Construction of vacuum referred binding energy diagram for understanding electronic structure of Ce^{3+} doped $Gd_3(Al,Ga)_5O_{12}$ phosphors

°Kazuki Asami [1], Jumpei Ueda [1], Mamoru Kitaura[2], Setsuhisa Tanabe [1]

[1] Kyoto University, [2]Yamagata University
E-mail: asami.kazuki.68m@st.kyoto-u.ac.jp

1. Introduction

Ce^{3+}- doped $Gd_3Al_{5-x}Ga_xO_{12}$ (GAG*G*) is a promising optical material for the scintillator [1]. It is known that the quantum efficiency (QE) of GAG*G*: Ce^{3+} becomes lower with increasing Ga content, *x* [2]. To understand optical properties of a phosphor, an electronic structure of host material should be investigated. Dorenbos suggested the construction method of the vacuum referred binding energy (VRBE) diagram [3]. This diagram can be constructed from the spectroscopy data of host exciton energy and charge transfer transition (CTS) of Eu^{3+}. To determine those transition energies, we measured photoluminescence excitation (PLE) spectra and investigated relationship with QE using constructed VRBE diagram.

2. Measurement

Phosphors of 0.2% Ce^{3+} doped and 0.2% Eu^{3+} doped $Gd_3(Al_{5-x}Ga_x)O_{12}$ (x = 1 - 4) were fabricated by solid-state reaction method. For these samples, PLE spectra were measured in the range between 100-500 nm at UVSOR (BL3B). From obtained data, the VRBE diagram of GAG*G*:Ce^{3+} was constructed.

3. Result and Discussion

Fig.1 (a) shows the PLE spectra of Ce^{3+}- doped GAG*G* phosphors with various Ga content. In PLE spectra, the host exciton peaks are observed at around 200 nm and three bands derived from Ce^{3+} are observed at 220 nm (*4f-5d*$_{3, 4, 5}$), 350 nm (*4f-5d*$_2$) and 450 nm (*4f-5d*$_1$). Several peaks at 270 nm and 310 nm are due to the intra – 4f transitions of Gd^{3+} in the host [1]. From the host exciton peaks, the bandgap energies of GAG*G* (x = 1, 2, 3 and 4) are estimated to be 6.84, 6.81, 6.63 and 6.55 eV, respectively. With increasing Ga content, the bandgap becomes narrower. Fig.1 (b) shows the PLE spectra of Eu^{3+}: GAG*G* phosphors. The strong broad band is located at around 250 nm, which is attributed to CTS of O^{2-}-Eu^{3+} →O^--Eu^{2+}. With increasing Ga content, the peak wavelength of CTS shifts to longer. The top of valence band is calculated by subtracting the CTS energy from the determined *4f* state energy of Eu^{2+}.

Based on the method of VRBE diagram construction by Dorenbos [3], the VRBE diagram of Ce^{3+}-doped GAG*G* are constructed by using measurement data obtained in Fig.2 . The energy E_v which is top of valence band shifts higher with increasing Ga content while the energy E_c which is the bottom of conduction band slightly changes. When the energy of Ce^{3+}:*5d*$_1$ is close to E_c, the excited electrons located at Ce^{3+}:*5d*$_1$ state tend to move to the conduction band by thermal ionization. From this diagram, with increasing Ga content, the energy gap between E_c and Ce^{3+}:*5d*$_1$ becomes smaller. Therefore QE of Ce^{3+} in GAG*G* system decreases by thermal ionization quenching.

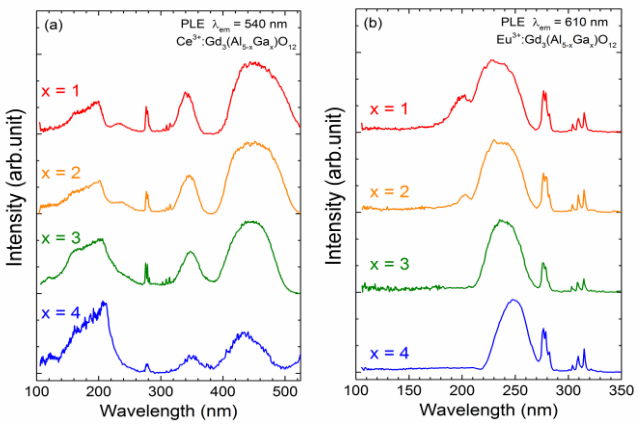

Fig.1. PLE spectra of (a) Ce^{3+} and (b) Eu^{3+} : GAG*G*.

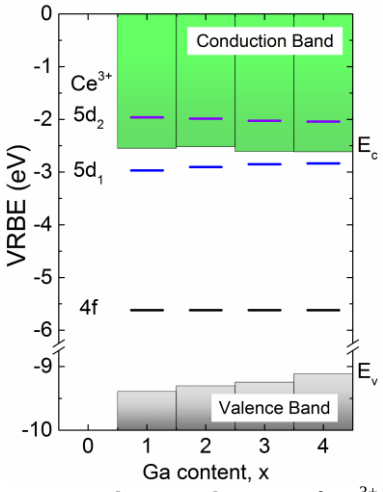

Fig. 2. Constructed VRBE diagram of Ce^{3+}:GAG*G*.

4. Conclusions

From PLE measurement of Ce^{3+} doped and Eu^{3+} doped samples, the VRBE diagram of Ce doped GAG*G* system is constructed. QE of Ce^{3+}:GAG*G* system decreases with increasing Ga content due to proximity between E_c and Ce^{3+}:*5d*$_1$.

Acknowledgements

We would like to thank the all staff members of UVSOR facility.

References

[1] M. Kitaura, A. Sato, K. Kamada, A. Ohnishi, M. Sasaki, J. Appl. Phys. **115** (2014) 083517.
[2] J.M. Ogiegło, A. Katelnikovas, A. Zych, T. Jüstel, A.Meijerink, C. R. Ronda, J. Phys. Chem. A, **117** (2013) 2479.
[3] P. Dorenbos, J. Lumin. **134** (2013) 310.