Temperature Dependence of Photoluminescence Intensity in Y₄Si₂O₇N₂:Eu³⁺ Red Phosphors Synthesized in NH₃ Atmosphere

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ABSTRACT

The charge transfer state (CTS) energy of $Y_4Si_2O_7N_2$: Eu^{3+} phosphor was 3.61 eV which is almost the same as that of La_2O_2S : Eu^{3+} . The activation energy from the CTS to 4f ground state is 0.24 eV The results suggest that $Y_4Si_2O_7N_2$: Eu^{3+} has several non-radiative transitions, due to crystal defects.

1 INTRODUCTION

Recently, the video format "Rec. ITU-R BT.2020 (and BT.2100)" has been advanced [1], and the development of RGB phosphors covering the wide color gamut is demanded. For the red phosphor, both a narrow red emission around CIE chromaticity diagram of (0.708, 0.292) and a strong excitation band located only in the blue wavelength region are essential. Eu³⁺ is one of candidate luminescent centers which meets these requirements. In general, the charge transfer state (CTS) of Eu³⁺ centers tend to shift to longer wavelength side with increasing electronegativity of anion atoms around Eu³⁺ [2][3]. Therefore, we have investigated Eu³⁺ activated oxynitrides phosphors, and reported Y4Si2O7N2:Eu3+ red phosphors synthesized in NH3 atmosphere [4]. As shown in Fig. 1, the CTS energy of Y₄Si₂O₇N₂:Eu³⁺ is 3.61 eV, which is almost the same as that of La₂O₂S:Eu³⁺ (3.58 eV). However, the luminescent intensity is very low. One of the reasons is considered to be due to the thermal quenching. In this study, the temperature-dependent photoluminescence (PL) intensity of the Y₄Si₂O₇N₂: Eu³⁺ phosphor has been investigated. A curve-fitting based on the Arrhenius equation has been attempted. The results were compared to those of the La₂O₂S:Eu³⁺ sample.

2 EXPERIMENT

The Y₄Si₂O₇N₂:Eu³⁺ phosphor sample was synthesized by a conventional solid state reaction method. Y₂O₃, Eu₂O₃, SiO₂, Si₃N₄, were used as source materials. The mixture was fired at 1350°C for 3h in NH₃ atmosphere. After that, a post annealing was treated at 450°C for 10h to oxidize Eu²⁺ centers. The La₂O₂S:Eu³⁺ sample was synthesized in air atmosphere. The PL temperature dependences were measured by using a fluorescence spectrometer (JASCO FP-6500). The optional unit of the PMU-183 (JASCO) the HPC-503 (JASCO) were also used for the lower (90 ~ 290 K) and higher temperature (270 ~ 520 K) measurements, respectively.

Figure 2 indicates the configurational coordinate model of the internal electron energy levels in Eu³⁺ centers. The activation energy (ΔE) from the CTS to 4f ground state strongly affects the thermal quenching. Assuming that the non-radiative transition is only one pass through this energy barrier, the curve-fitting based on the Arrhenius equation was performed for the measured temperaturedependent PL intensity by a least mean square approximation. Arrhenius equation is given as the following equation,

$$I(T) = \frac{I_0}{1 + \frac{B}{A}e^{-\frac{\Delta B}{kT}}}$$

here, *A* and *B* are the radiative and non-radiative transition rates from the CTS to the 4f ground state, respectively. The curve-fitting was executed using ΔE , *A*, and *B* as the fitting parameters.



Fig.1 PL Excitation spectra of Y₄Si₂O₇N₂:Eu³⁺, La₂O₂S:Eu³⁺ samples.



Fig.2 Configurational coordinate model of Eu³⁺.

3 RESULTS AND DISCUSSION

In Fig. 3, black circles show the PL temperature dependence of the La₂O₂S: Eu³⁺ sample measured under excitation wavelength at 340 nm, at which the CTS band are excited. The PL intensity gradually increases with increasing temperature, and reversely starts decreasing at 300 K. The solid line indicates the curve-fitting result calculated in the temperature range above 300 K. The obtained fitting parameters of ΔE and *B/A* are 0.45 eV and 51702, respectively.

Figure 4 shows the result of the Y₄Si₂O₇N₂: Eu³⁺ sample. The sample measured under excitation wavelength at 340 nm, at which the CTS band are excited. As seen in Fig. 4, the PL intensity decreases with increasing temperature, and a small shoulder is observed at around 230 K. The result implies that some energy relaxation processes exist. We assume that this energy relaxation above 230 K are due to the non-radiative from the CTS to the 4f ground state. The estimated ΔE and B/A are 0.24 eV and 12200, respectively.

The CTS energy corresponding to the PLE peek of the CTS band, ΔE and B/A are summarized in Table I. The ΔE value of Y₄Si₂O₇N₂:Eu³⁺ is about 1/2 compared to La₂O₂S:Eu³⁺, even though the CTS energy is almost the same. This fact suggests the existence of other energy relaxation processes through deep defect levels, such as oxygen and/or nitrogen vacancies. The B/A value of Y₄Si₂O₇N₂:Eu³⁺ is much smaller than that of La₂O₂S:Eu³⁺. It should be reminded that B/A is the non-radiative / radiative ratio. The result seems strange, because La₂O₂S:Eu³⁺ showing a much strong luminescence should have less non-radiative rate compared to Y₄Si₂O₇N₂:Eu³⁺. In addition, since A is ideally defined as 4f-4f internal electron transition probability in Eu³⁺, the value does not so much change in any host materials. In our previous study of the X-ray absorption near-edge structure (XAFS) analysis, the abundance ratio of Eu²⁺ to Eu³⁺ is drastically reduced from 16% to 1% by the post annealing in air atmosphere [4]. We also found that the 4f-5d excitation bands of Eu²⁺ overlaps with that of the CTS band of Eu³⁺. Therefore, even little amount of remaining Eu²⁺ centers might cause the energy cross relaxation, because the 4f-5d transition rate is much higher than that of the 4f-4f



Fig.3 Temperature dependences of PL intensity for La₂O₂S:Eu³⁺ phosphors. A line indicates the fitting curve based on Arrhenius equation.

transition. From these facts, it is considered that the *A* value of $Y_4Si_2O_7N_2$:Eu³⁺ is apparently high, resulting in lower B/A compared to La₂O₂S:Eu³⁺. Further investigations, such as PL decay curve and time response spectrum measurements, are required to clarify the detail mechanism.

4 CONCLUSIONS

The temperature-dependent PL intensity of the Y₄Si₂O₇N₂: Eu³⁺ was measured, and the curve-fitting based on the Arrhenius equation was performed. The results were compared to those of the La₂O₂S:Eu³⁺ sample. The obtained activation energy (ΔE) from the CTS to 4f ground state is 0.24 eV for Y₄Si₂O₇N₂:Eu³⁺ and 0.45 eV for La₂O₂S:Eu³⁺, even though both phosphors have almost the same CTS energy. The results of the curve-fitting suggest that Y₄Si₂O₇N₂:Eu³⁺ has several non-radiative transitions, which is considered to be due to crystal defects such as oxygen and nitrogen vacancies and/or remaining Eu²⁺ centers.

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- Fig.4 Temperature dependences of PL intensity for Y₄Si₂O₇N₂:Eu³⁺ phosphors. A line indicates the fitting curve based on Arrhenius equation.
- Table 1 CTS energy, activation energy and B/A of $Y_4Si_2O_7N_2$:Eu³⁺, La₂O₂S:Eu³⁺ samples.

	Y ₄ Si ₂ O ₇ N ₂ :Eu ³⁺	La ₂ O ₂ S:Eu ³⁺
CTS energy [eV]	3.61	3.58
Activation energy ΔE [eV]	0.24	0.45
B/A	12190	51702