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Effect of LiCl flux on the red ZnS:Sm phosphors fired in reductive atmosphere

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Abstract

ZnS:Sm phosphors with strong red emission can be prepared by solid state reaction fired in a reductive atmosphere. Using LiCl as the fluxing agent favors the crystal growth of ZnS as well as increasing the content of the hexagonal phase in ZnS. The higher content of the hexagonal phase and evenly-distributed samarium compound on ZnS can induce greater light energy absorption and result in better photoluminescence emission intensity and color purity. The red emission intensity of ZnS:Sm phosphors is increased about 5 times with the addition of LiCl flux agent compared with the addition of Sm alone without any flux agent. The optimal concentration of LiCl flux is 2.0 mol% for ZnS with doping 0.2 mol% Sm phosphors fired in a reductive atmosphere.

Keywords: ZnS; Phosphor; Flux; Firing

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1. Introduction

Phosphors find wide application in technology, such as in a fluorescent tube, cathode ray tube, picture tube, display, and coating materials. Currently, the available and commercial phosphors for blue or green light are made from ZnS as a host. However, for red emission, expensive Y_2O_2S phosphors play an important role [1,2].

Group II–VI compounds can emit sharp lines in the spectra and become more efficient when doped with minor rare-earth elements as activators [3]. Through Sm doping, ZnS under ultraviolet light excitation has exhibited three sharp light peaks attributed to the intra-4f transitions from the $^4G_{5/2}$ level to the $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ (red light) levels, respectively [4].

A current successful method for preparing ZnS:Sm as red phosphors is achieved mostly by MOCVD [4,5]. Previous study indicates the red light of ZnS phosphor can be prepared by solid state reaction, through doping 0.2 mol% Sm without flux fired in a reductive atmosphere at 1050°C [6]. Nevertheless, the intensity of red light emission is too low for commercial application. The larger ionic radius of Sm than that of Zn and the valence mismatch of Sm ion (trivalent) and Zn ion (divalent) make it difficult for the substitution of Sm into a Zn site in ZnS compound. The flux agent LiCl can promote growth of the CaS phosphors grain [7] and aids in the transfer of the electrons of the host lattice to Sm^{+3} B.E., thus increasing the emission spectra intensity [8–11]. This study attempts by adding NaCl or LiCl to ZnS:Sm as flux agent to enhance the red Sm characteristic emission and not to deteriorate the color purity. The effect of the concentration of flux agent on the photoluminescence of ZnS:Sm fired in a reductive atmosphere will also be investigated through analysis of the morphology and crystal structure of the phosphors.

2. Experimental

Starting powders of high purity, ZnS (>99.99%), activator $Sm(NO_3)3$ (>99.9%) and fluxes LiCl (>99.5%) or NaCl (>99.5%) 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 loaded in a platinum

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crucible was fired at 1050°C for 1 h in a reductive atmosphere. After air-cooling to room temperature, the photoluminescence emission and excitation spectra were obtained using a Shimadzu RF-5301 spectrofluorophotometer. The excitation spectra can be obtained with 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. Phases present in the phosphors were characterized by X-ray diffraction (XRD) using Rigaku-IIB X-ray diffractometer with CuK_α radiation at 40 kV, 15 mA and 4°(2θ)/min scanning rate. Observation of morphology and semi-quantitative composition determinations of the phosphor powders is carried out by scanning electron microscopy (SEM), using Hitachi S4100 model, equipped with energy dispersive (EDS) analysis.

3. Results and discussion

3.1. *Effect of different fluxes on luminescence characteristics*

As shown in Fig. 1, ZnS with 0.20mol% Sm^{+3} ion doping prepared from solid state reaction at 1050°C in a reductive atmosphere exhibits weak red emission and negligible S.A. luminescence, as in a previous report [6]. While adding NaCl as flux, the Sm characteristic emission is suppressed and the host luminescence (blue light), associated with a Sm-Vzn-Cl mechanism [2], enhanced. That implies that the NaCl flux cannot facilitate the transfer of the transition from S.A. to Sm characteristic emission, regardless of firing in the reductive atmosphere or not.

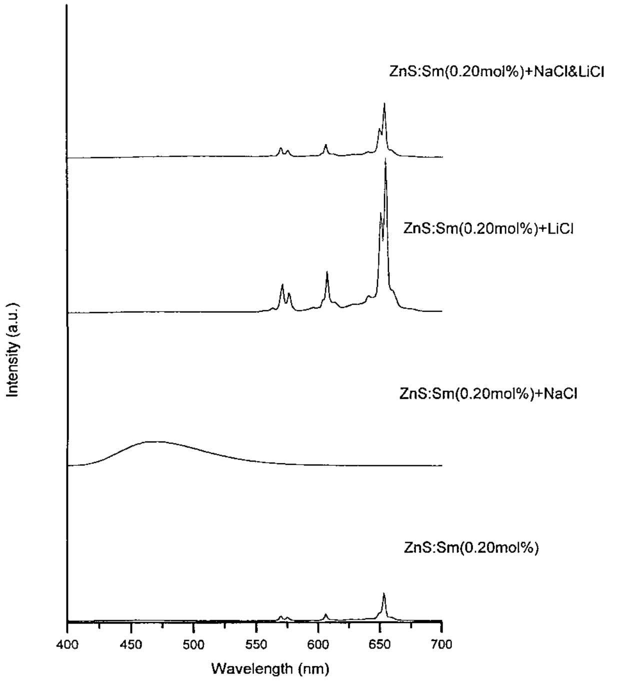


Fig. 1. The effect of flux on emission spectra of ZnS:Sm (0.20 mol%) phosphors with and without flux phosphors (S.A.: self-activator; Sm.A.: Sm-activator).

Owing to its small radius, the Li^{+} ion can readily enter the ZnS lattices interstitially and influence the transfer of Sm^{+3} B.E. (bound exciton). The transfer can aid the displacement of the electrons in Sm^{+}3 within the ZnS lattices, thus lowering the luminescence intensity of the host and improving the emission intensity of the Sm characteristic spectra. As shown in Fig. 1, the red emission intensity of ZnS:Sm phosphors is increased about 5 times with the addition of a LiCl flux agent compared with the addition of Sm alone without any flux agent. It can thus be appreciated that lithium has the effect of aiding electron transfer. The emission intensity is less when LiCl + NaCl are added than when LiCl is added alone, indicating that LiCl has the effect of enhancing the generation of the Sm characteristic spectra, whereas NaCl has the effect of inhibiting the generation of the Sm characteristic spectra. Although the existence of Cl ion in ZnS may increase intensity of luminescence [2,4,5], it seemingly plays a minor role in increasing the Sm characteristic emission.

3.2. *Effect of various concentrations of LiCl fluxes on luminescence characteristics*

The effects of LiCl concentration on the photoluminescence spectra are shown in Fig. 2. As opposed to the NaCl flux addition, the LiCl flux addition can fully suppress S.A. luminescence and induce the Sm characteristic emission. When the LiCl concentration is low, the intensity of the Sm characteristic emission increases as the LiCl concentration increases. Upon reaching 2.0 mol% LiCl concentration, the optimum emission effect can be obtained. However, when the LiCl concentration is further increased, the intensity of the characteristic emission drops.

3.3. *The crystal structure of phosphors*

Fig. 3 shows the effect of various amount of LiCl flux addition in ZnS with 0.2 mol% Sm^{+3} doping on the X-ray diffraction patterns. The host lattice of ZnS:Sm phosphors mainly consists of hexagonal phase (α) and cubic phase (β). The appearance of the peak at 26.5° (2θ), associated with the (100) and/or (002) diffraction peaks of Sm_2O_2S hexagonal phase, indicates that Sm_2O_2S phase appears. The appearance of the peak at 52.3° (2θ), associated with the (103) diffraction peaks of Sm_2O_3 hexagonal phase, indicates that Sm_2O_3 hexagonal phase appears.

The weight ratio (M_α/M_β) of α to β can be obtained from the intensity ratio of the $(100)_\alpha$ to $(200)_\beta$ [12].

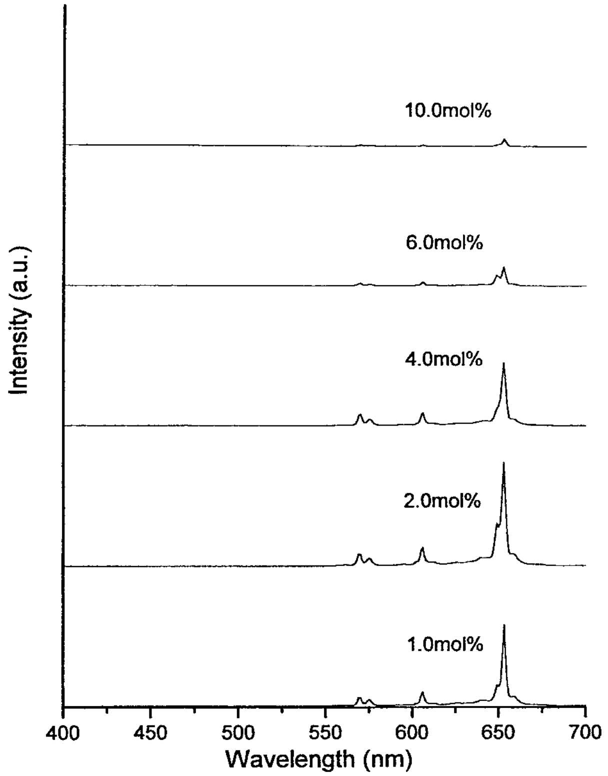


Fig. 2. Effect of LiCl flux concentration (1.0–10.0 mol%) on emission spectra of ZnS:Sm (0.2 mol%) phosphors.

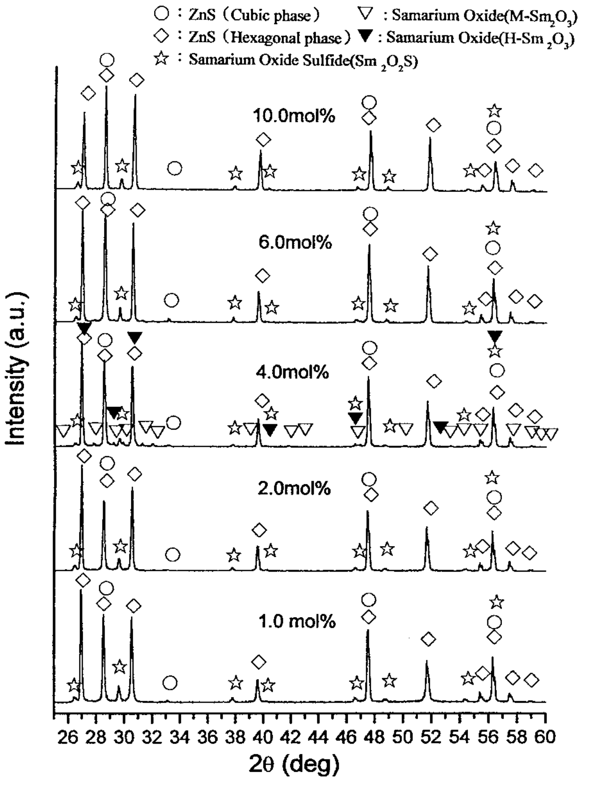


Fig. 3. X-ray diffraction pattern of ZnS:Sm (0.2 mol%) phosphors in 1.0–10.0 mol% LiCl.

$$\frac{M_\alpha}{M_\beta} = 0.968\frac{I_\alpha}{I_\beta}$$

The content of hexagonal phase can be calculated and is illustrated in Table 1. According to previous study, the hexagonal phase of ZnS can raise the excitation energy and result in the increase of the PL intensity [6]. In contrast to the maximum value of 75% hexagonal phase in previous report, the introduction of LiCl flux can further enhance the content of the hexagonal phase to 75% and above, while the second phase consists of the Sm_2O_2S hexagonal phase and Sm_2O_3 hexagonal phase. All three hexagonal phases favor the Sm characteristic emission. For low concentration (below 2 mol%) of LiCl addition, as shown in Fig. 4, the increase of hexagonal phase due to the increase in LiCl can enhance the intensity of the Sm characteristic emission, as predicted. However, for high LiCl concentration, the Sm characteristic emission intensity reduce substantially compared to the decrease in the content of the hexagonal phase. That implies that the content of the hexagonal phase is not the only factor to affect the emission intensity.

Morphologies of ZnS:Sm fired with various amounts of LiCl flux are shown in Fig. 5. Obviously, the particle size increases with the increase in the content of LiCl

Table 1
The relationships between luminescnce spectra and phase composition for ZnS:Sm (0.2 mol%) with various concentration of LiCl

LiCl (mol%)	Luminescence spectra		X-ray spectra			
	S.A.	Sm A.	Hex. (%)	Sm_2O_2S	H-Sm_2O_3	M-Sm_2O_3
1.0	Absent	Strong	84	Strong	Absent	Absent
2.0	Absent	Very strong	89	Strong	Absent	Absent
4.0	Absent	Strong	86	Strong	Weak	Weak
6.0	Absent	Weak	75	Strong	Absent	Absent
10.0	Absent	Very weak	83	Strong	Absent	Absent

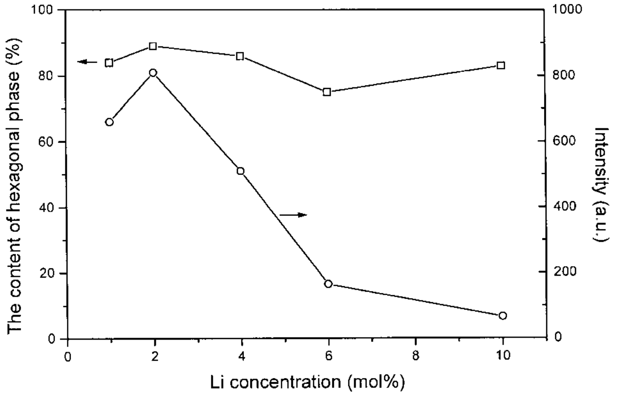
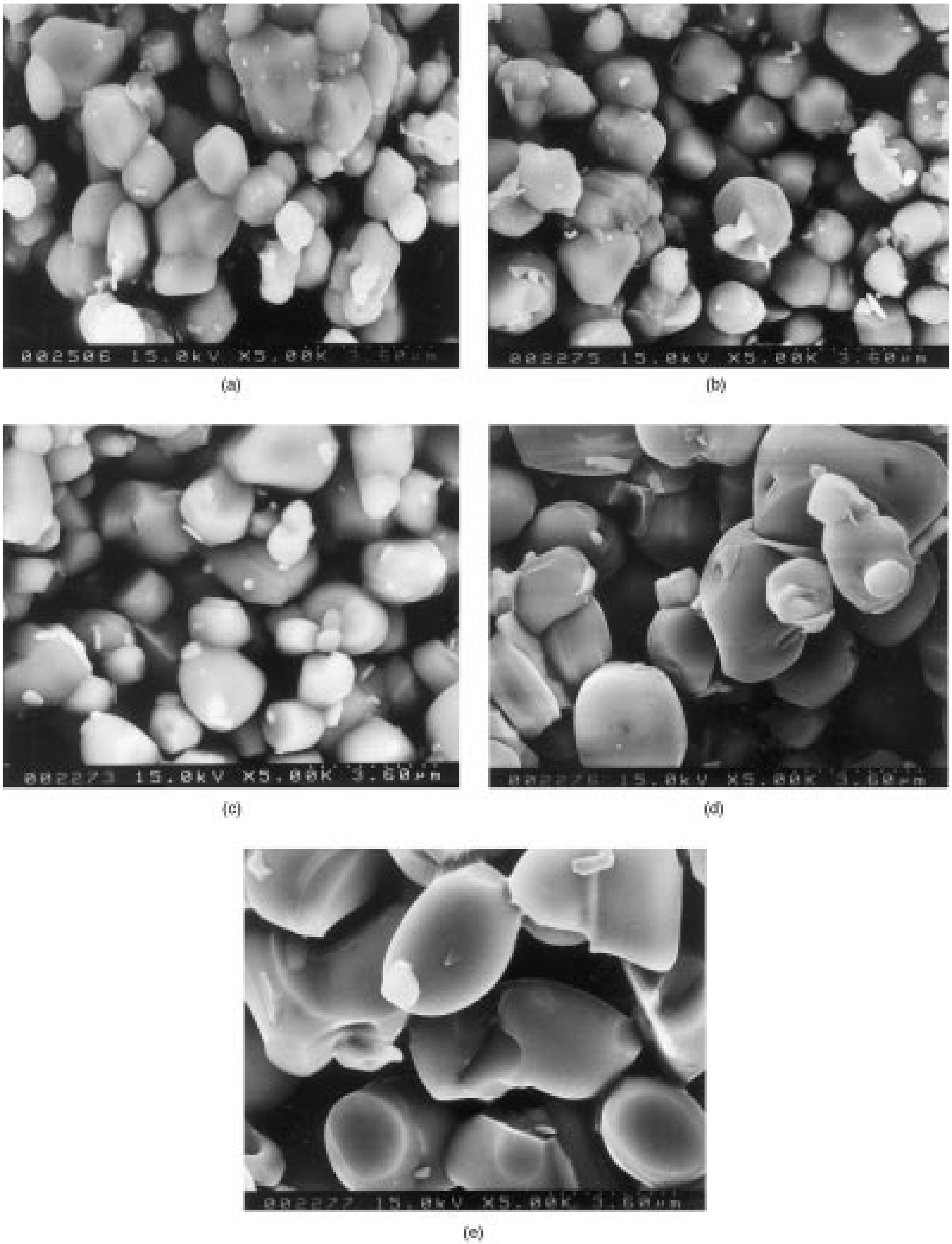


Fig. 4. Effect of the concentration of LiCl on the content of hexagonal phase and red Sm characteristic emission intensity of ZnS:Sm (0.2 mol%).



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

Fig. 5. Morphologies of ZnS:Sm phosphors with various amount of LiCl flux: (a) 1.0 mol%; (b) 2.0 mol%; (c) 4.0 mol%; (d) 6.0 mol%; (e) 10.0 mol%.

flux, as predicted [7]. The protrusions attached on ZnS particles were confirmed as samarium compound in previous report [6]. For ZnS:Sm with low concentration of LiCl flux, the small protrusion are uniformly attached on ZnS particles, as indicated by Sm mapping in Fig. 6(b). As the concentration of LiCl increases, the protrusions on ZnS become larger and sparse. That will result in uneven distribution of Sm, as shown in Fig. 6(d).

In contrast to the evenly-distributed Sm of ZnS:Sm with 2 mol% LiCl flux, the local accumulation of Sm for the ZnS:Sm phosphors with 10 mol% LiCl flux may be another factor to reduce the Sm characteristic emission. That is, in addition to the reduction of hexagonal content, the local accumulation of Sm may further reduce the Sm characteristic emission due to the interference between the Sm^{+3} B.E. luminescent centers.

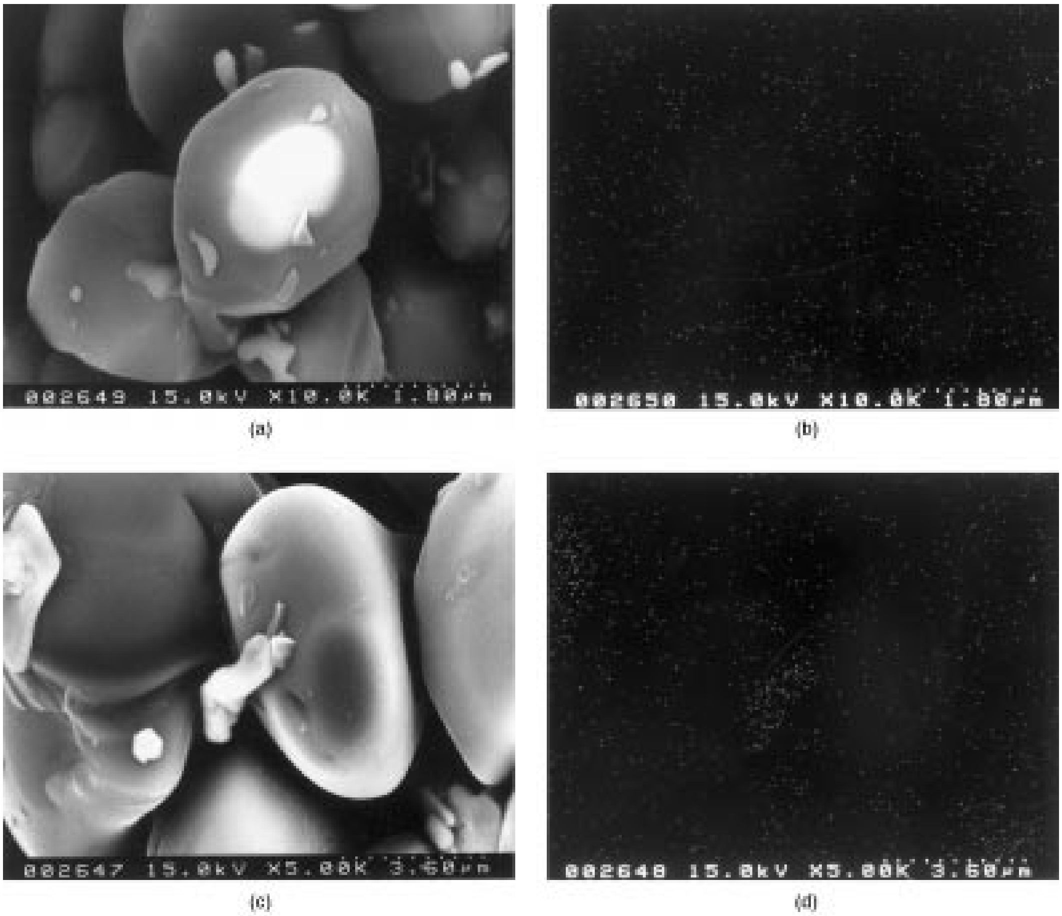


Fig. 6. Sm mapping for ZnS:Sm (0.2 mol% Sm) phosphors: (a) 2.0 mol% LiCl (10,000×) (b) 2.0 mol% LiCl (10,000× Sm mapping; (c) 10.0 mol% LiCl (5000×);(d) 10.0 mol% LiCl (5000×) Sm mapping.

4. Conclusions

1. LiCl can enhance the generation of the Sm characteristic spectra, whereas NaCl has the effect of inhibiting the generation of the Sm characteristic spectra. The addition of LiCl flux agent favors electron transfer from the host to the Sm^{+3} B.E. luminescent center, thus enhancing the intensity of the main characteristic peaks. When the LiCl concentration is further increased, the intensity of the characteristic emission decreases. This might be related to the Sm compound being melted by LiCl, coagulating and then being unable to disperse uniformly by itself. The optimal concentration of LiCl flux is 2.0 mol%.
2. Only fired in a reductive atmosphere, the red Sm characteristic emission can be obtained for ZnS:Sm phosphors with or without the addition of LiCl flux.
3. The higher content of hexagonal phase and evenly-distributed Sm compound seem to be requisites for ZnS:Sm phosphors to emit strong red photoluminescence.

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References

[1] J.E. Yang (Ed.), The Application and Investigation of Luminescent Materials in Electronic Industry, Technical Report, ITRI, Hsinchu (Taiwan), 1992, p. 58.
[2] Phosphor Members Committee (Ed.), Phosphors Handbook, OHM Society, Tokyo, 1987, p. 279.
[3] G. Blasse, B.C. Grabmaier, Luminescenct Materials, Springer–Verlag, New York, 1994, p. 44.
[4] A. Kato, M. Katayama, A. Mizutani, Y. Hattori, N. Ito, T. Hattori, Satellite peak generation in the electroluminescence spectrum of ZnS: Sm grown by metalorganic chemical vapor deposition with Cl codoping, J. Appl. Phys. 76 (5) (1994) 3206–3208.
[5] A. Kato, M. Katayama, A. Mizutani, Y. Hattori, N. Ito, T. Hattori, ZnS: Sm grown by metalorganic chemical vapor deposition with Cl codoping, J. Appl. Phys. 77 (9) (1995) 4616–4622.

[6] T.P. Tang, M.R. Yang, K.S. Chen, Photoluminescence of ZnS:Sm phosphor prepared in a reductive atmosphere, Ceram. Int. 26 (2) (2000) 153–158.

[7] O. Kanehisa, H. Yamamoto, Local environment of Ce^{+3} ions in CaS prepared with or without flux, J. Electrochem. Soc. 141 (11) (1994) 3188–3193.

[8] D.S. McClure, Excitons trapped at impurity centers in highly ionic crystals, Phys. Rev. B32 (1985) 8465–8468.

[9] K. Swiatek, M. Godlewski, Recombination processes in ZnS:Sm, Phys. Rev. B43 (1991) 9955–9958.

[10] K. Swiatek, M. Godlewski, Deep europium-bound exciton in a ZnS lattice, Phys. Rev. B42 (1990) 3628–3633.

[11] J. Lin, Q. Su, H.J. Zhang, S.B. Wang, Crystal structure dependence of the luminescence of rare earth ions (Ce^{3+},Tb^{3+},Sm^{3+}) in Y_2SiO_5, Mater. Res. Bull. 31 (2) (1996) 189–196.

[12] B.L. Li, C.X. Guo, Y.T. Wan, Influence of doping by trace Cu or Mn in sintering process on structural transformations of ZnS electroluminescent phosphor, Acta Physica Sinica 40 (3) (1991) 490–497.