

# Blue- and red-emitting phosphor nanoparticles embedded in a porous matrix

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## Abstract

Eu<sup>3+</sup>- and Ce<sup>3+</sup>-doped yttrium silicate, as well as Eu<sup>2+</sup>-doped zinc silicate nanoparticles, were grown in a porous SiO<sub>2</sub> matrix using an impregnation method. For Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>:Eu<sup>3+</sup>, particles of about 50 nm size were obtained that exhibited several photoluminescence (PL) peaks in red. Different peaks showed slightly different decay times; however, their excitation mechanism was found the same. Increasing the Eu concentration increased the PL intensity while reducing the decay time. Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>:Ce<sup>3+</sup> nanoparticles in the porous matrix showed bright blue emission, consisting of two peaks at 358 nm and 378 nm. Re-impregnation process was found effective in changing the relative intensity of the two peaks. Zn<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> nanoparticles in porous glass consisted of amorphous particles of about 20 nm size inside the porous matrix. The luminescence was a broad peak centered at 418 nm. These phosphor systems, together with our previously reported Zn<sub>2</sub>SiO<sub>4</sub>:Mn<sup>2+</sup> in porous SiO<sub>2</sub> structure, comprise a red–green–blue system that can be used in display applications.

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## 1. Introduction

Phosphors are luminescent materials that usually comprise a transparent matrix doped by active ions. Commercial phosphors are crystalline powders of large bandgap materials with a few micrometers size, activated by transition or rare-earth ions. Phosphor powders are obtained by solid-state reaction of starting materials, usually oxides, at relatively high temperatures. As the particle size of the starting materials is in micrometer range, the process of solid-state diffusion requires long times and relatively high firing temperatures. It is therefore expected that phosphor particles form faster and at lower temperatures if starting materials with nanostructured features are used.

We have developed methods of forming nanoparticle silicate phosphors in a transparent mesoporous SiO<sub>2</sub> [1–5]. The porous

matrix was porous glass, as well as the porous SiO<sub>2</sub> obtained by oxidation of porous silicon. The synthesis process involved the diffusion of solutions in the pores, followed by appropriate heat treatment. Zn<sub>2</sub>SiO<sub>4</sub>:Mn<sup>2+</sup> nanoparticles were formed in this way inside porous glass and oxidized porous silicon [1–4]. It was shown that depending on the synthesis conditions, Zn<sub>2</sub>SiO<sub>4</sub>:Mn<sup>2+</sup> with green or yellow luminescence could be obtained. This was found to be due to the formation of α or β phases of Zn<sub>2</sub>SiO<sub>4</sub>. It was also observed that Mn ions introduced into the porous material are effectively located inside Zn<sub>2</sub>SiO<sub>4</sub> crystalline particles rather than in porous SiO<sub>2</sub> skeleton or on the walls. This was found due to the fact that MnO<sub>x</sub> reacts readily with Zn<sub>2</sub>SiO<sub>4</sub>, while its reaction with SiO<sub>2</sub> is extremely slow. This leads to a kind of self-controlled doping process and is an important element in the overall success of this technique.

The idea employed for Mn-doped zinc silicate can be used for other silicate phosphors to synthesize phosphor particles in porous media. Silicate phosphors are an important class of phosphors and are already used in various applications [6]. Efficient red, green and blue silicate phosphors have been

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already synthesized and developed for certain applications. These phosphors if synthesized in porous media would have the advantage that they can be patterned in higher resolutions and phosphor distribution is uniform.

In a previous paper, we reported the structural properties of  $\text{Eu}^{3+}$ -doped yttrium silicate particles inside oxidized porous silicon [5]. The firing was performed in a relatively low temperature of 1100–1250 °C, compared to 1550 °C used in conventional powder synthesis. As in  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ , a high doping efficiency for Eu in yttrium silicate was observed which was attributed to the role of Eu species as the nucleation sites for the growth of yttrium silicate particles. The crystalline phase of the yttrium silicate phase was found as  $\text{Y}_2\text{Si}_2\text{O}_7$ . In this paper, we mainly focus on the luminescence properties. We will show that efficient red and blue phosphor systems can be obtained by this method.  $\text{Y}_2\text{Si}_2\text{O}_7:\text{Eu}^{3+}$  is reported as the red phosphor, and  $\text{Y}_2\text{Si}_2\text{O}_7:\text{Ce}^{3+}$  and  $\text{Zn}_2\text{SiO}_4:\text{Eu}^{2+}$  are reported as blue phosphors [7]. These phosphors together with  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$  comprise a red–green–blue system that could be used in displays.

## 2. Experimental details

To make the notation simpler, hereafter, we will use the abbreviated forms of ZS and YS for “zinc silicate” and “yttrium silicate.” Also, we will use PS and VPG for “porous silicon” and “Vycor porous glass.” For instance, PS:YS:Eu represents the Eu-doped yttrium silicate embedded in oxidized porous silicon. Vycor is a trade name for a commercial porous glass, also known as Corning 7930. The size of pores in VPG is about 4–5 nm.

The preparation method is in principle the same as that of PS:ZS:Mn reported earlier [1–4]. Porous silicon layers were formed on a  $p^+$ -type (100) Si wafer by the conventional electrochemical process. The average porosity and pore size were 70% and 10 nm, respectively. The thickness was about 15  $\mu\text{m}$ . For PS:YS:Eu samples, a 1 M chemical solution containing  $\text{Y}(\text{NO}_3)_3$  and  $\text{Eu}(\text{NO}_3)_3$  with Eu/Y ratio of 2–20% was diffused into the pores of porous silicon for several minutes. This was done by putting the samples in the solution or by putting a drop of solution on the sample. The diffusion process continues until it fills the whole space of the pores.

The samples were then dried in air and put into an electrical furnace. Temperature was raised with 1 °C/min rate up to 500 °C in order to evaporate water, dehydrate the nitrates and dissociate the nitrate molecules into the corresponding oxides. Then the temperature was increased to 1100–1250 °C and samples were fired for 10 h in air. The skeleton of porous silicon oxidizes completely soon after the temperature reaches about 900 °C. At the firing temperature  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  react to form Eu-doped yttrium silicate phase in a porous  $\text{SiO}_2$  matrix formed.

In case of PS:YS:Ce, the same procedure was carried out using a 1 M solution of  $\text{Y}(\text{NO}_3)_3$  and  $\text{Ce}(\text{NO}_3)_3$  as the starting solution. Ce/Y ratio was 7% in this case. The firing was done at 1100–1250 °C for 10 h in a slightly reducing atmosphere

(Ar+5%  $\text{H}_2$ ), in order to avoid  $\text{Ce}^{4+}$  formation, since  $\text{Ce}^{4+}$  ions are not efficient luminescent centers.

VPG:ZS:Eu samples were prepared by putting VPG plates with 0.5 mm thickness in a 1 M solution of mixed  $\text{Zn}(\text{NO}_3)_2$  and 7%  $\text{Eu}(\text{NO}_3)_3$ , so that the solution completely diffused in the pores. The samples were then dried and put into a furnace. The temperature was raised slowly up to 500 °C, and then rapidly increased to 1100 °C and fired at this temperature for several hours in the presence of Ar+5% $\text{H}_2$ . Reducing atmosphere is required to keep Eu ions in 2+ valency and prevent them from oxidation to 3+ valency.  $\text{Eu}^{2+}$  ions are blue emitting centers while  $\text{Eu}^{3+}$  ions emit in the red.

Transmission electron microscopy (TEM) images were taken using a JEOL-2000EX machine with 200 keV electron beam. Energy-dispersive spectroscopy (EDS) was performed in the same machine. Photoluminescence (PL) measurements were carried out using a low-pressure mercury lamp (254 nm) or a He–Cd laser (325 nm) as the excitation source. The source for the photoluminescence excitation (PLE) measurements was a 500-W Xe lamp, dispersed by a monochromator. Time resolved PL experiments were done using the fourth harmonic of a Nd:YAG pulsed laser, and the output signal from the photomultiplier tube was recorded using a digital oscilloscope.

## 3. Results and discussion

### 3.1. $\text{Eu}^{3+}$ doped yttrium silicate

Fig. 1 shows a top view TEM image of the PS:YS:Eu sample. Eu content in the starting solution was 7%. The black areas are yttrium silicate phase, as indicated by EDS. The white areas are pores and the gray areas are the skeleton of porous  $\text{SiO}_2$ . YS phase is formed along the skeleton or as individual particles. There is a wide size distribution, with average of about 50 nm. It should be noted that the holes in the sample are considerably larger than the holes in the original porous silicon (10 nm). This issue has been discussed earlier [1].

Fig. 2a shows PL spectrum for a PS:YS:Eu sample. The sample was prepared at 1250 °C firing temperature and Eu/Y ratio was 7%. The peaks appearing between 575 nm and 720 nm originate from  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  transitions, where  $J=0-4$ , as indicated in the figure. There is no luminescence coming from the porous  $\text{SiO}_2$  host. The luminescence from  $\text{Eu}^{3+}$  comes from

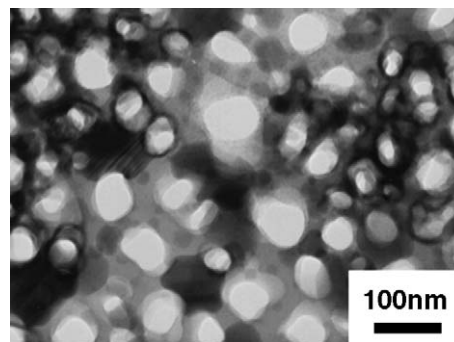


Fig. 1. Top view TEM image of a PS:YS:Eu sample.

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