A white light phosphor suitable for near ultraviolet excitation

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Abstract

Luminescent properties of Eu\textsuperscript{2+}-doped phosphors with nominal composition of 2SrO·MgO·xSiO\textsubscript{2} (0.8 ≤ x ≤ 1.2) are studied. The emission spectra consist of a blue band (460 nm) and a yellow band (550 nm), the relative intensities of which change with the SiO\textsubscript{2} composition x. It is found that a combination of the blue and yellow bands can generate white light at x around 1 under near-ultraviolet excitation. X-ray diffraction patterns of the phosphors demonstrate both Sr\textsubscript{3}MgSi\textsubscript{2}O\textsubscript{8} and Sr\textsubscript{2}SiO\textsubscript{4} phases, in which Eu\textsuperscript{2+} contributes to the blue and yellow emissions, respectively. The relative intensity variation of the two bands is attributed to the relative proportion of the two phases dependent on SiO\textsubscript{2} composition. A white light emitting diode fabricated using a GaN chip (λ\textsubscript{em} = 400 nm) and this phosphor is obtained, exhibiting color coordinates of x = 0.33, y = 0.34, color rendering index of 85 and luminous efficiency of 6 lm/W.

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1. Introduction

In recent years, the study on white light phosphors suitable for near-ultraviolet (NUV) excitation has been attracting more attention for fabricating white light emitting diode (LED) with NUV GaN chip for white lighting [1–4]. In comparison with the commercial white LED fabricated with a blue chip and yellow phosphor YAG:Ce\textsuperscript{3+}, the white LED fabricated with NUV chip and corresponding phosphor has higher color stability because all the colors are determined by the phosphors. Up to now, a few white phosphors suitable for NUV excitation have been reported [1–4], the phosphors with better optical properties are still in development. Rare-earth-ions-doped silicate hosts have demonstrated good photoluminescence properties and chemical–physical stability. Eu\textsuperscript{2+} in such kinds of host may emit various colors demanded by white lighting.

In this paper, we report luminescent properties of Eu\textsuperscript{2+}-doped silicate phosphors with nominal compositions of 2SrO·MgO·xSiO\textsubscript{2}. White light emission is obtained under NUV excitation. A white LED fabricated through combining NUV chip (λ\textsubscript{em} = 400 nm) with the new phosphor exhibits good color coordinates, high color rendering index (CRI) and luminous efficiency.

2. Experimental

The phosphors with nominal composition of 2SrO·MgO·xSiO\textsubscript{2}:Eu\textsuperscript{2+} were synthesized through a solid-state reaction technique. The samples were doped with 1 mol\% of Eu\textsuperscript{2+}. The starting materials were SrCO\textsubscript{3}, SiO\textsubscript{2}, MgO and Eu\textsubscript{2}O\textsubscript{3}. All the above materials were of analytical grade exceeding 99.99% purity. These raw materials in the desired ratio were well milled by an agate mortar and pestle. The mixture is fired at 1300 °C for 4 h in a reducing atmosphere. Photoluminescence and excitation spectra were measured with a Hitachi F-4500 Spectrometer. In measurement of fluorescence lifetime, a third (355 nm) harmonic of Nd–YAG pulsed laser (Spectra-Physics, GCR 130) was used as an excitation source, and the signal was detected with a TDS-3052 oscilloscope.
3. Results and discussion

Fig. 1 shows the emission spectra of the phosphors with nominal composition of $2\text{SrO} \cdot \text{MgO} \cdot x\text{SiO}_2:1\text{mol}\%\text{Eu}^{2+}$ under 385 nm excitation. It is observed that when $x = 1.20$, the phosphor has a blue emission band (460 nm) only. As $x$ decreases, a yellow band appears at 550 nm, and becomes dominant emission as $x = 0.8$. When $x$ is close to 1, the phosphors emit excellent white light.

Fig. 2 depicts the powder XRD pattern of the phosphors for different $x$. It is demonstrated that there are mainly two crystal phases, $\text{Sr}_3\text{MgSi}_2\text{O}_8$ and $\text{Sr}_2\text{SiO}_4$. At $x = 1.2$, $\text{Sr}_3\text{MgSi}_2\text{O}_8$ phase is dominant, indicating that the blue emission is originated from $\text{Eu}^{2+}$ in this phase [5]. Phase $\text{Sr}_2\text{SiO}_4$ appears at $x = 1.1$, and increases with decreasing $x$, and becomes dominant at $x = 0.8$. As a result, the yellow emission is attributed to $\text{Eu}^{2+}$ in $\text{Sr}_2\text{SiO}_4$ phase [5], and the color variation is therefore resulted from the change of the relative proportion of the two phases. It is also indicated from XRD that high concentration of $\text{SiO}_2$ is in favor of formation of $\text{Sr}_3\text{MgSi}_2\text{O}_8$ phase, thus leading to the variation of the relative proportion of the two phases as $x$ is changed. It is worth noting that if the composition of the phosphor is designed as a mixture of $\text{Sr}_3\text{MgSi}_2\text{O}_8$ and $\text{Sr}_2\text{SiO}_4$ in a proportion, no white emission can be obtained. Thus, in order to obtain white light emission, the starting material with nominal composition of $2\text{SrO} \cdot \text{MgO} \cdot x\text{SiO}_2:\text{Eu}^{2+}$ is necessary although extra $\text{MgO}$ and $\text{SrO}$ may be left in the materials. It is speculated that such extra alkaline metal oxides may play an important role in the formation of $\text{Sr}_3\text{MgSi}_2\text{O}_8$ and $\text{Sr}_2\text{SiO}_4$ phases in a proper proportion in material preparation process.

Emission and excitation spectra of the phosphor with $x = 1$ are depicted in Figs. 3 and 4, respectively. The intensity ratio of the blue to the yellow bands varies with the change of excitation wavelengths, indicating differences of the excitation spectra for the blue and yellow emissions, as shown in Fig. 4. It is observed that the phosphor displays good white color with coordinates of $x = 0.33$, $y = 0.34$ under 400 nm excitation. Kim et al. reported the white-light emitting properties of $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$. The phosphor has two emissions peaked at 470 and 570 nm. The two emission bands are attributed to $\text{Eu}^{2+}$ ion substituted by $\text{Sr}^{2+}$ (I) site and $\text{Sr}^{2+}$ (II,III) sites, respectively [4]. The two emissions have similar excitation spectra and widely different lifetimes, for example, 470 ns for the
blue band much shorter than 1400 ns for the yellow one, indicating effective energy transfer from the blue to the yellow center [4]. On the contrary, we can see from Fig. 4 that the two emission bands have distinctly different excitation spectra due to different phases. Moreover, the lifetimes of the blue and the yellow bands of the present phosphors have no big differences, as shown in Fig. 5. The lifetimes of the blue and yellow bands are 520 ns and 730 ns, respectively, indicating weak or no energy transfer between the two luminescent phases.

A white LED was fabricated through combining the white light phosphor with NUV GaN chip (λ_em = 400 nm). The white LED exhibits high color rendering index (CRI > 85) and excellent color coordinates (x = 0.33, y = 0.34) when the forward-bias current is 20 mA [6]. The luminous efficiency is 6 lm/W, higher than that (3.8 lm/W) fabricated with NUV chip and Sr2SiO4:Eu2+ phosphor [7]. The color coordinates and CRI of the white LED in this work almost do not change with the variation of forward-bias current, that is to say, the present white LED has higher color stability than the commercial white LED fabricated using a blue chip and YAG:Ce3+ phosphor.

4. Conclusions

White light phosphors with nominal composition of 2SrO·MgO·xSiO2:Eu2+ suitable for NUV excitation is prepared. The emission spectra consist of a blue and a yellow band, which originates from Eu2+ in phase Sr3MgSi2O8 and Sr2SiO4, respectively. High concentration of SiO2 is in favor of formation of Sr3MgSi2O8 phase. When x is around 1, the phosphor can emit white light resulted from the mixing of the blue and yellow colors. A white LED was fabricated through combining the phosphor with NUV InGaN chip (λ_em = 400 nm). The LED demonstrates high CRI (>85), excellent color coordinates (x = 0.33, y = 0.34), high color stability and luminous efficiency (6 lm/W). The phosphor presented in this work would be a promising material for use in white LED pumped by NUV chip.

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References