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# Photoluminescence of ZnS: Sm phosphor prepared in a reductive atmosphere

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**Abstract**

The characteristic emission of $Sm^{+3}$ in Zn phosphors, fired in inert atmosphere ($N_2$ gas) at various temperatures, was not detected. However, fired in reductive atmosphere at 1050°C, the characteristic $Sm^{+3}$ emission appears, which exhibits intra-4f transitions at 570, 606 and 653 nm, as predicted from the $^4G_{5/2}$ level to the $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ levels. Sm doping favors the formation of hexagonal phase in host lattice of ZnS:Sm. The increase in hexagonal phase content will boost the overall photoluminescence emission intensity. The self-activated luminescence intensity increases with the increase in the amount of Sm doping up to a maximum at 0.2 mol% of Sm dopant. According to the phase identification by X-ray diffraction, the $Sm_2O_2S$ phase favors the $Sm^{+3}$ characteristic luminescence but it deteriorates in $Sm_2O_3$. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* Phosphors; Rare-earth element; Self-activated luminescence; Sm

## 1. Introduction

Currently, phosphors using ZnS as host have been widely investigated and commercially applied for the emission of blue or green light. However, to obtain red emission, more expensive $Y_2O_2S$ phosphors are essential [1,2].

II–VI compounds can emit sharp lines in the spectra; and they are also more efficient when lightly doped with rare-earth elements as activators [3]. Among these elements, Sm, by providing an effective luminescent center, can shift the emission peak toward longer wavelengths. Instead of a self-activated (S.A.) luminescence of the host lattice, Sm-doped ZnS, with Cl codoping, excited by ultraviolet light exhibits three sharp peaks which can be attributed to the intra-4f transitions from the $^4G_{5/2}$ level to the $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ levels, as depicted in Fig. 1 [4–9]. Nevertheless, the larger ionic radius of Sm compared to Zn, together with the valence mismatch of the Sm ion (trivalent) and the Zn ion (divalent) makes substitution of Sm into the Zn site in the ZnS compound difficult. Although some successful doping of Sm into ZnS through co-doping has been reported, the role of Sm in phosphors has not yet been reported and investigated.

In this study, Sm is used to dope to the ZnS without co-doping or flux, by solid state reaction. The relationships between photoluminescence and both the firing temperature, as well as the amount of doping element are investigated by firing in various atmospheres. Through analysis of the morphology of the crystal structure and of the photoluminescence of the fired phosphors, the luminescence mechanism is derived and confirmed. A less expensive ZnS host with red emission has been successfully prepared.

## 2. Experimental

Starting powders of high purity, ZnS (>99.99%) and activator $Sm(NO_3)_3$ (>99.9%) were weighed on an analytical balance to an accuracy of ±0.1 mg, and then mixed with distilled water. The mixed slurry was dried in a hot water bath. The powder was loaded into a platinum crucible and then fired at 1050°C for 1 h in inert ($N_2$) or reductive (CO gas) atmospheres. After air-

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cooling to room temperature, the photoluminescence emission and excitation spectra of polycrystalline phosphors were obtained using a Shimadzu RF-5301 spectrofluorophotometer. The excitation spectra were obtained from scanning wavelength from 250 to 400 nm monitored at 650 nm. The emission wavelength was scanned from 400 to 700 nm excited at 343 nm. The phases present in the phosphors were characterized by X-ray diffraction (XRD) using Rigaku-B X-ray diffractometer with Cu$K_\alpha$ radiation at 40 kV, 15 mV and 4°(2$\theta$)/min scanning rate. Observation of morphology and semi-quantitative composition determinations of phosphor powders were carried out by scanning electron microscopy (SEM), equipped with energy dispersive (EDS) analysis.

## 3. Results and discussion

### 3.1. *The effect of firing atmosphere on luminescence of phosphors*

ZnS:Sm (0.5 mol%) prepared by MOCVD method exhibits weak S.A. luminescence and strong $Sm^{+3}$ characteristic emission [4]. ZnS:Sm (0.5 mol%) prepared by conventional sintering under inert atmosphere at 650~1050°C for 1 h does not exhibit the $Sm^{+3}$ characteristic emission. A typical example of the excitation and emission spectra of ZnS:Sm fired under inert atmosphere is shown in Fig. 2. The excitation spectrum exhibits two peaks. The major peak, located at 343 nm, is associated with host lattice absorption. The minor peak at 375 nm can be attributed to charge transfer transition. The ZnS:Sm can be excited by ultraviolet light with lower energy. The emission peak at 475 nm (blue light) excited under 343 nm is attributed to S.A. luminescence of host lattice [3]. The half width of the peak of S.A. luminescence is relatively broad and the $Sm^{+3}$ characteristic emission does not occur.

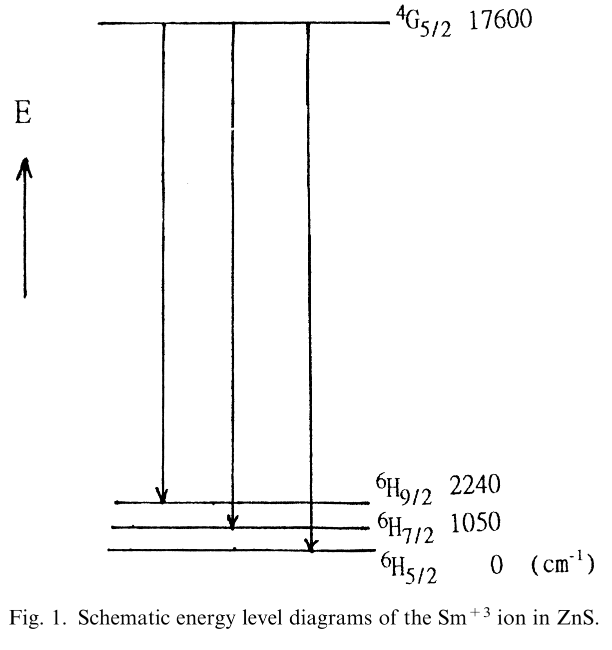


Fig. 1. Schematic energy level diagrams of the $Sm^{+3}$ ion in ZnS.

Due to the highly chemical activity of Sm, firing in a reducing atmosphere (CO gas) was used to mitigate oxidation of Sm in order to prevent or inhibit the formation of samarium oxide. The emission spectra of ZnS:Sm (0.5 mol%) firing under CO gas at 650–1050°C is given in Fig. 3. Only phosphors fired at 1050°C exhibit intra-4f transitions at 570, 606 and 653 nm, as predicted from the $^4G_{5/2}$ level to the $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ levels, respectively. Hence, ZnS:Sm fired under CO gas at 1050°C deserves further investigation.

### 3.2. *The effect of $Sm^{+3}$ dopant on luminescence of phosphors*

The effect of the amount of $Sm^{+3}$ dopant on luminescence firing at 1050°C under reductive atmosphere is shown in Fig. 4. Pure ZnS emits only very weak (negligible) self-activated luminescence at 475 nm. The intensity of S.A. luminescence of ZnS:Sm phosphors increases monotonically with increase of Sm concentration. The intensity of the $Sm^{+3}$ characteristic emission peak increases with increasing the amounts of Sm dopant until 0.20 mol%. At the same time, the S.A. luminescence is weak. An excellent red ZnS:Sm (0.2 mol%) phosphor, compared with ZnS:Sm (0.5 mol%), is expected. Further addition of Sm dopant (0.5~1.2

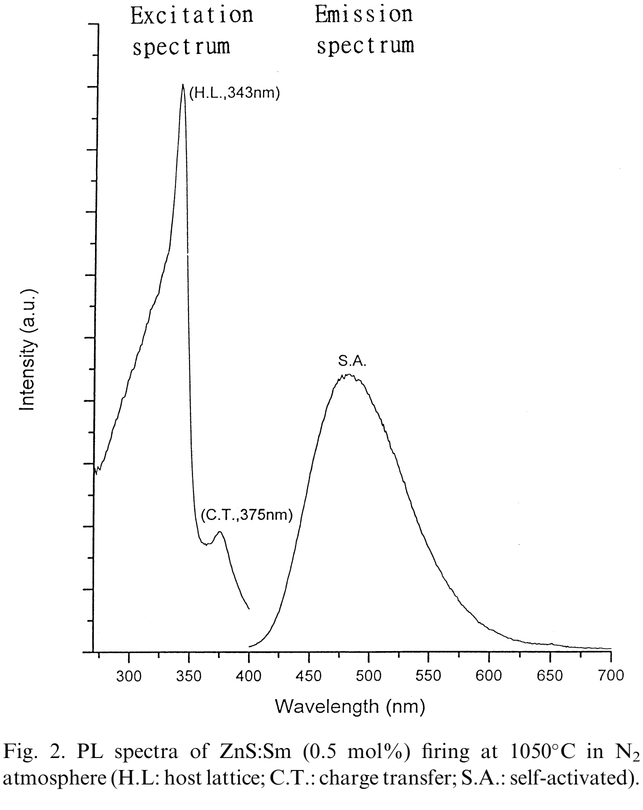


Fig. 2. PL spectra of ZnS:Sm (0.5 mol%) firing at 1050°C in $N_2$ atmosphere (H.L: host lattice; C.T.: charge transfer; S.A.: self-activated).

mol%) will suppress the $Sm^{+3}$ characteristic emission peak and enhance the S.A. luminescence. This may imply that the crystal structure has been modified after 0.5~1.2 mol% $Sm^{+3}$ doping.

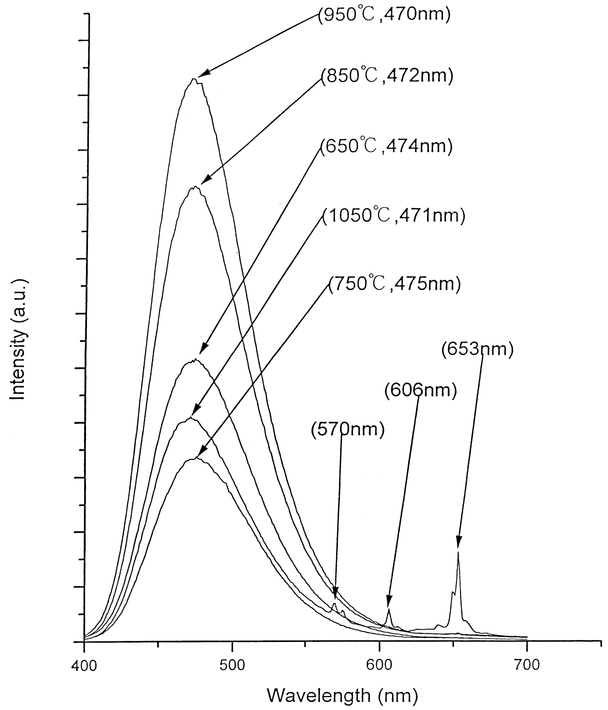


Fig. 3. Effect of firing temperature on emission spectra of ZnS:Sm (0.5 mol%) phosphors firing in reductive (CO gas) atmosphere.

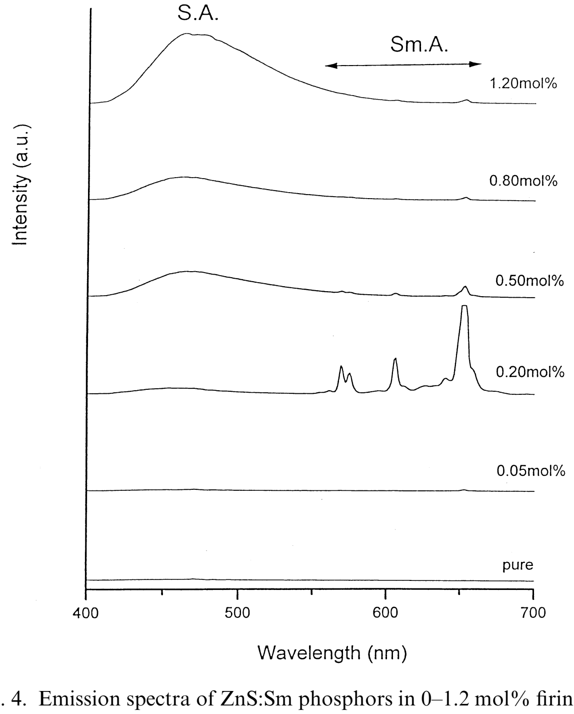


Fig. 4. Emission spectra of ZnS:Sm phosphors in 0–1.2 mol% firing at 1050°C in reductive (CO gas) atmosphere. (S.A.: self-activator; Sm.A.: Sm-activator).

### 3.3. The crystal structure of phosphors

The host structure of doped ZnS:Sm phosphors 0–1.2 mol% Sm, mainly consist of hexagonal (α) and cubic phases (β), determined from the X-ray diffraction patterns, as shown in Fig. 5. The weight ratio ($M_\alpha/M_\beta$) of α to β can be obtained from the intensity ratio of the $(100)_\alpha$ to $(200)_\beta$ [10].

$$\frac{M_\alpha}{M_\beta} = 0.0968\frac{I_\alpha}{I_\beta}$$

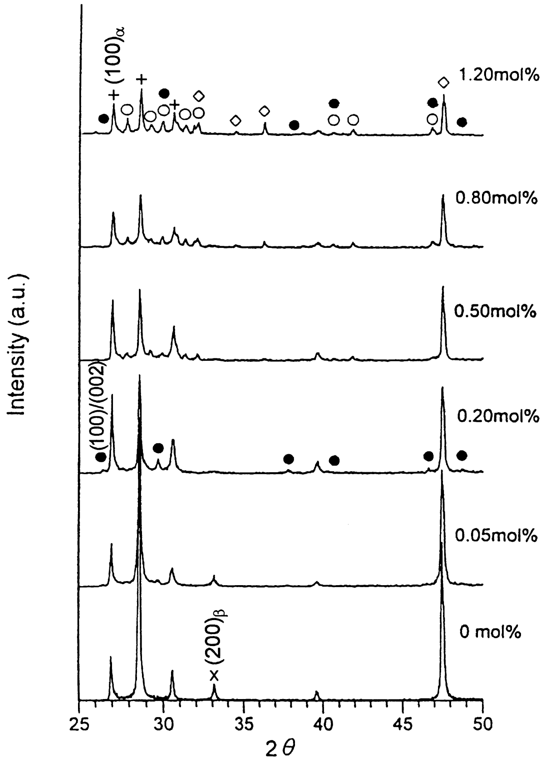


Fig. 5. X-ray diffraction pattern of ZnS:Sm phosphors in 0–1.2 mol% firing at 1050°C in reductive (CO gas) atmosphere. (●:$Sm_2O_2S$; □: $Sm_2O_3$; ◇: ZnO; +: hexagonal; ×: cubic).

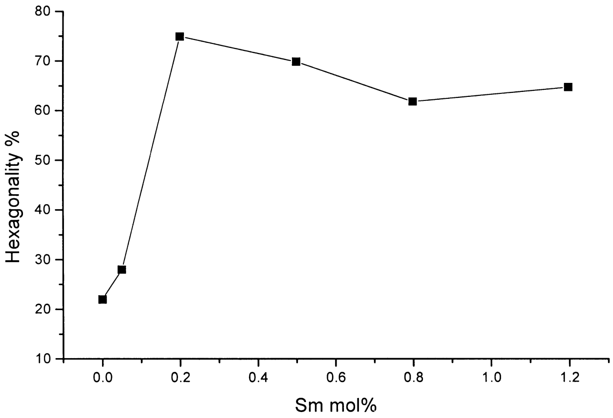
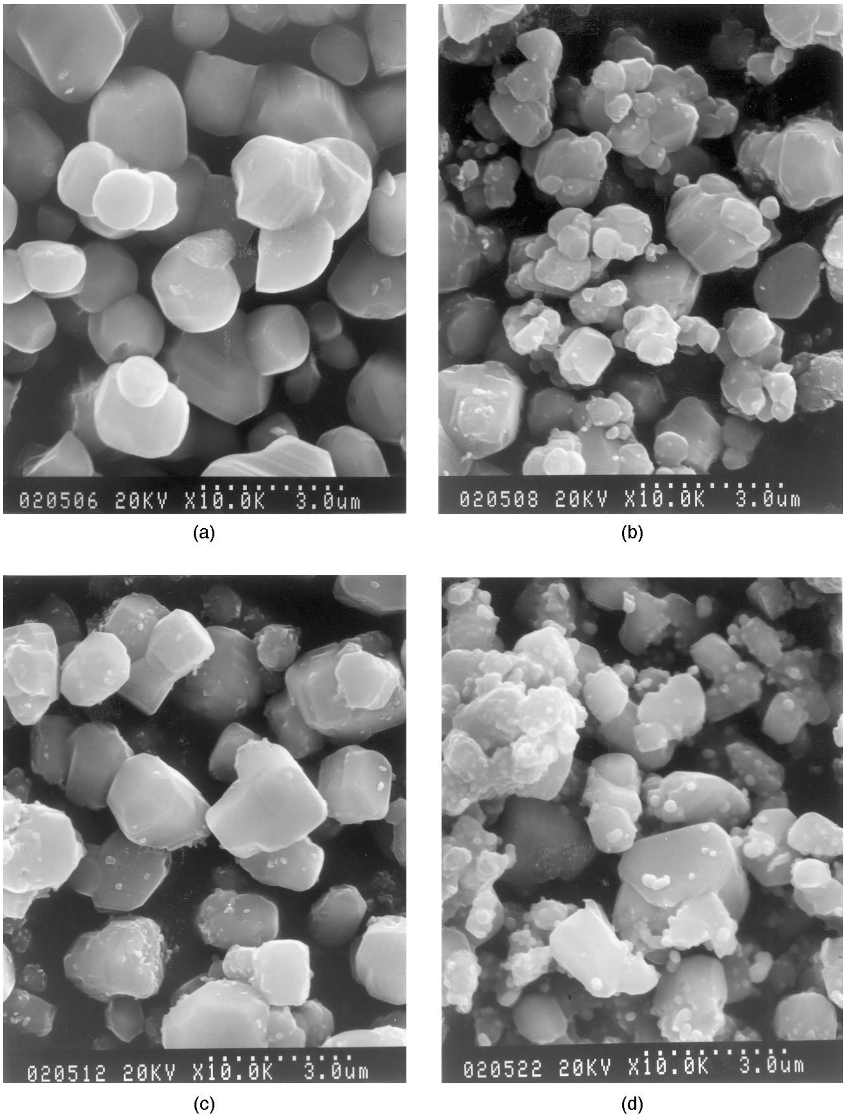


Fig. 6. Effect of Sm doping on the hexagonality of ZnS:Sm phosphors.

The content of hexagonal phase of ZnS:Sm fired in CO atmosphere at 1050°C increases from 22% for pure ZnS to a maximum (about 75%) for ZnS:Sm (0.2 mol%) as shown in Fig. 6. Further increase of Sm doping, from 0.2 to 1.2 mol% results in slight decrease in hexagonal content. However, the hexagonal phase is still $\geqslant 60\%$. Compared with Fig. 4, the hexagonal phase seems to favor an increase of the overall photoluminescence emission intensity. The result is in agreement with the fact that the phase transition from cubic to hexagonal phase at 1020°C will enhance the emission intensity [2].

Table 1
The relationships between luminescence spectra and phase composition for ZnS:Sm with various concentration of Sm

| Sm concentration (mol%) | Luminescence spectra | | X-ray spectra | | | |
|---|---|---|---|---|---|---|
| | Self-activator | Sm-activator | Hexagonal (%) | $Sm_2O_2S$ | $Sm_2O_3S$ | ZnO |
| 0 | Negligible | Absent | 22 | Absent | Absent | Absent |
| 0.05 | Very weak | Weak | 28 | Weak | Absent | Absent |
| 0.20 | Weak | Very strong | 75 | Strong | Absent | Absent |
| 0.50 | Strong | Strong | 70 | Weak | Weak | Weak |
| 0.80 | Strong | Weak | 62 | Weak | Strong | Strong |
| 1.20 | Very strong | Weak | 65 | Weak | Strong | Strong |



(a) (b) (c) (d)

Fig. 7. Morphologies of ZnS:Sm phosphors firing at 1050°C in reductive (CO gas) atmosphere: (a) pure (b) 0.05 mol% (c) 0.20 mol% (d) 1.20 mol%.

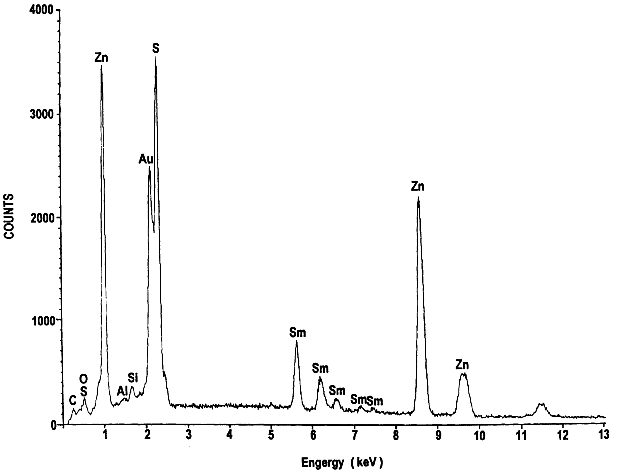
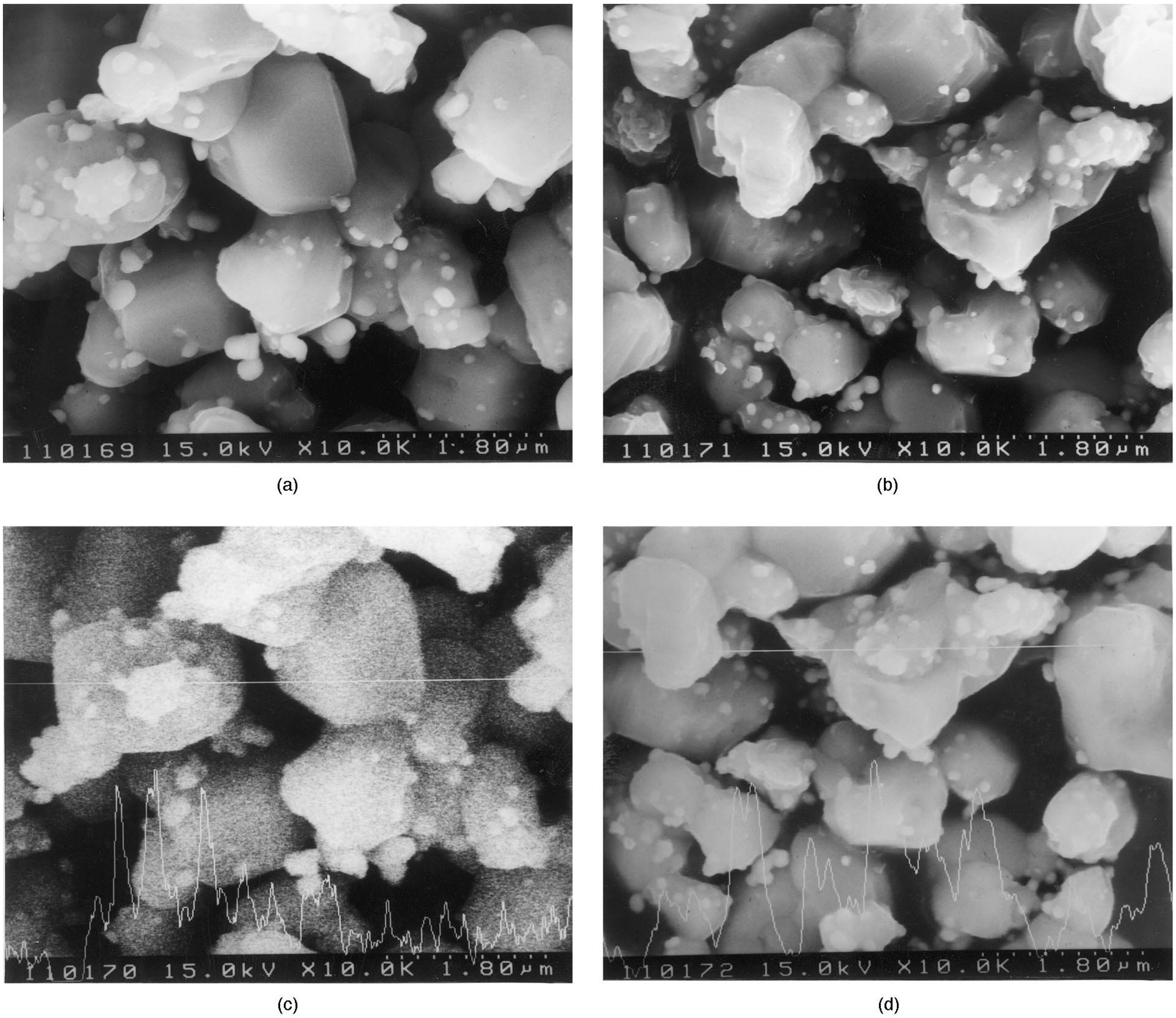


Fig. 8. The EDS analysis spectra of ZnS: Sm (0.2 mol%) phosphors firing at 1050°C in reductive (CO gas) atmosphere.

When the Sm concentration increases to 0.20 mol%, the appearance of the peak at 26.5° (2θ), associated with the (100) and/or (002) diffraction peaks of hexagonal $Sm_2O_2S$, appear. The amount of $Sm_2O_2S$ decreases obviously with increasing Sm doping from 0.5 to 1.2 mol%. At the same time, ZnO and $Sm_2O_3$ phases appear and increase as Sm doping increases from 0.5 to 1.2 mol%. In contrast to the emission spectrum, the $Sm^{+3}$ characteristic emission can be attributed to the presence of $Sm_2O_2S$ phase. The $Sm_2O_2S$ phase is structurally related to the $Sm_2O_3$ by S substitution on an oxygen site [11]. The $Sm_2O_2S$ phase may induce the bound-exciton (B.E.) Sm ($3^{+}\Rightarrow 2^{+}$) photoionization transition in ZnS [7]. The introduction of sulfur into the hexagonal phase will facilitate the $Sm^{+3}$ ($Sm^{+2}$ transition when excited. Moreover, compared with Fig. 4, the increase of ZnO and $Sm_2O_3$ can enhance the S.A. lumi-



(a) (b)

(c) (d)

Fig. 9. Sm line scanning for ZnS: Sm phosphors firing at 1050°C in reductive (CO gas) atmosphere: (a) 0.20 mol% (b) 1.20 mol% (c) 0.20 mol% Sm line scan, (d) 1.20 mol% Sm line scan.

nescence and suppress the $Sm^{+3}$ characterization emission [12]. The relationships between luminescence spectra and phase composition were summarized as indicated in Table 1.

The increase in the S.A. luminescence and the suppression of the $Sm^{+3}$ characterization emission will impair the properties of this compound as a red phosphor. According to the reaction equation

$$[S] + Sm_2O_3 = [O] + Sm_2O_2S,$$

lower oxygen partial pressure will favor the formation of $Sm_2O_2S$ and suppress the amount of $Sm_2O_3$. That is why the $Sm_2O_2S$ increases when fired in the CO atmosphere. The reductive atmosphere firing is suitable for the preparation of red ZnS:Sm phosphors.

### 3.4. *The morphology of phosphors*

The Sm dopant into phosphors has little influence on the particle size of phosphors, as shown in Fig. 7, indicating a particle size around $1 \sim 2$ μm. At the same time, Sm will cluster and form small particles attached to the ZnS particles. The attached particles apparently increase with increasing the amount of Sm dopant. Through the EDS analysis, as shown in Fig. 8, the attached particles are verified as the $Sm_2O_2S$ phase, as shown in Fig. 9.

## 4. Conclusions

1. The emission spectra of ZnS:Sm firing $N_2$ gas were mainly of blue light (475 nm), that is S.A. luminescence. But after firing in a reductive atmosphere at 1050°C, there are additional emissions at 570, 606 and 653 nm. These may be due to the intra-4f transitions from the $^4G_{5/2}$ level to the $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ levels, respectively.
2. ZnS:Sm fired in a reductive atmosphere at 1050°C with $0.05 \sim 1.2$ mol% Sm dopant range also emitted the $Sm^{+3}$ characteristic luminescence. The maximum intensity of the $Sm^{+3}$ characteristic emission is at the 0.2 mol% of Sm dopant. The S.A. luminescence will increase along with the increased Sm concentration.
3. The hexagonal phase of the host lattice can facilitate the increase of the overall emission intensity. In the ZnS:Sm phosphors, the $Sm_2O_2S$ phase, which exists as satellite particles attached to ZnS, will invoke the $Sm^{+3}$ characteristic emission luminescence at 570, 606 and 653 nm. The increase of ZnO and $Sm_2O_3$ can enhance the S.A. luminescence and suppress the $Sm^{+3}$ characterization emission.
4. The optimal parameters for preparing a red phosphors based on ZnS are the ZnS:Sm (0.2 mol%) firing under reductive atmosphere at 1050°C.

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