

# Crystal Growth of Silicate Phosphors from the Vapor Phase

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**SUMMARY** Well-crystallized  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  powders were grown on a substrate by the vapor phase reaction between a mixed powder (barium carbonate and europium oxide) and SiO gas. The vaporization of SiO occurs at 1400–1600°C from the  $\text{SiO}_2$  source (or SiO powder) in a reducing atmosphere. The formed SiO gas was transported by 95 vol% Ar - 5 vol%  $\text{H}_2$  gas and reacted with the raw material powders. The emission intensity of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor synthesized by the new vapor phase technique is about 2.6 times higher than that of a conventional solid-state reaction sample.

**key words:** phosphor, green emission, silicon monoxide,  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$

## 1. Introduction

In general, small particle phosphors have higher specific surface areas including many defects than that of bulk phosphors [1]. Therefore, a bulk phosphor with over a ten-micron diameter has been usually used in the applications of LED phosphors. Nano-sized phosphor powders were sometimes fabricated by a vapor phase technique (chemical vapor deposition) using metal-organic precursors. Such metal-organic compounds are expensive and difficult to handle in air, which is unsuitable for the mass production of the powders. Different methods to fabricate the well-grown bulk silicate phosphors are required. To the best of our knowledge, no such synthetic vapor process for the production of well-grown silicate phosphors has been developed to date.

In this study, we disclose a new vapor synthesis technique for the silicate phosphors. The conventional gas phase synthesis of phosphor materials uses organic metal sources or a high-purity sputtering target in a high vacuum [2], [3]. The conventional method is optimized for thin film production, but unsuitable for bulk powders. In the newly developed vapor synthesis technique, an expensive high vacuum system is not required and the reactions of conventional starting materials, such as silica powder and alkaline earth carbonates, are completed at atmospheric pressure in the reducing gas, 5%  $\text{H}_2/\text{Ar}$ , at around 1500°C. The well-crystallized  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  sample synthesized by this new

vapor-phase technique shows a green emission more intense than that of samples synthesized by the conventional solid-state reaction method.

## 2. Experimental

The phosphor samples were synthesized by a novel hybrid method in the gas-solid phase. This method requires SiO gas and the binary Ba - Sc - O, ternary Ba - Sc - Al - O or quaternary Ba - Sc - Al - Eu - O substrate as the starting materials. The substrate was a mixture of  $\text{BaCO}_3$  (Kanto Chemical Co., Inc., 3N),  $\text{Sc}_2\text{O}_3$  (Shin-Etsu Chemical Co., Ltd., 4N),  $\text{Al}_2\text{O}_3$  (Sumitomo Chemical Co., Ltd., 4N) and  $\text{Eu}_2\text{O}_3$  (Shin-Etsu Chemical Co., Ltd., 4N). The stoichiometric materials were weighed out for the  $\text{Ba}_3\text{Sc}_4\text{O}_9$  or  $(\text{Ba}_{0.99}\text{Eu}_{0.01})_7\text{Sc}_6\text{Al}_2\text{O}_{19}$  composition and then wet-mixed in acetone. The mixture was pressed into a 15-mm diameter disk pellet at a pressure of 30 MPa for several minutes. The SiO gas was produced from  $\text{SiO}_2$  powder (Kanto Chemical, Co., Ltd., 3N). The substrate was placed downstream of the  $\text{SiO}_2$  powder. The pellets were fired in alumina boats at 1500–1600°C for 12 h in 95 vol% Ar - 5 vol%  $\text{H}_2$  gas. The heating of the  $\text{SiO}_2$  powder in the reducing atmosphere generates SiO gas at 1400–1600°C [4], then the SiO gas reacted with the surface of the ternary Ba - Sc - Al - O or quaternary Ba - Sc - Al - Eu - O substrate. For comparison between the new vapor phase and the conventional solid-state techniques, a reference sample was synthesized by the conventional solid-state reaction method, i.e., 4h at 1200°C in the same atmosphere [4], [5].

The synthesized phosphors were identified by X-ray powder diffraction (MX-Labo; Mac Science, Ltd.) operated at 40 kV and 25 mA using  $\text{Cu K}\alpha$  radiation. The photoluminescence excitation–emission spectra and quantum efficiency were measured at room temperature using a fluorescence spectrofluorometer (FP-6500; Jasco, Inc.) equipped with a 150 W Xenon lamp. Raman spectroscopy was carried out at room temperature (Lab RAM HR; Horiba-Jobin Yvon). A 532 nm Nd:YAG laser was used for the excitation.

## 3. Results and Discussion

The SiO gas reacted with the raw material powders on the  $\text{BaO}-\text{Sc}_2\text{O}_3-\text{Al}_2\text{O}_3$  ternary system substrate surface. The stable compounds in the ternary system are  $\text{BaAl}_{12}\text{O}_{19}$ ,  $\text{BaAl}_2\text{O}_4$ ,  $\text{Ba}_3\text{Al}_2\text{O}_6$ ,  $\text{Ba}_3\text{Sc}_4\text{O}_9$ ,  $\text{Ba}_2\text{ScAlO}_5$ ,

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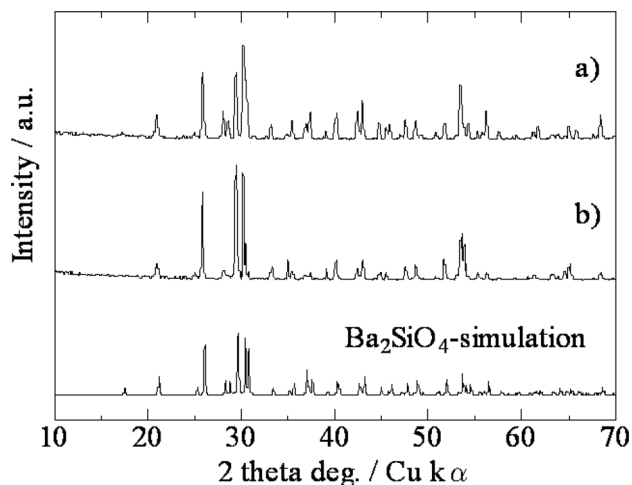


Fig. 1 XRD patterns of  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor. a)  $1500^\circ\text{C}$  for 12 h, b)  $1400^\circ\text{C}$  for 12 h.

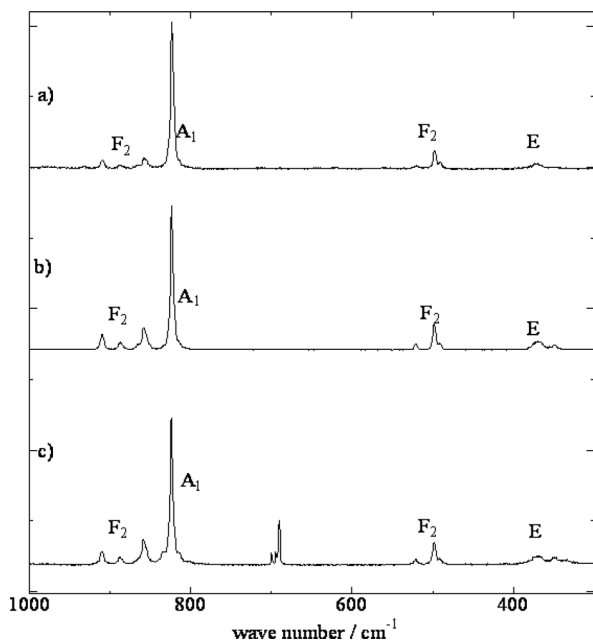


Fig. 2 Raman spectra of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor samples. a)  $1500^\circ\text{C}$  for 12 h in  $\text{H}_2/\text{Ar}$  treatment on  $\text{Ba}_3\text{Sc}_4\text{O}_9$  substrate, b)  $1300^\circ\text{C}$  for 6 h in  $\text{H}_2/\text{Ar}$  treatment, c)  $1300^\circ\text{C}$  for 6 h in air treatment.

and  $\text{Ba}_7\text{Sc}_6\text{Al}_2\text{O}_{19}$ . The  $\text{Ba}_3\text{Sc}_4\text{O}_9$  compound has the highest melting point of these compounds of  $2050^\circ\text{C}$  in air. Due to high melting points, all of these compounds can possibly be used as substrates. Using these compounds with high melting points, the substrates can act as a Ba-source for the  $\text{Ba}_2\text{SiO}_4$  at high temperature in a reducing atmosphere. In this study,  $(\text{Ba}_{0.99}\text{Eu}_{0.01})_7\text{Sc}_6\text{Al}_2\text{O}_{19}$  was used as the substrate. Figure 1 shows the XRD patterns of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor synthesized by the new vapor phase technique. Green emitting phosphor powders were deposited on the substrate by heating at  $1400\text{--}1500^\circ\text{C}$  for 12 h.

Figure 2 shows the Raman spectra of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  samples. At  $1500^\circ\text{C}$ , the  $\text{Ba}_2\text{SiO}_4$  was generally formed

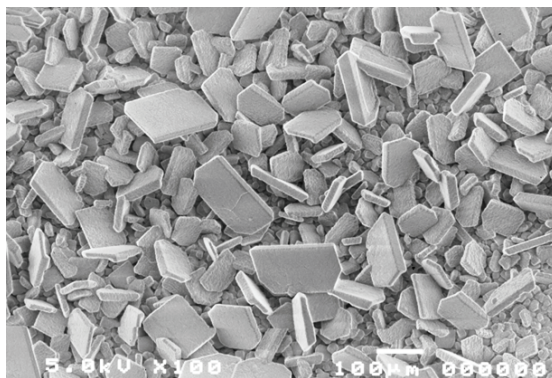


Fig. 3 SEM image of  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  crystals grown on the substrate at  $1500^\circ\text{C}$  for 12 h.

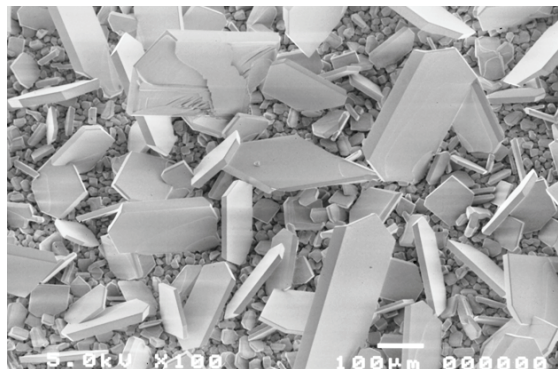
the melted glass phase. Based on the results, the obtained samples were a crystal phase, using this technique. These spectra of  $\text{Ba}_2\text{SiO}_4$  show sharp bands in the  $350\text{--}900\text{ cm}^{-1}$  region due to the internal vibrations of the  $\text{SiO}_4$  anions. The  $A_1$  mode ( $820\text{ cm}^{-1}$ ) and  $F_2$  mode ( $905\text{--}850\text{ cm}^{-1}$ ) are stretching modes, and the  $F_2$  mode ( $500\text{--}520\text{ cm}^{-1}$ ) and E mode ( $350\text{--}370\text{ cm}^{-1}$ ) are the bending modes. Generally, Raman spectroscopy is utilized to evaluate the vacancies in inorganic compounds. Due to the monophase single crystal particles, the observed Raman spectra of the samples by the new process are almost same as the spectrum of Ref. [6]. This result means that the vapor phase products form fine crystals and not glasses at the high synthesis temperature. Due to the difficult thermal decomposition in air, the peaks around  $700\text{ cm}^{-1}$  originated from the unreacted  $\text{BaCO}_3$  raw material. In other words, sintering in a reducing atmosphere produces a highly crystalline Eu-doped  $\text{Ba}_2\text{SiO}_4$  host material.

Figure 3 shows an SEM image of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  crystals grown on the surface of the substrate at  $1500^\circ\text{C}$  for 12 h. Well-grown single crystals with a  $10\text{--}40\text{ }\mu\text{m}$  size were mainly observed because of the relatively slow nucleation. Heating of the  $\text{SiO}_2$  source (or  $\text{SiO}$  powder) with the samples in a strong reducing atmosphere generates gaseous  $\text{SiO}$ , which reacted with the Ba- and Eu-components in the substrate. These crystals were confirmed as single crystals under a polarizing microscope.

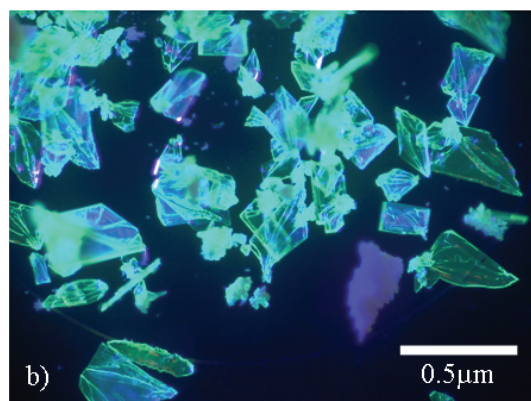
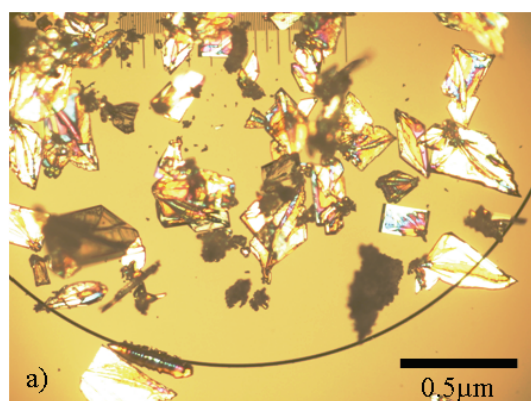
Figure 4 shows an SEM image of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  crystals grown on the surface of the substrate by firing at  $1600^\circ\text{C}$  for 12 h. Bigger well-grown single crystals with a few hundreds micrometer size were observed. The size of the phosphor single crystal was easily controlled by the reaction temperatures. According to Refs. [7], [8], the generation of the  $\text{SiO}$  gas was dependent on the temperature and atmosphere of the following chemical formulas.



The  $\text{SiO}$  gas was generated by the overall reaction with  $\text{H}_2$  gas according to reaction (a) or by decomposition at a low oxygen partial pressure according to reaction (b).



**Fig. 4** SEM image of  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  crystals grown on the substrate at  $1600^\circ\text{C}$  for 12 h.

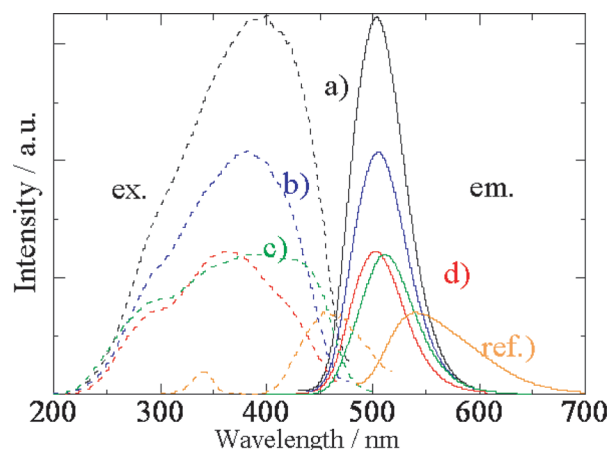


**Fig. 5** Polarized microscope images of  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  single crystals. ( $1500^\circ\text{C}$  synthesized) a) Under an incandescent lamp, b) under 365 nm UV light excitation.

Therefore, the SiO gas can be generated by heat-treating  $\text{SiO}_2$  powder in a reducing atmosphere at high temperature. For example, the generated SiO gas concentration at  $1500^\circ\text{C}$  for 3 h is about 5.3 times higher than that at  $1400^\circ\text{C}$  for 3 h from  $\text{SiO}_2$  in a reducing atmosphere [7]. According to the BaO-SiO<sub>2</sub> phase diagram, the melting point of  $\text{Ba}_2\text{SiO}_4$  is  $1877^\circ\text{C}$  in air [9]. Under a reducing atmosphere, the melting point of  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  dropped. In our experiment,  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  melted in the reducing atmosphere at a temperature as low as  $1400^\circ\text{C}$ . This temperature is not high enough to reduce the Eu emission center ions from trivalent

**Table 1** The quantum efficiency of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor synthesized by the vapor technique and conventional technique.

sample	External quantum efficiency	Internal quantum efficiency
Vapor technique	61.3	80.4
Conventional technique	43.6	81.2
Ref.) YAG (P46)	45.7	68.1



**Fig. 6** Excitation and emission spectra of  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  and reference (YAG:P46 commercialized product) phosphors at room temperature. a) Vapor technique at  $1500^\circ\text{C}$  ( $\lambda_{\text{ex}} = 387 \text{ nm}$ ,  $\lambda_{\text{em}} = 503 \text{ nm}$ ), b) Vapor technique at  $1400^\circ\text{C}$  ( $\lambda_{\text{ex}} = 382 \text{ nm}$ ,  $\lambda_{\text{em}} = 505 \text{ nm}$ ), c) Vapor technique at  $1600^\circ\text{C}$  ( $\lambda_{\text{ex}} = 386 \text{ nm}$ ,  $\lambda_{\text{em}} = 511 \text{ nm}$ ), d)  $\text{Eu}^{2+}$  1% doped conventional technique at  $1300^\circ\text{C}$  ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $\lambda_{\text{em}} = 504 \text{ nm}$ ), ref.) YAG:P46 ( $\lambda_{\text{ex}} = 460 \text{ nm}$ ,  $\lambda_{\text{em}} = 557 \text{ nm}$ ).

to divalent. Thus, it is not an easy process to obtain silicate phosphors with a low defect density concentration by a conventional solid-state diffusion reaction in a reducing atmosphere at high temperature. The gas phase crystal growth is a dilute phase reaction, which is a more homogeneously dispersed emission center than the condensed phase. On the other hand, the conventional solid-state reaction is driven by the ionic diffusion of each raw material having different diffusion rates. Based on a microscopic image, unreacted raw materials remained. Figure 5 shows a polarized microscope image of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  crystals synthesized by the new vapor-phase technique. The crystals emit a strong green light under UV (365 nm) excitation. Therefore, the vapor phase technique is also a general and powerful tool for the single crystal growth of the  $\text{Eu}^{2+}$  doped silicate phosphor materials.

According to the quantum efficiency measurement result (Table 1), there is no appreciable change in the internal quantum efficiency. On the other hand, the external quantum efficiency of the vapor phase sample was about 1.5 times higher than that of the conventional one. This means that the vapor phase synthesis improved the efficiencies of the absorption and extraction of light.

Figure 6 shows the excitation and emission spectra of the  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor at room temperature. The



$\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor synthesized by the new vapor-phase technique has a relatively strong absorption band on the long wavelength side. The emission intensity of the phosphor synthesized by the new vapor-phase technique at  $1500^\circ\text{C}$  is about 2.6 times higher than that of a conventional solid-state reaction sample. There are two main reasons for this phenomenon. The most likely cause is a longer optical path length. Due to the larger grain size compared to the conventional synthesis, the ratio of the excitation energy absorption was improved. On the other hand, at  $1600^\circ\text{C}$ , the prepared sample becomes too large for the absorption and extraction of light. Another reason is the concentration of  $\text{Eu}^{2+}$  in the host compound of  $\text{Ba}_2\text{SiO}_4$ . According to Nakanishi's report [10], as the  $\text{Eu}^{2+}$  concentration of the Eu-doped alkaline silicate phosphor increases, the excitation spectra show a red shift. In this study, we also observed this shift in Fig. 6. This is due to acceleration of the Eu ion reduction from trivalent to divalent at high temperature.

#### 4. Conclusions

A well-crystallized and well-grown  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor was synthesized by a new vapor-phase technique using gaseous SiO. The relative emission intensity of the sample synthesized by the new vapor phase reaction was about 260% compared to the conventional  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor made by the solid-state reaction. The novel vapor-phase techniques also made it possible to synthesize other conventional silicate phosphors such as  $\text{Zn}_2\text{SiO}_4:\text{Mn}$ . This new vapor synthesis has the significant possibility to prepare nano-scale to bulk silicate materials using a common substance, i.e., the silica powder.

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