A novel bluish green-emitting RbBaScSi$_3$O$_9$ : Eu$^{2+}$ phosphor for white LEDs

Takeshi Abe$^a$, Sun Woog Kim$^a$, Tadashi Ishigaki$^a$, Kazuyoshi Uematsu$^b$, Kenji Toda$^a$* and Mineo Sato$^b$

$^a$Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan
$^b$Department of Chemistry and Chemical Engineering, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan

A novel bluish green-emitting silicate phosphor, RbBaScSi$_3$O$_9$ : Eu$^{2+}$, was synthesized by a conventional solid state reaction method. The RbBaScSi$_3$O$_9$ : Eu$^{2+}$ phosphor can be excited by a near-UV and blue light irradiation and presents a bluish green band centered at 500 nm due to the allowed transition from 4f$^6$5d$^1$ to 4f$^7$ of Eu$^{2+}$. The maximum emission peak intensity was obtained at the composition of RbBaScSi$_3$O$_9$ : 10 mol% Eu$^{2+}$, and the emission intensity was 13% compared with that of the commercial YAG phosphor.

Key words: White LEDs, Bluish green-emitting phosphor, RbBaScSi$_3$O$_9$.

Introduction

Recent years, white light-emitting diodes have been widely used in lamps and displays as a next generation white light source because the white LEDs have a number of advantages, such as a high luminescent efficiency, a long life time, environmental consideration, compactness and designable features [1-3]. In order to enhance the luminescence efficiency of the white LEDs, it is important to develop new phosphor materials which can show high luminescent efficiency under near-UV and blue light irradiation. Recently, Eu$^{2+}$ activated nitrides and oxynitrides phosphors have been applied to the white LEDs because they show strong optical absorption in near-UV to blue light region, and have high chemical and thermal stability [4-11]. However, these nitrides and oxynitrides phosphor materials are hard to synthesize in a single phase form and require a special high-temperature and high-pressure furnace [12, 13]. Furthermore, raw materials of these phosphors such as Ca$_3$N$_2$ and Sr$_2$N$_2$ can easily react with oxygen in air and need to be treated in an inactive gas. Therefore, investigations have been devoted to the search for new phosphor materials based on oxides such as silicate, aluminate and phosphate, which can be relatively easy to synthesize in a single phase form [14-18]. In particular, Eu$^{2+}$ doped silicate phosphors have been extensively researched because they can show good luminescence properties due to strong crystal fields with the covalent Si-O bond. Since the splitting of 4f$^5$5d energy level of the Eu$^{2+}$ becomes wider with the increase of the crystal field strength, the energy gaps between the ground state $^5$S level and lower excited state 4f$^6$5d component of Eu$^{2+}$ becomes smaller. Therefore, the silicate phosphors are expected to be obtained the excitation and emission band in the longer wavelength range.

In this study, we have focused on rubidium barium scandium silicate, RbBaScSi$_3$O$_9$, as a host material for the phosphors to realize a novel phosphor material with high luminescence efficiency under a near-UV or blue light excitation. The crystal form of RbBaScSi$_3$O$_9$ adopts a monoclinic structure [19], in which tetrahedral SiO$_4$ and octahedral ScO$_6$ connected to form a rigid three-dimensional structure and the Rb$^+$ and Ba$^{2+}$ ions are located in the three-dimensional framework, as illustrated in Fig. 1(a). In the case of present phosphor, the doping Eu$^{2+}$ may be preferably occupy the Ba$^{2+}$ site in the crystal structure, because the ionic radius of Eu$^{2+}$ (0.120 nm for 7 coordination and 0.125 nm for 8

Fig. 1(a). The crystal structure of monoclinic RbBaScSi$_3$O$_9$. 
coordination) is similar to that of Ba\(^{2+}\) (0.138 nm for 7 coordination) but it is too smaller than that of Rb\(^{+}\) (0.161 nm for 8 coordination), and the valences of Eu\(^{2+}\) is same to that of Ba\(^{2+}\). As shown in Fig. 1(b), 7-coordinated Ba\(^{2+}\) site in the monoclinic RbBaScSi\(_3\)O\(_9\) is distorted by the different bond length of Ba-O, and the distortion leads to strong crystal field around the Eu\(^{2+}\) ion. Therefore, excitation and emission band in the longer wavelength range. Therefore, this phosphor is expected to be obtained the excitation and emission band in the longer wavelength range.

In this work, the RbBaScSi\(_3\)O\(_9\) : Eu\(^{2+}\) phosphor was synthesized by the conventional solid state reaction method, and the photoluminescence properties of the RbBaScSi\(_3\)O\(_9\) : Eu\(^{2+}\) were characterized.

**Experimental**

The RbBaScSi\(_3\)O\(_9\) : Eu\(^{2+}\) phosphors were synthesized by the conventional solid state reaction method. A stoichiometric mixture of Rb\(_2\)CO\(_3\) (98%, Wako Pure Chemical Industries Ltd.), BaCO\(_3\) (99.9%, Kanto Chemical Co., Inc.), Sc\(_2\)O\(_3\) (99.99%, Shin-Etsu Chemical Co., Ltd.), SiO\(_2\) (99.9%, Wako Pure Chemical Industries Ltd.) and Eu\(_2\)O\(_3\) (99.99%, Shin-Etsu Chemical Co., Ltd.) was mixed using a mortar with acetone, in which the Eu\(^{2+}\) concentration in the phosphors was adjusted between 1 mol% and 15 mol%, and then the mixtures were pre-calcinated at 1200 °C for 12 hrs in air. After pre-calcination, the phosphor samples were reground in a mortar, and then calcinated at 1200 °C for 12 hrs in a flow of 95 vol% Ar-5 vol% H\(_2\) gas for the reduction of Eu\(^{3+}\) to Eu\(^{2+}\).

Powder X-ray diffraction (XRD) data were obtained using an X-ray diffractometer (MX-Labo; Mac Science Ltd.). The photoluminescence emission (PL) and excitation (PLE) spectra were measured for the powder samples using a spectrofluorometer (FP-6500/6600; Jasco Corp.) at room temperature. The photoluminescence emission intensity of the samples was compared with that of a commercial yellow-emitting YAG phosphor (P-46). The crystal structure was illustrated by the VESTA program [20].

**Results and Discussion**

The XRD patterns of the RbBaScSi\(_3\)O\(_9\) : xmol%Eu\(^{2+}\) phosphors were shown in Fig. 2. The XRD patterns of all samples were identical to a single phase of the monoclinic RbBaScSi\(_3\)O\(_9\) structure with high crystallinity, and there is no diffraction peak corresponding to any impurities in the patterns.

Fig. 3 presents the photoluminescence excitation and emission spectra of the RbBaScSi\(_3\)O\(_9\) : 10 mol%Eu\(^{2+}\) phosphor. The excitation spectrum of the phosphor is consisted of a broad band covering from the UV to blue light region. This indicates that the phosphor can be applied in the white LEDs which including near-UV LED chip and blue LED chip as an excitation source. The emission spectra exhibit a broad bluish green band centering at 500 nm, corresponding to the allowed
A novel bluish green-emitting RbBaScSi₃O₉ : Eu²⁺ phosphor for white LEDs

The dependence of the photoluminescence emission peak intensities on the Eu²⁺ concentrations in the RbBaScSi₃O₉ : xmol%Eu²⁺ phosphors. The excitation wavelength are 405 nm for RbBaScSi₃O₉ : 10 mol%Eu²⁺ and 460 nm of commercial YAG phosphor. The photoluminescence emission peak intensity of the Eu²⁺ ions under either excitation wavelength. There are no significant changes in the emission spectrum except the wavelength at 405 nm and 450 nm. There are no RbBaScSi₃O₉ of commercial YAG phosphor, and then decreased due to thermal quenching effect. Fig. 5 shows the temperature dependence of the emission peak intensity of the RbBaScSi₃O₉ : 10 mol%Eu²⁺ phosphor normalized with respect to the value at 20 °C. Result of commercial YAG phosphor is also included for the comparison. With increasing the temperature up to 150 °C, the emission peak intensity of the RbBaScSi₃O₉ : 10 mol%Eu²⁺ decreased to 68% of initial value at 20 °C, which is equivalent to that of the commercial YAG phosphor (73% of initial value at 20 °C). This result suggests that the RbBaScSi₃O₉ : Eu²⁺ phosphor is expected to find application as green-emitting phosphor for use in white LEDs, although the emission intensity of this phosphor is not sufficient at the present stage. In addition, improvement of the optical properties is expected by optimization of the preparation method and modification of the crystal field around the Eu²⁺ ions by doping different cations in the Rb⁺ and Ba⁺ site.

Conclusions

A near-UV and blue light excitable bluish green-emitting RbBaScSi₃O₉ : Eu²⁺ phosphors were synthesized by a conventional solid-state reaction method. These phosphors obtained in the present study adopt the monoclinic RbBaScSi₃O₉ structure in a single phase form with high crystallinity. The highest emission intensity was obtained for RbBaScSi₃O₉ : 10 mol%Eu²⁺, and the relative emission intensity was 13% of the commercial YAG phosphor. The RbBaScSi₃O₉ : Eu²⁺ has a relatively good thermal stability on the temperature quenching effect. Therefore, the RbBaScSi₃O₉ : Eu²⁺ phosphor material is expected to be a suitable candidate as a green-emitting phosphor for use in the white LEDs.

References

9. R.J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, T.