

# Preparation and Characterization of white ZnS:Pr,Mn,KCl Phosphor

Su-Hua Yang, Chien-Hung Wang, Yin-Hsuan Ling, Ci-Fong Do

Department of Electronic Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan, R.O.C.  
Phone: +886-7-3814526 Email: shya@cc.kuas.edu.tw

## 1. Introduction

In II-VI group phosphor materials, ZnS has been identified as a promising host material, and it has a wide range of applications in electroluminescence devices, field emission displays, and optical sensors [1-2]. In order to prepare efficient ZnS phosphor, doping processes are carried out in which rare-earth materials and transition-metals are preferred dopants, especially the materials produce white-light emission are most used. In this study, white ZnS-based phosphors were synthesized and its characteristics are investigated.

## 2. Experimental

White ZnS-based phosphors were synthesized using the conventional solid-state reaction method. The starting materials were ZnS, MnO<sub>2</sub>, PrCl<sub>3</sub>, and KCl. First, the source powders were mixed with deionized water and milled for 24 hours. Subsequently, the mixed solution was dried in an oven at a temperature of 80°C for 8 h. The mixed powders were then sintered in a tube furnace at temperatures of 800–1000°C for 1 h in N<sub>2</sub> atmosphere.

In order to measure the properties of the phosphors, phosphor films were prepared by screen-printing. The crystallinity of phosphors was evaluated by X-ray diffraction (XRD) and field emission electron microscope (SEM). The photoluminescence (PL) characteristics of phosphors were measured and discussed.

## 3. Result and Discussion

The XRD measurements showed that the composition of hexagonal phase was increased with the increase of sintering temperature and the XRD patterns were the same even though the doping concentration of PrCl<sub>3</sub> was varied. The full-width at half maximum (FWHM) values of XRD were 0.118°, 0.108°, 0.110°, 0.105°, 0.091° for phosphor prepared at temperatures of 800, 900, 1000, 1100 and 1200°C, respectively. Obviously, the crystallization of phosphor was improved as the sintering temperature was increased. The maximum PL intensity was obtained when the phosphor was sintered at 900°C. If the sintering temperature was higher than 900°C, the emission intensity of phosphor was decreased; this was referred to the increases in grain size and structural composition ratio of hexagonal to cubic phase. When the ZnS:Pr,KCl was sintered with different concentrations of KCl flux, the ratio of hexagonal to cubic phase was reduced; this shows that the growth of hexagonal phases were suppressed when KCl was doped. Figure 1 shows the X-ray photoelectron spectrometer (XPS) spectra of the S 2p of the ZnS:Pr,KCl

phosphor synthesized with 4 mol% PrCl<sub>3</sub> together with various KCl concentrations of 0, 2, and 6 mol%. The S 2p peak of the pure ZnS showed a peak at about 161.6 eV, however, this peak was shifted by approximately 1 eV when 4 mol% PrCl<sub>3</sub> and 6 mol% KCl were doped.

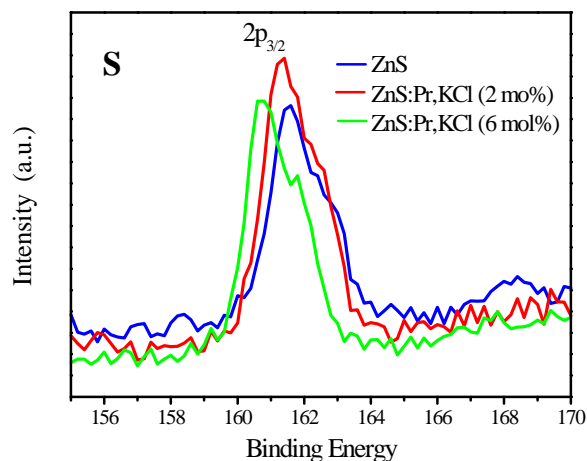


Fig. 1 XPS of S 2p of the ZnS:Pr,KCl phosphor for different doping conditions.

Two emission bands of the ZnS:Pr,KCl phosphor were observed when doping concentration of PrCl<sub>3</sub> was low. The blue emission peak at 454 nm was attributed to 4f-5d transition from excited state <sup>3</sup>P<sub>0</sub> to the ground state <sup>3</sup>H<sub>4</sub> of the Pr ions. The green emission peak at 520 nm was ascribed to the transition from the energy level of sulfur vacancy to the valence band or by the donor-acceptor pair recombination from sulfur vacancy to zinc vacancy. The relative intensity of blue to green emission was increased when the doping concentration of PrCl<sub>3</sub> was increased, the maximum emission intensity at wavelength of 454 nm was measured when PrCl<sub>3</sub> concentration was 4 mol%; and the emission intensity was then decreased due to the concentration quenching effect when the doping concentration of PrCl<sub>3</sub> was higher than 4 mol%. Furthermore, the maximum emission intensity was obtained when 2 mol% KCl was doped. The emission intensity was decreased as KCl concentration was over 2 mol%; this is due to the increased grain size of phosphor.

In order to obtain white ZnS-based phosphors, the ZnS:Mn-mixed ZnS:Pr,KCl phosphor was prepared with different weight ratios of ZnS:Pr,KCl to ZnS:Mn, where the ZnS:Pr,KCl phosphor was synthesized with 4 mol% of PrCl<sub>3</sub> and 2 mol% of KCl and sintered at 900°C; and the ZnS:Mn phosphor was synthesized with 4 mol% of MnO<sub>2</sub> and sintered at 900°C. The PL spectra exhibited two bands

at around 458 nm and 578 nm, which were corresponding to the blue and yellow-orange emissions, respectively. The intensity of blue emission was significantly decreased when the weight ratio of ZnS:Pr,KCl was decreased. On the other hand, the intensity of yellow-orange emission was only slightly increased when the weight ratio of ZnS:Mn was increased. The CIE coordinates of the ZnS:Mn-mixed ZnS:Pr,KCl phosphor were linearly red-shifted when the mixing weight ratio of ZnS:Mn was equivalently increased, as shown in Fig. 2. When the weight ratio of ZnS:Pr,KCl/ZnS:Mn was 1/2.5, the mixed phosphors exhibited a near white light emission, with CIE coordinates of (0.35, 0.32).

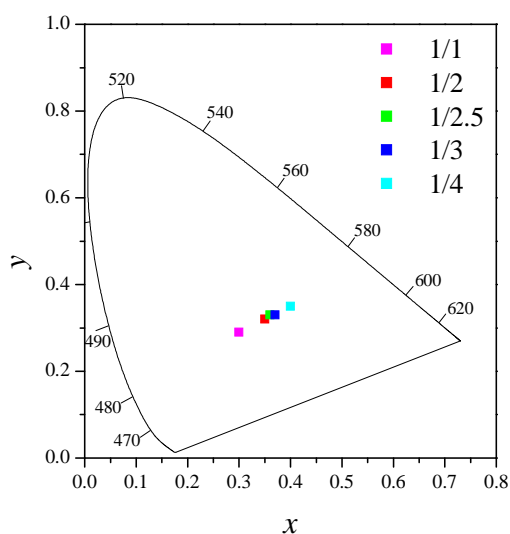


Fig. 2 CIE coordinates of the ZnS:Mn-mixed ZnS:Pr,KCl phosphor prepared at different weight ratios of ZnS:Pr,KCl/ZnS:Mn.

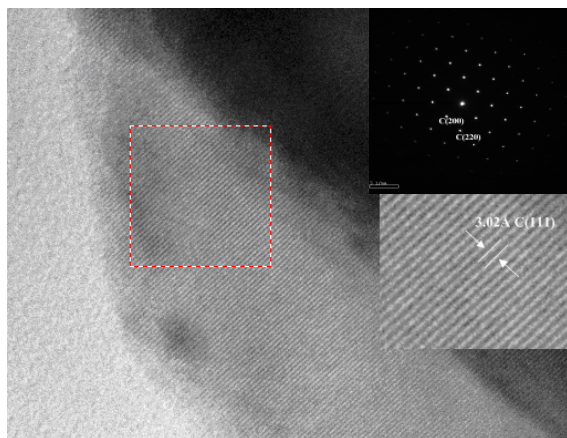


Fig. 3 HRTEM images of the ZnS:Pr,Mn,KCl phosphor.

It was not only the white ZnS-based phosphor was prepared by mixing complementary phosphors but also by means of codoping of complementary activators to produce white-light emission was studied. Figure 3 shows the high-resolution TEM (HRTEM) images of the ZnS:Pr,Mn,KCl phosphor doped with 1 mol% of KCl and

sintered at 900°C for one hour, where the concentrations of PrCl<sub>3</sub> and MnO<sub>2</sub> were 4 and 0.4 mol%, respectively. It shows that the high crystallinity of ZnS:Pr,Mn,KCl phosphor was sintered. The lattice fringes separated by a distance of 3.02 Å was corresponding to the spacing of the (111) plane of cubic ZnS. The selected area electron diffraction (SAED) pattern of the ZnS:Pr,Mn,KCl phosphor showed that the phosphor was a single crystalline, as exhibited in the inset of Fig. 3.

Figure 4 shows the PL spectra of the white ZnS:Mn-mixed ZnS:Pr,KCl phosphor and the white ZnS:Pr,Mn,KCl phosphor. It is found that the PL intensity of the ZnS:Pr,Mn,KCl phosphor is higher than that of the ZnS:Mn-mixed ZnS:Pr,KCl phosphor. The CIE coordinates of the ZnS:Pr,Mn,KCl phosphor were (0.36, 0.32), exhibiting a white-light emission.

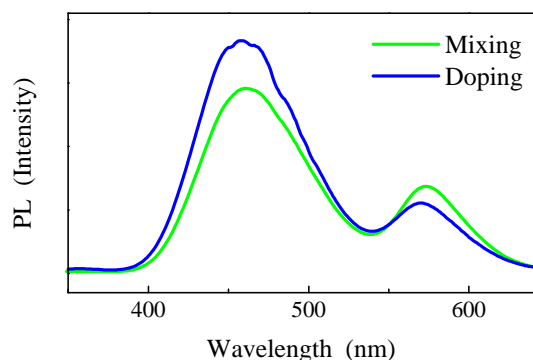


Fig. 4. PL spectra of the white ZnS:Mn-mixed ZnS:Pr,KCl phosphor (mixing) and the white ZnS:Pr,Mn,KCl phosphor (doping).

#### 4. Conclusion

In this study, approaches of mixing complementary phosphors and codoping of complementary activators were used to prepare white ZnS-based phosphors. In order to enhance the emission intensity of phosphors, flux of KCl was doped to improve the crystallization of the phosphors. From the measurements, it shows that the CIE coordinates of the ZnS:Mn-mixed ZnS:Pr,KCl phosphor and the ZnS:Pr,Mn,KCl phosphor were (0.35, 0.32) and (0.36, 0.32), respectively, and the PL intensity of the phosphor prepared by codoping was higher than that of the phosphor prepared by complementary mixing.

#### 5. Acknowledgement

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