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Insight into thermal degradation mechanism of $Sr_2Si_5N_8:Eu^{2+}$ phosphor during high-temperature aging processes

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ABSTRACT

The thermal degradation is considered as one the most common limitations of $Sr_{2-x}Eu_xSi_5N_8$ nitride phosphors due to the elevated working temperatures in LED. In order to examine the origin of the thermal degradation, $Sr_{2-x}Eu_xSi_5N_8$ was synthesized using high-temperature solid-state reaction. The nitride with activators and the nitride host lattice were studied separately. The diffuse reflectance spectra, the internal quantum efficiency, and optical absorption rate, as well as the element binding energy and element content before and after annealing at high temperature, were investigated. Also, the morphology and surface layers were observed using high-resolution transmission electron microscopy (HRTEM). The results suggested the formation of an amorphous layer on the grain surface, which decreased luminescence efficiency after the heat treatment. It was found that oxidation of both the europium and $Sr_2Si_5N_8$ host lattice caused the formation of the amorphous layer.

1. Introduction

Advances in phosphor-conversion white light-emitting diodes (WLEDs) as the next-generation lighting sources have been made during the past years due to their low-energy consumption, long service time, and highlight efficiencies. The most widely adopted WLEDs are combinations of InGaN devices with 460 nm blue lights and yellow emitting phosphors (YAG:Ce). A red light emitting phosphor that could be excited by blue light is often required to yield high color-rendering index (CRI) and warm-light LEDs. In the past few years, rare-earth doped nitridosilicates have been investigated as promising new red phosphors in WLEDs. This includes Eu-doped (Sr,Ca)$AlSiN_3$ [1–6], $M_2Si_5N_8$ (M = Ca, Sr, Ba) [7–10], $SrSiN_2$ [11,12], $SrAlSi_4N_7$ [13,14], and $SrLi_2Si_2N_4$ [15]. Among these, (Sr,Ca)$AlSiN_3:Eu^{2+}$ and $Sr_2Si_5N_8:Eu^{2+}$ have been applied in commercial products. However, the synthetic methods of $SrAlSiN_3$ structures employ harsh reaction conditions such as high pressure (190 MPa) and high temperature (1900 °C), which further limited the commercial applications [16]. $Sr_2Si_5N_8:Eu^{2+}$ can be synthesized using mild reaction conditions while (Sr,Ca)$AlSiN_3$ requires harsh conditions. The usual synthesis temperature lies around 1500–1600 °C under normal air pressure. When excited at 460 nm wavelength, $Sr_2Si_5N_8:Eu^{2+}$ gives strong emission in the red region of 616–670 nm with high quantum efficiency. The host lattice containing SiN_4 tetrahedral three-dimensional network structure is highly stable chemically. Although $Sr_2Si_5N_8:Eu^{2+}$ phosphor has several advantages, one of its limitation concerns the thermal degradation. The working temperature in WLEDs can often reach 150 °C [17], where the luminescence properties could decline at this temperature as the intensity reduces more quickly when the temperature increases.

Thermal degradation of nitride phosphors has been discussed in several relevant literature accounts. Zhang et al. [18] recorded moisture-induced degradation of phosphors and proposed an improving method, which consisted of modifying the hydrophobic nanolayer (8 nm) of amorphous silicon dioxide by CH_3 groups at the surface. The induced hydrophobic surface layer boosted the stability of phosphor at high-pressure water steam conditions and 150 °C. The origin of thermal degradation in $Sr_2Si_5N_8:Eu^{2+}$ was recently reported and found to be caused by the oxidation of Eu

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ions from divalent to trivalent ions. The increased trivalent europium would make the surface amorphous, which was confirmed on the surface of heat-treated samples [17]. However, the damage of host lattice could also result in a decrease of luminescence. The research did not consider that if the host lattice without europium can be oxidized to form an amorphous layer on the surface of the crystal grain. Cho et al. [19] examined the stability and reliability of $Sr_{1-x}Ba_xSi_2O_2N_2:Eu^{2+}$ phosphors for white LED applications. Although their findings pointed out to oxidation of the host lattice at higher temperatures, they unveiled that degradation in electroluminescent (EL) intensity of the device might be the result of thermally assisted photoionization of Eu^{2+} ions in the phosphor.

The present account reports on the nitride phosphors thermal degradation, by focusing on variations of Eu ions. The relationship between the host lattice decay and the thermal degradation has not been discussed. Thus, more factors should be investigated and discussed in order to gain a better understanding. The variation of host lattice during heating can be investigated by studying the nitride compound without the presence of Eu^{2+} activator. In this study, the thermal degradation of $Sr_2Si_5N_8$ with and without Eu activators has been examined and variations in the host lattice after heat treatment were considered in order to clarify the thermal degradation mechanisms.

2. Experimental

All powder samples of $Sr_{2-x}Eu_xSi_5N_8$ (x = 0, 0.02, 0.1, 0.24, 1) were synthesized from the raw materials of Sr_3N_2, Si_3N_4, and Eu_2O_3. The binary nitride precursors Sr_3N_2 was prepared by the reaction of pure strontium metal under flowing dried nitrogen at 800 °C for 10 h in a horizontal tube furnace. The stoichiometrically weighed raw materials were first mixed thoroughly under N_2 atmosphere in a glove box in presence of trace impurities (O_2 < 0.1 ppm, H_2O < 0.1 ppm). The mixture was then poured into a Molybdenum crucible and fired at 1500 °C for 8 h under 0.12 MPa N_2 atmosphere in a sintering furnace with a graphite tube. The graphite containing oxides (Eu_2O_3 and O in Si_3N_4/Sr_3N_2) in a nitrogen atmosphere yielded a carbothermal reaction at high temperature following the reaction: oxide + C + N_2 → nitride + CO. The flowing N_2 at 50 ml/min was provided during the whole heating process. After sintering, the samples were cooled down in the furnace and coarse phosphors were eventually obtained. The as-prepared $Sr_2Si_5N_8$ with or without Eu^{2+} powders were thermally treated at 100 °C, 150 °C, 200 °C, 300 °C and 500 °C under either air or N_2 atmospheres.

The phase identification was performed by powder X-ray diffraction (XRD RINT2200, Rigaku with Cu Kα radiation) operating at 40 kV and 30 mA. The photoluminescence (PL) spectra were measured using fluorescent spectrophotometers (Hitachi F-7000) at room temperature equipped with a Xe-lamp as an excitation source. Temperature-dependent PL properties were recorded in the range of 30 °C–175 °C (increased and decreased) with 5 min holding time to reach thermal equilibria. Internal quantum efficiencies (QEs) and absorption were determined using an absolute PL quantum yield spectrometer (C11347, Hamamatsu). X-ray photoelectron spectroscopy (XPS) of the samples was performed with a system (Thermo Scientific, ESCALAB 250Xi) with an Al Kα X-ray source. The elemental content as a function of etch depth were calculated from the XPS spectra. The diffuse reflectance spectra were measured with a Cary 5000 UV–vis–NIR spectrophotometer equipped with an internal diffuse reflectance accessory. Finally, the TEM micrographs were obtained using an FEI Tecnai G2 electron microscope.

3. Results and discussion

The results of temperature-dependent PL spectra of $Sr_2Si_5N_8:Eu^{2+}$ heated from 30 to 175 °C and then cooled down from 175 to 30 °C under air are shown in Fig. 1. It can be seen that the emission intensity decreased and the wavelength displayed clear blue shifts as temperature increased. As the temperature was cooled down to 30 °C, the emission intensity showed a reverse trend during the initial intensity without recovering the initial value. The losing emission intensity with a recovery trend belonged to thermal quenching, while the irreversible losing part belonged to thermal degradation. The mechanism of thermal quenching in nitrides was extensively discussed in the literature. Usually, thermal quenching of $Sr_2Si_5N_8:Eu^{2+}$ was linked to thermal ionization of Eu^{2+} ions [20]. However, the mechanism of thermal degradation in nitride phosphors is still unclear. Fig. 2 shows the relative photoluminescence intensity of $Sr_{1.9}Eu_{0.1}Si_5N_8$ heated in air at 200 °C as a function of time [21]. It will be noted that the thermal degradation increased quickly during the first 3 days, and then the intensity declined in a slow trend. Results from additional experiments using similar heat treatments under an N_2 atmosphere in a glove box (O_2 < 0.1 ppm, H_2O < 0.1 ppm) depicted a decrease in the emitting intensity, though N_2 induced less thermal degradation than air. As it was quite difficult to obtain a 100% free-oxygen environment, and

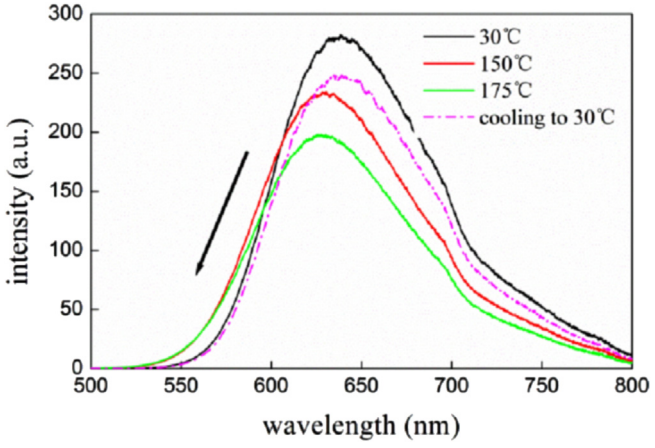

Fig. 1. Temperature dependence of emission spectra of $Sr_{1.76}Eu_{0.24}Si_5N_8$ heated from 30 to 175 °C (solid line), then cooled from 175 to 30 °C (dash line) under air.

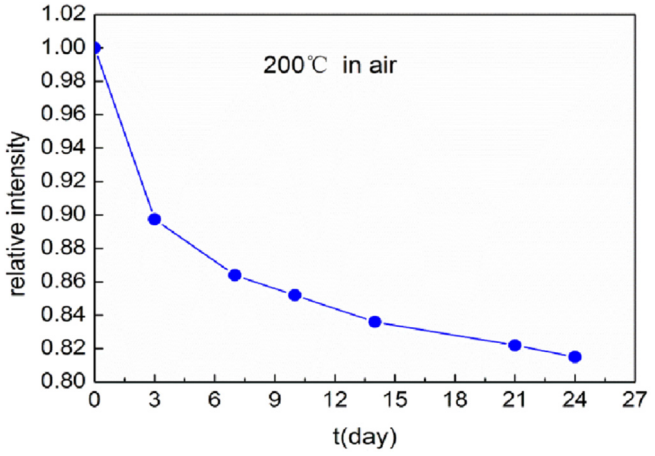

Fig. 2. Relative PL intensity of $Sr_{1.9}Eu_{0.1}Si_5N_8$ heated in air at 200 °C as a function of time.