5}N_{11.5}O_{0.5}:Eu_{0.06} are shown in Fig. 2. Although both peak intensity and integrated intensity

gradually decreased with temperature, the degree of decline was very small.

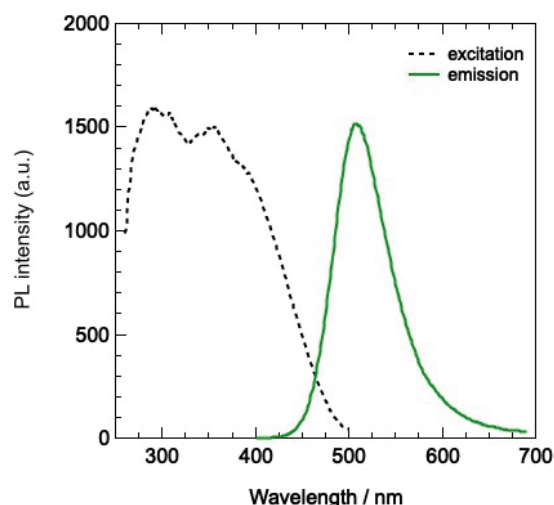


Fig.1 Emission and excitation spectra of $\text{Ba}_2\text{LiSi}_{7-x}\text{Al}_{1+x}\text{N}_{12-x}\text{O}_x\text{:Eu}$.

The integrated intensities at 200 °C and 300 °C were 100% and 96% of that at room temperature, respectively. The temperature dependence improved from the data for the single particle (Eu 7.5 at%) due to the small Eu^{2+} concentration in the powder sample (Eu 3 at%).

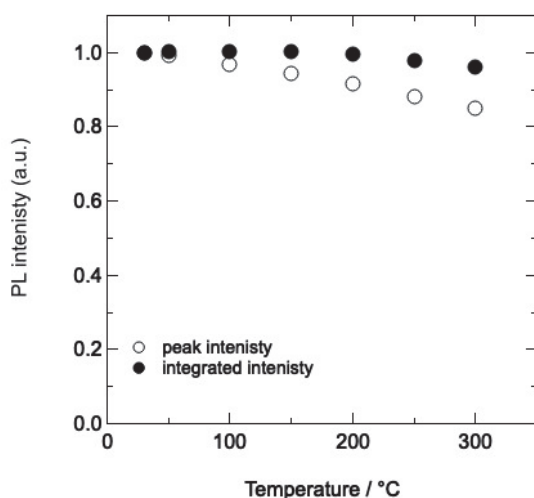


Fig.2 Temperature dependence of PL peak and integrated intensity of $\text{Ba}_2\text{LiSi}_{7-x}\text{Al}_{1+x}\text{N}_{12-x}\text{O}_x\text{:Eu}$.

In the chemical analysis, Li added in excess still remained in the product. In the XRD pattern, however, there was no impurity phase. There is a possibility that the Li containing phase remains as a phase not detected by the XRD analysis such as an amorphous phase. If there is absorption by the phase in the green range, the PL intensity of $\text{Ba}_2\text{LiSi}_{7-x}\text{Al}_{1+x}\text{N}_{12-x}\text{O}_x\text{:Eu}^{2+}$ will decrease. We washed the product by hydrochloric acid solution (pH = 0).

After acid washing, the body color changed from muddy green to bright green. The PL intensity increased as shown in Fig. 3 and the internal QE increased to 93% from 79% before washing.

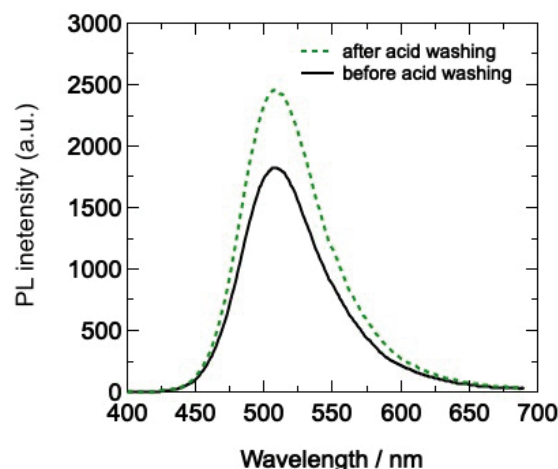


Fig.3 Emission spectra of $\text{Ba}_2\text{LiSi}_{7-x}\text{Al}_{1+x}\text{N}_{12-x}\text{O}_x\text{:Eu}$ before and after acid washing.

Another is $\text{BaSi}_7\text{N}_{10}\text{:Eu}$ derived phosphor. The original $\text{BaSi}_7\text{N}_{10}\text{:Eu}$ shows blue luminescence. We found white luminescent particles isostructural with $\text{BaSi}_7\text{N}_{10}$ in the product from Ba_3N_2 , EuN , Si_3N_4 , AlN and Li_3N fired at 1900 °C. However, there is only one Ba site for Eu doping in the $\text{BaSi}_7\text{N}_{10}$ crystal structure. A structural change to produce the some Ba sites is anticipated. In the single crystal XRD analysis, residual electron densities around the Ba site were recognized. LA-ICP-MASS analysis showed Li is included in the white luminescent particle. These results indicate that the incorporated Li in the crystal has effect on the multiple Ba sites for Eu doping.

4 CONCLUSIONS

Both Li containing phosphors show interesting luminescence properties. Further discovery of interesting Li containing phosphors are anticipated by a combination of a sealed tube and Li analysis.

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