Synthesis and characterization of ZnS:Mn,Cl phosphor by combustion method

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Abstract

The preparation of ZnS:Mn,Cl phosphor has been carried out by combustion method. Manganese nitrate was decomposed with an organic fuel at 500°C to give fine sized crystallites in presence of alkali metal halides at a lower temperature than the conventional synthesis. The phosphors thus obtained were then heated at 900 to 1200°C in an inert atmosphere, for 3hours to get better luminescent properties. The phosphors were prepared at different temperatures and at different doping concentrations of manganese to determine the optimal conditions for synthesizing the phosphors with superior optical properties. Scanning electron microscopy (SEM) investigations have been carried out to observe the particle morphology and the grain size. Powder X-ray diffraction(XRD) was also performed to characterize the phosphors.

Key words: ZnS:Mn,Cl phosphor, combustion method

1. Introduction

Zinc sulfide is a well known phosphor that emittes different radiations when doped with different metallic ions impurities[1]. It gives green, blue and orange-yellow bands when doped with copper, silver and manganese respectively. The luminance properties of these materials are strongly dependent on the purity of the starting compounds and also on the method of their preparation. The phosphors prepared at different temperatures and doping concentration are found to have varied values of luminescent properties[2]. In conventional methods the stochiometeric amounts of zinc sulfide and doping metallic ions are mixed and heated at high temperatures for a certain period. In general, ZnS phosphors prepared by firing above 1000°C have wurtzite structure, while those prepared below this temperature have zinc blend structure. During the preparation of phosphors it has to be kept in mind that the contamination even with a very small amount of iron, nickel or cobalt greatly reduce the luminescence intensity[3] and should be removed to a lowest level before the synthesis process is started. All these processes presented to this date are very tough and require drastic conditions. In this paper a simplified process for the preparation of ZnS:Mn,Cl phosphor has been presented and further the optimal conditions of temperature and doping concentration of manganese in the ZnS matrices have been determined to get maximum luminescence.

2. Experimental

High purity commercially available zinc sulfide(Korea Zinc Co.) was taken as a base material 1.0gm of zinc sulfide 100-500ppm

of manganesein the form of manganese nitrate, varying mixtures of NaCl, $MgCl_2$ and $BaCl_2$ in 2-3 weight% of zinc sulfide as flux and ammonium nitrate in appropriate proportions equimolar to zinc sulfide were taken. An appropriate amount of organic decomposing agent(urea)acting as a fuel[4] was mixed. A homogeneous paste was prepared and then fired at 500℃ in air for about 15min. The mixture was cooled and milled to a fine powder and then again fired at 900-1200℃ for 3hrs in an inert atmosphere of N_2 gas. The sintered cake of the phosphors after firing was washed in hot deionized water at 80°C to remove the excess flux. Then the phosphor was again washed with dilute HCl solution. Finally, phosphor was washed 3-4 times with pure deionized water. All chemicals except ZnS, used were of high purity procured from Aldrich Chemical Co.

Photoluminescence spectra were measured at room temperature, after exiting the sample at a 400nm with radiation from a xenon lamp, using a photometer(Minolta CS-1000). The morphology and particle size of the phosphors were determined by SEM and XRD techniques using Philips XL-30 and D/Max 2000-Ultima plus respectively.

3. Results and discussion

When appropriate amounts of ZnS with metals as activators are fired at temperatures between 900-1200°C, generally lead to the formation of phosphor having bigger particles with inhomogeneous distribution of active contres. But in the present combustion method, we noticed that the metal nitrates when heated with an organic fuel, urea in present case, at about 500°C, produced a large amount of heat due to evolution of combustible gases those burnt to produce a high enthalpy of reaction[4]. This heat was sufficient to produce the phosphor. However, when appropriate amount of NH_4NO_3 almost equivalent to molar ratio of ZnS was added with urea, the mixture melted and homogeneous doping of manganese occurred. One of the advantage of using NH_4NO_3 is that it completely decomposes at a temperature around 500°C producing sufficient heat to make the phosphor. Addition of small amounts of alkali halides in 2-3 weight% of ZnS also acted as co-activators. The paste of ZnS, $Mn(NO_3)_2$, Urea, NH_4NO_3, NaCl, $MgCl_2$ and $BaCl_2$ in water was prepared and fired in preheated furnace at 500°C for 15 minutes. The prepared phosphor was milled to fine powder and again heated in inert atmosphere of N_2 gas at temperatures 700, 900, 1000 and 1200°C for three hours separately.

The emission spectra of these phosphors are shown in Fig.1. It may be observed that 1000°C is the optimal temperature for the preparation of ZnS:Mn,Cl phosphor to give best luminescence intensity.

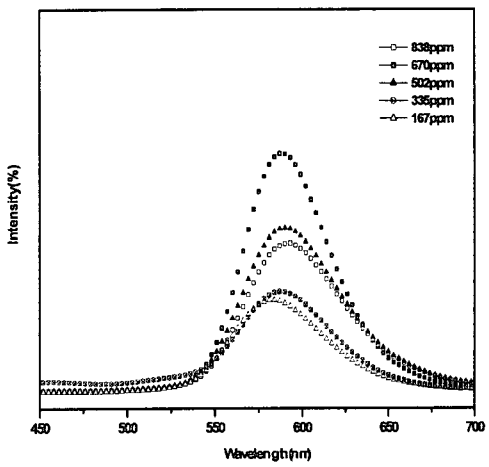


Fig. 1. The emission spectra of ZnS:Mn,Cl phosphors prepared at different firing temperatures.

In Fig.2, the emission spectra of phosphors doped with varying amounts of manganese prepared at 1000°C is presented.

Concentration of manganese 670ppm at a level of 670ppm produced the best phosphor as evidenced by SEM and XRD micro graphs of these phosphors. The SEM micrographs of phosphors prepared at 1000, 1100 and 1200°C are presented in Fig.3(a, b, c). It may be observed that the average particles size is in the range of 1 to 2μm, when the phosphor was sintered at 1000°C.

The phosphors prepared at 1100°C and 1200°C have round shaped crystallites(fig.3(a, b, c)), whereas the phosphor prepared at 1000°C has fine sized particles with well defined shapes. It clearly indicates that the morphology of the phosphors is governed by sintering temperature.

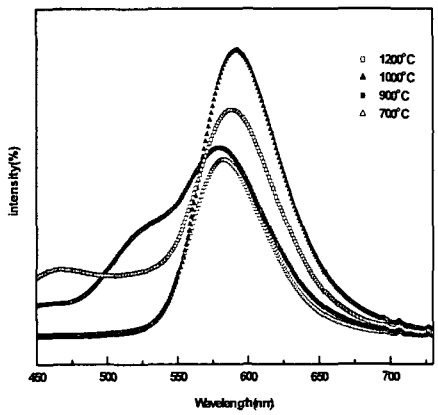
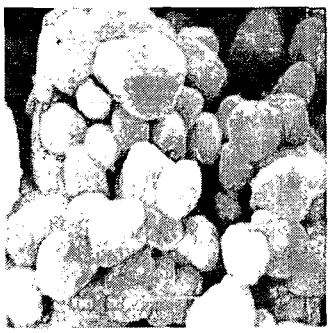
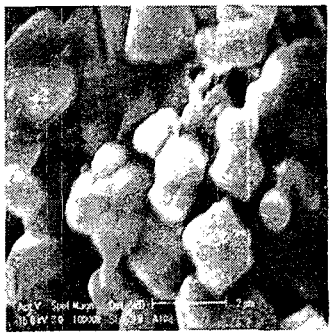


Fig. 2. The emission spectra of ZnS:Mn,Cl phosphors doped with varying amounts of manganese.



(a) 1000°C



(b)1100°C

(c)1200°C

Fig.3. SEM micrographs of the phosphors prepared at different firing temperature.

The XRD pattern of phosphor sintered at 1000°C is shown in Fig.4. The expanded range from 26 to 34 degree of Fig.4 is shown in Fig.5. It may be observed that the cubic phase is dominant in phosphors prepared at low temperatures. Both hexagonal and cubic phase are found in phosphors sintered at 1200°C. It seems that for the phosphor prepared at 1000°C have the best homogeneous combination of cubic and hexagonal phases with small sized crystallites to give superior luminescent properties.

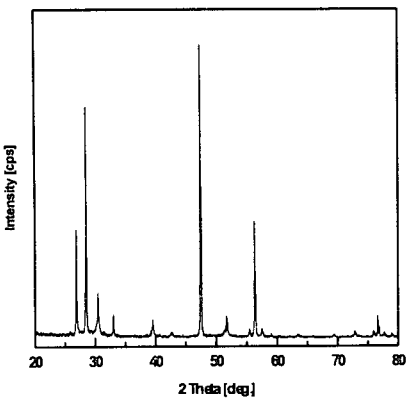


Fig. 4. The XRD pattern of ZnS:Mn,Cl phosphor prepared at 1000°C.

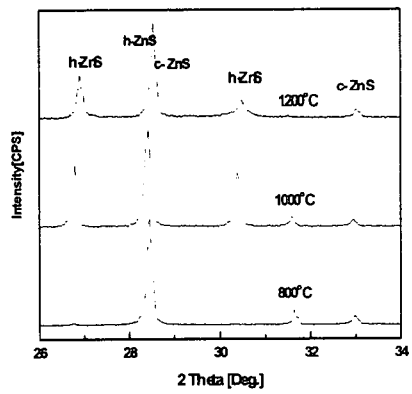


Fig. 5. The XRD pattern of ZnS:Mn,Cl phosphor of the range 26 to 34 degree.

4. Conclusion

ZnS phosphors doped with Mn^{2+} are obtained by combustion method. The photoluminescence experiments showed that a strong orange-yellow band was emitted by the phosphor prepared at 1000°C. with 649ppm of Mn^{2+} doping. The well defined crystallites of small size having cubic and hexagonal phases were formed under these conditions.

References

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