Lanthanoid Activated Phosphors with 5d - 4f Visible Luminescence for Lighting Applications: Development and Characterization Based on Control of Electronic Structure and Ligand Field

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In the study described in this dissertation, the electronic structure and ligand field of Ce^{3+} doped garnet phosphors and Eu^{2+} barium silicate phosphors that can be used for InGaN LEDs were investigated. On the basis of the relationship between the electronic structure and the energy levels of the luminescent center obtained from the spectroscopic data, the electron transfer processes such as the trapping/de-trapping and thermal ionization processes were investigated, as well.

In Chapter 1, the overview of phosphor and basic theoretical aspects on photoluminescence are presented.

In Chapter 2, persistent and thermoluminescence properties in Ce^{3+}-Cr^{3+} co-doped $Gd_3Al_{5-x}Ga_xO_{12}$ garnet solid solution have been investigated. The persistent luminescent color is shifted from orange to yellowish green with increasing Ga content. The samples with x = 2.5 and 3 showed long persistent luminescence for 6.5 h by blue-light illumination.

In Chapter 3, we proposed the use of yellow persistent luminescent garnet phosphors to compensate the flicker effect in alternative current driven light emitting diode. The time evolution of luminescence intensity measurement of Ce^{3+} and Cr^{3+} co-doped $Gd_3Al_2Ga_3O_{12}$ phosphor using a modulated blue laser diode was performed. From this measurement, the flicker percent of Ce^{3+} and Cr^{3+} co-doped $Gd_3Al_2Ga_3O_{12}$ phosphor is calculated to be about 60%. This result demonstrates that persistent phosphor is expected to solve the problem of flicker caused in the AC-driven LED lighting system.

In Chapter 4, the luminescence quenching and persistent luminescence properties of Ce^{3+} (- Cr^{3+}) doped $Gd_yY_{3-y}Al_{5-x}Ga_xO_{12}$ garnet (GYAGG) were discussed by constructing the vacuum referred binding energy (VRBE) diagram including information on these energy locations. The quantum yield of Ce^{3+}:5d−4f in Ce^{3+} doped GYAGG phosphors is clearly related to the energy gap between the lowest 5d level and the bottom of conduction band in the constructed VRBE diagram.

In Chapter 5, structural and photoluminescence properties of Ce^{3+}-doped $Y_3Al_{4.75}Si_{0.25}O_{11.75}N_{0.25}$ garnet (YASiONG:Ce) phosphor has been investigated by neutron powder diffraction (NPD) measurement. The obtained NPD pattern confirmed the presence of N atoms by Rietveld refinement for the first time. In the photoluminescence and excitation spectra, additional excitation and emission bands of Ce^{3+} :4f-5d_1 appeared. The additional band can be attributed to the 4f-5d_1 transition of Ce^{3+} in the dodecahedral site with one N^{3-} and seven O^{2-} coordination.

In Chapter 6, the luminescence properties of Ce^{3+}-doped $Gd_xY_{3-x}Al_{5-y}Si_yO_{12-y}N_y$ (x = 0, 1 and 2; y = 0.25) oxynitride garnet phosphors were investigated and compared with corresponding oxide garnet phosphors (y = 0). The measured photoluminescence spectra exhibit redshift of the emission peak wavelength by the partial nitridation of oxide garnet phosphors because of the strong crystal field splitting and the nephelauxetic effect. Temperature dependence studies of the photoluminescence intensity revealed that the quenching temperature decreased by partial nitridation and Gd substitution.

In Chapter 7, the VRBE diagram of the Ba_2SiO_4 host with the 4f ground states of divalent and trivalent lanthanide ions in the host band gap was constructed from the obtained spectroscopic data and the Dorenbos's procedure. From the energy gap between the bottom of the conduction band and 4f ground states of divalent lanthanide ions in constructed diagram, we selected the Er^{3+} ion as an efficient co-dopant because the trap depth was suitable for improving the persistent luminescence duration. The Eu^{2+}-Er^{3+}-codoped sample showed persistent luminescence intensity of over 0.32 mcd/m^2 for 7 h duration.

In Chapter 8, Eu^{2+}-Dy^{3+} co-doped barium silicate glass was prepared by a melt quenching method and cerammed at various temperatures between 800 ºC and 1250 ºC to obtain the glass ceramic (GC) persistent phosphors. The GC sample heat-treated at 1250 ºC (GC1250) exhibited the longest persistent luminescence over 16 h until the luminance becomes 2 mcd/m^2. In addition, GC1250 showed photochromism strongly in which the surface color of the sample is changed from white to blue by UV illumination and then it is bleached by red-light illumination.