学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on UV Excitable Lanthanide Doped M-SiAlON (M = La, Sr) Phosphors for White LEDs
（白色 LED に向けた UV 励起可能な希土類ドープ M-SiAlON (M = La, Sr)蛍光体に関する研究）

Phosphor-converted white light-emitting diodes (pc-wLEDs) have been widely used for lighting and displays because of their high energy conversion efficiency, long lifetime and environmental benefits. However, pc-wLEDs with a higher luminous efficacy and better color rendition are urgently required, especially for illumination-grade light sources. Pc-wLEDs based on a blue LED chip and a yellow-emitting phosphor (typically $Y_3Al_5O_{12}:Ce^{3+}$) suffer from a low color rendering. A better color rendering can be achieved if a near-UV LED chip is combined with multiple phosphors. Moreover, the color will be more stable for near-UV pumping LEDs as it is independent of the driven current and the temperature of the chips. Since the energy of UV or near UV light is much stronger than blue light, the phosphors required for UV or near UV-LEDs need to be more thermally stable and robust. However, the number of phosphors that can be efficiently excited with UV or near UV light and have high quantum efficiency and good thermal stability is very limited. Ce^{3+} and Eu^{2+} doped nitride and oxynitride phosphors have been reported with good chemical and thermal stability, as well as high luminescence efficiency. In this thesis, the focus is on developing novel UV or near-UV excitable oxynitride phosphors for white LEDs. The synthesis, structure and photoluminescence properties of these phosphors are investigated.

Chapter 1 elaborates on the scope of my PhD research. The concept of pc-wLEDs is described, discussing different approaches to obtain white LEDs by using luminescent materials. In addition, I focus on the theoretical background of luminescence and the selection criteria of white LED phosphors. The effects of host lattice on the energy levels of lanthanide activators, such as centroid shift, crystal field splitting and Stokes shift are discussed. The method to contruct an energy level scheme that positions 4f and 5d levels of lanthanide ions with respect to the valence band of the host material is explained.

Chapter 2 describes the solid-state reaction method that is used to synthesize the oxynitride phosphors that are investigated. The structural characterization techniques such as XRD, NMR and SEM are briefly explained. Also discussed are the optical characterization methods that have been used to study the luminescence properties. Examples hereof are photoluminescence spectroscopy, temperature dependent measurements, quantum efficiency and time-resolved luminescence decay.

Chapter 3 and chapter 4 study synthesis and photoluminescence properties of Eu, Ce, Sm, Yb doped $LaAl(Si_{6-z}Al_z)(N_{10-z}O_z)$ (termed JEM, $z \approx 1$) phosphors. Ce doped JEM phosphor has been reported as a promising blue-emitting phosphor for white LEDs using near-UV excitation, particularly for home illumination. However, the unavailability of a phase pure JEM:Ce phosphor prevents widespread application. In addition, there was no report on the photoluminescence properties of an Eu^{2+} doped JEM phosphor. Chapters 3 focuses on synthesis and photoluminescence properties of Eu doped JEM phosphor. Phase pure JEM:Eu phosphors have been obtained by carefully controlling the sintering temperature and chemical composition of starting materials (z value, N/O ratio and Si/Al ratio). Photoluminescence properties including photoluminescence spectra, the red-shift of emission, thermal quenching and luminescence decay have been investigated for the first time. It was found that JEM:Eu phosphor emits green light after UV excitation and its emission band largely redshifts with increasing Eu concentration. This phosphor shows an unusual thermal quenching behavior and double exponential decay due to different Eu local environments, although there is only one crystallographic site which Eu can occupy.

Chapter 4 further studies the synthesis and photoluminescence properties of Ce, Sm, Yb doped JEM phosphors. JEM:Ce phosphor shows higher quantum efficiency and better thermal stability than JEM:Eu phosphor. An energy level scheme has been constructed by investigating the redshift of Ce^{3+} and Eu^{2+} ions, the charge transfer transitions of Yb and Sm, the centroid shift of Ce^{3+} and the chemical shift of Eu^{2+} ions in JEM. The scheme contains the positions of the 4f and 5d levels of all divalent and trivalent lanthanide ions with respect to the valence band of JEM, and allows the prediction and explanation of the photoluminescence properties of lanthanide ions doped JEM phosphors.

Chapter 5 investigates the photoluminescence properties of Ce doped Al-containing La N(ew)-phase $La_3Si_{8-x}Al_xN_{11-x}O_{4+x}$ (x = 1.5) phosphor and its application for white LEDs. The effect of Al-O substitution for Si-N and the effect of Ce concentration on phosphor performance have been studied. Solid state ^{29}Si and ^{27}Al NMR have been used to study the local coordinations. $La_3Si_{6.5}Al_{1.5}N_{9.5}O_{5.5}$:Ce phosphor shows deep blue emission with a narrow emission band after UV or near-UV excitation with high quantum efficiency and color purity. A white LED containing $La_3Si_{6.5}Al_{1.5}N_{9.5}O_{5.5}$:0.05Ce phosphor as the blue phosphor has high color rendering index, showing the great potential of the phosphor for white LEDs.

In chapter 6, a new Sr-sialon phase $Sr_{4-x}(Si,Al)_{19+x}(N,O)_{29+x}$ is described that I discovered during my PhD research. The crystal structure of this material and photoluminescence properties when doped with Eu or Ce are investigated. Ce^{3+} doped Sr-sialon phosphor shows strong blue emission around 435 nm with a fwhm ≈ 90 nm after 355 nm light excitation. The blue luminescence exhibits a small thermal quenching behavior at high temperature. Upon doping with Eu^{2+}, the emission band can be tuned from 487 nm to 541 nm by increasing Eu concentration.

Finally, in chapter 7 the most important conclusions are summarized and an outlook is given on the potential of the UV-excitable sialon phosphors for white LED applications.