Preparation of Phosphor Fine Particles for Mercury-Free Lamps by Using Liquid-Phase Synthesis Method

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Abstract

The liquid-phase synthesis method for preparing phosphor ($\text{Y}_2\text{O}_3\text{:Eu}$) fine particles, which was expected in the application for mercury-free fluorescent lamps, was investigated. The monodispersed sols as the precursor of phosphor fine particles were first synthesized by the co-precipitation method under different conditions in the aqueous-phase. The colloidal particles of precursor sols were spherical and almost uniform. The particle sizes of the sols were under $1\text{ }\mu\text{m}$, and the size distributions were sufficiently narrow. The metal element ratio of the sol particles could be controlled by adjusting the initial concentration of the synthesis solution. The as-prepared precursor sols were converted into well crystalline phosphor particles by heat-treatment over approximately 600°C . The phosphor particles showed emission spectra with a remarkable emission line of Eu^{3+} activator, and the emission intensity was sensitively influenced by the concentration of Eu^{3+} in the precursor solution. A morphological feature as the monodisperse of the phosphor particles remained after the heat-treatment.

Introduction

Conventional fluorescent lamps excel in energy efficiency and color-rendering properties compared with incandescent bulbs, but may introduce the environmental problem of waste disposal because they contain toxic mercury. This also causes an adverse load on the recycling system for fluorescent lamps. The recycling system requires troublesome processes to eliminate mercury from the tubes of lamps without releasing it into the atmosphere. In Japan, the recycling ratio of fluorescent lamps accounts for only approximately 10% of the production now. Globally, the use of mercury in manufactured products now also has severe restrictions imposed on it or the amount of the mercury content is limited. Therefore, the development of a lighting system without mercury is desired. Mercury-free fluorescent lamps are expected as one possibility for replacing conventional lamps for some instrumental usage. In spite of their safety for disposal, however, these lamps have inadequate energy efficiency and stability for emitting light. It is necessary to improve them

before using them for industrial production. The most critical difference between these two lamp systems (with and without mercury) is the specific emission wavelength of the UV radiation of their enclosed gas. Xenon gas is better suited for this replacement due to its UV-emitting property and chemical inertness, but its UV resonance line (wavelength = 147, 172 nm) is shorter than that of mercury vapor gas (184, 254 nm). The visible light from fluorescent lamps is emitted by the phosphor particles coated on the inner surface of the glass tubes of the lamps, and the phosphor particles are excited by the UV radiation of these enclosed gases. Since the fluorescence property of phosphor particles depends on the excitation wavelength, which is specifically equal to above the UV-emission wavelength in this case, every fluorescent lamp system requires the appropriate phosphor particles. The commercial products of phosphor particles are not tuned to a shorter excitation wavelength for the xenon resonance line, so the performance of visible light emission is insufficient. More improvement or new development for phosphor particles suited to excitation by the UV radiation of xenon gas is necessary in order to promote the practical application of mercury free fluorescent lamps. Recently, as one of the ap-

proaches for this purpose, colloidal precipitation techniques are being studied to apply them to preparing phosphor particles. These techniques generally have an advantage for controlling the composition, morphology, and size of the synthesized particles. Optimizing these particle characteristics is important for improving luminescent performance. In this case, some reports indicate that a uniform shape, such as a sphere, and a single micrometer size are suited for this shorter excitation wavelength, but it is difficult for the conventional combustion method to produce these micro-features [1,2]. These physical properties improve the packing density and screen performance of the lamps. In addition, these high-performance phosphors should also be optimized for applying to flat-plane displays such as PDP and FED [3].

The liquid phase synthesis methods are extensively studied to prepare the uniform fine particles as these methods excel at controlling the composition and morphology of particles as mentioned above [4,5]. B. Aiken et al. [6] and Kobayashi et al. [7] prepared spherical monodispersed fine particles of a rare-earth monocomponent from a homogeneous solution by one of the liquid-phase methods. In this study, multicomponent fine particles of Eu³⁺ doped Y oxide phosphor (Y₂O₃:Eu), which is expected to apply to the above inert gas fluorescent lamp systems, were synthesized from the homogenous solution by the liquid-phase method, and the effect of different reaction conditions to the morphological characteristics and the luminescent properties of prepared phosphor particles was investigated.

Experimental

1. Synthesis and Characterization of Phosphor Fine Particles

Red phosphor Y₂O₃:Eu particles were synthesized by liquid-phase precipitation in aqueous so-

lution and following heat-treatment in the air. The precursor solutions were prepared by dissolving YCl₃·6H₂O, EuCl₃·6H₂O, Y₂O₃, Eu₂O₃ (>99.9% purity) and urea (reagent grade) into 1.0 dm³ pure water. In this precipitation process, urea was used as a precipitant generator. The experimental conditions are summarized in Table 1. Precipitation reactions were carried out for 60 min at 77~97°C in a glass reactor with a reflux condenser. The synthesized precipitates were rinsed with distilled water, and then the solvent was replaced by 2-propanol to prevent granulation during drying. Heat-treatment was carried out after vacuum drying in order to convert them from basic carbonate into oxide [8]. The total metal ion concentration was varied from 1.0×10^{-2} to 4.0×10^{-2} mol/dm³, and the concentration ratio of Y to Eu in the precursor solution was kept constant [9.5]/[0.5]. The average particle size and the size distribution of the precipitates were calculated from the two hundred measurements for one sample photographed by transmission electron microscopy (TEM). The yields of Y and Eu as the precipitated particles were calculated from the rare-earth ion concentration in the residual and precursor solutions. The part of the dried particles was dissolved again in fixed amount of acid solution, and the ratio of Y to Eu in the particles was obtained by measuring the concentration ratio of Y to Eu in this solution. ICP emission spectrometry was used for measuring the metal element concentration in the solution. The emission spectra of the particles were measured with a spectrofluorophotometer (excitation λ : 254 nm).

Results and discussion

1. Structure and Fluorescence Spectrum of Prepared Particles

Figure 1 shows the TEM photographs of as-prepared sol-colloidal fine particles prepared by

Table 1 Experimental conditions and results

Experimental	Concentration (10^{-2} mol/dm ³)			Reaction temp. (°C)	Reaction time (min)	Precipitation ratio (%)	Precipitate shape	Volume mean diameter (μm)
	EuCl ₃ ·H ₂ O	YCl ₃ ·H ₂ O	Urea					
A-1	0.05	0.95	10	97	60	63	sphere	0.24
A-2	0.05	0.95	10	77	60	34	sphere	0.33
A-3	0.05	0.95	50	97	60	>99	sphere	0.28
A-4	0.05	0.95	50	77→97	20+40	>99	sphere	0.78
A-5	0.10	1.90	50	97	60	>99	sphere	0.33
A-6	0.20	3.80	50	97	60	89	agglomerate	—
A-7	0.20	3.80	100	97	60	>99	agglomerate	—
A-8	0.05	0.95	10	97	60	>99	sphere	0.32

Fig. 1 TEM photographs of the particles.

precipitation reaction for 60 minutes in the liquid-phase and the corresponding phosphor particles after heat-treatment at over 600°C. The shape of the as-prepared fine particles is spherical and monodispersed. The total metal element concentration of the precursor solution was lower than a certain threshold level to avoid agglomerating (or coagulating) the precipitate. These morphological properties did not remarkably change after heat-treatment. Then, the spherical and monodispersed phosphor $\text{Y}_2\text{O}_3\text{:Eu}$ fine particles can be obtained by this procedure. The shapes of the as-prepared precipitates and the mean diameters of the resultant spherical particles are summarized in Table 1, and a representative size distribution of the monodispersed particles is shown in Fig. 2. The coefficients of variance were $<10\%$ in most cases. The particle size of the spheres was the submicron order, and the width of the size distribution might be sufficiently narrow for utilization as phosphors. Figure 3 shows the X-ray diffraction patterns of the resultant particles, in which the lower is as-prepared and the upper is heat-treated. The after heat-treatment particles are well-crystallized single-phase $\text{Y}_2\text{O}_3\text{:Eu}$, while the as-prepared particles are amorphous. Figure 4a shows the emission

Fig. 2 The volume frequency distribution of A-3.

Fig. 3 X-ray diffraction patterns of A-3.

spectra of the as-prepared particles and the heat-treated particles. The after heat-treatment particles showed remarkable emission lines which correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} in the region of the 580~630 nm wavelength. The main emission peak was 611 nm, which signified red light emission. The above results show that this liquid phase synthetic method could be applied to prepare the spherical monodispersed $\text{Y}_2\text{O}_3\text{:Eu}$ phosphor fine particle.

2. Effect of Anionic Species

The effect of the anionic species (SO_4^{2-} , Cl^- , NO_3^-) in synthesizing fine particles of phosphor $\text{Y}_2\text{O}_3\text{:Eu}$ from a homogeneous solution in which Y_2O_3 and Eu_2O_3 were dissolved by adding acid; H_2SO_4 , HCl , or HNO_3 , was examined for the following reasons. Rare-earth oxides are generally used as starting materials of rare-earth sources because of their inexpensive costs compared with their other chemical compounds in commercial use, and they are usually dissolved in acid solution for using liquid-phase processing. In the recycling or refining processes of the materials containing rare-earths, metal elements are also

Fig. 4 Emission spectra of A-3 and B-1.

handled with the same sort of procedure using acids.

In this study, oxide reagents were dissolved in each acid solution shown in Table 2, and the solutions were adjusted to pH 2.3. Phosphor particles were synthesized under the same condition as A-3 in Table 1. The shapes of the obtained precipitates are different according to the anionic species in the precursor solutions. For the precursor solution containing NO_3^- or Cl^- , monodispersed spherical fine particles were obtained. Irregular-shaped precipitate was obtained from the solution containing SO_4^{2-} , however, as is shown in Fig. 5. The former spherical particles were both amorphous basic carbonate, and they were converted into the mono-phase $\text{Y}_2\text{O}_3:\text{Eu}$ by heat-treatment at a temperature over 600°C as mentioned above. The latter irregular-shaped precipitate obtained from the solution containing SO_4^{2-} showed crystal structure, however, and that is a different composition containing sulfate ion. In these preparations, it was also confirmed that the heat-treatment process did not remarkably influence their morphology or size. The monodispersed $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor

Fig. 5 TEM photograph of the particles prepared from the solutions including SO_4^{2-} .

fine particles prepared from the precursor solution containing NO_3^- or Cl^- showed the fluorescence spectra with a strong emission line at 611 nm, which were almost equal to the phosphor particles of A-3 shown in Fig. 4a. For the synthesis including SO_4^{2-} though, the different spectrum shown in Fig. 4b was measured, and the intensity of the emission lines was lower than the former phosphor particles. In the synthesis of the latter phosphor particles, sulfate ion contained in the as-prepared precipitate remained after heat-treatment, and the crystallinity after heat-treatment was lower than for the former. These deterioration factors seem to be the reason for lower luminescent performance.

The above results prove that the precursor solution containing SO_4^{2-} is inappropriate for this synthesis for obtaining fine phosphor particles, which are monodispersed spheres of mono-phase $\text{Y}_2\text{O}_3:\text{Eu}$, although sulfuric acid is inexpensive compared with other acids and may be suitable for the leaching process of phosphor particles in the recycling plants of fluorescent lamps.

3. Effect of Eu Doping Ratio

The effect of the Eu^{3+} doping ratio on the phosphor particles was investigated in the synthesis from the precursor solution containing Cl^- , in which the monodispersed spherical $\text{Y}_2\text{O}_3:\text{Eu}$ particles were obtained. The precursor solutions with different ratios of Y to Eu with a total concentration equal to A-3 in Table 1 were prepared for the synthesis. Precipitation reactions were also carried out under the same conditions as A-3. Monodispersed spherical fine particles were obtained from all ratios of Y to Eu in this synthesis. Meanwhile, the particle size decreased with the in-

Table 2 Conditions of precursor solution

Experimental	Concentration (10^{-3}mol/dm^3)			Additives for pH adjustment	Initial pH
	Y_2O_3	Eu_2O_3	Urea		
B-1	4.75	2.50	500	H_2SO_4	2.3
B-2	4.75	2.50	500	HCl	2.3
B-3	4.75	2.50	500	HNO_3	2.3

Fig. 6 The relationship between Eu^{3+} doping ratio in prepared particles and Eu^{3+} concentration ratio in precursor solution.

crease in the ratio of Eu^{3+} . The relationship between the concentration ratio of rare-earths in the precursor solution and the component ratio in the prepared particles is shown in Fig. 6. This result indicates that the Eu^{3+} doping ratio of phosphor particle can be accurately controlled by the concentrations of the component ions in the precursor solution.

The phosphor particles which were converted from as-prepared particles by heat-treatment at a temperature over 600°C indicated a red light emission that was almost equal to that of A-3 shown in Fig. 4. Figure 7 shows the relationship between the relative intensities of the emission line at 611 nm and concentrations of Eu^{3+} in the resultant phosphor particles. The emission inten-

Fig. 7 The relationship between emission intensity and Eu^{3+} concentration in prepared particles.

sity was changed with the ratio of Eu^{3+} and it became the maximum in the case of 5 mol %. This ratio corresponds with that of the commercial product, which is designed to derive the maximum efficiency of light emission, and the relationship between the doping ratio and emission intensity agrees with other reports of recent work [1]. The brightness of the phosphor particles tuned to suitable properties, such as the morphology, size, and Eu^{3+} doping rate, by this method is about 20% stronger than that of the same composite phosphor particles prepared by the conventional combustion method.

Conclusion

The fine particles of Eu^{3+} doped Y oxide phosphor ($\text{Y}_2\text{O}_3:\text{Eu}$), which are expected to be applied to mercury-free inert gas fluorescent lamps, were synthesized from the homogenous solution by the liquid-phase method, and the effect of the various reactions to the morphological characteristics and luminescent properties of the prepared phosphor particles was investigated. Monodispersed spherical $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor fine particles were prepared from the precursor solution containing NO_3^- or Cl^- , but irregular-shaped precipitate was obtained from the solution containing SO_4^{2-} . The Eu^{3+} doping rate can be accurately controlled by the initial concentration of precursor solution. These characteristics should improve screen brightness for mercury-free lamp applications.

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