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白光LED用$SrSi_2O_2N_2$: Eu^{2+} 荧光粉的化学合成与表征

Chemical Synthesis and Characterizations of $SrSi_2O_2N_2$: Eu^{2+} Phosphors for White LEDs Applications

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Chemical Synthesis and Characterizations of $SrSi_2O_2N_2$: Eu^{2+} Phosphors for White LEDs Applications

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Original Statement

The work and research presented in this dissertation **"Chemical Synthesis and Characterizations of $SrSi_2O_2N_2$: Eu^{2+} Phosphors for White LEDs Applications"** was conducted under the supervision of **Professor Renjie Zeng** at the Department of Materials Science and Engineering, College of Materials, Xiamen University, P. R of China**.** I'm delighted to declare this dissertation is my own work, and that appropriate acknowledgment was made where reference was made from the work of others. Furthermore, I realize that this dissertation has not been in whole or part for the award of a degree, diploma or other qualifications at this or another university.

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摘 要

白光发光二极管(white light-emitting diodes, WLEDs)具有寿命长、能耗低以及结构紧凑等优点，因此被广泛的关注。目前，基于蓝光 LED 的荧光粉转换 WLEDs (phosphor-converted-WLEDs, PC-WLEDs)是市场的主流，该方案需要搭配荧光粉以产生白光。因此，荧光粉是 PC-WLEDs 的关键材料之一。

为了获得较高显色指数的 PC-WLED，绿色荧光粉是必不可少的。$SrSi_2O_2N_2$: Eu^{2+} (SSON)是一种性能优异的绿色荧光粉，具有较高的量子效率，较宽的吸收带(紫外到蓝光)以及良好的稳定性。通常使用高温固相法(high-temperature solid-state method, SS)来制备该荧光粉，而采用湿化学法可以在较低的热处理温度下，获得较高相纯度和颗粒均匀的 SSON 荧光粉。因此，本研究采用了多种湿化学法以制备绿色 SSON 荧光粉以应用于 WLEDs。

(1) 首次以聚合物-金属配合物为原料，采用了 Pechini 溶胶−凝胶(Pechini sol−gel, PSG)法制备 SSON。通过 DTA-TG 来设计每阶段的热处理工艺。XRD 证实在 1400 °C 保温 3 h 可以得到纯相，颗粒晶面清晰，具有较好的分散性。当 Eu^{2+}浓度为 0.04 mol% 时得，强度最高，峰值波长为 531.4 nm。对所得荧光粉的量子效率和 CIE 色坐标进行了研究。通过搭配红色$(Sr,Ca)AlSiN_3$:Eu^{2+}荧光粉和蓝光(450 nm)LED 芯片得到了暖白光的 WLEDs。结果表明，该制备法有潜力代替固相法制备 SSON 荧光粉。

(2) 研究了以 Sr_2SiO_4:Eu^{2+}(SSO)作为前驱体制备 SSON 过程中，不同 Eu^{2+}浓度的 α'与 β 相 SSO 的相变过程。两步法所制样品较于一步法具有更高的发光效率和更大的晶粒尺寸。研究发现，在 SSON 中，可形成 X_2 相，并表现出强烈的绿光发射，峰值位于 530 nm。其粒径约为 13.63 μm，颗粒分布均匀，晶粒尺寸为 60-65 nm。研究了 SSO 和 SSON 的发光性能与其晶体结构的关系。结果表明，对 SSON 的发光性能而言，Eu^{2+}浓度的影响比 α'相与 β 相比例的影响要更加明显。

(3) 研究了两步法制备 SSON 过程中，第一步合成的 SSO 中 α'相和 β 相的比对 SSON 荧光性质的影响。第一步采用共沉淀(co-precipitation, CO), SG, PSO 和 SS 合成 SSO，第二步使用 SS 法合成 SSON。第一步中，不同方法制备的 SSO，对第二步所制得 SSON 的发光性能有明显影响。研究了第一步中 α'和 β 相 SSO 对第二步产物 SSON 的发光强度、晶粒尺寸和量子效率的影响。研究表明，SS 合成的 SSON 具有更高的发光强度，而采用 SG、PSG 和 CO 法制得的 SSON，其发光强度依次递减。结果显示，通过不同制备方法，使第一步骤中的 β-SSO 相含量改变，而 β-SSO 的含量是获得高效率 SSON 荧光粉的关键所在。这将有助于制备高性能的 SSON 荧光粉，以使得其可在 WLEDs 中的应用。

关键词：溶胶–凝胶；氮氧化物；相变

Abstract

White light-emitting diodes (WLEDs) have attracted great attentions due to their advantages of long lifetime, compact structure, and low power consumption. The phosphor-converted WLEDs (PC-WLEDs) that are based on blue LEDs are the mainstream of the market. This strategy requires phosphor to generate white light. Thus, the phosphor is a key material of PC-WLEDs.

The green phosphor is very important to get high color rendering index (CRI) in blue chip based WLED. $SrSi_2O_2N_2$: Eu^{2+} (SSON) has received great attention due to its high quantum efficiency, wide absorbance (from near-UV to blue region), and good thermal/ chemical stability. Conventional high-temperature solid-state method (SS) is commercially used to prepare the phosphors. The chemical methods are alternative-efficient ways to improve the luminescent properties of the phosphors. Phosphors can be prepared by chemical methods at relatively low temperature, and are expected to have high purity and good morphology. Thus, in the present work, several chemical ways are used to synthesis the green SSON phosphors for PC-WLEDs.

(1) Polymer-metal complex or Pechini sol−gel (PSG) method has been used to prepare the SSON phosphor for the first time. The multi-heated stages were designed depending on the DTA-TG curve. The XRD results confirmed that pure SSON phase could be obtained at 1400 °C (for 3 h). Additionally, the particles were uniform and well-dispersed. The photoluminescent properties indicate that the maximum PL intensity was found in the sample doped with 0.04 mol% Eu^{2+} with a green emission peak at 531.4 nm. The quantum efficiency and the CIE chromaticity coordinates of the prepared phosphors are investigated. The fabricated WLED lamp, which is consist of the SSON, (Sr,Ca)$AlSiN_3$: Eu^{2+}red phosphor, and blue chip InGaN (λ = 450 nm), has warm white light. The result indicates that Pechini method is an alternative way and showed close efficiency to the solid-state method to prepare

SSON phosphor with higher homogeneity and more uniform size distribution for applications of WLEDs in the blue region.

(2) The transformation of α'-phase to β-phase in Sr_2SiO_4: Eu^{2+} (SSO) with increasing the Eu^{2+} concentration was investigated. SSO was used as a precursor in the first step and then reacted with silicon nitride (Si_3N_4) in the second step to prepare SSON phosphor by solid-state two-steps synthesis method. The phosphor prepared by this method showed a higher luminescence efficiency and larger crystallite size than that of the one-step method. The X_2-phase in SSON was formed and showed a strong green emission band at 530 nm. The particles were homogeneous and well-dispersed with the size around 13.63 μm and crystallite size between 60-65 nm. The relation between the crystal structure and the photoluminescence of SSO and SSON was studied.

(3) The effect of α'- and β-phases of SSO on the photoluminescent properties of SSON phosphors was investigated. The SSON phosphor was prepared using a two-steps process. The first step was involved the synthesis of SSO by four different routes: co-precipitation (CO), PSG, sol−gel (SG), and solid-state reaction (SS) methods while the second step was performed using the SS method to prepare SSON. The differences in the preparation methods of SSO in the first step have a significant effect on the luminescent properties of SSON in the second step. The effects of the α'- and β-SSO ratio on the luminescent intensity, crystallite size and quantum efficiency of SSON are investigated. The higher luminescence intensity of the SSON phosphor was found in SS method and then decrease in the order of SG, PSG and CO methods. The increasing of β-SSO phase in the first step using a specific preparation method is an important key to obtain high-efficiency SSON phosphors for their promising application in WLEDs.

Keywords: Sol−gel; Oxynitride; Phase transformation.

Abbreviations

SSL	Solid-State Lighting
WLED	White Light Emitting Diode
RGB	Red Green Blue
CIE	The Commission Internationale de l'éclairage
CCT	Correlated Color Temperature
CRI	Color Rendering Index
PSG	Pechini Sol−gel
CO	Co-precipitation
SG	Sol−gel
SS	Solid-State Reaction
SSON	$SrSi_2O_2N_2$: Eu^{2+}
SSO	Sr_2SiO_4: Eu^{2+}
DTA-TG	Differential Thermal Analysis-Thermogravimetric
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
PL	Photoluminescent
QE	Quantum Efficiency
FTIR	Fourier Transform Infrared Spectroscopy

Content

Chapter 1

1.1 Introduction

1.1.1 Solid-state lighting

Solid-state lighting (SSL) is a type of lighting which uses solid-state materials by using a combination of semiconductor chips as light generators and phosphors as light converters, which exhibit higher energy conversion efficiency, compact structure, and longer life compared to conventional lamps.

The first demonstration of a light emitting diode source was in 1907 by Henry J. Round, by applied a high voltage on a silicon carbide crystal (carborundum) to produce a light emission. The first visible light emitting diodes (LEDs) emerged commercially at 1960's[1, 2]. After the investigation of the gallium nitride (GaN) LED by Shuji Nakamura in 1993[3] at the Nichia Corporation in Japan, make it possible to use a semiconductor to produce white light. Recently, the LEDs have received a big attention because of their performance has become increasingly rivals the traditional light sources, see Fig. 1.1[4].

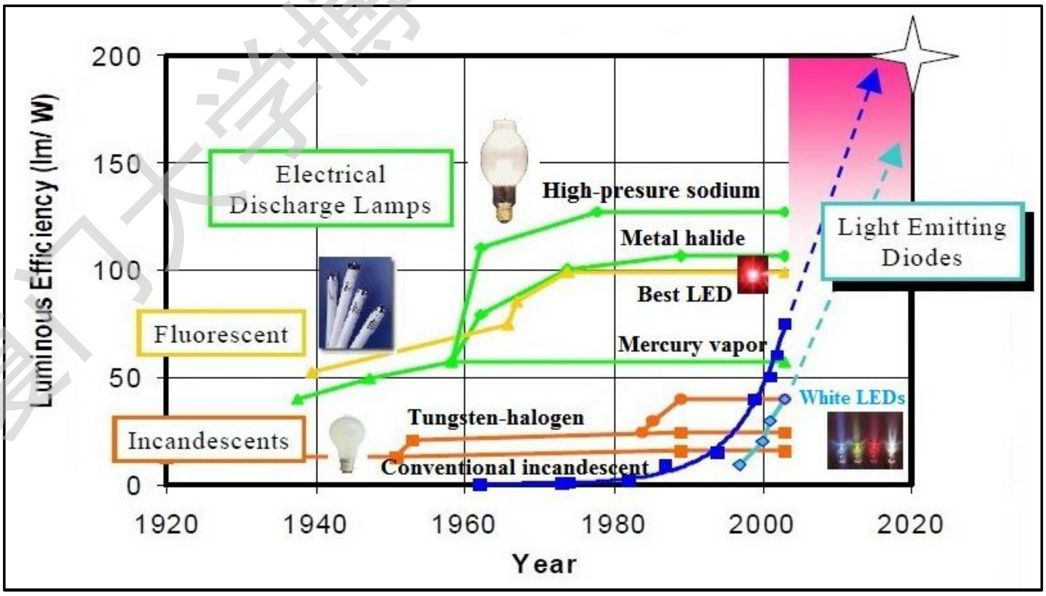

Fig. 1.1 The evolution of lighting illustrated LED performance and compared to conventional light sources[4]