Effect of heat treatment condition on optical properties of ZnS:Mn,Cu,Cl phosphor

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Abstract

ZnS-based orange-emitting phosphors were synthesized by two-step firing process: above 1000°C to obtain hexagonal phase, and at 750°C for cubic phase. The effect of heat treatment condition on the optical properties was investigated to find an optimum condition for high-performance ZnS:Mn,Cu,Cl phosphor.

1. Introduction

ZnS:Mn,Cu,Cl phosphor is synthesized by many different steps such as material selection, blending, drying, firing, washing, milling, and so on. The firing step is important for synthesis of phosphors to control the particle size and uniformity, and the properties [1]. The optical property of the ZnS:Mn,Cu,Cl phosphor was investigated altering heat treatment conditions during the synthesis process.

2. Experimental

The powders of ZnS:Mn,Cu,Cl phosphor were synthesized by solid-liquid state reaction with two firing step. A proper quantity of flux - NaCl, $MgCl_2{\cdot}6H_2O$ and $BaCl_2{\cdot}2H_2O$ - was mixed with ZnS host material and impurities of Mn^{2+} and Cu^{2+} [1]. As-mixed samples were heat-treated at 1000, 1100, 1150, 1200, or 1300ºC with an extra amount of sulfur, followed by washing and drying. After the resulting products were ground with impurity precursors, they were treated at 750ºC (the 2nd firing), washed, and dried. At the 2nd firing step, samples were quenched after heating at 750ºC for a couple of hours. The quenching temperatures were 750, 500 and 300ºC. Non-quenched sample was also prepared to compare with the above-samples quenched at different temperatures.

The structure and morphology of phosphor particles and their PL properties were studied by means of X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and PL emission spectra. The phosphor samples were excited with UV light λ_{exc} = 352 nm. Emission spectra were recorded on Minolta CS-1000. Using the obtained phosphor powders, EL devices were fabricated by screen-printing method. PL and EL spectra of the phosphors synthesized with different conditions of heat treatment were investigated.

3. Results and discussion

SEM images in Fig. 1 shows the morphology of ZnS:Mn,Cu,Cl phosphors treated at 1000, 1150, or 1300°C of the 1st firing step. The phosphor from 1000°C does not have round-shape particles unlike those from 1150 and 1300°C. According to XRD patterns of these samples (Fig. 2), phosphor obtained by 1000°C-heat treatment of the 1st firing step exhibits mainly cubic phase after the 1st firing as well as after the 2nd firing, while phosphors synthesized by 1150 and 1300°C-heat treatment of the 1st firing step show hexagonal phase after the 1st firing, and mainly transfer to cubic phase through the milling and the 2nd firing processes.

Table 1 shows PL and EL intensity data of ZnS:Mn,Cu,Cl phosphors synthesized with different temperatures of the 1st firing step. The optimum temperature for the 1st firing was found to be 1150°C to obtain the highest PL and EL intensities. The EL intensity of phosphors is dramatically affected by the 1st firing temperatures compared with the PL intensity changes.

Samples treated at 1150°C for the 1st firing was treated at 750°C for the 2nd firing after done whole process necessary. At the 2nd firing step, quenching conditions differed for the sample cooling as shown in Table 2. No matter what condition was for cooling, the PL intensities were not significantly different from each other. However, maximum EL intensity was obtained from a sample quenched at 750°C, firing temperature of the 2nd step, which is ~260 % of EL intensity of non-quenched sample. The EL spectra of ZnS:Mn,Cu,Cl phosphors synthesized with different heat treatment conditions are shown in Fig. 3.

4. Summary

Heat treatment conditions could be optimized for optical properties of ZnS:Mn,Cu,Cl phosphor, controlling firing and cooling temperatures during the synthesis. It was found that the temperature quenching at the 2nd firing step significantly increases the EL intensity of ZnS:Mn,Cu,Cl phosphor, even though other synthesis conditions such as impurity concentration in ZnS are all same.

5. References

1. A.K. Kwon, M.Sc. Thesis, "Studies on the synthesis and luminescent properties of ZnS:Mn,Cu,Cl phosphor for ACPEL", Yonsei Univ., Seoul, Korea, (2006).

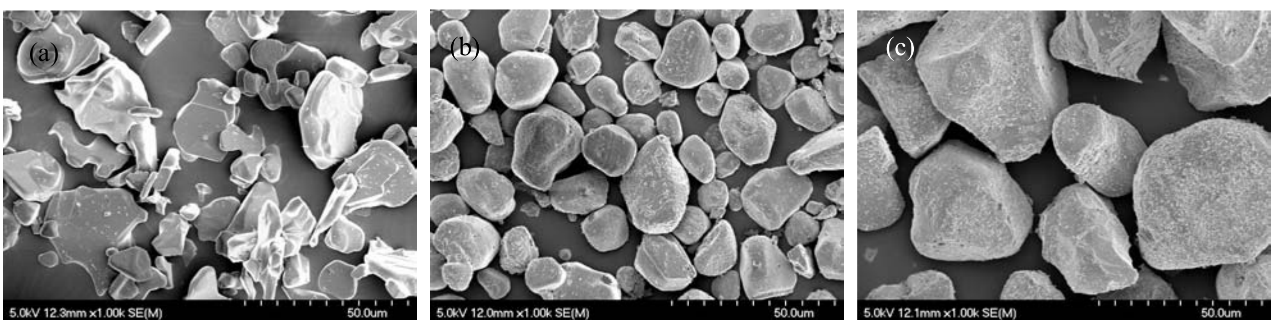

Fig. 1. SEM images of ZnS:Mn,Cu,Cl phosphors synthesized with different temperatures of the 1st firing step: (a) 1000°C; (b) 1150°C; (c) 1300°C

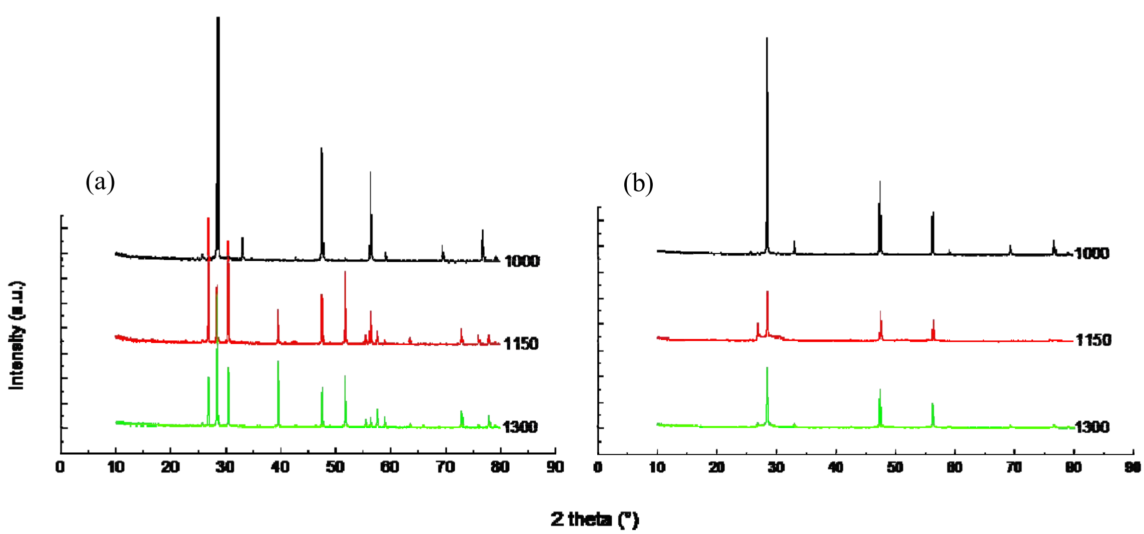

Fig. 2. XRD patterns of ZnS:Mn,Cu,Cl phosphors synthesized with different temperatures of the 1st firing step: (a) after the 1st firing; (b) after the 2nd firing step

Table 1. Luminescence properties of ZnS:Mn,Cu,Cl phosphors synthesized with different temperatures of the 1st firing step.

Temperature of the 1st firing step	1000°C	1100°C	1150°C	1200°C	1300°C
PL (after the 1st firing step)	43.44 (0.3755, 0.4396)	46.63 (0.4723, 0.4337)	45.49 (0.4503, 0.4387)	59.40 (0.4585, 0.4403)	74.00 (0.4719, 0.4592)
PL (final)	92.28 (0.5473, 0.4445)	98.11 (0.5369, 0.4545)	99.76 (0.5354, 0.4567)	98.95 (0.5423, 0.4511)	48.77 (0.5412, 0.4513)
EL (final)	6.35 (0.5402, 0.4439)	36.61 (0.5266, 0.4526)	**50.92** (0.5261, 0.4509)	45.18 (0.5285, 0.4506)	11.41 (0.5268, 0.4624)

Table 2. Optical properties of ZnS:Mn,Cu,Cl phosphors synthesized with different cooling conditions at the 2nd firing step.

Quenching temperature	750°C	500°C	300°C	non-quenching
PL (x,y color coordinates)	118.2 (0.5263, 0.4572)	110.8 (0.5356, 0.4577)	106.3 (0.5238, 0.4557)	119.0 (0.5256, 0.4569)
EL (x,y color coordinates)	**52.44** (0.5316, 0.4607)	41.25 (0.5327, 0.4605)	24.59 (0.5331, 0.4581)	19.97 (0.5294, 0.4606)

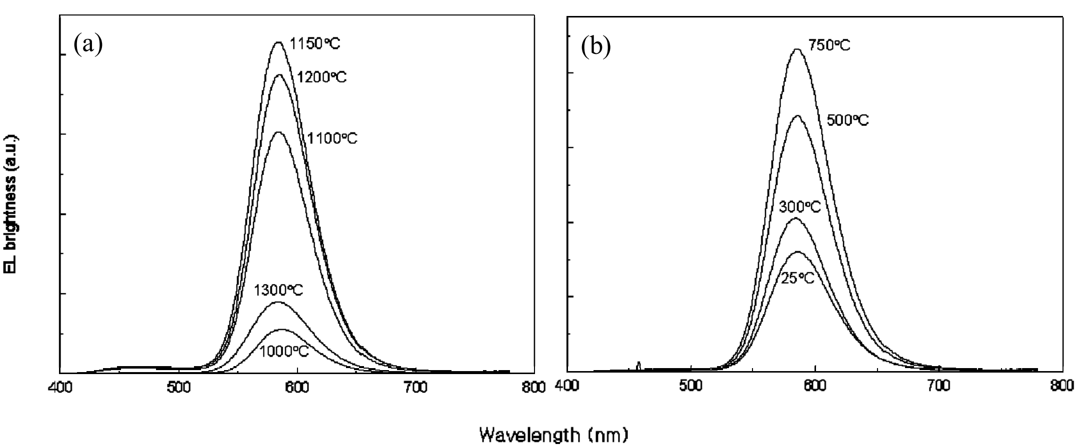

Fig. 3. EL spectra of ZnS:Mn,Cu,Cl phosphors synthesized with different heat treatment conditions: (a) different 1st firing temperatures; (b) different quenching temperatures at the 2nd firing step