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Elaboration of blue-emitting blue pigments based on Eu^{2+}/Co^{2+} codoped $BaMgAl_{10}O_{17}$ through the heterogeneous distribution of dopants

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Photoluminescence and coloring properties of Eu^{2+}/Co^{2+} codoped $BaMgAl_{10}O_{17}$ were investigated to produce inorganic blue-luminescent pigments. Two kinds of synthesis methods were employed for $BaMgAl_{10}O_{17}:Eu^{2+},Co^{2+}$ powders based on a conventional solid-state reaction and a newly developed precipitation method. Powder samples through the solid-state reaction exhibited blue photoluminescence from Eu^{2+}, which was quenched considerably by codoping with Co^{2+} due to the occurrence of a $Eu^{2+} \rightarrow Co^{2+}$ energy transfer. The precipitation method was then conceived to separate Eu^{2+} and Co^{2+} spatially in a $BaMgAl_{10}O_{17}$ particle. Powder samples through the precipitation method could be colored blue by optical absorption of Co^{2+} without degrading blue photoluminescence from Eu^{2+}. The inhomogeneous distribution of the Eu^{2+}/Co^{2+} dopants in the $BaMgAl_{10}O_{17}$ particles was instrumental to the suppression of the $Eu^{2+} \rightarrow Co^{2+}$ energy transfer.

1. Introduction

Conventional inorganic phosphor materials are generally colorless and their emission colors and intensities have been a major concern in relation to their application in lighting and display devices. It is known that the coloring of host crystals in phosphors leads to some improvements in the contrast of emitting light. For example, cathode-ray tube phosphors have been coated with pigments to absorb additional unnecessary emissions that may degrade the color purity [1,2]. Recent developments of flat panel displays and solid-state lighting require novel phosphor materials with high color purities. However, the current pigment-coated phosphors are not necessarily suitable for such applications because the presence of coating layers can disturb the excitation through a low-voltage electron beam or near ultraviolet (UV) light.

We have been working on colored phosphor materials, which are expected to be applied as novel luminescent pigments. Their practical or potential application includes paints, plastics, inks, building materials, and ceramic glazes [3]. Pigments may be considered as inorganic crystalline materials which absorb a certain range of wavelengths in the visible light region. Non-absorbed light is recognized as their crystal color reaching the eyes. Therefore, luminescent colors should be the same as the crystal colors when designing luminescent pigments. In our previous study, green-colored and green-luminescent phosphors could be obtained by using Y_2BaZnO_5 as a host material, Tb^{3+} as a luminescent rare-earth center, and Cu^{2+} as a coloring transition metal ion [4]. Initially, green emissions from Tb^{3+} were quenched significantly by codoping Cu^{2+} due to the occurrence of a $Tb^{3+} \rightarrow Cu^{2+}$ energy transfer in samples synthesized by a conventional solid-state reaction. We then conceived a modified synthesis process to suppress the luminescent quenching effectively. This success motivated us to elaborate blue-emitting blue pigments of high optical quality because of the commercial demand for making up three primary colors.

Eu^{2+}-activated $BaMgAl_{10}O_{17}$ (BAM:Eu), which is one of the most famous blue-emitting phosphors [5–7], has been widely used for fluorescence lamps and, more recently, for plasma display panels. Divalent Eu^{2+} ions can stably exist in host crystals containing alkaline earth ions and replace Ba^{2+} ions in the BAM:Eu crystal [7]. The intense blue emission from BAM:Eu is due to the allowed 5d → 4f transition of the Eu^{2+} ions located at lattice sites with high crystal-field strength and a high degree of covalency [8]. Interestingly, the substitution of Co^{2+} for Mg^{2+} in $BaMgAl_{10}O_{17}$ gives the crystal a blue color similarly to well-known $CoAl_2O_4$ pigments [9]. In the present work, we attempted to codope Eu^{2+} and Co^{2+} in $BaMgAl_{10}O_{17}$ with the expectation of obtaining a blue luminescent pigment. Two kinds of synthesis methods were examined based on

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the conventional solid-state reaction and a newly developed precipitation method. Optical properties of the resultant Eu^{2+}/Co^{2+} codoped $BaMgAl_{10}O_{17}$ (BAM:Eu,Co) were investigated by measuring photoluminescence and diffuse reflectance. The precipitation method was superior in that the blue emission from the Eu^{2+} ions was not disturbed by the blue coloring Co^{2+} ions due to their inhomogeneous distribution in BAM particles.

2. Experimental

2.1. Synthesis

In the conventional solid-state reaction method, $BaCO_3$ (99%, Wako Pure Chemical Industries, Co., Ltd., Japan), MgO (99%, Wako), Eu_2O_3 (99.9%, Wako), $Co(CH_3COO)_2 \cdot 4H_2O$ (99%, Wako), and alumina powders were used as starting materials. Total amounts of the materials were adjusted to give nearly 1 g of each final product. They were thoroughly mixed in pertinent compositions of $Ba_{1-m}Eu_mMg_{1-n}Co_nAl_{10}O_{17}$ ($0 \leq m \leq 0.14$ and $0 \leq n \leq 0.01$) using a mortar, placed in an alumina crucible, and heated at a temperature in the range 1300–1500 °C for 10 h in air to obtain "SS-BAM:Eu,Co" powders. The Eu^{2+} and Co^{2+} dopant levels are indicated by the atomic percentage (100m and 100n%) hereafter.

In the precipitation method, Co^{2+}-containing compounds were precipitated preferentially on BAM:Eu phosphor particles, which were synthesized by the solid-state reaction, through heterogeneous nucleation in aqueous solutions. The BAM:Eu powder of the $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ composition was synthesized first by the same solid-state reaction method as described above. $Co(CH_3COO)_2 \cdot 4H_2O$ in varying concentrations from 0.02 to 0.10 mM and urea ($(NH_2)_2CO$; 0.10 M) were dissolved in ion-exchanged water (100 mL). BAM:Eu powder (0.3 g) was added to the solution and kept at 80 °C under stirring for 1 h. The thermohydrolysis of urea was promoted at this temperature to generate OH^- and CO_3^{2-} ions as follows [10].

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \tag{1}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{2}$$

$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+ \tag{3}$$

Compounds containing Co^{2+} were then precipitated on the surface of the BAM:Eu particles, as judged by the change of the color of the powder. The resultant powders were collected, dried, and heated at 1500 °C for a relatively short period of 10 min in air to obtain "P-BAM:Eu,Co" powders.

2.2. Characterization

The phase identification of the powder samples was performed with an X-ray diffractometer using Cu Kα radiation (Bruker AXS, type D8-02). Diffuse reflectance spectra were recorded with a UV-visible spectrophotometer (JASCO, type V-670). Photoluminescence (PL) spectra were measured at room temperature with a spectrofluorophotometer (JASCO, type FP-6500) using a xenon lamp (150 W) as a light source. A filter was used to remove a second-order peak of the excitation light in the PL measurement. The thermal decomposition behavior of the Co^{2+}-containing compound was examined by thermogravimetry-differential thermal analysis (TG-DTA) with a Mac Science 2020S analyzer using a heating rate of 2 °C/min in flowing air.

3. Results and discussion

3.1. Samples from the solid-state reaction method

The heat-treatment temperature suitable for the solid-state reaction was examined first using the composition of $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ without codoping Co^{2+}. Fig. 1 shows X-ray diffraction (XRD) patterns of the samples heated at 1300, 1400, or 1500 °C for 10 h in air. At 1300 and 1400 °C, diffraction peaks due to the $BaMgAl_{10}O_{17}$ phase (ICDD 00-026-0163) are observed with some additional peaks coming from a $BaAl_2O_4$ impurity (ICDD 01-082-1349). At the higher temperature of 1500 °C, the sample is identified as the single $BaMgAl_{10}O_{17}$ phase. This temperature is typical of the synthesis of $BaMgAl_{10}O_{17}$ by the solid-state reaction [7]. In the present case, we did not use a reducing atmosphere such as H_2/N_2 because the high-temperature treatment in air promoted the reduction of Eu^{3+} in the starting material to Eu^{2+} in the final product, as evidenced by the PL measurement below.

Fig. 2 shows PL excitation ($\lambda_{em.} = 450$ nm) and emission spectra of the $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ samples, without codoping Co^{2+}, heated at 1300, 1400, or 1500 °C for 10 h in air. There appear two kinds of characteristic peaks in the PL emission spectra. One is a broad-band emission corresponding to the allowed 5d → 4f electronic transition of Eu^{2+} around 450 nm. The excitation for this emission is caused by electronic transitions between the ground state ($4f^7$) and the crystal-field split configuration ($4f^65d^1$) of Eu^{2+}. The other band is comprised of a group of several sharp emission peaks due to 4f → 4f electronic transitions ($^5D_0 \rightarrow {}^7F_0$, $^7F_1$, and $^7F_2$) of Eu^{3+} ($4f^6$) observed around 600 nm. In the sample heated at 1300 °C, the latter Eu^{3+} emissions are dominant and actually weak red luminescence could be observed under the irradiation with UV light. When the heating temperature is increased to 1400 °C, a strong blue-emission band due to Eu^{2+} appears in the PL emission spectra. This result suggests that Eu^{3+} can be reduced to Eu^{2+} at the higher temperature even in air. The sample heated at 1500 °C exhibits the strongest blue emission and simultaneously the weaker red emissions. The surviving red emissions are not a problem in the present case because they are absorbed by codoped Co^{2+}, as described later. From these experimental results, we judged that the heat-treatment

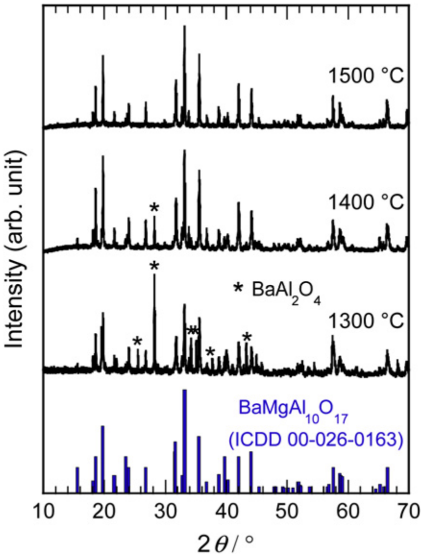

Fig. 1. XRD patterns of the samples with the $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ composition synthesized through the solid-state reaction by heating at 1300, 1400, or 1500 °C for 10 h in air. The ICDD of $BaMgAl_{10}O_{17}$ is also shown as a reference.

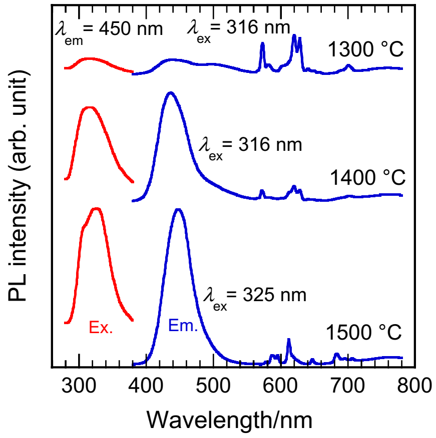

Fig. 2. PL excitation and emission spectra of the samples with the $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ composition synthesized through the solid-state reaction by heating at 1300, 1400, or 1500 °C for 10 h in air.

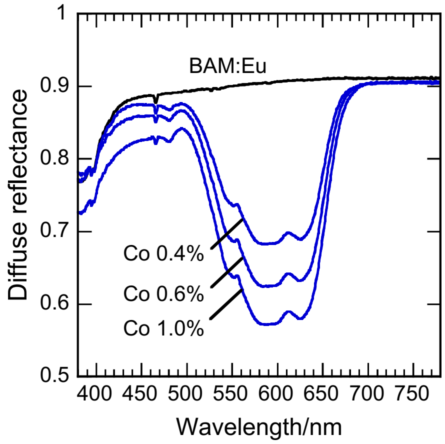

Fig. 4. Diffuse reflectance spectra of $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ co-doped with 0–1.0% of Co^{2+} against Mg^{2+}. The samples were synthesized by the solid-state reaction method.

temperature should be fixed at 1500 °C in the solid-state reaction, which was also adopted in the precipitation method.

Next the dependence of PL properties on the Eu^{2+} dopant concentration in BAM was examined in detail. This information is quite significant for adjusting intensities of blue emission and hues of blue color in the luminescent pigments. Fig. 3 shows PL excitation and emission spectra of the BAM:Eu (with Eu^{2+} concentrations of 4–14% against Ba^{2+}) samples prepared through the solid-state reaction by heating at 1500 °C. All the samples exhibit the broad emission band (5d → 4f in Eu^{2+}) centered at 450 nm and additionally the weaker sharp peaks around 610 nm ($^5D_0 \rightarrow {}^7F_2$ in Eu^{3+}) in the emission spectra. Since the Eu^{3+} emissions are relatively weak even with the higher concentrations (10 and 14%) of Eu^{3+} in the starting mixture, the Eu^{3+}-to-Eu^{2+} reduction is effectively promoted during the heat treatment at 1500 °C. The BAM:Eu sample with the Eu^{2+} concentration of 10% has the strongest blue emission as seen from Fig. 3. Note that all the samples described above are colorless and appear white due to light scattering.

Co^{2+} ions with the $3d^7$ electronic configuration were then incorporated into the Mg^{2+} sites of the BAM:Eu phosphor with the Eu^{2+} concentration fixed at 10% to obtain a blue crystal color. The samples (SS-BAM:Eu,Co) were synthesized under the same condition as that employed in the solid-state reaction for BAM:Eu. Fig. 4 shows diffuse reflectance spectra of the SS-BAM:Eu,Co samples, with Co^{2+} concentrations of 0–1% against Mg^{2+}, heated at 1500 °C for 10 h in air. The Co^{2+}-free sample maintains high reflectance more than 90% in the visible light region and is actually colorless. The crystal color becomes bluish by the Co^{2+}-doping due to appearance of absorption bands between 550 and 650 nm corresponding to the green–red region. These absorption bands due to Co^{2+} do not overlap with the emission bands due to Eu^{2+} shown in Fig. 3. The well-known $CoAl_2O_4$ blue pigment has similar optical absorptions [11] with the SS-BAM:Eu,Co samples. $CoAl_2O_4$ has the normal spinel structure where Co^{2+} ions are accommodated in the tetrahedral sites and Al^{3+} ions are in octahedral sites. The $3d^7$ Co^{2+} ion occupying the tetrahedral site exhibits triple absorption bands attributable to the spin-allowed $^4A_2(F) \rightarrow {}^4T_1(P)$ electronic transition. Therefore, the SS-BAM:Eu,Co samples have the similar Co^{2+}/Mg^{2+} sites in the spinel block of BAM to those present in the $CoAl_2O_4$ crystal lattice. It is also seen that the intensity of the triple absorption bands increases with increasing the Co-doping level to 0.4, 0.6, and 1.0%, resulting in the generation of the deeper blue color.

Unfortunately, the PL properties of the SS-BAM:Eu,Co samples underwent considerable degradation by the Co^{2+} codoping. Fig. 5 shows PL excitation and emission spectra of the SS-BAM:Eu,Co (with the Eu^{2+} concentration of 10% against Ba^{2+} and the Co^{2+} concentrations of 0–1% against Mg^{2+}) samples prepared by the

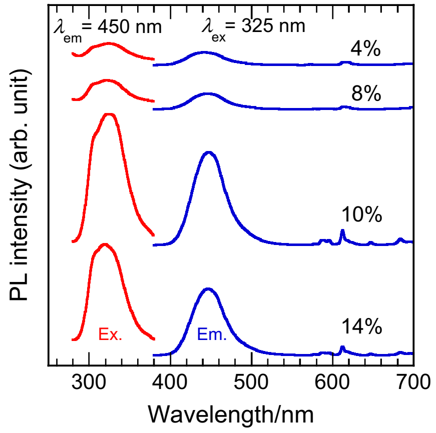

Fig. 3. PL excitation and emission spectra of $BaMgAl_{10}O_{17}$ doped with 4–14% of Eu^{2+} against Ba^{2+}. The samples were synthesized by the solid-state reaction method.

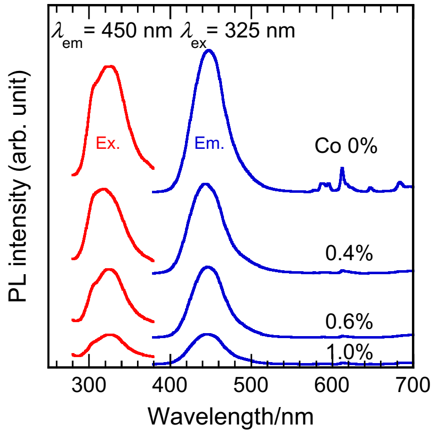

Fig. 5. PL excitation and emission spectra of $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ co-doped with 0–1.0% of Co^{2+} against Mg^{2+}. The samples were synthesized by the solid-state reaction method.

solid-state reaction by heating at 1500 °C. Obviously the intensity of the blue emission is decreased in accordance with the Co^{2+} concentration, indicating that the blue emission by Eu^{2+} and the blue coloring by Co^{2+} are in a trade-off relationship. Quantitative analysis was made by integrating the blue emission intensity at wavelengths between 380 and 550 nm and results are summarized in Table 1. The blue PL intensity is diminished to as low as 18.2% of the initial intensity with only 1% of the Co^{2+} codoping. A main reason for the observed luminescence quenching is supposed to be the occurrence of the energy transfer from the excited Eu^{2+} to the Co^{2+} ions, followed by non-radiative transitions in Co^{2+}. A similar phenomenon was observed in the Y_2BaZnO_5:Tb,Cu system which was developed as the green-colored, green-emitting phosphor [4]. It is suggested that a careful control of distribution of the Eu^{2+}/Co^{2+} dopants in the BAM particles may lead to effective suppression of the $Eu^{2+} \rightarrow Co^{2+}$ energy transfer and hence the luminescence quenching.

3.2. Samples from the precipitation method

In order to suppress the $Eu^{2+} \rightarrow Co^{2+}$ energy transfer, we conceived a core–shell-like particle structure where Eu^{2+} and Co^{2+} are separately distributed in cores and shells, respectively. The precipitation method was employed to obtain the core–shell-like structure through the formation of Co^{2+}-containing compounds on the surface of the BAM:Eu (with the Eu^{2+} concentration of 10% against Ba^{2+}) particles in the aqueous solution containing urea. The thermohydrolysis of urea is promoted at 80 °C, followed by the generation of OH^- and $CO_3{}^{2-}$ ions as mentioned above (Eqs. (2) and (3)). The solution is then supersaturated with Co^{2+}-containing compounds (counter anions would be OH^-, $CO_3{}^{2-}$, or CH_3COO^-) having the lower solubility than that of the starting $Co(CH_3COO)_2 \cdot 4H_2O$, leading to the heterogeneous nucleation on the surface of the BAM:Eu particles. Heat treatment of the precipitated BAM:Eu powders at 1500 °C results in the thermal decomposition of the Co^{2+}-containing compounds and the diffusion of the Co^{2+} ions to form the P-BAM:Eu,Co powders. The short period of heating (10 min) is indispensible to avoid further Co^{2+} diffusion inside the particles. The blue-colored powders thus obtained were optically characterized.

The degree of blue coloring was controlled by the concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in the aqueous solutions between 0.02 and 0.10 mM. Fig. 6 shows diffuse reflectance spectra of the P-BAM:Eu,Co samples. Triple absorption bands are observed, which are ascribed to the electronic transition in Co^{2+} located at the tetrahedral site. This result indicates that the Co^{2+} ions in the surface precipitates could be incorporated into the BAM lattice by heat treatment. The blue coloring is well controlled by the $Co(CH_3COO)_2 \cdot 4H_2O$ concentration as evidenced by a monotonical increase in the absorption intensity. With regard to the diffuse reflectance, there appears no significant difference in the blue coloring property between the SS-BAM:Eu,Co and the P-BAM:Eu,Co samples.

Table 1
The integrated PL intensity at wavelengths between 380 and 550 nm for the blue emission from the Eu^{2+}/Co^{2+} codoped $BaMgAl_{10}O_{17}$ powders synthesized by the solid-state reaction or the precipitation method. The Co^{2+} concentration for the precipitation method corresponds to that of $Co(CH_3COO)_2 \cdot 4H_2O$ in the aqueous solution.

Synthesis method	Co^{2+} concentration	Integrated PL intensity
Solid-state reaction	0%	100
Solid-state reaction	0.4%	58.1
Solid-state reaction	0.6%	41.9
Solid-state reaction	1.0%	18.2
Precipitation	0.02 mM	96.7
Precipitation	0.04 mM	83.3
Precipitation	0.10 mM	75.1

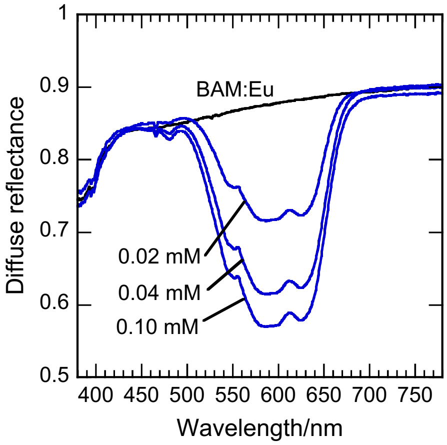

Fig. 6. Diffuse reflectance spectra of the Co^{2+}-codoped $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ samples prepared by the precipitation method with the $Co(CH_3COO)_2 \cdot 4H_2O$ concentrations of 0.02–0.10 mM.

To identify the Co^{2+}-containing compounds precipitated in the aqueous solution, another sample was prepared by keeping a high-concentration aqueous solution (0.10 M of $Co(CH_3COO)_2 \cdot 4H_2O$ and 1.0 M of urea) at 80 °C for 24 h. The thermal decomposition behavior of the precipitated sample was examined by TG-DTA performed in flowing air. As shown in Fig. 7, a first gradual weight loss is observed at temperatures between 50 and 200 °C due to the release of hydrated or adsorbed water. An abrupt weight loss then begins at 240 °C, accompanied by a sharp and intense exothermic peak. This is attributed to the decomposition reaction of the precipitated compounds. Fig. 8 compares XRD patterns of the precipitated sample and the heat-treated sample at 900 °C for 10 min. The pattern of the precipitated sample has no definite diffraction peaks and basically is an amorphous phase. Minor peaks appearing at $2\theta = 17.5°$ and 33.8° may be assigned to diffraction from a crystalline phase similar to $Co_{0.49}Cu_{0.51}(CO_3)_{0.43}(OH)_{1.14}$ (ICDD 00-048-0084). It has been reported that the cobalt carbonate hydroxide compounds are formed in the aqueous solutions containing urea [12,13], which may also be the present case. After calcination of the powder at 900 °C, diffraction peaks due to Co_3O_4 (ICDD 00-042-1467) appear in the pattern. Therefore the large

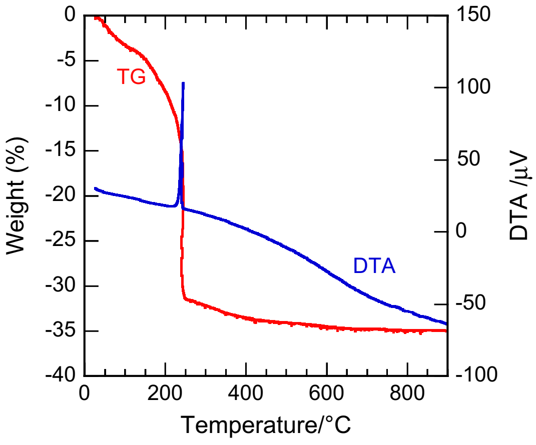

Fig. 7. TG-DTA curves for the precipitated Co^{2+}-containing compound.

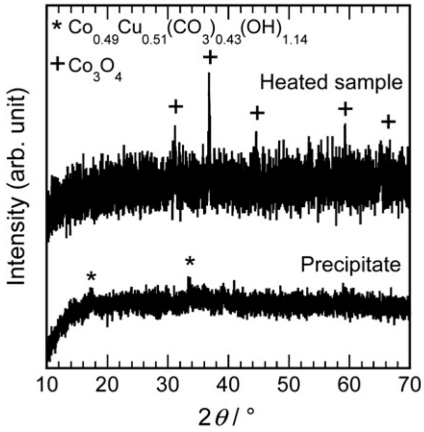

Fig. 8. XRD patterns of the precipitated Co^{2+}-containing compound and its heated product at 900 °C for 10 min.

weight loss caused by the decomposition reaction corresponds to the transformation from the cobalt carbonate hydroxide to Co_3O_4. From the TG data in Fig. 7, the weight loss of this transformation is approximately 25%. The composition of the precipitation is then tentatively estimated as $Co(CO_3)_{0.285}(OH)_{1.43}$. Since Co_3O_4 contains both Co^{2+} and Co^{3+} and is black in color, it would not be formed when $Co(CO_3)_{0.285}(OH)_{1.43}$ precipitated on the BAM:Eu was heated at 1500 °C. Instead, the Co^{2+} ions in $Co(CO_3)_{0.285}(OH)_{1.43}$ diffused into the BAM:Eu particles and incorporated into the lattice.

A difference in the PL properties is expected to appear between the SS-BAM:Eu,Co and the P-BAM:Eu,Co samples. Fig. 9 shows PL excitation and emission spectra of the P-BAM:Eu,Co samples. The spectral structure is almost the same as that observed for the SS-BAM:Eu,Co samples shown in Fig. 5, indicating that the P-BAM:Eu,Co samples also work well as blue-emitting phosphors. The emission intensity was integrated between 380 and 550 nm, as summarized in Table 1. Contrary to the SS-BAM:Eu,Co samples, the P-BAM:Eu,Co samples maintain the blue emission intensity even at a high degree of blue coloring. In the P-BAM:Eu,Co samples synthesized by the precipitation method, the coloring Co^{2+} ions are distributed only near the surface of the particles (shells). On the other hand, the blue-emitting Eu^{2+} ions are distributed mainly inside the particles (cores). This inhomogeneous distribution of the dopants suppresses the $Eu^{2+} \rightarrow Co^{2+}$ energy transfer, resulting in the higher blue emission intensity from the blue-colored phosphors.

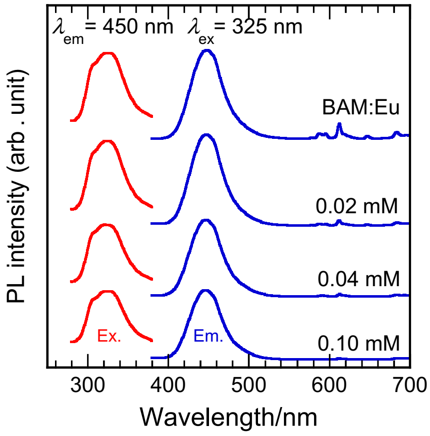

Fig. 9. PL excitation and emission spectra of the Co^{2+}-codoped $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ samples prepared by the precipitation method with the $Co(CH_3COO)_2 \cdot 4H_2O$ concentrations of 0.02–0.10 mM.

Table 2
The CIE chromaticity coordinate (x, y) of the blue emission from the Eu^{2+}/Co^{2+} codoped $BaMgAl_{10}O_{17}$ powders synthesized by the precipitation method. The Co^{2+} concentration corresponds to that of $Co(CH_3COO)_2 \cdot 4H_2O$ in the aqueous solution.

Co^{2+} concentration/mM	CIE chromaticity coordinate	
	x	y
0	0.1651	0.0542
0.02	0.1519	0.0412
0.04	0.1509	0.0404
0.10	0.1508	0.0391

It should be emphasized that the weaker red-emission peaks located at around 610 nm in the PL emission spectra shown in Figs. 5 and 9 are significantly decreased by blue-coloring the host crystals. This is due to the optical absorption between 550 and 650 nm coming from the electronic transitions in Co^{2+}. As a result, the color purity of the emissions could be improved by coloring the host crystal. The chromaticity (x, y) coordinates in the Commission Internationale d'Eclairage (CIE) diagram were calculated from the emission spectra and are summarized in Table 2 for the P-BAM:Eu,Co samples. In the (x, y) coordinates, moving away from the center of the diagram indicates approach to spectrally purer colors. Both the x and y values are decreased with increasing the Co^{2+} concentration, thereby indicating that the blue color purity can be enhanced in the P-BAM:Eu,Co samples by the codoping.

4. Conclusions

The luminescence and coloring properties of the Eu^{2+}/Co^{2+} codoped $BaMgAl_{10}O_{17}$ powders were examined, directed towards the creation of blue-colored and blue-luminescent phosphors. In a solid-state reaction, heating the starting mixture at 1500 °C led to the formation of a single-phase $BaMgAl_{10}O_{17}$ and the reduction of Eu^{3+} to be incorporated as Eu^{2+} in the host lattice. Although the Eu^{2+}-doped $BaMgAl_{10}O_{17}$ exhibited the strong blue emission due to the 5d → 4f transition of the Eu^{2+} ions, the codoped Co^{2+} ions quenched the emission due to $Eu^{2+} \rightarrow Co^{2+}$ energy transfer. In a precipitation method, cobalt carbonate hydroxide was precipitated on the Eu^{2+}-doped $BaMgAl_{10}O_{17}$ powders in the aqueous solution utilizing the thermohydrolysis of urea. Subsequent heating of the precipitated powders resulted in the incorporation of Co^{2+} in the host lattice, as evidenced by the blue coloring. The blue-colored Eu^{2+}/Co^{2+} codoped $BaMgAl_{10}O_{17}$ powders thus obtained also exhibited strong blue emissions upon irradiation with UV light. Our results demonstrate that the inorganic luminescent pigments can be produced by designing absorption and emission colors under the inhomogeneous distribution of the dopants.

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