Luminescence of orange-emitting ZnS:Mn,Cu,Cl for EL device

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Abstract

An orange-emitting phosphor for inorganic electroluminescent device has been studied. Cu and Cl were co-doped in Mn-doped ZnS for a high-performing phosphor. The effect of Mn^{2+}-doping concentration as well as Mg^{2+}-sensitizer addition on the luminescence characteristics has been investigated.

1. Introduction

It has been known that impurity doped zinc sulfide as well as thin films, single crystals and semiconductors exhibits electroluminescence (EL) phenomenon converting electrical energy to luminous energy without thermal energy generation [1,2]. EL devices have lately attracted considerable attention due to the solid-state construction and self-emissive characteristics, which can improve display performances for many applications [3,4]. Designing of the EL phosphor is one of the most important factors for a high-performing EL device. It is imperative to optimize phosphor properties to increase brightness and stability, etc. in the EL device development.

Currently the red phosphor in full-color EL devices is obtained by filtering the orange emission of ZnS:Mn [5]. It seems important to improve the luminescence properties of orange phosphor to get high efficiency and color saturation without filtering, since a considerable loss of luminance efficiency results from the use of a color filter. Concentration of impurities such as activator and co-activator in ZnS host material is very important condition to obtain a phosphor exhibiting commercially desirable brightness and color characteristic.

In this study, Cu,Cl co-doped ZnS:Mn orange phosphor has been investigated altering Mn concentration. The electroluminescent and the photoluminescent properties were characterized in the operating condition of 100V-400Hz and the excitation wavelength of 380 nm, respectively. The effect of sensitizer Mg^{2+} on the luminescence characteristics has been studied as well.

2. Results

Photoluminescence and electroluminescence spectra of the phosphors with various manganese concentrations were investigated. Cu concentration added in ZnS before the 1st and 2nd sintering steps was decided based on the results of previous work as the sample without Cu has no EL emission [6]. Mn- doping concentration in ZnS was 0.34 mol% (0.4 wt% $MnCO_3$ relative to the weight of ZnS) at the 1st sintering step and in the range of 0~8.5 mol% (0~10 wt% of $MnCO_3$) at the 2nd sintering step. The phosphor particle morphology and the crystal structure are characterized in ref. [7].

5.1 mol% Mn (6 wt% $MnCO_3$)-added sample in the 2nd mixing step showed the highest photoluminescence by 380 nm-excitation among the tested samples (175 % PL intensity compared with the 1st-sintered product), while the highest EL intensity of main emission peak at 582 nm and a color coordinate at x=0.5242, y=0.4674 was obtained with the sample of 5.9 mol% Mn concentration (7 wt% $MnCO_3$) in the 2nd mixing step. Figure 1 shows the orange-emitting EL device prepared using the as-synthesized phosphor. As another attempt, additional sulfur in the 2nd mixing step was used for the orange-phosphor synthesis. Although it was effective to increase luminescence of blue and green ZnS:Cu,Cl phosphor prepared in same process [8], small amount of sulfur added in the 2nd mixing step negatively affected not only the photoluminescence but also the electroluminescence.

Mg^{2+}-added samples were also prepared in order to investigate the effect of sensitizer on the luminescent property of orange-emitting ZnS:Mn,Cu,Cl phosphor. $MnSO_4$ added at the second mixing step was 0~2 mol%. The EL intensity increased over 20 %, while the increase of PL intensity by addition of 2 mol% $MgSO_4$ was only 3 %, compared with the sample without Mg^{2+}. The change by Mg^{2+}-addition is shown in Figure 2 with the EL spectra of phosphors synthesized with different Mg^{2+}-concentration. The EL intensity of the synthesized ZnS:Mn,Cu,Cl was 117 without Mg^{2+} addition and 142 with 2 mol% Mg^{2+}

addition, where the EL intensity of commercial one (Durel co.) was set to 100. The color coordinates of the synthesized phosphor with 2 mol% Mg^{2+}-sensitizer and the commercial one were x=0.5225, y=0.4697 and x=0.5417, y=0.4511, respectively, falling in the orange region of the diagram, as shown in Figure 3. Further investigations are in progress.

3. Conclusion

The luminescence characteristics of ZnS:Cu,Mn,Cl orange-emitting phosphor is dependent on manganese concentration in the mixing step before the 2nd sintering. Sulfur addition at the 2nd-mixing step decreases the luminescence while sensitizer Mg^{2+} favors the PL as well as the EL of the orange-emitting phosphor. The addition of 5.9 mol% Mn^{2+}-activator and 2.0 mol% Mg^{2+}-sensitizer at the 2nd mixing step during the synthesis process resulted in the best luminescent property of the orange-emitting ZnS phosphor, which is remarkably better than commercial one in terms of the EL intensity.

4. Acknowledgements

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5. References

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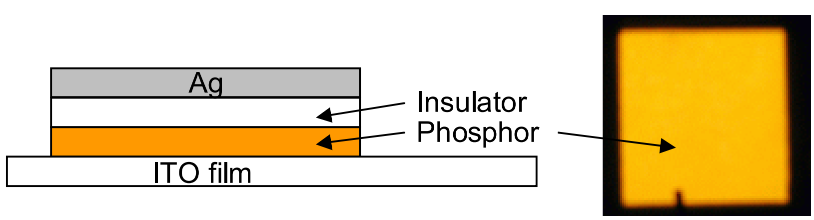

Figure 1. Schematic structure of EL device (left) and orange-emitting EL device operated at 100V-400Hz (right).

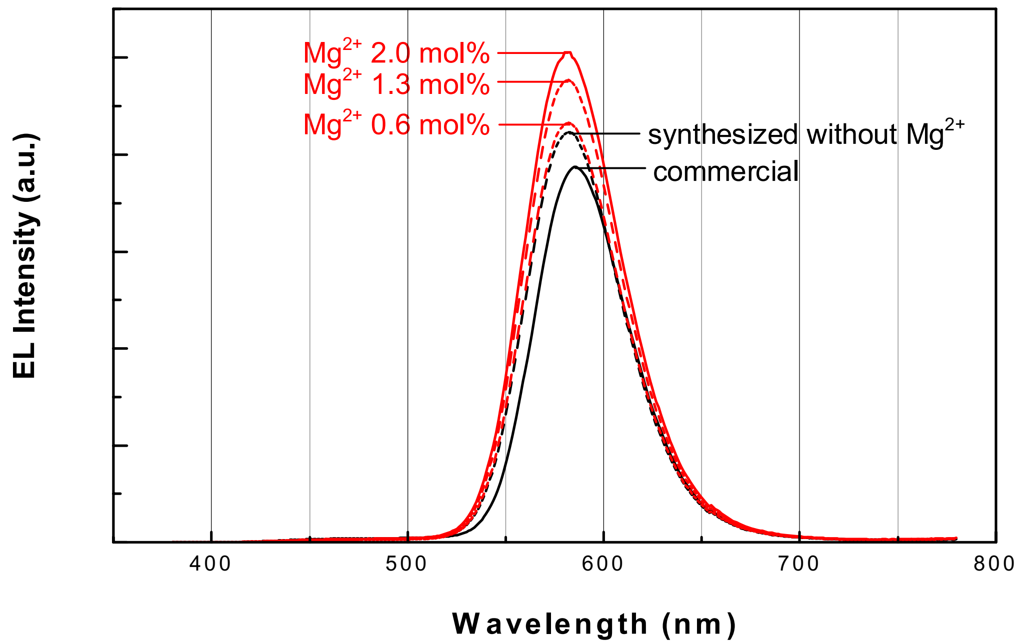

Figure 2. EL spectra of the orange-emitting phosphors with different concentration of Mg^{2+}-sensitizer and the comparison with commercial orange phosphor.

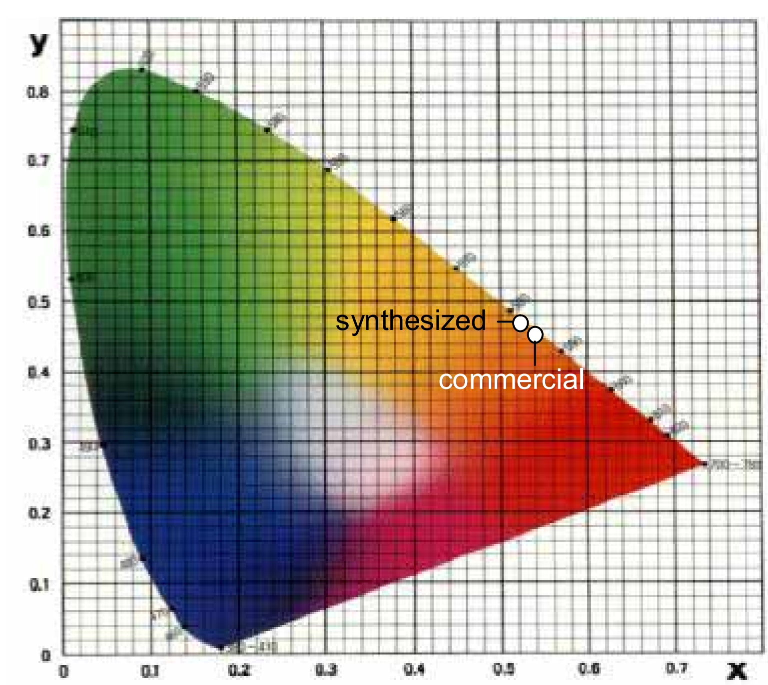

Figure 3. EL color coordinates of the synthesized and the commercial orange phosphors.