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学位論文の要約

博士（総合化学）

氏名　Chunyun Wang

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, as shown in Figure 1. 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.

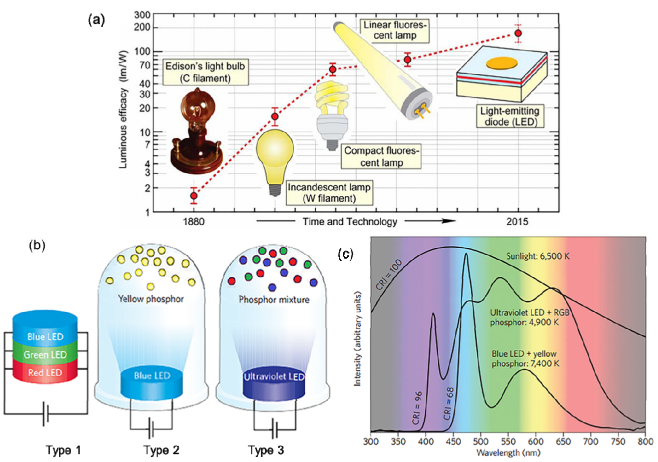


Figure 1 (a) Comparison of the luminous efficacy of several lighting technologies; (b) three dominant ways to produce white LEDs; (c) comparison of the spectrum of ideal sunlight with two LED-based white-light sources.

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, which is displayed in Figure 2. 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.

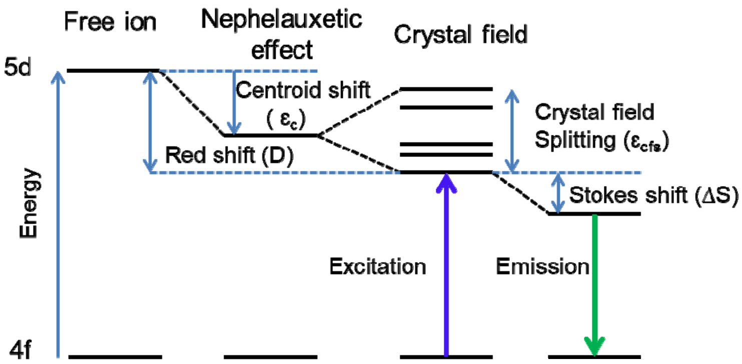


Figure 2 A diagram of the effects of centroid shift, crystal field splitting and Stokes shift on lowering of the energy of the 5d levels for Eu^{2+} or Ce^{3+} ion in a compound.

Chapter 2 describes the solid-state reaction method that is used to synthesize the oxynitride phosphors that are investigated, which can be seen in Figure 3. 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.

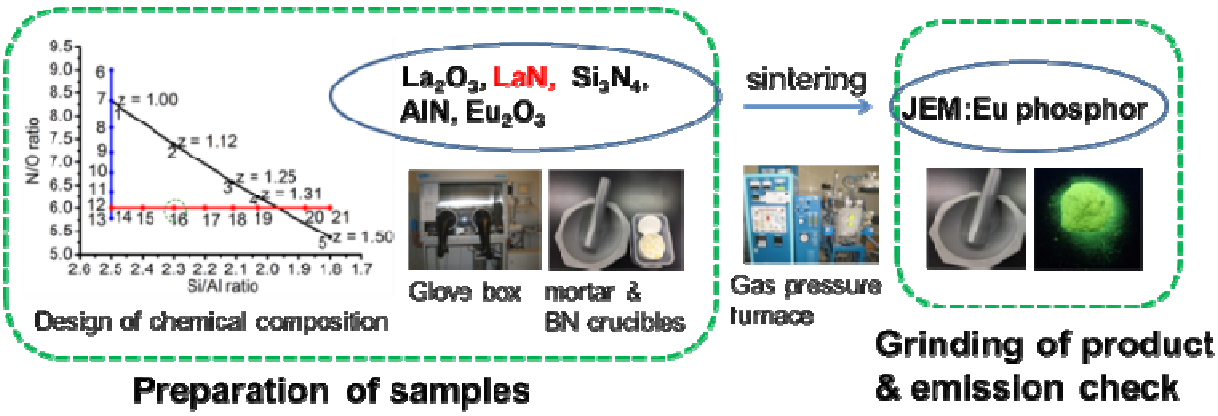
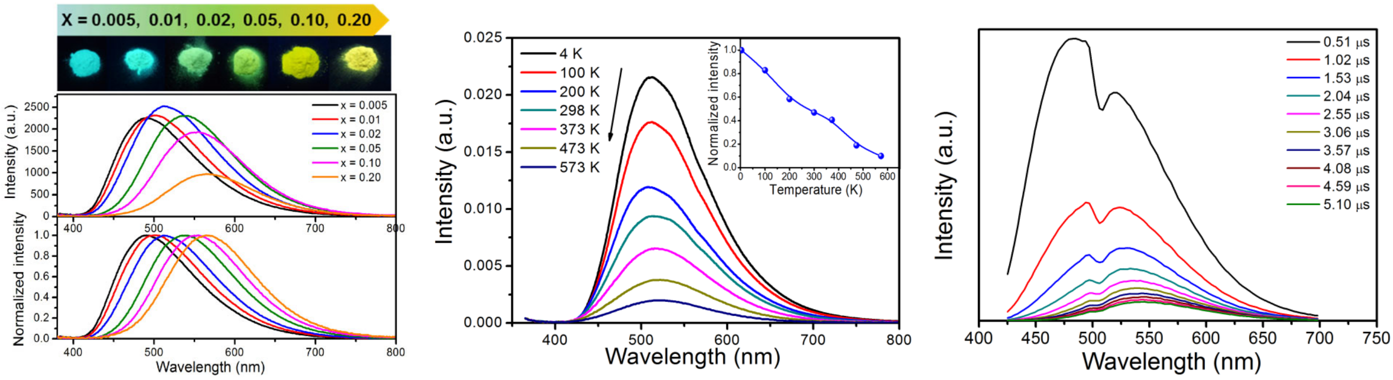


Figure 3 A schematic diagram of process to synthesize JEM:Eu phosphor.

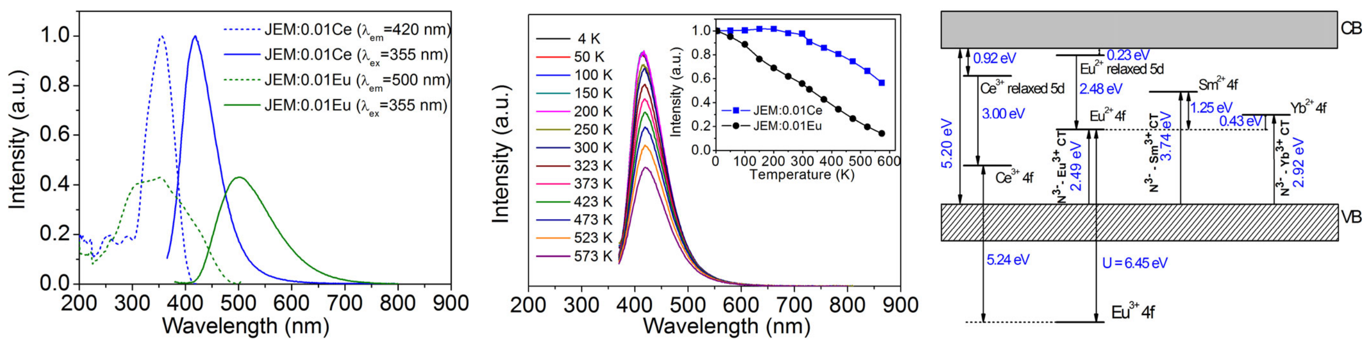
Chapter 3 and chapter 4 study synthesis and photoluminescence properties of Eu, Ce, Sm, Yb doped $LaAl(Si_{6-z}Al_z)(N_{10-z}O_z)$ (termed JEM, $z \approx 1$) phosphors. Ce doped JEM phosphor has been reported as a promising blue-emitting phosphor for white LEDs using near-UV excitation, particularly 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, as shown in Figure 4. 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.



(a) (b) (c)

Figure 4 (a) Emission spectra of JEM:Eu phosphors with different Eu concentrations, thermal quenching behavior (b) and time resolved emission spectra (c) of JEM:0.02Eu phosphor.

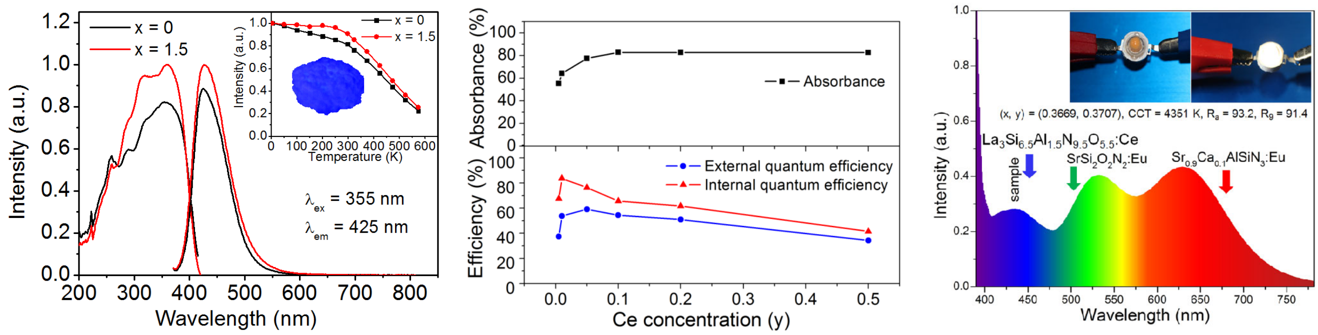
Chapter 4 further studies the synthesis and photoluminescence properties of Ce, Sm, Yb doped JEM phosphors. JEM:Ce phosphor shows higher quantum efficiency and better thermal stability than JEM:Eu phosphor, as seen in Figure 5a. In order to understand the difference of quantum efficiency and thermal stability (see Figure 5a and 5b), 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, which is shown in Figure 5c. 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.



(a) (b) (c)

Figure 5 (a) Photoluminescence spectra of JEM:0.01Eu and JEM:0.01Ce phosphors; (b) thermal quenching behavior of JEM:0.01Ce phosphor and (c) an energy level scheme of JEM:Ln phosphors (Ln = Ce, Eu, Sm, Yb).

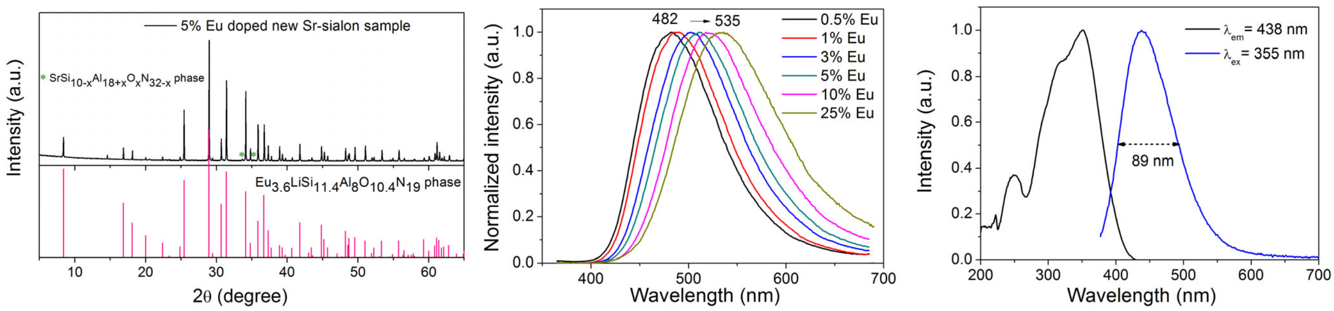
Chapter 5 investigates the photoluminescence properties of Ce doped Al-containing La N(ew)-phase $La_3Si_{8-x}Al_xN_{11-x}O_{4+x}$ (x = 1.5) phosphor and its application for white LEDs. The effect of Al-O substitution for Si-N and the effect of Ce concentration on phosphor performance have been studied (see Figure 6a). 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, as shown in Figure 6c.



(a) (b) (c)

Figure 6 (a) A comparison of photoluminescence spectra and thermal stability for $La_3Si_{8-x}Al_xN_{11-x}O_{4+x}$ (x = 0, 1.5) phosphors; (b) quantum efficiency of $La_3Si_{6.5}Al_{1.5}N_{9.5}O_{5.5}$:Ce phosphors with different Ce concentrations and (c) Electroluminescence spectrum of a white LED using a UV-LED chip (365 nm) and $La_3Si_{6.5}Al_{1.5}N_{9.5}O_{5.5}$:5%Ce, $SrSi_2O_2N_2:Eu^{2+}$ and $Sr_{0.9}Ca_{0.1}AlSiN_3:Eu^{2+}$ phosphors.

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 ≈ 89 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 482 nm to 535 nm by increasing Eu concentration, which can be seen in Figure 7.



(a) (b) (c)

Figure 7 (a) XRD pattern of 5% Eu doped new Sr-sialon phase sample; (b)Eu concentration dependent emission spectra and (c) photoluminescence spectra of 5% Ce,Li doped new Sr-sialon phase.

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.

The research described in this thesis shows some interesting results that seem to be promising for application or pave the way to future research. The availability of highly pure JEM phase will make it possible to investigate the structure in more detail, and the obtained high efficiency and good thermal stability make it more likely that JEM:Ce may be applied as an LED phosphor for home illumination. The energy level scheme of the lanthanides in JEM showed to be helpful in the interpretation of the optical data, and constructing an energy level scheme may be useful for other hosts as well to predict and interpret the luminescence results. The Ce doped N phase seems to be promising for backlighting of displays, due to its efficient and narrow deep blue emission. For application in high power LEDs, the thermal stability would need to be further improved, which may be done by changing the chemical composition, optimizing the synthesis approach or by adding a protective coating layer on the phosphor surface. The newly discovered Ce doped Sr sialon phase also has a deep blue emission and a better thermal stability, making it very promising for white LEDs. However, its complex structure still requires a more thorough investigation.