Spectroscopic characterization of electroluminescent ZnS:Cu,Cl phosphor coated by sol-gel process

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Abstract
The photoluminescence, electroluminescence and surface properties of ZnS:Cu,Cl phosphor coated by sol-gel process were studies. Na-silicate was used as precursor coating material. pH of solution and the concentration of Na-silicate are the important conditions to obtain the uniform coating on the phosphors. Also, the electroluminescent devices were made with Na-silicate coated phosphor. The spectroscopic characterization is performed by photospectrometer.

1. Introduction
The value of electroluminescent (EL) phosphors having commercial applications such as for LCD, copy machines, automotive dash-board display etc., lies in their long-life and stability against high electrical resistance [1]. However, one of the main draw-back of ZnS-type of phosphors to be used in EL device is their instability against moisture and environmental components during their use. Surface of the phosphor material plays important role in its luminescence since surface structural defects and functional groups may serve as electron or hole traps [2]. Therefore, the phosphors were coated with thin layers of inert materials viz. SiO_2, Al_2O_3 or other oxides by different techniques to enhance the stability of the sulfide phosphors [3-5]. In this communication, our emphasis is to coat a thin protective layer by sol-gel on the ZnS:Cu,Cl phosphor particles to make resistant against moisture or chemical deterioration and then to measure the EL performance of ZnS:Cu,Cl phosphor with thick film EL devices.

2. Experimental
ZnS:Cu,Cl phosphor with average 20~32㎛ particle size was used as a base material for coating. NaOH solution was added in the mixture solution of boric acid and KCl, to attain a particular value of pH. Then Na-silicate solution was added drop-wise to this buffer solution. The solution containing phosphor was repeatedly washed with decantation while adding distilled water to remove electrolytes. The solid was recovered by filtration then dried at 60℃ and further heated to 500℃ for 1 hour in the furnace. The experiments were performed at different pH, with different amount of Na-silicate and at different sintering temperatures.

The thick film EL devices were made by silk printing process and EL properties have been measured with EL device as a function of driving voltages and frequencies.

3. Results
The coating of SiO_2 by Na-silicate has much variability that can affect the surface morphology of the coatings. The amount of SiO_2 particles deposited on the surface increases with the increase of Na-silicate amount added to the phosphor suspension. The concentration of Na-silicate is 20wt.% [Fig. 1]. Smooth and evenly distributed coating over the phosphor particles was observed when the pH of buffer solution was 10~11[Fig. 2]. Effect of the firing temperature to transform the $Si(OH)_4$ identified as an amorphous phase to crystalline SiO_2 was also studied. The most suitable temperature based on the results was proved between 400~500℃, in which suppression of ZnS oxidation and crystallization of SiO_2 were simultaneously confirmed. The hydrolyzed surface of ZnS not only facilitates the growth of SiO_2 on the surface, but it also tends to adhere SiO_2 particles in a better way. Bonding situation between coating oxide particles and the surfaces of ZnS phosphor may be

like as shown in Fig. 3[6-7]

Emission properties of the device were also studied by recording the EL spectra at different voltages and frequencies. In particular, the measurements at fixed voltages were performed at 100V by varying the frequency from 100Hz to 900Hz while the measurements at fixed frequency were carried out at 400Hz by varying the voltage from 40V to 200V[Table 1]. As a result, on increasing voltage and frequency, EL intensity and brightness were increased [Fig. 4]. Also, the life-time of the electroluminescent device was improved by coating phosphors [Fig. 5].

4. Conclusion

This paper reveals that smooth coating on particles was achieved by Na-silicate by sol-gel process and better EL properties were observed for driving voltage and frequency.

A continuous, evenly thick and transparent SiO_2 coating on ZnS:Cu,Cl phosphor could be obtained by adding 20% Na-silicate amount by drop-wise to the buffer solution maintained at pH=10~11 and then by sintering at the temperature between 400~500℃.

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In addition, with EL devices, we tested EL luminance properties of the uncoated and coated phosphors at different applied voltages and frequencies. Remarkable improvement with EL properties was noticed of the coated phosphor.

5. References

[1] H. Chander, V Shanker, D. Haranath, Suman Dudeja and Pooja Sharma, Material Research Bulletin, 38, 2003, 279-288

[2] V. Dimitrova and J. Tate, Thin solid films, 365, 2000, 134-138

[3] Rhim youl Lee, Sung woo Kim, J. Lumin. 93(2001)93

[4] K. Inoue, M. Watanabe, [p] US Patent No. 5224750

[5] W. Park, K. Yasuda, B. K. Wagner, C. J. Summers, Y. Do, H. G. Tang, [P] US Patent No. 2002/119247 Al.

[6] C. Feldmann, J. Merikhi, J. Colloidal and Interface Science 223, 229-234(2000)

[7] Myers, D. “Surfaces, Interfaces and Colloids.” VCH, Weinheim, 1991.

Table 1 EL brightness of the phosphor at different voltages and frequency

Voltage/ frequency	EL (cd/m^2)	Color coordinates	
		x	y
100/400	83.02	0.1708	0.4156
150/400	158.4	0.1796	0.4242
200/400	201.0	0.2070	0.4646
100/900	170.5	0.1766	0.4102
150/900	288.0	0.1994	0.4463
200/900	380.4	0.2080	0.4573

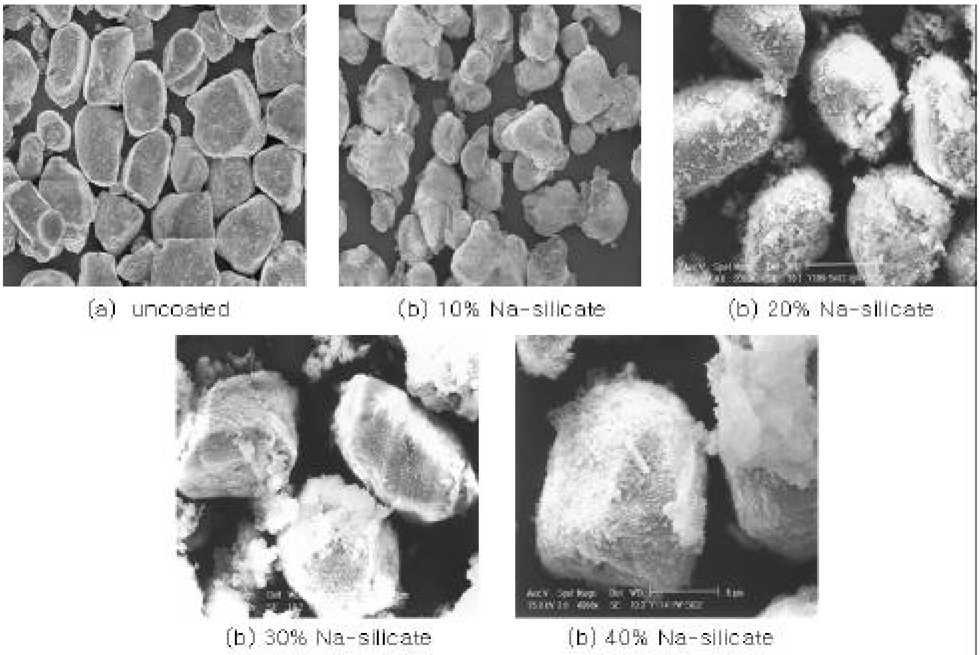

Fig. 1 SEM micrographs of ZnS:Cu,Cl phosphors coated with different Na-silicate amount

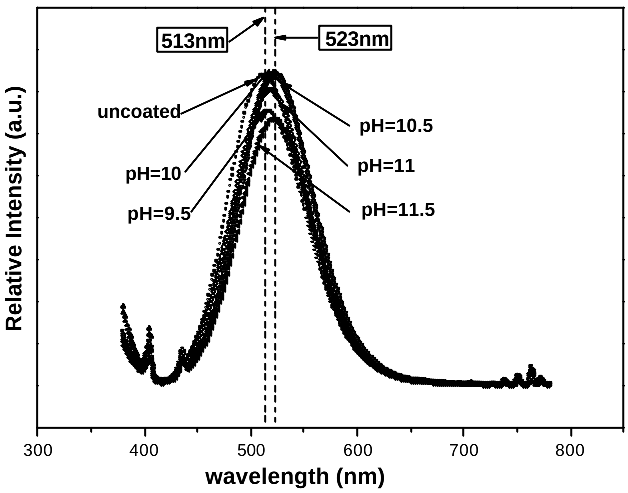

Fig. 2 PL spectrum of ZnS:Cu,Cl phosphors coated with different pH values

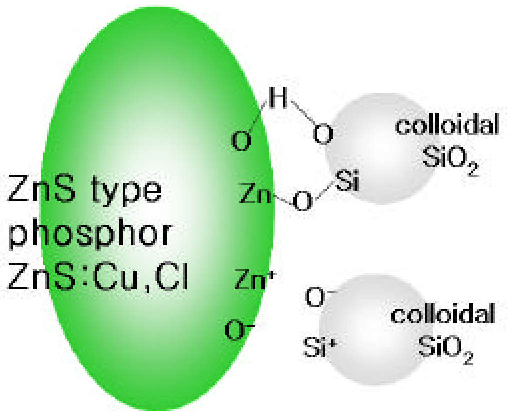

Fig. 3 Model of bonding between SiO_2 particles and ZnS:Cu,Cl particle

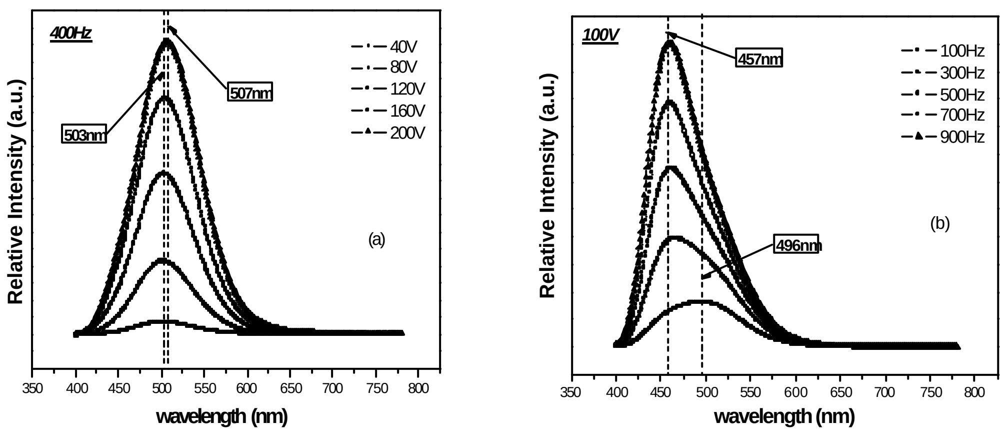

Fig. 4 EL spectrum at different voltages and frequencies (a) at fixed frequency, (b) at fixed voltage

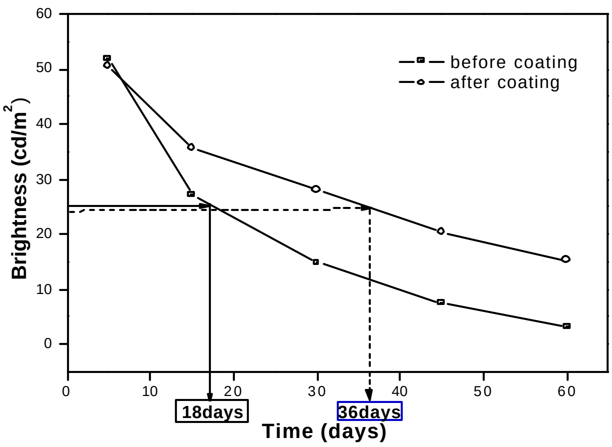

Fig. 5 EL properties of uncoated and coated phosphors