

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

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A novel bluish green-emitting silicate phosphor, $\text{RbBaScSi}_3\text{O}_9 : \text{Eu}^{2+}$, was synthesized by a conventional solid state reaction method. The $\text{RbBaScSi}_3\text{O}_9 : \text{Eu}^{2+}$ 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 $4f^65d^1$ to $4f^7$ of Eu^{2+} . The maximum emission peak intensity was obtained at the composition of $\text{RbBaScSi}_3\text{O}_9 : 10 \text{ mol}\% \text{Eu}^{2+}$, and the emission intensity was 13% compared with that of the commercial YAG phosphor.

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

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_3N_2 and Sr_3N_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 $4f^65d$ energy level of the Eu^{2+} becomes wider with the increase of the crystal field strength, the energy gaps between the ground state ^8S level and

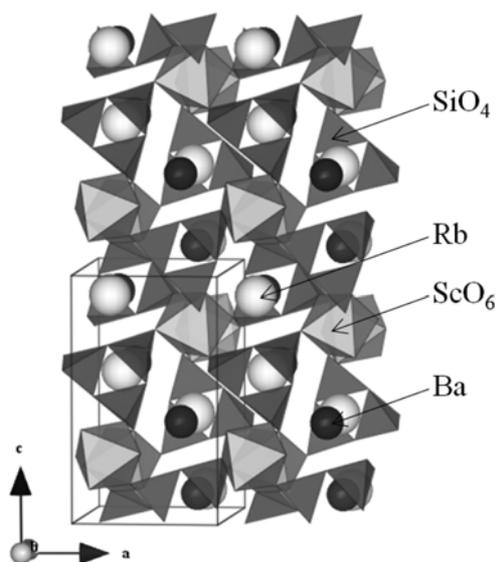


Fig. 1(a). The crystal structure of monoclinic $\text{RbBaScSi}_3\text{O}_9$.

lower excited state $4f^65d$ 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, $\text{RbBaScSi}_3\text{O}_9$, 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 $\text{RbBaScSi}_3\text{O}_9$ 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

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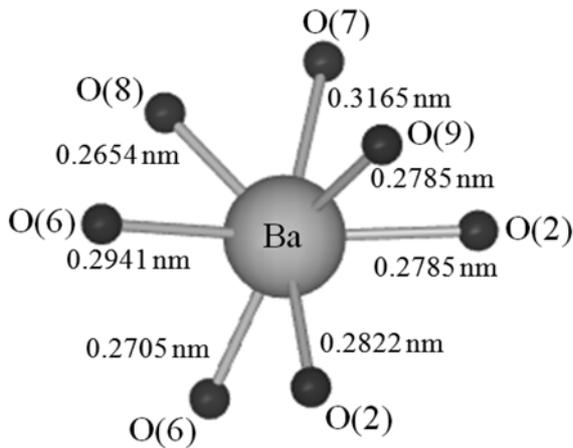


Fig. 1(b). The coordination environment of Ba²⁺ in monoclinic RbBaScSi₃O₉.

coordination) is similar to that of Ba²⁺ (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 Eu²⁺ is same to that of Ba²⁺. As shown in Fig. 1(b), 7-coordinated Ba²⁺ site in the monoclinic RbBaScSi₃O₉ is distorted by the different bond length of Ba-O, and the distortion leads to strong crystal field around the Eu²⁺ 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 RbBaScSi₃O₉ : Eu²⁺ phosphor was synthesized by the conventional solid state reaction method, and the photoluminescence properties of the RbBaScSi₃O₉ : Eu²⁺ were characterized.

Experimental

The RbBaScSi₃O₉ : Eu²⁺ phosphors were synthesized by the conventional solid state reaction method. A stoichiometric mixture of Rb₂CO₃ (98%, Wako Pure Chemical Industries Ltd.), BaCO₃ (99.9%, Kanto Chemical Co., Inc.), Sc₂O₃ (99.99%, Shin-Etsu Chemical Co., Ltd.), SiO₂ (99.9%, Wako Pure Chemical Industries Ltd.) and Eu₂O₃ (99.99%, Shin-Etsu Chemical Co., Ltd.) was mixed using a mortar with acetone, in which the Eu²⁺ concentration in the phosphors was adjusted between 1 mol% and 15 mol%, and then the mixtures were pre-calcined 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% H₂ gas for the reduction of Eu³⁺ to Eu²⁺.

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

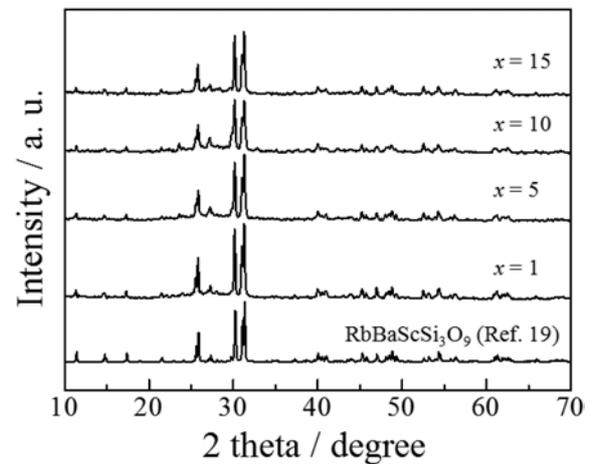


Fig. 2. The XRD patterns of the RbBaScSi₃O₉ : x mol% Eu²⁺ phosphors.

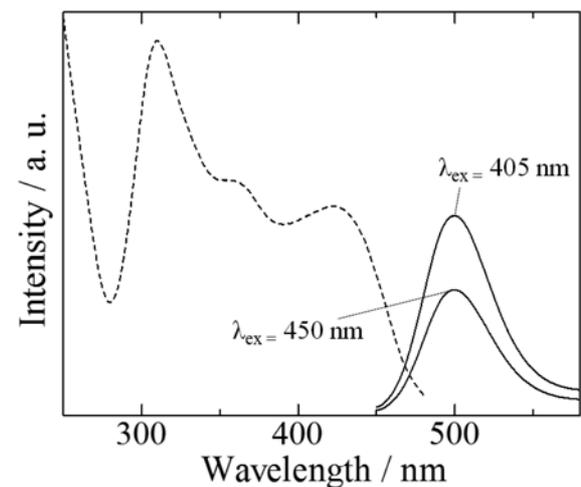


Fig. 3. The photoluminescence excitation and emission spectra of the RbBaScSi₃O₉ : 10 mol% Eu²⁺ phosphor.

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 RbBaScSi₃O₉ : x mol% Eu²⁺ phosphors are shown in Fig. 2. The XRD patterns of all samples were identical to a single phase of the monoclinic RbBaScSi₃O₉ 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 RbBaScSi₃O₉ : 10 mol% Eu²⁺ 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

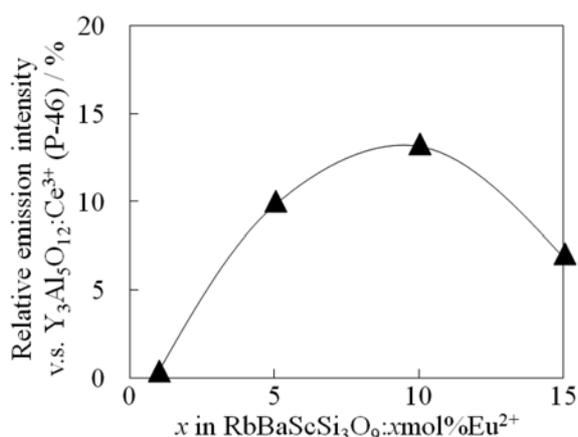


Fig. 4. The dependence of the photoluminescence emission peak intensities on the Eu^{2+} concentrations in the $\text{RbBaScSi}_3\text{O}_9 : x\text{mol}\%\text{Eu}^{2+}$ phosphors. The excitation wavelength are 405 nm for $\text{RbBaScSi}_3\text{O}_9 : 10\text{mol}\%\text{Eu}^{2+}$ and 460 nm of commercial YAG phosphor.

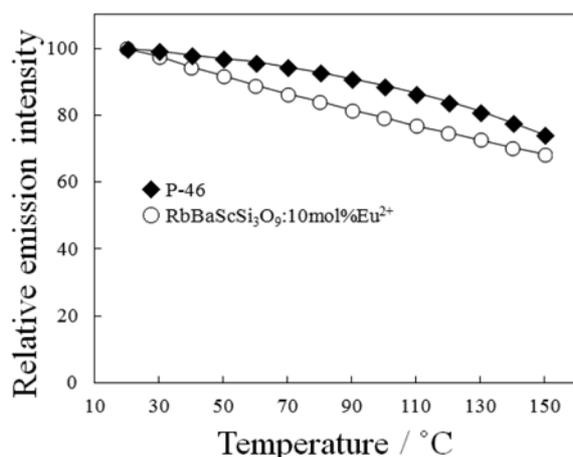


Fig. 5. The temperature dependence of the emission peak intensity of the $\text{RbBaScSi}_3\text{O}_9 : 10\text{mol}\%\text{Eu}^{2+}$ phosphor normalized with respect to the value at 20 °C.

transition from $4f^65d^1$ to $4f^7$ of Eu^{2+} , under excitation wavelength at 405 nm and 450 nm. There are no significant changes in the emission spectrum except the emission peak intensity under either excitation wavelength.

The dependence of the photoluminescence emission peak intensities on the Eu^{2+} concentrations in the $\text{RbBaScSi}_3\text{O}_9 : x\text{mol}\%\text{Eu}^{2+}$ phosphors under excitation wavelength at 405 nm is shown in Figure 4. The emission peak intensity increased with increasing Eu^{2+} concentration until it reached a highest value at $x = 10$ in the $\text{RbBaScSi}_3\text{O}_9 : x\text{mol}\%\text{Eu}^{2+}$ phosphors, where the relative emission peak intensity was about 13% of that of commercial YAG phosphor, and then decreased due to concentration quenching.

In addition, the temperature dependence of the $\text{RbBaScSi}_3\text{O}_9 : 10\text{mol}\%\text{Eu}^{2+}$ phosphor was investigated, which is important in the white LEDs application because it has great influence on the light output and color-rendering index. In addition, it is well known that

the photoluminescence emission peak intensity of phosphor generally decreases with an increase in the temperature due to thermal quenching effect. Fig. 5 shows the temperature dependence of the emission peak intensity of the $\text{RbBaScSi}_3\text{O}_9 : 10\text{mol}\%\text{Eu}^{2+}$ phosphor normalized with respect to the value at 20 °C. Result of the commercial YAG phosphor is also included for the comparison. With increasing the temperature up to 150 °C, the emission peak intensity of the $\text{RbBaScSi}_3\text{O}_9 : 10\text{mol}\%\text{Eu}^{2+}$ 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 $\text{RbBaScSi}_3\text{O}_9 : \text{Eu}^{2+}$ 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 Eu^{2+} ions by doping different cations in the Rb^+ and Ba^{2+} ions site.

Conclusions

A near-UV and blue light excitable bluish green-emitting $\text{RbBaScSi}_3\text{O}_9 : \text{Eu}^{2+}$ phosphors were synthesized by a conventional solid-state reaction method. These phosphors obtained in the present study adopt the monoclinic $\text{RbBaScSi}_3\text{O}_9$ structure in a single phase form with high crystallinity. The highest emission intensity was obtained for $\text{RbBaScSi}_3\text{O}_9 : 10\text{mol}\%\text{Eu}^{2+}$, and the relative emission intensity was 13% of the commercial YAG phosphor. The $\text{RbBaScSi}_3\text{O}_9 : \text{Eu}^{2+}$ has a relatively good thermal stability on the temperature quenching effect. Therefore, the $\text{RbBaScSi}_3\text{O}_9 : \text{Eu}^{2+}$ phosphor material is expected to be a suitable candidate as a green-emitting phosphor for use in the white LEDs.

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