Preparation of Eu-Doped CaGa₂S₄–CaS Composite Bicolor Phosphor for White Light Emitting Diode

Jian ZHANG, Masahide TAKAHASHI, * Yomei TOKUDA and Toshinobu YOKO
*Institute for Chemical Research, Kyoto University, Uji-shi, Kyoto 611–0011
*PRESTO, Japan Science and Technology Agency, 4–1–8, Honcho, Kawaguchi–shi, Saitama 332–0012

A CaGa₂S₄–CaS composite doped with Eu²⁺ has been prepared by cooling the corresponding melt of the composition of 65CaS·35Ga₂S₄ containing 1 mol% EuS in order to obtain an efficient bicolor phosphor applicable to white light emitting diode. Efficient green and red fluorescence were simultaneously observed at around 555 and 645 nm, respectively, under 476 nm excitation. Especially, the red emission was about three times as intense as a simple mixture of CaGa₂S₄: Eu²⁺ and CaS: Eu²⁺ powders with the same composition. It was also found that the post-heat-treatment doubled the red fluorescence. The obtained CaGa₂S₄–CaS composite doped with Eu²⁺ showed more intense fluorescence rich in color rendering than a commercially available Y₃Al₅O₁₂: Ce phosphor.

[Received June 11, 2004; Accepted July 30, 2004]

Key-words: White light LED, Bicolor phosphor, Thiogallate, Composite, Rare earth ion

1. Introduction

In recent years, white LED (Light emitting diode) has been widely applied to torches, lighting, automotive interior lighting, and so on. White light is currently achieved by two different methods. The first white light LED was demonstrated by a combination of the three primary color LEDs. In this case, the output color can be controlled by a proportion of electric current of each LED. It was, however, reported that the multiple LED method gave a poor white. Secondly, a blue light GaN (gallium nitride) LED chip loaded with a phosphor such as Y₃Al₅O₁₂: Ce was proposed to obtain white light, which is now widely used as a conventional white LED. The Y₃Al₅O₁₂: Ce phosphor exhibits yellow fluorescence under blue light (~470 nm) excitation. Therefore, a combination of blue light from LED and yellow one from phosphor is perceived as white. This type of white light LED has a great advantage over the multiple type LED because of the simple structure. The color rendering of white light LED using Y₃Al₅O₁₂: Ce phosphor is, however, still scant, especially of red color. Therefore, phosphor materials with high color rendering, which emits multiple colors, green and red luminescence, have been intensively investigated aiming at obtaining high performance white LED.

Among the transition metal ions and rare earth ions, divalent rare earth ions such as Eu³⁺ emit intense and broad luminescence due to 4f⁵5d¹⁴f⁷ transition. In addition, the wavelength of their luminescence is strongly dependent on the crystal field strength and covalency of the local structure of divalent rare earth ions. For example, the Eu²⁺-doped CaGa₂S₄ phosphor exhibits a broad green emission band at around 550 nm under ~470 nm excitation. On the other hand, red luminescence around 650 nm can be obtained by CaS: Eu²⁺ phosphor under ~550 nm excitation. It is then expected that the composite phosphor of CaGa₂S₄: Eu and CaS: Eu can emit green and red fluorescence simultaneously under blue light (~470 nm) excitation, where the red fluorescence is caused by cascading fluorescence from CaGa₂S₄: Eu²⁺ to CaS: Eu²⁺.

In the present work, we have prepared the CaGa₂S₄–CaS composite phosphor doped with Eu²⁺ from the corresponding homogeneous melt consisting of CaS, Ga₂S₄ and EuS. The much more efficient cascading excitation from CaGa₂S₄: Eu²⁺ to CaS: Eu²⁺ can be expected for the composite phosphor due to the close contact between the crystal grains of each phase on a micro or nanometer scale compared with a simple mixture of the individual phosphors prepared separately.

2. Experimental procedures

Starting materials consisting of CaS (99.99%), Ga₂S₄ (99.99%), and EuS (>99.9%, Kojundo Chemical Laboratory Co., Ltd.) were loaded in a silica glass tube and outgassed under vacuum at 150°C for 12 h, and then were vacuum sealed. A composition of the starting mixture was 65CaS·35Ga₂S₄ containing 1 mol% EuS. The optimum CaS: Ga₂S₄ ratio and EuS concentration for attaining intense photoluminescence was estimated beforehand and the results will be reported elsewhere. The sealed mixture was melted at 900°C for 30 min and 1000°C for another 30 min. The melt was then cooled down to room temperature in a furnace by turning off the heater. In order to enhance fluorescence intensity, the sample was subjected to post heat-treatment at 700°C for 60 min in a sealed silica tube. The emission property of CaGa₂S₄–CaS composite phosphor was compared with that of a simple mixture of CaGa₂S₄: Eu²⁺ and CaS: Eu²⁺. CaGa₂S₄: Eu²⁺ (Eu doping concentration was 3 mol%) and CaS: Eu²⁺ (Eu doping concentration was 1 mol%) were prepared individually. The doping concentration was chosen so as to yield the maximum emission intensity. Photoluminescence and phospholuminescence excitation spectra of the samples were measured at room temperature using a Hitachi 850 fluorescence spectrophotometer equipped with a Xe lamp as an excitation source. X-ray diffraction (XRD) measurements were
performed with a Rigaku RINT2100 X-ray diffractometer using Cu Kα radiation operated at 40 kV and 40 mA.

3. Results and discussion
The obtained CaGa$_2$S$_4$-CaS composite was ground into powder, whose color was bright orange. XRD patterns of the obtained composite are shown in Fig. 1. All the diffraction peaks were assigned to CaGa$_2$S$_4$ and CaS phases. It is seen that relative intensities of the diffraction peaks due to CaS phase increased after post heat-treatment.

Figure 2 compares the photoluminescence spectra of the CaGa$_2$S$_4$–CaS composite with the mixture of CaGa$_2$S$_4$:Eu$^{2+}$ and CaS:Eu$^{2+}$ under 476 nm excitation. Similarly to Eu$^{2+}$-activated CaGa$_2$S$_4$ phosphor, both the composite and mixed phosphors also show a green broad emission band at 555 nm. A distinct red emission at 645 nm assignable to CaS:Eu$^{3+}$ is observed for the composite phosphor. The intensity of red emission from the composite phosphor is three times as large as that from a simple mixture of the individual phosphors, indicating that the direct excitation of CaS:Eu$^{3+}$ by 476 nm blue light is negligible. That is, the red emission of the composite phosphor would be excited by reabsorbing the green emission from CaGa$_2$S$_4$:Eu$^{2+}$, which is excited by the blue excitation source. Therefore, it can be said that under blue light excitation, the present composite phosphor shows green and red bicolour cascading emission.

When the sample was annealed at 700°C for 60 min, the emission intensity at 555 nm increased to a certain extent. Moreover, the emission of 645 nm band of the post-heated composite increased twice as intense as that of the as-prepared one. This can be explained by considering that the formation of CaS:Eu$^{2+}$ phase was enhanced by the post heat-treatment as indicated in Fig. 1. Hereafter, all the measurements were carried out using the post-heated composite.

Figure 3 shows the photoluminescence and photoluminescence excitation spectra of the composite phosphor. The green emission band showed a broad excitation band from 400 to 500 nm, indicating that the phosphor can be excited by a wide range of the wavelength of excitation source. On the other hand, the red luminescence band exhibited an absorption maximum at around 550 nm which is very close to the green luminescence band. Therefore, the efficient reabsorbing was realized for the present composite phosphor. In addition, CaGa$_2$S$_4$:Eu$^{2+}$ and CaS:Eu$^{2+}$ crystals in the present composite are in close contact with each other, or one type of crystal is surrounded by the other type of crystal and vice versa. The quantitative analysis of the cascading excitation of red photoluminescence is under way by the time resolved spectroscopy and electron microscopy.

Since YAG:Ce is the most widely studied phosphor for white LED, the emission properties of the composite phosphor in comparison with YAG:Ce were also investigated. Photoluminescence spectra of the present composite and a commercially available YAG:Ce phosphor are shown in Fig. 4. A broad emission band at about 526 nm under 460 nm excitation, which was the optimum excitation wavelength, was observed for YAG:Ce. On the other hand, the composite phosphor showed more intense green luminescence than YAG:Ce. Therefore, it is expected that the brighter and higher color rendering white LED can be obtained using the present CaGa$_2$S$_4$–CaS composite phosphor combined with blue LED.

4. Conclusion
A CaGa$_2$S$_4$–CaS composite phosphor doped with Eu$^{2+}$ was
prepared for high performance white LED. Intense green and red simultaneous emission were observed under 476 nm excitation, where the red emission was considered to be due to the cascading excitation from CaGdS₂:Eu²⁺ to CaS:Eu²⁺. Therefore, we have concluded that the present composite phosphor will be a promising candidate for white LED excited by blue LED.

Acknowledgement We thank the Ministry of Education, Science, Sports and Culture, Japan, for the Grant-in-Aids for COE Research on Elements Science, No. 12CE2005.

References