ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 898–902

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Preparation of Eu-doped alkaline-earth silicate phosphor particles by using liquid-phase synthesis method

Yoshihiro Nishisu [a,*], Mikio Kobayashi [a], Hitoshi Ohya [a], Toshiyuki Akiya [b]

[a] *Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba 305-8569, Japan*

[b] *Faculty of Engineering, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino 275-0023, Japan*

Received 2 August 2004; received in revised form 18 December 2004; accepted 13 January 2005
Available online 17 June 2005

Abstract

The liquid-phase synthesis method for preparing Eu-doped alkaline-earth silicate phosphor particles, which is expected to be applied for lighting apparatuses, such as mercury-free fluorescent lamps and flat-plane displays, such as PDP, was investigated. The sols, as the phosphor particle precursors, were synthesized by sol–gel processes under various conditions in the liquid-phase. The particle sizes of the sols were almost uniform, and they were under 200 nm. The metal elements ratio of the sol-particles could be controlled by the initial concentration of the synthesis solutions. The sol-particles were converted from an amorphous composition into an Eu-doped alkaline-earth silicate phosphor by heat-treatment at a lower temperature compared to the conventional premixed combustion method. The crystallinity of the phosphor particles was increased with a heat-treating temperature up to 1300 °C, but an undesirable aggregation was enhanced at a higher temperature closer to its melting point (1391 °C). Therefore, these properties of reactivity and crystallinity at a lower temperature, as the precursors indicated, are very important characteristics for dispersibility because phosphor particles must be well dispersed in order to apply them to the lamp and display applications. The phosphor particles showed spectra with an emission peak of Eu^{2+} at a 446 nm wavelength and the emission intensity was sensitive to the composition.

Keywords: Eu-doped alkaline-earth silicate; Phosphor; Particles; Liquid-phase synthesis

1. Introduction

Alkaline-earth silicate ($CaMgSi_2O_6$) has been expected to be applied to the host subtracts of the fluorescence materials because of its chemical and structural stability. Recently, several research projects have been reported on preparing it with modifications of its particular characteristics through using novel chemical synthesis methods in the liquid phase or solid-state reactions. Eu-doped alkaline-earth silicate phosphor particles ($CaMgSi_2O_6$:Eu^{2+}) [1,2] are considered as one possibility for replacing the conventional blue phosphor for the xenon lamp system. The commercial products of blue phosphor particles are not tuned to a shorter excitation wavelength for the xenon resonance line compared with mercury, so the luminance degradation under exposure with higher energy VUV emission of xenon gas is a critical problem for long lifetime applications, such as fluorescent lamps. $CaMgSi_2O_6$:Eu^{2+} has higher stability on durable property for luminance degradation [2] but its luminance performance is desired to be advanced by optimizing its chemical and physical properties. The synthesis processes of phosphor particles require advanced control on composition and particle morphology to increase their optical and structural ability. Additionally, optimization of the diameter and size distribution of the phosphor particles is also a factor that influences luminescent performance [3]. Some reports indicate that a uniform shape and size less than a single micrometer are suited for this shorter excitation wavelength [4,5], but it is difficult for the conventional combustion method to

---

* Corresponding author. Tel.: +81 29 861 8487; fax: +81 29 861 8459.
E-mail address: n-nishisu@aist.go.jp (Y. Nishisu).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.01.101

produce these micro-features. 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 particles composition and morphology [6,7]. Therefore, it is expected that the liquid-phase synthesis methods would control the micro-features on composition, uniformity, crystallinity, and morphological characteristics for optimizing phosphor particles. In this study, the liquid-phase synthesis method was applied for preparing fine particles of $CaMgSi_2O_6:Eu^{2+}$.

2. Experimental

The particles of $CaMgSi_2O_6:Eu^{2+}$ were synthesized with the liquid-phase co-precipitation process and the following heat-treatment in a reducing atmosphere. $Si(OC_2H_5)_4$ (>95%, Wako Pure Chemical), SiO_2 (99.9%, Wako Pure Chemical), $Ca(NO_3)_2{\cdot}4H_2O$ (99.9%, Wako Pure Chemical), $Mg(NO_3)_2{\cdot}6H_2O$ (99.5%, Wako Pure Chemical), $Eu(NO_3)_3{\cdot}6H_2O$ (99.95%, Kanto Chemical), $CaCl_2{\cdot}2H_2O$ (99.9%, Wako Pure Chemical), $MgCl_2{\cdot}6H_2O$ (99.9%, Wako Pure Chemical), and $EuCl_3{\cdot}6H_2O$ (99.9%, Wako Pure Chemical) were used as starting materials without further purification. At first, the stock solutions were prepared by suspending Si sources and dissolving metal chlorides or nitrates of alkaline earth and rare-earth into 0.20 dm^3 ethanol or water. The concentration conditions are summarized in Table 1. These chemical amounts were not settled stoichiometry because it was reported that Si-rich precursors prevent the formation of impurities in the combustion process [2]. The precipitation reactions were started by adding the acid catalyst, e.g., hydrochloric acid, or the bass catalyst, e.g., aqueous ammonia, into the stock solutions. The reactions were carried out for 48 h at room temperature with agitation using a magnetic stirrer. The precipitates were rinsed with ethanol, and then the solvent was replaced by 2-propanol to prevent granulation during vacuum drying in case of using the base catalyst. Meanwhile, the produced gels were dried directly in an oven at 200 °C in case of using the acid catalyst. Heat-treatment was carried out for as-prepared precursor particles under a reducing atmosphere (Ar/H_2) in order to reduce Eu ions from trivalence to bivalence, and to convert precursor particles from amorphous composite into crystalline phosphor ($CaMgSi_2O_6:Eu^{2+}$) particles [7]. The particles shapes were observed with a transmission electron microscope (TEM) and a scanning electron microscope (SEM). The ratio of Si and metallic elements in the particles was measured by energy dispersive X-ray analysis (EDAX). X-ray diffraction (XRD) patterns were obtained for the as-prepared precursor particles as well as for the heat-treated phosphor particles. The emission spectra of the phosphor particles were measured with a spectrofluorophotometer.

3. Results and discussion

3.1. As-prepared precursor particles

Fig. 1 shows the TEM photographs of as-prepared sol-colloidal fine particles prepared by precipitation reaction using the base catalyst. The sol-particles were homogenous in shape and size. The size of primary particles was less than 200 nm. There is no obvious difference in the morphology and body colors between the nitrate and chloride as starting sources. However, solidified gels are obtained by preparation with the acid catalyst. When using citric acid as the catalyst, the dried gels were foamy and fragile for pulverization with a mortar and pestle. This effect was due to the decomposition reaction of the citric ion within the Si network in the dried gel, which caused the weakening of polymer bonds and foaming of gel during the drying process in the 200 °C oven. From the synthesis with the SiO_2 as the Si source, cloudy slurried gel was obtained, as the SiO_2 was not dissolved in the solution.

On energy dispersive X-ray analysis for the well-dispersed as-prepared particles obtained by base catalyst synthesis, the ratio of components in sol-particles was almost constant for the several beam spot locations within the TEM bright field of each sample. The average values of elemental ratio measured by EDAX for each sample are summarized in the inlet table in Fig. 2. These ratios are almost equal to those of each component concentration in the stock solutions. Fig. 2

Table 1
Experimental conditions and composites of resultant products

No.	Si source	Metal elements	Concentration ($\times 10^{-2}$ mol/dm^3)			Catalyst	Eu/Ca (%)	Produced compound	Body color of product
			Si	Mg	Ca				
A00	$Si(OC_2H_5)_4$	Nitrate	10	4.5	4.8	Base	3.0	Diopside	Grayish
A01	$Si(OC_2H_5)_4$	Chloride	10	4.5	4.8	Base	2.0	Diopside	White
A02	$Si(OC_2H_5)_4$	Chloride	10	4.5	4.8	Base	3.0	Diopside	White
A03	$Si(OC_2H_5)_4$	Chloride	10	4.5	4.8	Base	4.0	Diopside	White
B00	$Si(OC_2H_5)_4$	Nitrate	10	4.5	4.5	Acid	3.0	Diopside	Grayish
B01	$Si(OC_2H_5)_4$	Chloride	10	4.5	4.5	Acid	3.0	Diopside	White
C01	SiO_2	Nitrate	10	4.5	4.5	–	3.0	Diopside/akermanite	Grayish
C02	SiO_2	Chloride	10	4.5	4.5	–	3.0	Diopside/akermanite	White

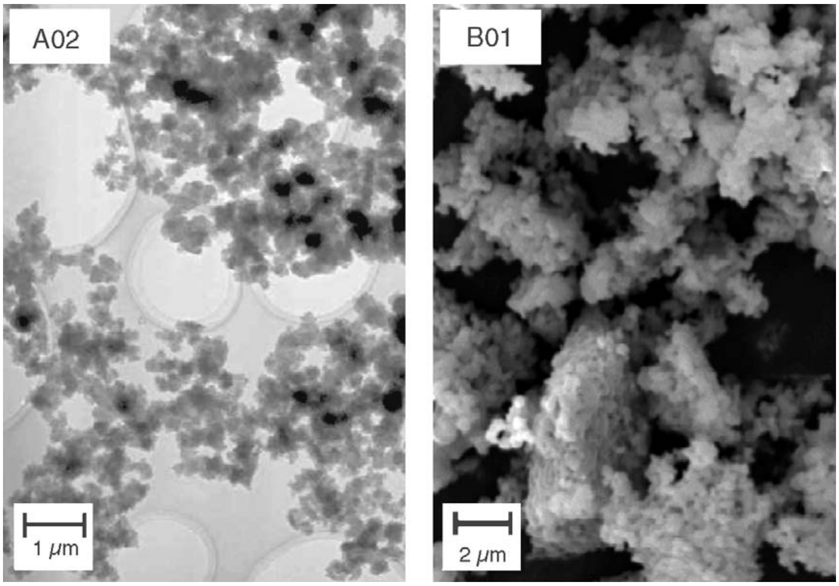
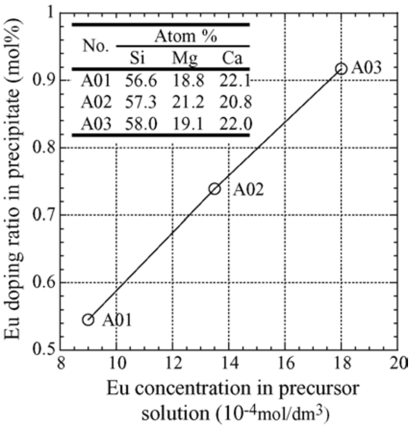


Fig. 1. TEM photograph of as-prepared precursor particles of A02 and SEM photograph of heat-treated phosphor particles of B01.

shows the relationship between the Eu doping ratio in the sol-particles and the Eu concentration in the stock solutions. The Eu doping ratio was also controlled by the initial concentration of the starting stock solutions. Eu is an activator as a luminescence centre, and its amount for the host crystal severely influenced the brightness of light emission of synthesized phosphor materials. For the Eu-doped alkaline-earth silicate phosphor $CaMgSi_2O_6$:Eu^{2+} as the objective of this study, the suitable Eu doping ratio is only a few percent at the most for the substitute Ca ratio. In this method, it is possible to precisely control the composition of the products or amount of additives with the initial concentration condition of the stock solutions. The results of TEM observation and EDAX measurement indicate that there was not any detectable variation in composition and shape in synthesized particles.



No.	Atom %		
	Si	Mg	Ca
A01	56.6	18.8	22.1
A02	57.3	21.2	20.8
A03	58.0	19.1	22.0

Fig. 2. The result of EDAX analysis for as-prepared precursor particles of A01–A03.

3.2. Heat-treated phosphor particles

Fig. 3 shows TG and DTA curves of as-prepared particles (sample A02, B01). TG continues to decrease up to about 900 °C and total weight loss was about 30% for original gravity. A remarkable exothermic peak was observed on DTA curves at 900–950 °C for the particles except for those from the citric acid catalyst system. The particle obtained from the citric acid system shows extra exothermic peak at approximately 400 °C on the DTA curve, which indicates the combustion reaction of the citric ion. Then, the weight loss of the citric acid system was much higher than in other systems.

Fig. 4 shows X-ray diffraction patterns of the particles of C01, and A02 before and after heat-treatment. For synthesis using $Si(OC_2H_5)_4$ as an Si source, the as-prepared precursor particles were amorphous. After heat-treatment at under 800 °C, the amorphous phase was consider to have remained predominant. However, by heat-treatment at over 1000 °C, particles were converted into well-crystallized almost single-phase alkaline-earth silicate ($CaMgSi_2O_6$). When using SiO_2 as a Si source though, calcium salt crystals originated in starting materials were predominant under 800 °C. The XRD pattern also shows the presence of not only $CaMgSi_2O_6$ but also the contamination of $Ca_2MgSi_2O_7$ after the heat-treatment above 1000 °C when using SiO_2. Furthermore, synthesized as-prepared particles in liquid phase indicated higher reactivity and constituent homogeneity than solid compound mixture. The crystallinity of synthesized particles was increased up to 1300 °C, but undesirable aggregation was enhanced at higher temperature close to its melting point (1391 °C). Then, the well-crystallized property at the lower temperature is very important because phosphor particles must be well dispersed for using lamp or display applications. It is hypothesized that

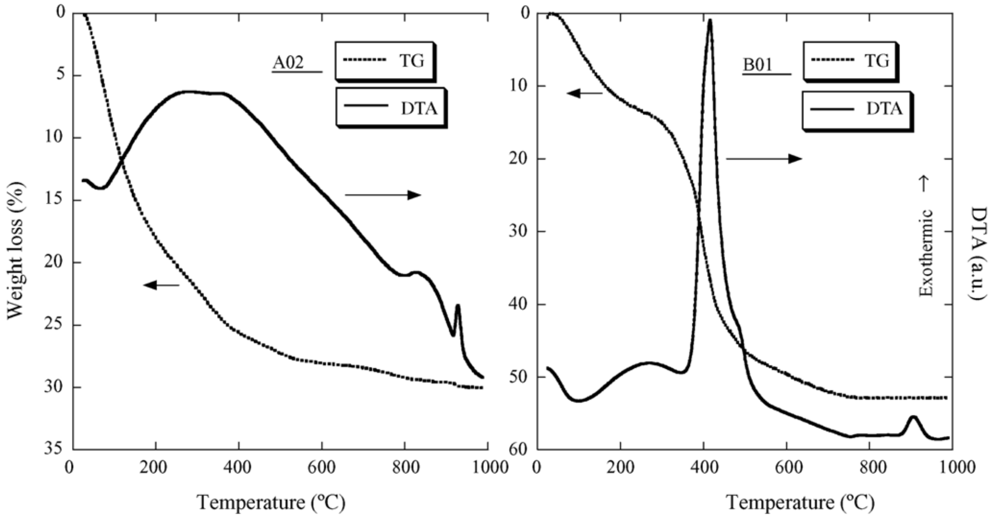


Fig. 3. TG–DTA curves of as-prepared precursor particles of A02 and B01.

liquid phase reactions are hydrolysis of silica, ethyl silicate, and metal cations if their single elements of each component react in aqueous solution separately, but the reactions are actually considered to be co-precipitation reactions, producing complex compositions containing both Si and metal ions.

3.3. Luminescent property of phosphor particles

Fig. 5 shows the emission spectra of synthesized $CaMgSi_2O_6:Eu^{2+}$ particles of A02 heat-treated at 1200 °C in a reducing atmosphere. The phosphor particles heat-treated in a reducing atmosphere showed a remarkable emission peak that corresponds to $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} in the region of the 400–500 nm wavelength. The main emission peak was 446 nm, resulting in Blue light emission. However, the phosphor particles contaminated by $Ca_2MgSi_2O_7$, which were produced by a synthesis using SiO_2 as the starting material for the Si source in this work, indicated greenish light emission. This was due to the emission peak of $Ca_2MgSi_2O_7:Eu^{2+}$ being placed at a longer-wavelength compared to that of $CaMgSi_2O_6:Eu^{2+}$. The peak-intensity on the emission spectrum of phosphor particles that had a grayish body color was significantly lower than that with whitish body color. Therefore, this grayish body color may indicate the occurrence of crystal defects, which quench the luminescence emission.

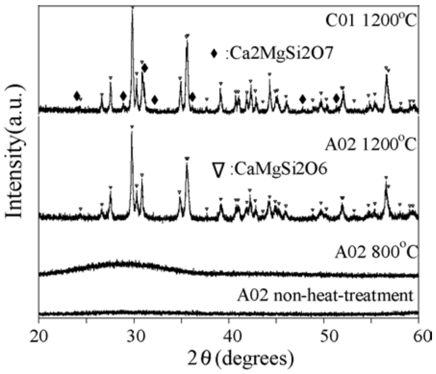


Fig. 4. XRD patterns of as-prepared precursor particles A02 and heat-treated phosphor particles of A02 and C01.

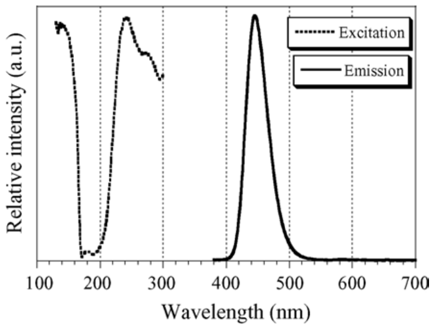


Fig. 5. Excitation and emission spectra of the heat-treated phosphor particles of A02.

From these results, it is considered that the Eu ion was doped at the correct site of the single phase crystalline of $CaMgSi_2O_6$, and Eu^{3+} derived form starting compound, such as chloride reduced to Eu^{2+} by this synthesis process using appropriate starting materials, such as $Si(OC_2H_5)_4$ and chloride salt. Additionally, the doping ratio of Eu^{2+}, which strongly affects the intensity of luminance, was controlled by the initial concentration in stock solutions. These results show that this liquid-phase synthesis method could be applied to prepare the uniform Eu-doped alkaline-earth silicate phosphor $CaMgSi_2O_6:Eu^{2+}$.

4. Conclusions

The liquid-phase synthesis method for preparing Eu-doped alkaline-earth silicate phosphor particles $CaMgSi_2O_6:Eu^{2+}$, which is expected for applying inert gas systems, such as for mercury-free fluorescent lamps and plasma panel displays, was investigated. Synthesized sol-particles were almost uniform, and their size was under 200 nm. The metal elements ratio of the sol-particles was controlled by the initial concentration of the stock solution. As-prepared particles were converted into the Eu-doped silicate alkaline-earth silicate phosphor by heat-treatment at above about 900 °C. The phosphor particles indicate a blue light emission of Eu^{2+} with an emission peak of 446 nm.

Acknowledgement

This study was supported by the Industrial Technology Research Grant Program in 2003 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

[1] K. Yamamoto, H. Nakabayashi, Y. Kotera, A. Ueno, J. Electrochem. Soc. 133 (1986) 657.
[2] T. Kunimoto, R. Yoshimatsu, K. Ohmi, S. Tanaka, H. Kobayashi, IEICE Trans. Elect. E85-C (2002) 1888.
[3] S. Oshio, K. Kitamura, T. Shigeta, T. Matsuoka, S. Tanaka, H. Kobayashi, J. Electrochem. Soc. 146 (1999) 392.
[4] S.H. Cho, J.S. Yoo, J.D. Lee, J. Electrochem. Soc. 145 (1998) 1017.
[5] Y.C. Kang, H.S. Roh, H.D. Park, Ceram. Int. 29 (2003) 41.
[6] P. Sangmoon, C.L. Benjamin, K.A. Douglas, B.P. Jeffrey, W.F. John, R.A. Thomas, H.S. Gregoy, Science 297 (2002) 65.
[7] T. Sugimoto, Adv. Colloid Interface Sci. 28 (1987) 65.