

## Luminescence of $Y_{2-x}Ce_xSiO_5$ Phosphor

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(Received September 14, 1997)

Photoluminescence (PL) and cathodoluminescence (CL) characteristics of Ce-activated  $Y_{2-x}Ce_xSiO_5$  have been investigated as functions of Ce concentration and firing condition. According to the X-ray, PL and CL results,  $Y_2SiO_5$  is found to have two phases depending on the firing temperature. For the specimen fired above 1270°C, the emission band peaked at 395 nm with a shoulder at 424 nm under ultraviolet (u.v.) and cathode-ray (c.r.) excitation. However, for the specimen fired below 1200°C in air the peak was observed at 424 nm and it shifted to longer wavelength with reduction level. The reduced specimen for  $x=0.02$  showed the brightest emission under u.v. excitation whereas under c.r. excitation the brightest emission was observed for the reduced specimen for  $x=0.06$ .

**Key words :**  $Y_2SiO_5$ , Cerium, Photoluminescence, Cathodoluminescence

### I. Introduction

Low-voltage oxide phosphors with high-efficiency have recently regained much attention, because they are considered as possible alternatives to ZnS-based cathodoluminescent phosphors for the new low-voltage luminescence applications, such as the field emission display technology. Oxide phosphors are considered to be superior to commonly used sulfide phosphors in the stability under high vacuum and to be without corrosive gas emission under irradiation of cathode ray.

A number of Ce-activated phosphors are known to show emission with a maximum intensity in the region of 380 to 560 nm and a relatively short decay time. Two features of Ce activation are of major significance. Since the lowest excited state of  $Ce^{3+}$  belongs to the 5d configuration, the radiative transition to the ground state is Laporte-allowed and therefore extremely fast. The excited states typically lies some 40,000  $cm^{-1}$  above the ground state and this large energy gap makes the probability of nonradiative deactivation by multiphonon mechanism almost vanishingly small, so that the quantum yield is often very high. The wavelengths of emission peaks for the Ce-activated yttrium silicates,  $Y_2SiO_5$  and  $Y_2Si_2O_7$ , were reported to be 415 and 385 nm, respectively.<sup>1)</sup> According to the phase diagram of  $Y_2O_3$ - $SiO_2$  system, there seem to be only two compounds, namely,  $Y_2SiO_5$  and  $Y_2Si_2O_7$ . However, previous investigators reported several compounds to occur in the system.<sup>2)</sup> If there are several compounds as reported, the PL characteristics of Ce-activated  $Y_2O_3$ - $SiO_2$  system may vary appreciably with composition and preparation procedure.

Sometimes success in producing good phosphor ma-

terials can be attributed simply to the preparation procedures. Therefore, it was thought to be worthwhile to investigate the effect of preparation procedure on the photoluminescence characteristics. And furthermore, with increased demands on improving the efficiency of established phosphors, it is thought that more scientific approaches to phosphor synthesis have to be developed.

### II. Experimental Procedure

Phosphors with the general formula,  $Y_{2-x}Ce_xSiO_5$ , were prepared by solid-state reaction technics with x ranging from 0.005 to 0.10. The raw materials  $Y_2O_3$  (Alfa, 99.999%) and  $SiO_2$  (Alfa, 99.999%) were weighed to an accuracy of  $\pm 0.1$  mg, incorporated with  $CeCl_3$  aqueous solution (Alfa), hand-mixed under ethanol in an agate mortar and pestle for more than 2 hrs, and allowed to dry. The dried mixtures were put into a fused silica tube and fired at temperatures from 1050 to 1600°C for 4 hrs.

A Rigaku diffractometer was used for X-ray diffraction analysis. The photoluminescence excitation and emission spectra were obtained with a Amico-Bowman luminescence spectrometer. A powder holder was loaded at a suitable angle to the excitation and emission beams to achieve maximum signal and minimum scattering. Samples were excited with appropriate radiations. The emission was monitored in the range of 380 to 650 nm to locate the wavelength of the maximum point in the emission spectra and the excitation wavelengths were scanned in the range of 220 to 380 nm. Attenuators were used to eliminate the second order Rayleigh scattering of the excitation wavelength and the monochromator was operated with a slit width of 4 nm. The CL was measur-

ed at room temperature using a demountable ultrahigh-vacuum chamber ( $10^{-7}$  Torr) equipped with in-house assembled CL spectrometer and a multiple-specimen holder.

### III. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of  $Y_2SiO_5$  phosphors prepared at various temperatures.  $Y_2SiO_5$  compound is known to have two phases,  $X_1$ , the low temperature phase,<sup>3)</sup> and  $X_2$ , the high temperature phase.<sup>4)</sup> The crystal structure of  $X_2$  phase is listed as monoclinic, however, that of  $X_1$  phase is unknown. The X-ray diffraction pattern of the compound prepared at 1200°C or below is identical to that of  $X_1$  phase, and the X-ray diffraction pattern of the compound prepared at 1350°C or above is virtually identical to that of  $X_2$  phase. However, it has been noted that there is always a trace amount of  $X_1$  phase in the compound prepared at temperatures between 1350 and 1600°C, and the amount of  $X_1$  phase decreases with increasing annealing temperature. It has also been noted that X-ray diffraction pattern of  $X_2$  phase formed at a higher temperature is not affected by prolonged annealing of the specimen at a lower temperature (1100°C).

Shown in Figs. 2(a) and 2(b) are excitation and emission spectra of  $Y_{2-x}Ce_xSiO_5$  phosphors fired in air at 1100 and 1350°C respectively. In the excitation spectrum of  $Y_{2-x}Ce_xSiO_5$  phosphors prepared at 1350°C, four absorption bands appeared at 357, 301, 264, and 224 nm. The similar results were observed by the previous investigators.<sup>5)</sup> However, for  $Y_{2-x}Ce_xSiO_5$  phosphors prepared at 1100°C, the excitation spectrum exhibits two peaks at 362, and 280 nm. The difference of excitation spectra of two phases cannot be explained at this moment.

The overall shape of emission bands did not vary with  $x$  in the composition range investigated. However, a significant variation in peak intensities with  $x$  was observed. In both phases, the maximum emission in-

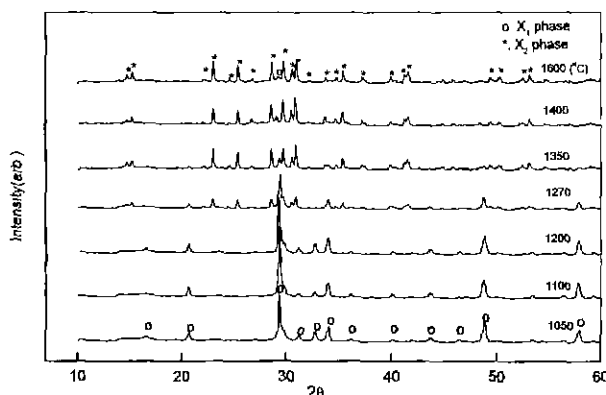


Fig. 1. X-ray diffraction patterns of  $Y_2SiO_5$  prepared at various temperatures.

tensities were obtained for  $x=0.02$ .  $Y_{2-x}Ce_xSiO_5$  fired at unspecified temperature has been reported to show an emission band with a maximum at 415 nm.<sup>2)</sup> However, in this investigation the specimen fired at 1100°C ( $X_1$  phase) showed a broad emission band peaking at 424 nm under u.v. excitation. On the other hand, there seem to be two components in the emission band of phosphor annealed at 1350°C, one at about 395 nm and the other at about 424 nm. And the emission peak wavelength of the second component is considered to be the peak wavelength of  $X_1$  phase. Based on these results, it is concluded that the 395 nm component is due to the emission of  $X_2$  phase (the high temperature phase) and the 424 nm component to the emission of  $X_1$  phase (the low temperature phase).

To investigate the effect of reducing atmosphere on the PL characteristics,  $Y_{2-x}Ce_xSiO_5$  phosphors were prepared at 1100°C in various atmospheres. Some typical excitation and emission spectra are given in Fig. 3. Note that there is a significant overall increase in the emission intensity for the phosphor annealed in the most reducing atmosphere (90%  $N_2$ -10%  $H_2$ ) as compared with the phosphors annealed in air or  $N_2$ . It is well known that  $Ce_2O_3$  is converted spontaneously to  $CeO_2$  in air.<sup>6)</sup> Therefore, a great number of Ce ions in  $Y_{2-x}Ce_xSiO_5$  phosphor prepared in air are thought to exist in the state of

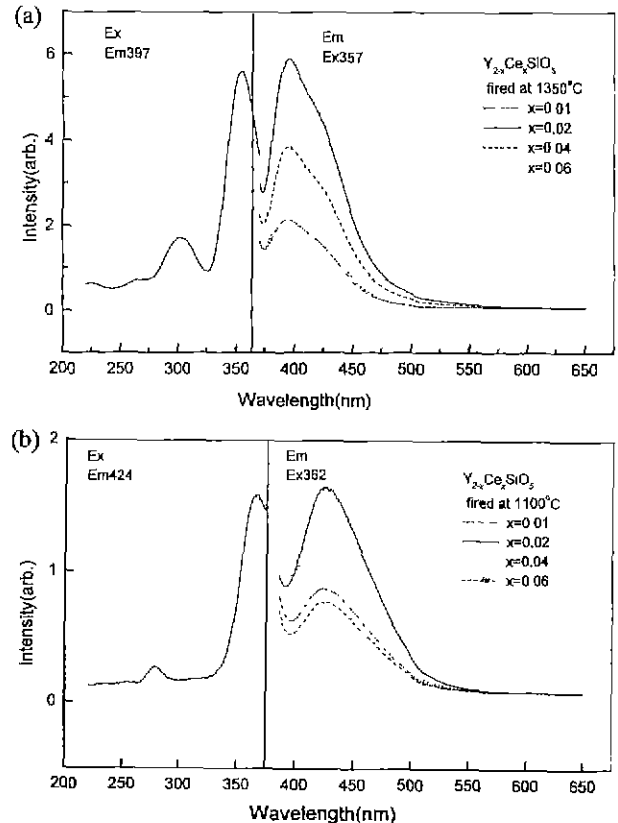
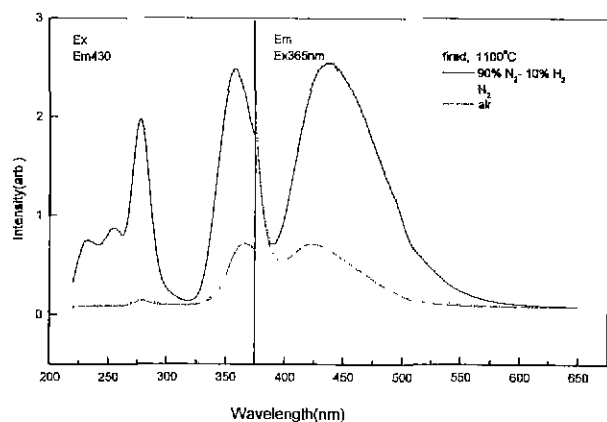
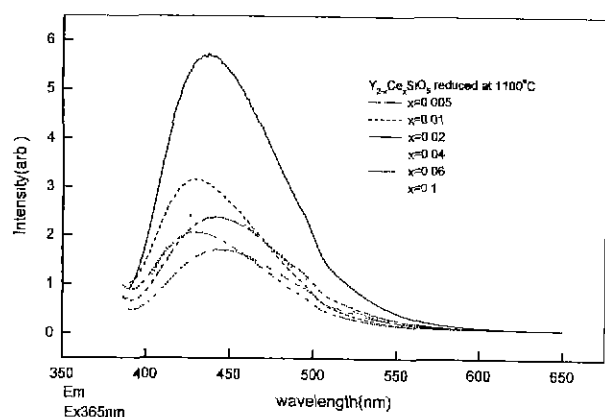


Fig. 2. PL excitation and emission spectra of  $Y_{2-x}Ce_xSiO_5$  prepared in air at (a) 1350 and (b) 1100°C.



**Fig. 3.** PL excitation and emission spectra of  $Y_{1.98}Ce_{0.04}SiO_5$  fired at  $1100^\circ C$  for 4 hrs in various atmospheres.



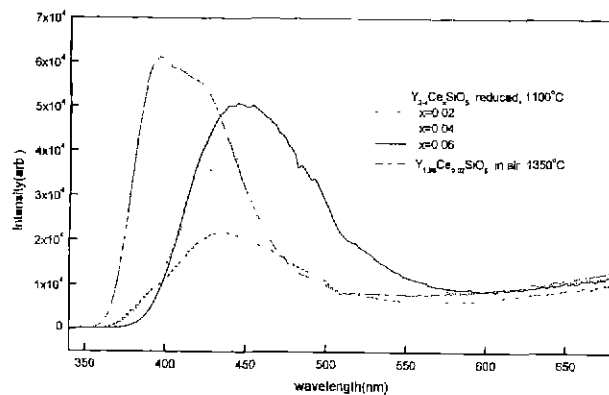
**Fig. 4.** PL spectra of  $Y_{2-x}Ce_xSiO_5$  as a function of  $x$  (reduced in atmosphere of  $90\% N_2-10\% H_2$  at  $1100^\circ C$  for 4 hrs).

$Ce^{4+}$ . When the specimen is reduced in most of  $Ce^{4+}$  ions in  $90\% N_2-10\% H_2$  atmosphere,  $Y_{2-x}Ce_xSiO_5$  phosphor are considered to be reduced to  $Ce^{3+}$  ions. Because only  $Ce^{3+}$  ion can emit blue light, it can be concluded that the increase in the emission intensity for the phosphor annealed in the most reducing atmosphere ( $90\% N_2-10\% H_2$ ) is due to the increase of  $Ce^{3+}$  ions during the reduction firing.

Additionally, as can be seen in Fig 3,  $\lambda_{max}$  shifted from 424 to 438 nm with reduction level for the phosphor fired at  $1100^\circ C$ . However, the reason for the shift of  $\lambda_{max}$  is not clear. On the other hand,  $\lambda_{max}$  for the phosphor fired at  $1350^\circ C$  or higher, was not affected by reduction treatment.

In Fig. 4, PL spectra of  $Y_{2-x}Ce_xSiO_5$  annealed at  $1100^\circ C$  in reducing atmosphere of  $90\% N_2-10\% H_2$  are shown as a function of  $x$ . It is seen that  $\lambda_{max}$  of  $Y_{2-x}Ce_xSiO_5$  shifts from 428 to 447 nm as  $x$  varies from 0.005 to 0.1 and the maximum intensity is observed for  $x=0.02$ .

Shown in Fig. 5 are the CL spectra of  $Y_{2-x}Ce_xSiO_5$  fired at  $1100^\circ C$  in reducing atmosphere ( $90\% N_2-10\% H_2$ ) and  $Y_{1.98}Ce_{0.02}SiO_5$  fired at  $1350^\circ C$  in air. The overall  $x$  dependence of energy distribution is virtually the same as



**Fig. 5.** CL spectra of  $Y_{2-x}Ce_xSiO_5$  fired in reducing atmosphere of  $90\% N_2-10\% H_2$  at  $1100^\circ C$  and  $Y_{1.98}Ce_{0.02}SiO_5$  fired in air at  $1350^\circ C$ .

that observed under u.v. excitation except for the slight increase of the 424 nm component for the specimen fired at  $1350^\circ C$ . The emission spectra of phosphor fired at  $1100^\circ C$  exhibit a single emission band with a maximum in the range of 435 to 447 nm. The similar results were observed by previous investigators.<sup>2)</sup> The brightest emission was observed for  $x=0.06$ . For higher values of  $x$ , intensity decreased with  $x$  (not shown). However,  $\lambda_{max}$  continuously shifted toward longer wavelength with  $x$  in the composition range investigated.

#### IV. Summary

Photoluminescence and cathodoluminescence of  $Y_{2-x}Ce_xSiO_5$  have been found to be strongly dependent on  $x$  and the firing condition.  $Y_{2-x}Ce_xSiO_5$  was found to have two phases,  $X_1$  and  $X_2$ . For the specimen fired above  $1270^\circ C$  ( $X_2$  phase), the peak wavelength, being at 395 nm, under u.v. excitation was independent of  $x$  and reduction level. However, for the specimen fired in air at  $1200^\circ C$  or below ( $X_1$  phase), the peak was observed at 424 nm and it shifted to longer wavelength with reduction level. And further, it was found that under intensive reduction heat treatment, the peak shifted to longer wavelength with  $x$ . The overall emission intensity has been found to be significantly enhanced by reduction heat treatment. The reduced specimen for  $x=0.02$  showed the brightest emission under u.v. excitation whereas under c.r. excitation the brightest emission was observed for the reduced specimen for  $x=0.06$ .

#### References

1. A. H. Gomes de Mesquita and A. Bril, "The Afterglow of Some Old and New  $Ce^{3+}$ -Activated phosphors," *J. Electrochem. Soc.*, **116**, 871 (1969).
2. A. H. Gomes de Mesquita and A. Bril, *Mat. Res. Bull.*, "Preparation and Cathodoluminescence of  $Ce^{3+}$ -Activated Yttrium Silicate and Some Isostructural Compounds," **4**,

- 643 (1969).
- 3 JCPDS card (No. 21-1456) Private Communication, Ito and Johnson, *Am. Mineral.*, **53**, 1940 (1968).
  4. JCPDS card (No. 21-1458) Private Communication, Ito and Johnson, *Am. Mineral.*, **53**, 1940 (1968).
  - 5 J. Shmulovich, G. W. Berkstresser, C. D. Brandle and A. Valentino, "Single-Crystal Rare-Earth-Doped Yttrium Orthosilicate phosphors," *J. Electrochem Soc.*, **135**, 3141 (1988).
  6. M. Cannon Sneed and Robert C. Brasted, "Comprehensive Inorganic Chemistry," D. Van Nostrand Company, INC. **4**, 168 (1965).