

## Liquid-Phase Synthesis of Precursor Particles of Eu-Doped Phosphor for Mercury-free Lamps

Yoshihiro Nishisu, Mikio Kobayashi and Toshiyuki Akiya

Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology,

16-1 Onogawa, Tsukuba, Ibaraki 305, Japan

Fax: 81-29-861-8459, e-mail: n-nishisu@aist.go.jp

Faculty of Engineering, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275, Japan

Fax: 81-474-78-0329, e-mail: tos-akiya@aist.go.jp

The liquid-phase synthesis method for preparing Eu-doped phosphor ( $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$ ) precursor particles, which expected in the application of the mercury-free fluorescent lamps, was investigated. The dispersed precursor particles were synthesized under carefully controlled conditions in liquid-phase. The sizes of particles were almost uniform, and they were under 100nm. The metal element ratio of the precursor particles could be controlled by adjusting the initial concentration of the synthesis solutions. The precursors were converted into the  $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$  phosphor by heat-treatment at a lower temperature compared to the conventional premixed combustion method. The phosphor particles showed emission spectrum of Eu ions activator, and the fluorescence intensity was influenced by the crystallinity and composition of the substrate.

Key words: liquid-phase synthesis method,  $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$ , phosphor, particle

### 1. INTRODUCTION

Conventional fluorescent lamps excel in energy efficiency and color-rendering properties compared with incandescent bulbs, but may introduce an environmental problem of waste disposal because they contain toxic mercury. This also causes an adverse load on 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 account 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, 172nm) is shorter than that of mercury vapor gas (184, 254nm). The visible light from fluorescent lamps is emitted by 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. Additionally, faster rate of luminance degradation on conventional phosphor particles under exposure with higher energy UV emission of xenon resonance line is critical problem for long lifetime applications such as fluorescent lamp compared to lower energy UV emission of mercury system. Especially, durability of current popular blue phosphor  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  is poorer than that of other color phosphors. More improvement or new development for phosphor particles suited to excitation by the UV radiation of xenon gas is necessary in order to promote practical application of mercury free fluorescent lamps. Recently, as one of the approaches for this purpose, the synthesis processes of phosphor particles require advanced control on composition and particle morphology to increase the optical and structural ability of them. Additionally, optimization of the diameter and size distribution of the phosphor particles is also the factor that influences luminescent performance. In this case, some reports indicate that a uniform shape and a size less than single micrometer 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 [4, 5]. In this study, liquid-phase synthesis method was applied for preparing

the precursor particles of Eu-doped alkaline earth silicate phosphor particles  $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$  [6, 7], that is considered as one possibility for replacing the conventional blue phosphor for the xenon lamp system.  $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$  has higher stability on durable property for luminance degradation [7] but its luminance performance is desired to be advanced by optimizing its chemical and physical properties mentioned above. It is expected that liquid phase synthesis methods would control the micro features on composition, uniformity, crystallinity and morphological characteristics for optimizing the phosphor particle. In this study, the precursor particles of  $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$  were prepared, and the characteristics of their converted phosphor particles were investigated.

## 2. EXPERIMENTAL

### 2.1 Materials

Sodium metasilicate nonahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , >98%, Wako Pure Chemical), water glass ( $\text{SiO}_2/\text{Na}_2\text{O} = 2.06\text{--}2.31$ , first grade, Wako Pure Chemical), calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 99.9%, Wako Pure Chemical), magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.5%, Wako Pure Chemical), europium nitrate hexahydrate ( $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.95%, Kanto Chemical), calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 99.9%, Wako Pure Chemical), magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 99.9%, Wako Pure Chemical) and europium chloride hexahydrate ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ , 99.9%, Wako Pure Chemical) were used as starting materials without further purification.

### 2.2 Preparation of precursor particles

The experimental conditions are summarized in Table I. These values were established by the estimate of Ca solubility and the reference [7], which reported that Si-rich precursor beyond stoichiometry prevent the formation of impurities on a combustion process. The precursor particles of Eu-doped alkaline earth silicate phosphor  $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$  were synthesized by the liquid-phase co-precipitation method through the following steps. Two set of Stock solutions, (A) and (B) were prepared for the precipitation reaction; (A)  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  or water glass were dissolved into  $10\text{cm}^3$  pure water, (B) metal chlorides or nitrates of alkaline earth and rare-earth components were dissolved into  $95\text{cm}^3$  pure water. Precipitation reactions were carried out by mixing solution A and B, and the reactions were continued for 60 minutes at a room temperature with agitation using a magnetic stirrer. The yielded precipitates were rinsed with ethanol, and then the solvent was replaced by 2-propanol to prevent granulation during drying. The precursor particles were fully dried by a vacuum desiccator.

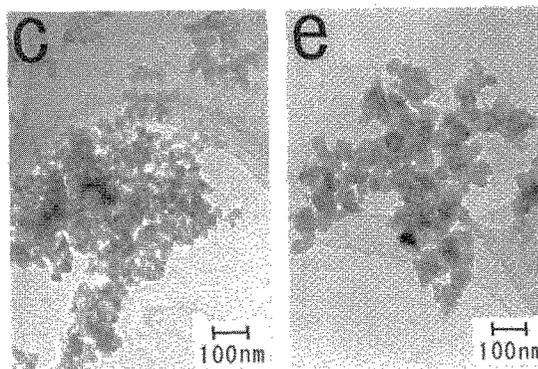


Fig.1 TEM photographs of the particles synthesized by liquid-phase precipitation from the stock solution containing; (c)  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , (e) water glass, as a Si source.

### 2.3 Heat-treatment and analysis

Heat-treatment was carried out for dried precursor particles under reducing atmosphere ( $\text{Ar}/\text{H}_2$ ) in order to reduce Eu ions from trivalence to bivalence, and to convert precursor particles from amorphous composite into the well crystalline alkaline earth silicate phosphor  $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$  [7]. The particles shapes were observed with transmission electron microscopy (TEM). The ratio of elements in the particles was measured by energy dispersive X-ray analysis (EDAX). X-ray diffraction (XRD) patterns were obtained for the dried precipitate as well as for the heat-treated particles. The emission spectra of the obtained phosphor particles were measured with a spectrofluorophotometer.

## 3. RESULTS AND DISCUSSION

### 3.1 Shape and composition of precipitate

Figure 1 shows the TEM photographs of as-prepared sol-colloidal fine particles prepared by precipitation reaction for 60 minutes in the liquid-phase. The particles in the sol were homogenous in shape and size. The size of the primary particles was less than 100nm. On the result of energy dispersive X-ray analysis (EDAX) for the several locations of the beam spot on the bright fields of TEM, the ratio of elements in the sol-particles was almost constant. The Average values of the elemental ratio on EDAX for each sample are summarized in Table II. In the case of using  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  as a Si source, these ratios are almost equal to the concentration ratios of corresponding components in the stock solutions. But in the case of water glass, Ca content value was far less than the target value. It was guess that one reason of this deficiency is lower alkalinity than the case of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  because of the difference in the ratio of Si/Na in the stock solution. The precipitation rate of Ca ions is sensitive

Table I Experimental conditions

No.	Si source	(Ca, Mg, Eu) source	Concentration ( $\text{mol}/\text{dm}^3$ )				Precipitation Time (min)	heat-treatment	
			Si	Ca	Mg	Eu		Temp. ( $^{\circ}\text{C}$ )	atmosphere
a	$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	Nitrate	0.14	7.4E-02	6.9E-02	1.4E-03	60	1200	$\text{Ar}+2\%\text{H}_2$
b	$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	Nitrate	0.14	6.6E-02	6.2E-02	1.2E-03	60	1200	$\text{Ar}+2%\text{H}_2$
c	$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	Chloride	0.14	7.4E-02	6.9E-02	1.4E-03	60	1200	$\text{Ar}+2%\text{H}_2$
d	Water glass	Nitrate	0.14	7.4E-02	6.9E-02	1.4E-03	60	1200	$\text{Ar}+2%\text{H}_2$
e	Water glass	Chloride	0.14	7.4E-02	6.9E-02	1.4E-03	60	1200	$\text{Ar}+2%\text{H}_2$

Table II Result of EDAX (TEM) analysis

No.	Atom %			
	Ca	Mg	Si	Eu
a	23	23	54	0.6
b	24	21	55	0.5
c	22	24	53	0.4
d	8	21	72	0.4
e	8	21	71	0.4

to alkalinity of the reacting solution since its solubility for aqueous solution is far higher than other metal elements in this condition. Meanwhile, the Eu ratio in the particles was almost constant and slightly less than its concentration ratio in the stock solution, however its EDAX value is too small to estimate precisely. However, these Eu doping ratios are within the aimed range, which is 0.4 to 0.7. The Eu ion is the activator as a luminescence centre, and its amount for the host crystal severely influenced to the brightness of light emission of phosphor materials.

These results of TEM observation and EDAX measurement indicate that the synthesized precursor particles were homogenous in composition and morphological feature. And, it is possible to control the elemental ratio of these precursor particles by the initial concentration in the stock solution.

### 3.2 Heat-treatment and structure of particles

Figure 2 shows TG and DTA curves of as-prepared precursor particles (sample c). The weight of the particles continued to decrease up to approximately 900 °C and the total weight loss was approximately 30% of the original. And a remarkable exothermic peak was observed on DTA curves at the range of 900~950 °C. It is guess that the as-prepared particles contain a hydroxyl group derived from the hydrolysis of silicate and metal cations.

Figure 3 shows X-ray diffraction patterns of the particles before and after heat-treatment. The as-prepared particles are amorphous and this amorphous phase predominantly remained after heat-treatment until 800 °C. However, by heat-treatment over 950 °C,

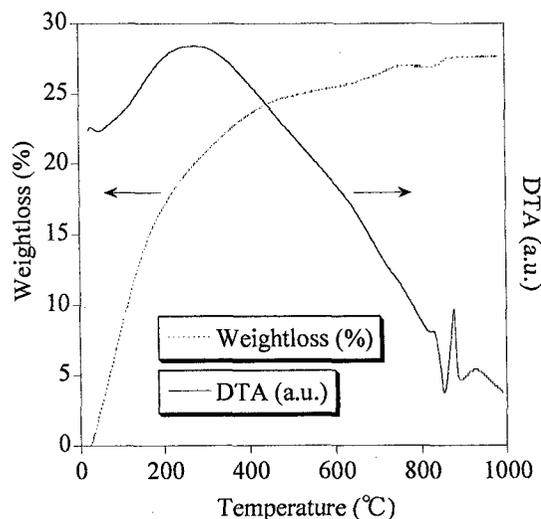


Fig 2 TG/DTA curves of as-prepared particles (c) synthesized by liquid-phase precipitation.

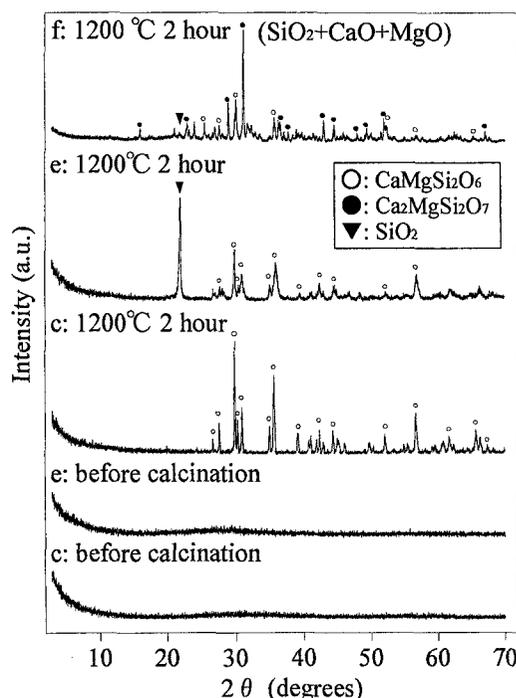


Fig 3 XRD pattern of particles (A01); (a) as prepared, (b) after heat-treatment at 800 °C, (c) after heat-treatment at 1200 °C, and (d) a comparative sample produced from mixture of corresponding

particles were converted into well-crystallized almost single-phase alkaline earth silicate ( $\text{CaMgSi}_2\text{O}_6$ ) in case of using  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  as a Si source. Figure 3 (f) shows a pattern for the comparative sample synthesized from the mixture of corresponding oxides powders by treating only a combustion process at 1200 °C. This pattern indicates that the sample include not only a  $\text{CaMgSi}_2\text{O}_6$  but also impurities such as  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  and a high-temperature phase of  $\text{SiO}_2$ . These results mean that as-prepared precursor particles may promise higher reactivity and homogeneity in the composition compared with the solid-stated mixture. Though, an exception was caused in the case of using the water glass as a Si source, which prominently yielded a high-temperature phase of  $\text{SiO}_2$  by a heat-treatment over approximately 1200 °C.

The crystallinity of aimed phosphor particles was increased with heat-treating temperature up to 1300 °C, but undesirable aggregation was enhanced at a higher temperature closed to its melting point (1391 °C) [8]. Therefore, the properties of reactivity and crystallinity at a lower temperature like these precursors are very important, because phosphor particles must be well dispersed in order to apply to the lamp or display applications.

### 3.3 Luminescent property of phosphor particles

Figure 4 shows the emission spectra of phosphor particles prepared by heat-treating the precursor precipitates at 1200 °C in a reducing atmosphere. The phosphor particles showed a remarkable emission peak, which correspond to the  $4f^7 \rightarrow 4f^6 5d$  transition of the  $\text{Eu}^{2+}$  in the range of a 400~500nm wavelength. The main emission peak located at 446nm, which implies a

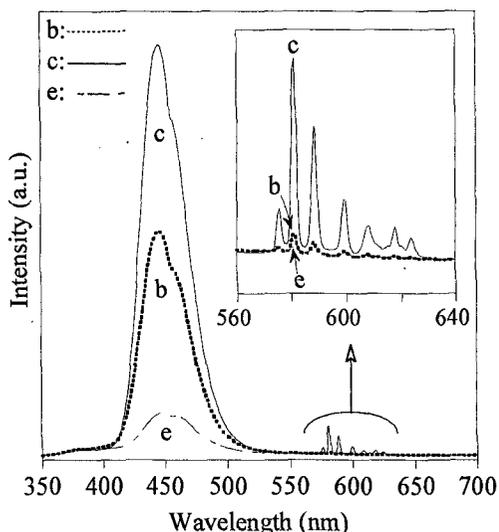
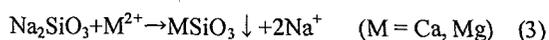
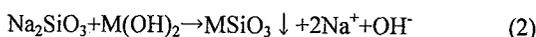


Fig.4 Emission spectra of particles heat-treated at 1200°C in reducing atmosphere (2% H<sub>2</sub> in Ar gas).

blue-light emission. However, the phosphor particles heat-treated in the air showed only a weak emission which correspond to the  $^5D_0 \rightarrow ^7F_2$  transition of the Eu<sup>3+</sup> in the region of a 580~630nm wavelength. This emission means a red-light emission. The latter emission indicates that a part of the Eu<sup>3+</sup> ions, derived from the starting material, remained after the heat-treatment, although most part of them were considered to be doped as the Eu<sup>2+</sup> at correct sites of the crystal lattice of the CaMgSi<sub>2</sub>O<sub>6</sub>. The insufficiency of the reduction mentioned above has not reported in other works [6-8], and the reason of this difference is discussed below.

On a EADX (SEM) measurement, Na was detected (Table III), and this contamination is considered to be the prime factor of the existence of the Eu<sup>3+</sup> in spite of a reducing atmosphere. It is possible that the doped Eu<sup>2+</sup> is substituted for Ca<sup>2+</sup> site in CaMgSi<sub>2</sub>O<sub>6</sub> [6], but ion radii of Eu<sup>3+</sup> (0.0947nm) and Na<sup>2+</sup> (0.102nm) are closer to Ca<sup>2+</sup> (0.100nm) than Eu<sup>2+</sup> (0.113nm). Therefore, the role of Na<sup>2+</sup> as charge compensator could facilitate a co-doping of the Eu<sup>3+</sup>. However, the results of EADX (SEM) summarized Table III indicate that amount of Na content was not so much compared to the original source in the stock solution. The most part of the Na ions remained supernatant after precipitation reaction.

The prospective reaction of alkaline earth elements and silicon in the liquid-phase is shown in below equations.



The Na<sup>+</sup> is replaced by other metal ions during precipitation reaction in the liquid-phase. But actually, it is considered that co-precipitation occurred in this reaction process and the Na<sup>+</sup> was contaminated in the precipitate. The phosphor particles were needed to eliminate the Na content by the additional process such as a further heat-treatment, or an ion exchange in the

Table III Result of EDAX (SEM) analysis

elements	Atom% (as prepared)			
	spot 1	Spot 2	spot 3	Average
Na	4.9	5.5	5.8	5.4
Mg	28	27	28	28
Si	48	48	47	48
Ca	19	19	19	19
Eu	0.4	0.2	0.4	0.3

elements	Atom% (after heat-treatment at 1200°C)			
	spot 1	Spot 2	spot 3	Average
Na	1.2	0.5	1.7	1.1
Mg	27	27	26	27
Si	46	46	45	46
Ca	26	23	25	25
Eu	0.6	0.6	0.4	0.5

liquid phase before the synthesis, in order to achieve an advance luminous performance.

These results show that there is a greater possibility to apply this liquid phase synthesis method to the preparation of uniform Eu-doped alkaline earth silicate phosphor CaMgSi<sub>2</sub>O<sub>6</sub>:Eu<sup>2+</sup>.

#### 4. CONCLUSION

The liquid-phase synthesis method for the preparation of the precursor particles of Eu-doped alkaline earth silicate phosphor CaMgSi<sub>2</sub>O<sub>6</sub>:Eu<sup>2+</sup>, which are expected to be applied to mercury-free fluorescent lamps, was investigated. The synthesized precursor sol-particles were almost uniform, and their sizes were under 100nm. The metal elements ratio of the sol particles was controlled by the initial concentration of the stock solution. This precursor particles were converted into CaMgSi<sub>2</sub>O<sub>6</sub>:Eu<sup>2+</sup> by a heat-treatment over approximately 900°C. The obtained phosphor particles indicated blue light emission of the Eu<sup>2+</sup>. This phosphor contained a small amount of Na<sup>+</sup>, which caused a Eu<sup>3+</sup> co-doping with the slight red light emission.

This research was granted a research fund from Science and Technology Agent (project No. 12317).

#### REFERENCES

- [1] Y. C. Kang, H. S. Roh and H. D. Park, *Ceramics International*, Vol. 29, 41-47 (2003).
- [2] S. Oshio, K. Kitamura, T. Shigeta, T. Matsuoka, S. Tanaka and H. Kobayashi, *J. Electrochem. Soc.*, 146, 392-399 (1999).
- [3] S. H. Cho, J. S. Yoo and J. D. Lee, *J. Electrochem. Soc.*, 145, 1017-1019 (1998).
- [4] T. Sugimoto, *Advance in Colloid and Interface Science*, 28, 65-108 (1987).
- [5] P. Sangmoon, C. L. Benjamin, K. A. Douglas, B. P. Jeffrey, W. F. John, R. A. Thomas and H. S. Gregoy, *Science*, 297, 65 (2002).
- [6] K. Yamamoto, H. Nakabayashi, Y. Kotera and A. Ueno, *J. Electrochem. Soc.*, 133, 657-660 (1986).
- [7] T. Kunimoto, R. Yoshimatsu, K. Ohmi, S. Tanaka and H. Kobayashi, *IEICE Transactions on Electronics*, E85C, 1888-1894 (2002).
- [8] Y. Nishisu and M. Kobayasi, "Proceeding of The 7th International Symposia on East Asian Resources Recycling Technology", 461-464 (2003).