Influence of Rare Earth Sc and La to the Luminescent Properties of FED Blue Phosphor Y$_2$SiO$_5$:Ce

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Luminescent properties of Sc$^{3+}$ and La$^{3+}$ doped (Y$_{0.995}$Ce$_{0.005}$)$_2$SiO$_5$ phosphors were studied. In the Sc$^{3+}$ doped system (Y$_{0.995}$-Sc$_{0.005}$)$_2$SiO$_5$, the solid solution extends to $x = 0.65$, but in the La$^{3+}$ doped system (Y$_{0.995}$-La$_{0.005}$)$_2$SiO$_5$, the solid solution range is not over the La$^{3+}$ content of $x = 0.05$. For La$^{3+}$ doped samples, the photoluminescence (PL) increases about 30% and cathodoluminescence (CL) increases about 10%. Additionally the color saturation is also improved with La$^{3+}$ doping. The mechanisms for these improvements are discussed. For the Sc$^{3+}$ doped samples, both PL and CL, clearly decrease. These phosphors may be useful in field emission displays (FED).

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Various types of multicomponent oxide phosphors have been widely researched for using in display technologies such as high definition television (HDTV), projection television (PTV), and flat panel displays (FPD). Since the beginning of the 1990s, a new type of flat panel display device, field emission display (FED) has been developed. In this device, the phosphors are excited by the cathode rays with low voltage (<5 kV) and high current density. Due to these excitation conditions, the general requirements for FED phosphors are more stringent than for conventional CRT (cathode ray tube) phosphors. At present, Y$_2$SiO$_5$:Ce is selected as a blue phosphor candidate for this device.

Y$_2$SiO$_5$ is a good host material for cathodoluminescent (CL) phosphors. Structural studies showed that this material contains isolated SiO$_4$ tetrahedral and nonsilicon-bonded oxygen. Two different monoclinic structures have been found, a low temperature phase (X1) and high temperature phase (X2). The X1 phase has the space group $P2_1/c$, whereas the space group $B2/c$ is assigned to the X2 phase. Both X1 and X2 phases have two different Y$^{3+}$ sites, the coordination numbers of which are 7 and 9 for the X1 phase and 6 and 7 for the X2 phase. Other rare earth elements also form these phases, La$^{3+}$-Tb$^{3+}$ tends to form the X1 phase; while Dy$^{3+}$-Lu$^{3+}$ tends to form the X2 phase. Recently, pure phase samples for X1 phases of Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$, and Yb$^{3+}$ were obtained.

The luminescence of Y$_2$SiO$_5$:Ce has been studied for several decades. Previous studies found that the luminescent intensity of X1-Y$_2$SiO$_5$:Ce is much weaker than that of X2-Y$_2$SiO$_5$:Ce. In this paper, luminescent properties for the X2 phase are mainly considered, thus formula Y$_2$SiO$_5$:Ce is used for short to represent the X2 phase phosphor. Previously, our group investigated the influence of Sc$^{3+}$, La$^{3+}$, Gd$^{3+}$, and Lu$^{3+}$ to the luminescence of Y$_2$SiO$_5$:Ce. It was found that Y$^{3+}$ could be replaced by Gd$^{3+}$ and Lu$^{3+}$ to form solid solutions in wide ranges. The replacement of Gd$^{3+}$ decreases the luminescence, whereas Lu$^{3+}$ enhanced the luminescence about 20% under cathode ray excitation. Lu$^{3+}$ doping also improves color saturation. Bosze and his co-workers reported Gd$^{3+}$ improving the luminescent efficiency of doping Y$_2$SiO$_5$:Ce under excitation of a low-voltage cathode ray. However, the effects of La$^{3+}$ and Sc$^{3+}$ doping were not carefully analyzed. In the present work, a careful study was conducted on the influence of Sc$^{3+}$ and La$^{3+}$ to the luminescent properties of Y$_2$SiO$_5$:Ce.

Experimental

The purity of all rare earth oxides as starting materials is over 99.99%. As the source of SiO$_2$, amorphous powder with luminescent purity was used. All starting materials were dried at 850°C. Powder samples were prepared by solid reactions at high temperatures. Suitable amounts of starting materials were weighed and mixed thoroughly by grinding. In order to obtain homogeneous mixtures, a small amount of ethanol was added during grinding. All samples were fired at 1500°C and in a reductive atmosphere (CO generated from spectrally pure carbon rods during firing). In all samples, 0.4 wt % BaF$_2$ was added as the flux.

The powder X-ray diffraction (XRD) patterns of the samples were recorded by using a Rigaku D/max 2000 X-ray powder diffractometer. The phase present was examined by analyzing the XRD patterns using software PowderX. The photoluminescence (PL) was measured by using a Hitachi F4500 fluorospectrometer and energy calibration was applied for the spectrum data collection. Cathodoluminescent (CL) measurements were conducted by using YFC-2 cathodoluminescentometer with the excitation voltage 10 kV and current density 1 mA/cm$^2$. The chromaticity coordinates were calculated based on the CIE 1931 system.

Results and Discussion

Solid solutions in the systems of (Y$_{0.995}$-R$_x$Ce$_{0.005}$)$_2$SiO$_5$ (R = Sc$^{3+}$ and La$^{3+}$) form a narrow solid-solution range; La$^{3+}$ can substitute for Y$^{3+}$ in Y$_2$SiO$_5$ in certain ranges. For different rare earth elements, the solid solution ranges are varied. In our previous work, it was reported that for the system (Y$_{1-x}$Gd$_x$)$_2$SiO$_5$, the solid solution region extends to $x = 0.4$ and for the system (Y$_{1-x}$Lu$_x$)$_2$SiO$_5$, to $x = 0.35$. In previous work, the substitutions of Sc$^{3+}$ and La$^{3+}$ were not carefully analyzed. Our present work shows that the system (Y$_{1-x}$La$_x$)$_2$SiO$_5$ forms a narrow solid-solution region; La$^{3+}$ content $x$ is not over 0.05. A broad solid-solution region forms in the system (Y$_{1-x}$Sc$_x$)$_2$SiO$_5$, in which Sc$^{3+}$ content, $x$, extends to 0.65. Figure 1 illustrates the variation of unit cell volume with Sc$^{3+}$ content. Since the radius of Sc$^{3+}$ is smaller than that of Y$^{3+}$, the unit cell volume decreases with Sc$^{3+}$ content in the range of $x < 0.65$. When $x$ is over 0.65, the samples are out of the solid-solution region; the unit cell volume is kept constant. The size of the rare earth ions is an important factor for the formation of the solid solutions. The radius difference between La$^{3+}$ ($r = 0.1172$ nm) and Y$^{3+}$ ($r = 0.1040$ nm) is much larger ($\Delta r = 0.0132$ nm) than the difference between Y$^{3+}$ and Sc$^{3+}$ or Gd$^{3+}$ or Lu$^{3+}$ (Gd$^{3+}$, $r = 0.1078$ nm, $\Delta r = 0.0038$ nm; Lu$^{3+}$, $r = 0.1001$ nm, $\Delta r = -0.0039$ nm; all data are six-coordinated Shannon radii). Thus in the La$^{3+}$ doped system, the solid-solution range is much narrower than in other systems. The radius difference between Sc$^{3+}$ ($r = 0.0885$ nm, $\Delta r = -0.0155$ nm) and Y$^{3+}$ is not comparatively small, but it forms wide range of solid solutions, possibly because the size of Sc$^{3+}$ is smaller than that of Y$^{3+}$. It can be seen that the solid solution region for the Sc$^{3+}$ doped system is clearly

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wider than that of Gd$^{3+}$ and Lu$^{3+}$ doped systems. A reasonable explanation for this has not been found.

Curve fitting for PL emission spectrum of $(Y_{0.995} Ce_{0.005})_2 SiO_5$.—Figure 2 shows the PL emission spectrum of $(Y_{0.995} Ce_{0.005})_2 SiO_5$ excited by 356 nm UV light, which is coincident with previous reports. It is well known that this emission band is the origin of the d-f transitions of Ce$^{3+}$ in $(Y_{0.995} Ce_{0.005})_2 SiO_5$. Each peak was simulated by a Gaussian profile on the emission energy and $\nu$ is the wavenumber. The fitting abided by the following criteria: (i) the spectrum is resolved into four peaks in two sets, P1 and P2 for Ce$^{3+}$(I), P3 and P4 for Ce$^{3+}$(II); (ii) the peaks in each set should have similar profiles, e.g., similar full width at half maximum (fwhm) values, since the peaks are generated from the same emission center; (iii) as the energy difference between $^2F_{5/2}$ and $^2F_{7/2}$ is about 2000 cm$^{-1}$, the peak position difference of the two peaks in each set should be close to this value. The phosphor spectrum is customarily represented as $E - \nu$, thus the fitting results are transformed to this form. The fitted peaks are represented in Fig. 2 and the related parameters are listed in Table I. Actually the above curve fitting is a mathematical fitting. Deviations from the criteria exist. However, comparing this result with the previous work, the former is more physically reasonable.

Reference 13 contributes two well-resolved excitation spectra for both emission centers, Ce$^{3+}$(I) and Ce$^{3+}$(II). The maximum of the excitation peak at the longest wavelength for Ce$^{3+}$(I) is at 350 nm and that for Ce$^{3+}$(II) is at 375 nm. Using these data and the peak positions of P1 and P3 from our curve fitting results, the Stokes shifts for both centers are estimated and listed in Table I.

Considering the coordinating environments, due to the covalency effects (nephelauxetic effect), the seven-coordinated center has lower energy of 5d level than the six-coordinated one; compared to the later, the excitation peak of the former should show a red shift. Additionally, because the seven-coordinated center is less stiff than the six-coordinated one, the former should have a larger Stokes shift. The expansion of the seven-coordinated center after excitation is also not more strongly restricted than that of the six-coordinated center and more nonradiative relaxations take place in the former than in the later. As a result, the seven-coordinated center should present a weaker emission. Based on these discussions, we may assign Ce$^{3+}$(I) to the six-coordinated center and Ce$^{3+}$(II) to the seven-coordinated center. The above ideas were proposed by Lin and Su for analyzing the luminescent differences between X$1$-Y$_2$SiO$_5$·Ce and X$2$-Y$_2$SiO$_5$·Ce.

Table I. Curve fitting parameters.

<table>
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<tr>
<th>Emission center</th>
<th>Peak</th>
<th>Peak position nm$^{-1}$</th>
<th>FWHM nm$^{-1}$</th>
<th>Peak area (%)</th>
<th>Peak position difference cm$^{-1}$</th>
<th>Stokes shift nm$^{-1}$</th>
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<tr>
<td>Ce$^{3+}$(I)</td>
<td>P1</td>
<td>397/25200</td>
<td>29/1600</td>
<td>85</td>
<td>1900</td>
<td>47/3400</td>
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<tr>
<td></td>
<td>P2</td>
<td>429/23300</td>
<td>37/1900</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce$^{3+}$(II)</td>
<td>P3</td>
<td>463/21600</td>
<td>44/2000</td>
<td>36</td>
<td>1500</td>
<td>88/5100</td>
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<tr>
<td></td>
<td>P4</td>
<td>497/20100</td>
<td>73/3100</td>
<td>36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Variation of unit cell volume with Sc$^{3+}$ content $x$ in the system $(Y_{1-x}Sc_x)_2SiO_3$.

Figure 2. PL emission spectrum of $(Y_{0.995} Ce_{0.005})_2 SiO_5$ ($\lambda_{ex} = 356$ nm).
The size difference between Y$^{3+}$ and Ce$^{3+}$ is quite large (Ce$^{3+}$, $r = 0.115$ nm, $\Delta r = 0.011$ nm). Possibly in phosphor $Y_2SiO_5:Ce$, Ce$^{3+}$ ions might not disperse homogeneously in the lattice, but accumulate to some extent. It is known that La$^{3+}$ has a size similar to Ce$^{3+}$, but slightly bigger. When La$^{3+}$ ions are doped in the lattice, they tend to enter the Ce$^{3+}$ accumulation zone and Ce$^{3+}$ concentration in this zone is diluted. Consequently, concentration quenching is reduced, and luminescent intensity increases. Figure 4 illustrates the variations of luminescent intensity with Ce$^{3+}$ content at various La$^{3+}$ contents in the systems $(Y_{0.995-x}La_xCe_0.005)_2SiO_5$. With the La$^{3+}$ content increase, the saturating concentration of Ce$^{3+}$ shifts from 0.005 to 0.01. These data support the discussion above.

La$^{3+}$ doping also affects color coordinates; the result is represented in Fig. 5. When the La$^{3+}$ content $x$ varies in the solid solution region from 0.0 to 0.05, the color coordinate $y$ reduces from 0.084 to 0.070, while the color coordinate $x$ does not change much ($0.157-0.158$). This indicates that the color saturation of $Y_2SiO_5:Ce$ is improved by La$^{3+}$ doping.

Careful comparisons were carried out in the emission spectra of La$^{3+}$ doped samples. It was found that the long wavelength tail in the spectra (around 470-550 nm) was reduced with La$^{3+}$ content increase. In order to well represent this reduction, curve fitting was applied to all spectra of the La$^{3+}$ doped samples. $P1/P2$ (the ratio of peak areas) is almost constant with the increase of La$^{3+}$ content, while $P3/P2$ and $P4/P2$ decreased obviously. Figure 6 exhibits the variation of $(P3 + P4)/P2$ with La$^{3+}$ content $x$. P3 and P4 are located in the blue-greenish region, thus their reduction leads to the improvement of color saturation.

For understanding color improvement, the following mechanism is proposed. The seven-coordinated sites have larger space than the six-coordinated one, thus the large ions of La$^{3+}$ preferentially occupy the former sites. Consequently more Ce$^{3+}$ ions are squeezed into the later sites and P3 and P4 intensities decreases.

**Cathodoluminescent measurement for $(Y_{0.995-x}La_xCe_0.005)_2SiO_5$** ($R$ = Sc$^{3+}$, La$^{3+}$). — The cathodoluminescent measurements were carried out on the systems $(Y_{0.995-x}La_xCe_0.005)_2SiO_5$. CL spectra are similar to PL ones. CL intensity increases about 10% in La$^{3+}$ doped

![Figure 4](image4.png)

**Figure 4.** Variations of PL intensity with contents of La$^{3+}$ and Ce$^{3+}$ in the systems $(Y_{0.995-x}La_xCe_0.005)_2SiO_5$.

![Figure 5](image5.png)

**Figure 5.** Variation of color coordinates with La$^{3+}$ content $x$ in the system $(Y_{0.995-x}La_xCe_0.005)_2SiO_5$.

![Figure 6](image6.png)

**Figure 6.** Variation of $(P3 + P4)/P2$ with La$^{3+}$ content $x$ in the system $(Y_{0.995-x}La_xCe_0.005)_2SiO_5$. 
system, while in the Sc$^{3+}$ doped system, the data show a trend to decrease with the increase of Sc$^{3+}$ content. When the Sc$^{3+}$ content is at $x = 0.4$, only ca. 50% emission remains. The data are exhibited in Fig. 7.

**Conclusions**

Luminescent properties of La$^{3+}$ and Sc$^{3+}$ doped $(Y_{0.995}Ce_{0.005})_2SiO_5$ phosphors were studied, and the results are summarized as follows.

Curve fitting resolves the emission spectrum of $(Y_{0.995}Ce_{0.005})_2SiO_5$ into four peaks for two emission centers, Ce$^{3+}$(I) and Ce$^{3+}$(II). The stronger peaks, P1 and P2, arising from the Ce$^{3+}$(I) center, may be assigned to the emission from the six-coordinated sites, while the weaker peaks, P3 and P4, arising from Ce$^{3+}$(II) center, may be assigned to the emission from the seven-coordinated sites.

In La$^{3+}$ doped $Y_2SiO_5:Ce$, the PL intensity increases about 30% and the CL intensity increases about 10%, although the solid-solution range is quite narrow. La$^{3+}$ doping also reduces the color coordinate $y$ and the color saturation is improved. Possible mechanisms for the improvements are proposed.

Sc$^{3+}$ can replace Y$^{3+}$ in $Y_2SiO_5$ to form solid solutions in a wide range ($x = 0.0$ to 0.65). Sc$^{3+}$ doping causes the dramatic decrease of both PL and CL.

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