

## Electroluminescence of $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$ Thin Film Phosphors

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The dependence of luminescent properties for Ce-doped  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  thin films on composition and annealing temperature was investigated. It has been found that the emission intensity of  $\text{Ce}^{3+}$  photoluminescence was enhanced by the incorporation of a small amount of Zn and the post-annealing at high temperature. The emission intensity is attributable to the crystallinity of the films and to valence state of Ce ions. An attempt to fabricate electroluminescent devices has been carried out, introducing  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  as a host material.

### 1. Introduction

With the success of orange  $\text{ZnS}:\text{Mn}$ -based high-field thin film electroluminescent (TFEL) displays, there has been increasing interest in developing a capability for full color TFEL devices. As red and green emitting TFEL displays have reached the required brightness,<sup>1-2)</sup> the current research has primarily been focused on the development of an efficient blue emitting TFEL devices. A alkaline earth thiogallate was introduced as a novel host material for blue phosphors<sup>3)</sup> and an improvement of luminescence intensity in a traditional  $\text{SrS}:\text{Ce}$  based TFEL was achieved by adding a small amount of Mn and/or Zn into SrS host.<sup>4)</sup>

Recently we have reported the formation and characterization of  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  thin films with whole composition in view of it being a novel wide band gap light emitter and especially we have elucidated fundamental crystal phases, optical band gap energies and chemical bonding states.<sup>5-7)</sup> Also, we have reported the luminescent properties of  $\text{Ce}^{3+}$  in a host matrix of the  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$ .<sup>8)</sup>

In this presentation, we describe the dependence of luminescent properties of Ce-doped  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  thin films on composition  $x$  and annealing temperature, and also discuss the origin of the enhancement of luminescence intensity. We also made an attempt to fabricate electroluminescent devices, introducing  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  as a host material.

### 2. Experiments

$\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films were deposited by a conventional diode-type rf sputtering system<sup>5)</sup>. As a target, a mixture of  $\text{ZnS}/\text{SrS}/\text{Ce}_2\text{S}_3$  powder with the required mole fraction was used after firing at 700°C in argon atmosphere for 2 hr. The typical deposition conditions were as follows: Ar gas was used for the sputtering and gas pressure was maintained at 3 Pa. An rf power density of about 4 W/cm<sup>2</sup> was applied. Samples were deposited on a quartz glass substrate for 180 min maintaining the substrate temperature of 200°C, and subsequently annealed at 600-850°C for 1 hr.

The composition  $x$  of the  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films was determined by energy dispersive X-ray (EDX) analysis. The

crystal properties of the films were investigated by X-ray diffraction (XRD) trace using  $\text{Cu-K}\alpha$  ( $\lambda=1.54065\text{\AA}$ ) radiation. The composition along the depth of film and chemical bonding states of constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS). The X-ray target employed was a Mg anode with a characteristic X-ray energy of 1253.6eV. An energy resolution is  $\pm 0.1\text{eV}$  at 368.2eV of Ag 3d<sub>5/2</sub>. Prior to the XPS measurements, *in situ* Ar<sup>+</sup> ion etching was performed to avoid the surface contamination. Shifts of the XPS spectra due to electrical charging of the sample surface were calibrated with reference to the XPS signal from C 1s at 284.6eV. PL and PL excitation (PLE) spectra were recorded using a conventional measurement system. D<sub>2</sub> lamp was used as an excitation light source. Spectra were measured at 300K. The electroluminescent characteristics were measured by conventional methods.

### 3. Results and Discussion

#### 3.1 Crystallographic characteristics

The compositional dependence of crystalline properties of the  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  thin films were investigated by XRD. Figure 1 shows typical XRD patterns for  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films with  $x=0(\text{SrS})$ , 0.05, 0.25, 0.49 and 1( $\text{ZnS}$ ). The  $\text{Zn}_{0.05}\text{Sr}_{0.95}\text{S}$  film crystallizes only in the rocksalt structure. It has been found that  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  mixed compounds formed solid solution with a single-phased rocksalt structure up to  $x\approx 0.08$ . The XRD patterns of the  $\text{Zn}_{0.25}\text{Sr}_{0.75}\text{S}$  and  $\text{Zn}_{0.49}\text{Sr}_{0.51}\text{S}$  thin films, however, show two clear peaks which assigned to be (111) peak for zincblende structure and (200) peak for rocksalt structure. This suggests that phase separation occurs in this composition.

#### 3.2 Photoluminescence

To investigate the emission properties by doping  $\text{Ce}^{3+}$  luminescent centers in a host matrix of the  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$ , PL and PLE were measured. PLE spectra obtained by monitoring the PL emission peak exhibited a strong broad excitation band at 200-270nm which is due to  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  host excitation, and a weak peak at around 430nm which corresponds to the  $4f\rightarrow 5d(T_{2g})$  transition of  $\text{Ce}^{3+}$  in a cubic crystal field. This result implies that energy transfer mechanism from host lattice to luminescent centers is predominant rather than direct impact excitation. The whole feature of PL spectra is almost the same irrespective of Zn

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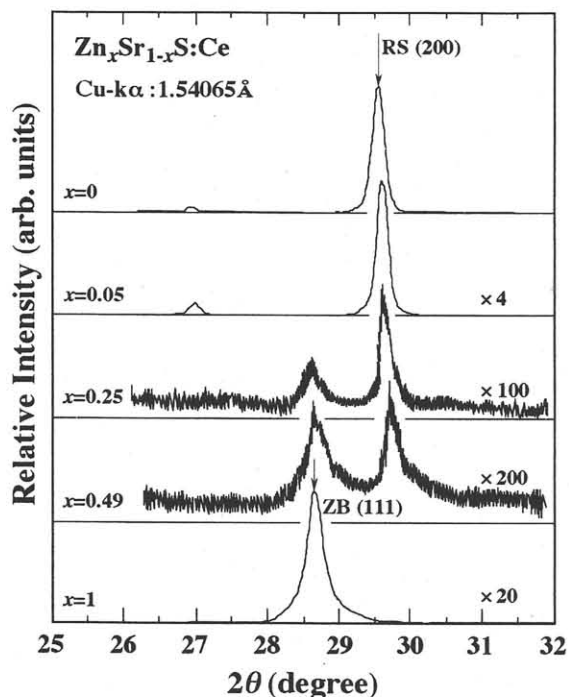


Fig. 1 Typical X-ray diffraction patterns for  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films with  $x=0$  (SrS), 0.05, 0.25, 0.49 and 1 (ZnS). Samples were measured after being annealed at  $800^\circ\text{C}$ .

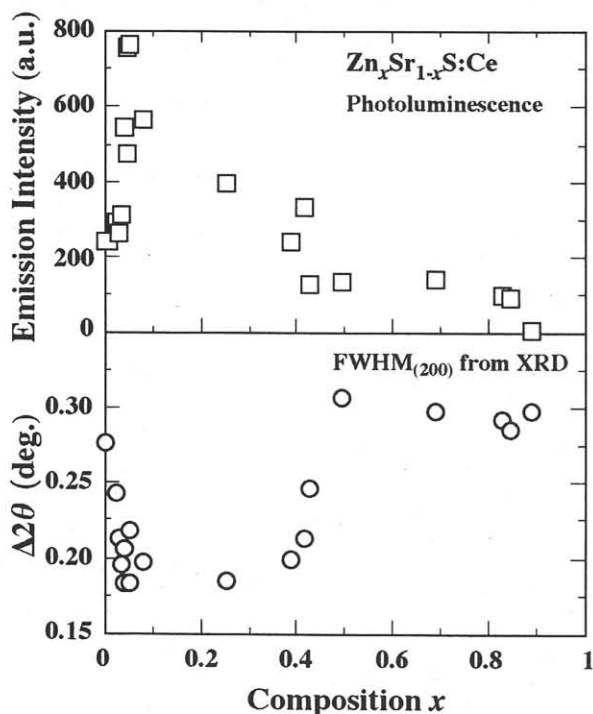


Fig. 2 Compositional dependence of PL intensity and  $\text{FWHM}_{(200)}$  of XRD measurement for  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films. Samples were measured after being annealed at  $800^\circ\text{C}$ .

composition. That is, the PL spectrum has two main emission bands with peaks at around 475nm and 540nm assigned to two parity allowed transitions of  $^2\text{D}(5\text{d})$ - $^2\text{F}_{5/2}(4\text{f})$  and  $^2\text{D}(5\text{d})$ - $^2\text{F}_{7/2}(4\text{f})$  for  $\text{Ce}^{3+}$  centers. However,

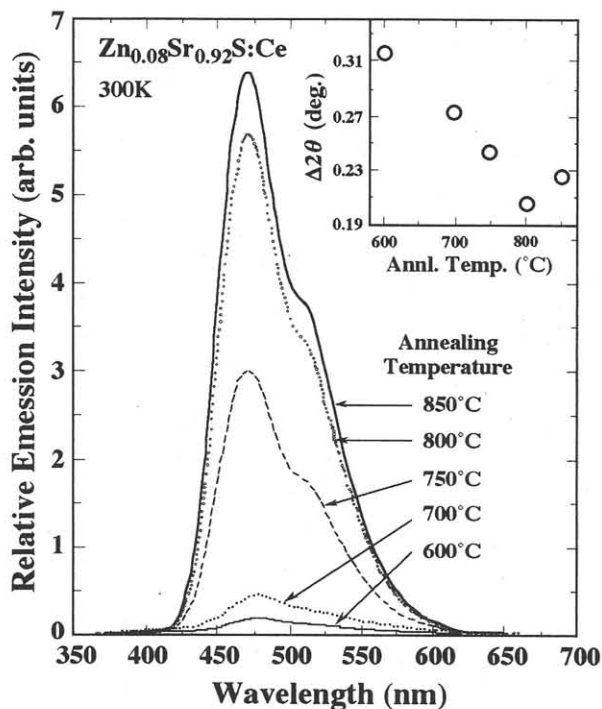


Fig. 3 PL spectra for  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films with  $x \approx 0.08$  as a function of annealing temperature. The dependence of  $\text{FWHM}_{(200)}$  of XRD on annealing temperature is also shown in inset.

emission intensity depended strongly on composition. Figure 2 shows the compositional dependence of PL intensity and full width at half maximum (FWHM) of (200) peak of XRD pattern for  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films. The emission intensity of  $\text{Ce}^{3+}$  photoluminescence was enhanced by the incorporation of a small amount of Zn up to  $x \approx 0.05$ . For the Zn composition higher than 0.05, intensity decreases with increasing composition. The reduction of  $\text{FWHM}_{(200)}$  of XRD was observed with increasing  $x$  from 0 to 0.05, which implies that the improvement of the crystallinity by the incorporation of a small amount of Zn results in the enhancement of luminescence.

Figure 3 shows PL spectra for  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films with  $x \approx 0.08$  as a function of annealing temperature. The dependence of  $\text{FWHM}_{(200)}$  of XRD on annealing temperature is also shown in the inset. The whole feature was almost the same for all the spectra, except that the intensity was enhanced more than one order of magnitude by increasing the annealing temperature from  $600^\circ\text{C}$  to  $800^\circ\text{C}$ . As can be seen in the inset, FWHM decreases with increasing annealing temperature. This result suggests that recrystallization takes place during annealing, which results in the increase of grain size and/or the improvement of the crystallinity.

To further investigate the effect of annealing, XPS analysis have been performed. It is known that Ce is mixed-valence ions and Vercaemst *et al.*<sup>9)</sup> reported that only 3+ state can produce visible light emission. Figure 4 shows XPS spectra from Ce 3d in  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films with  $x \approx 0.08$  for annealing temperature of 600, 700 and  $850^\circ\text{C}$ . The vertical lines indicate the reported Ce 3d line positions

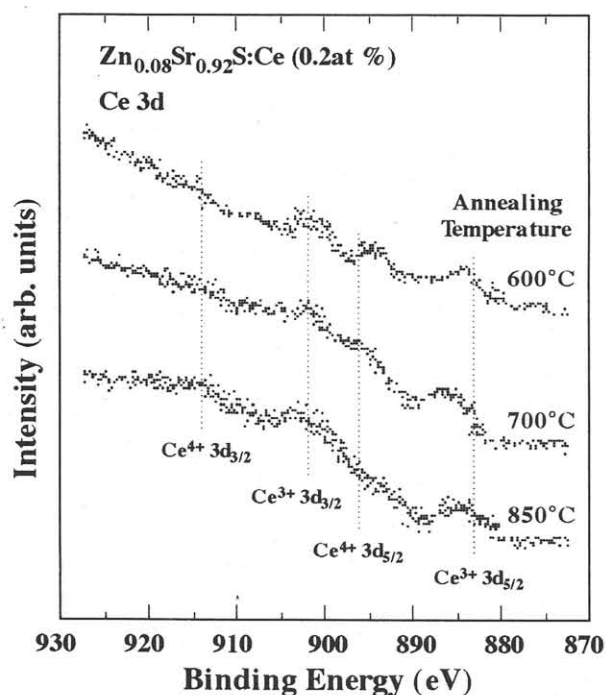


Fig. 4 XPS spectra from Ce 3d in  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  films with  $x \approx 0.08$  as a function of annealing temperature of 600, 700 and 850°C. The vertical lines indicate the reported  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  XPS lines from Ce 3d.

of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ .<sup>9)</sup> The spectrum of the 850°C annealed film indicates the existence of 3+ state of the Ce ions as a dominant valency, only a small amount of  $\text{Ce}^{4+}$  is detectable. In contrary, a significant amount of  $\text{Ce}^{4+}$  ions can be found for lower annealing temperature, which may be due to the formation of Ce clusters or  $\text{CeO}_2$ . By the increase of annealing temperature, the film may be recrystallized, which results in the improvement of crystalline quality as well as the decrease of Ce clusters. This result is in good agreement with PL result as shown in Fig. 3. However, the relationship between the activation of Ce clusters and the improvements of crystallinity is not clear at present.

### 3.3 Electroluminescence

Electroluminescent devices with  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films with several compositions, which have a conventional double insulating structure, were prepared. The phosphor layer was annealed at 600°C in Ar atmosphere. The devices showed broad greenish-blue EL emission under 1 kHz drive. However, the obtained luminance remained quite low for all samples. This may be due to the poor crystallinity of phosphor materials annealed at 600°C. Also, low luminance may be partially ascribed to the valence state. From the results shown in Figs. 3 and 4, further improvements in luminance can be expected by optimizing annealing temperature.

### 4. Conclusion

Novel Ce-doped  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  solid solutions have been prepared as blue-green emitting phosphor thin films. The

dependence of luminescent properties for  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  thin films on composition and annealing temperature was investigated. It has been found that the emission intensity of  $\text{Ce}^{3+}$  photoluminescence in  $\text{Zn}_x\text{Sr}_{1-x}\text{S}:\text{Ce}$  films was enhanced not only by the incorporation of a small amount of Zn but also by the increase of the post-annealing temperature. The increase of PL intensity is attributable to the improvement of the crystallinity of the films and partially to valence state of Ce ion. An attempt to fabricate electroluminescent devices has been carried out introducing  $\text{Zn}_x\text{Sr}_{1-x}\text{S}$  as a host material. Although the obtained luminance of the devices remained quite low, it will be much improved by optimization of the annealing process.

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