

# Synthesis of ZnS:Cu,Cl phosphor by combustion method

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## Abstract

*A new method for the preparation of copper activated zinc sulfide phosphors by combustion method has been proposed. Copper nitrate was decomposed with an organic fuel to give fine sized particles in presence of alkali metal halides at low temperature than the conventional synthesis. Organic compound also acted as fuel at 500 °C with rapid heating. The phosphors thus obtained were then heated at 900 °C in an inert atmosphere for 2-5 hrs to get better luminescent properties.*

## 1. Introduction

Since the discovery of ZnS phosphor about a century ago, researchers have been engaged in developing this phosphor doping with numerous impurities[1]. ZnS as green-emitting ZnS:Cu,Al phosphor and blue-emitting ZnS:Ag,Cl phosphor are very important for many practical purpose especially for cathode-ray tube. Small amounts of metal ions viz. copper, silver are called activators[1], while halide flux added in the firing process(usually 900-1200 °C) not only promote the crystal growth, but also halide ions in ZnS lattice particulate in the formation of luminescence centers[2]. Introduction of Al<sup>3+</sup> ions also showed a similar effect without using halide ions. These ions are thus called co-activators[1]. In general, ZnS phosphors prepared by firing above 1000 °C have the wurtzite structure, while those

prepared below this temperature have zinc blende 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. One aim of this paper is to present a simplified process for the preparation of some ZnS:Cu,Cl phosphors.

## 2. Experimental

High purity commercially available zinc sulfide(Korea Zinc Co.Ltd.) was taken as a base material. 1.0gm of zinc sulfide, 100-500ppm of copper in the form of copper nitrate, varying mixtures of NaCl, MgCl<sub>2</sub> and BaCl<sub>2</sub> in 2-3 weight% of zinc sulfide as flux and ammonium nitrate in appropriate proportions was taken as a fuel. An appropriate amount of organic decomposing agent [4] was mixed. A homogeneous paste was prepared and then fired at 500 °C in air for about 15min. The mixture was cooled and milled to a fine powder and then again fired at 900 °C for 2-5hrs in an inert atmosphere. The cooled mixture was treated with very dilute mineral acid, washed with hot water to remove the excess flux and then finally washed 3-4 times with pure water. All chemicals except ZnS,

used were of high purity procured from Aldrich Chemical Co.

### 3. Results and Discussion

Most of the methods presented till this date are the firing methods, where appropriate amounts of ZnS with metals as activators are fired at temperatures between 900-1200°C. One of the contributory factor for their high cost is the high temperature preparation and also lead to the formation of bigger particles with inhomogeneous distribution of active centers. We noticed that the metal nitrates when heated with an organic fuel at about 500°C, produced a large amount of heat due to evaluation of combustible gases those burnt to produce a high enthalpy of reaction[4]. This heat produced by facile combustion process was sufficient to produce a phosphor. Pure ZnS with little  $\text{Cu}(\text{NO}_3)_2$  when heated with stoichiometric amounts of fuel(i.e equivalent amount to copper) produced little amount of heat and was not sufficient to dope copper ions homogeneously. However, when appropriate amount of  $\text{NH}_4\text{NO}_3$  was added as reactant to produce heat with organic fuel, the mixture melted and homogeneous doping of copper occurred. One of the advantage of using  $\text{NH}_4\text{NO}_3$  is that it completely decomposes at high 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. Fig.1 shows the emission spectra of the zinc sulfide phosphors doped with varying amounts of copper in presence of chloride ions when fired at 500°C. Emission spectra of these phosphors showed less intensity (about 40%) in comparison to phosphors made by direct firing method at 900°C. However, the phosphors obtained at 500°C were milled to a fine powder and again fired at 900°C for 2-5hrs in an

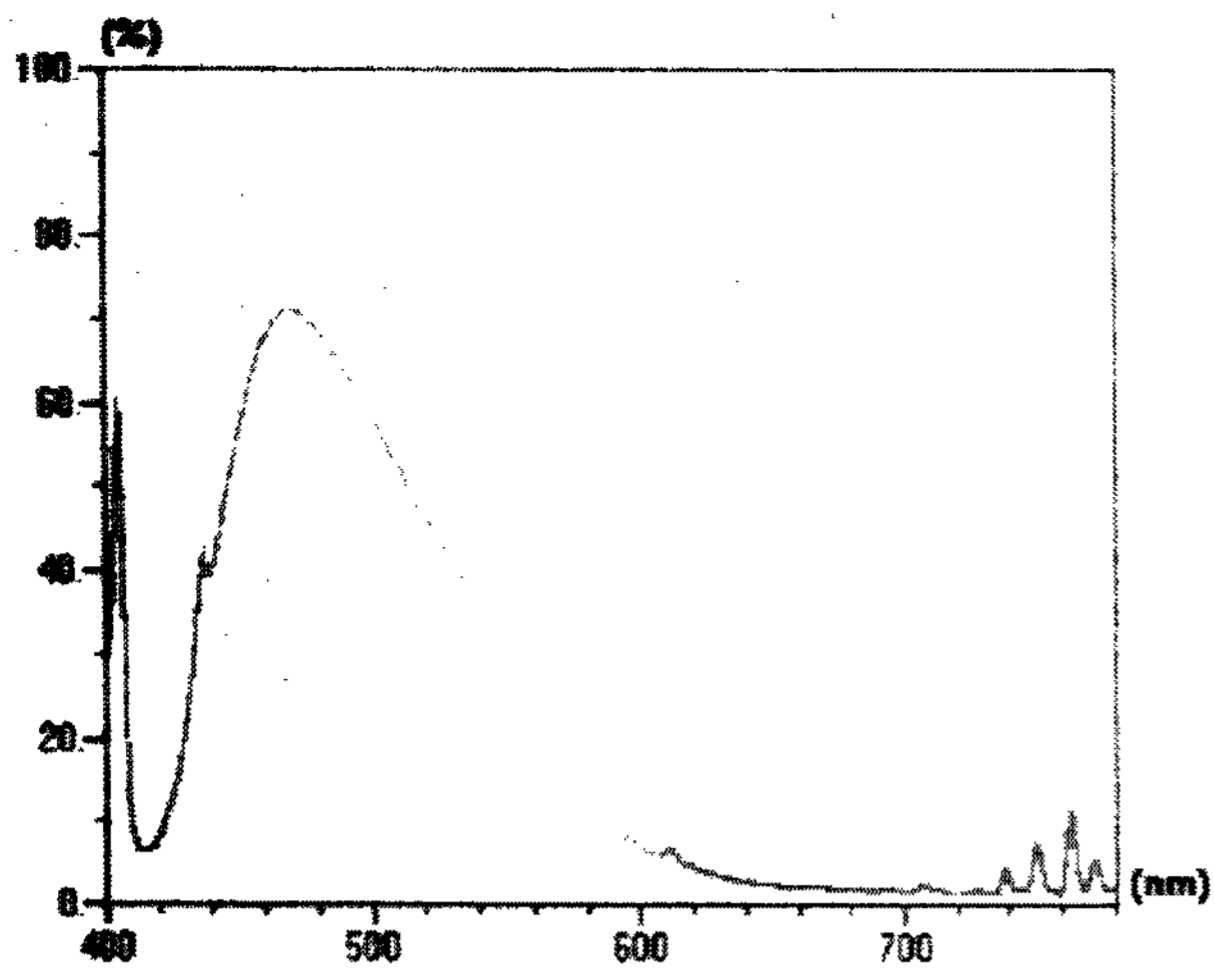
inert atmosphere. This step gave very bright phosphors, as shown by their emission spectra in Fig.2. It was noticed that when copper concentration was less, equivalent to 150ppm in the phosphor, the emission peak at 525nm was dominating, while a sub-emission peak at 460nm became dominant when concentration of copper was around 400ppm or more. Similar results have also been reported by Chen and co-workers[5]. Further investigations on these phosphor are in progress.

### 4. Conclusion

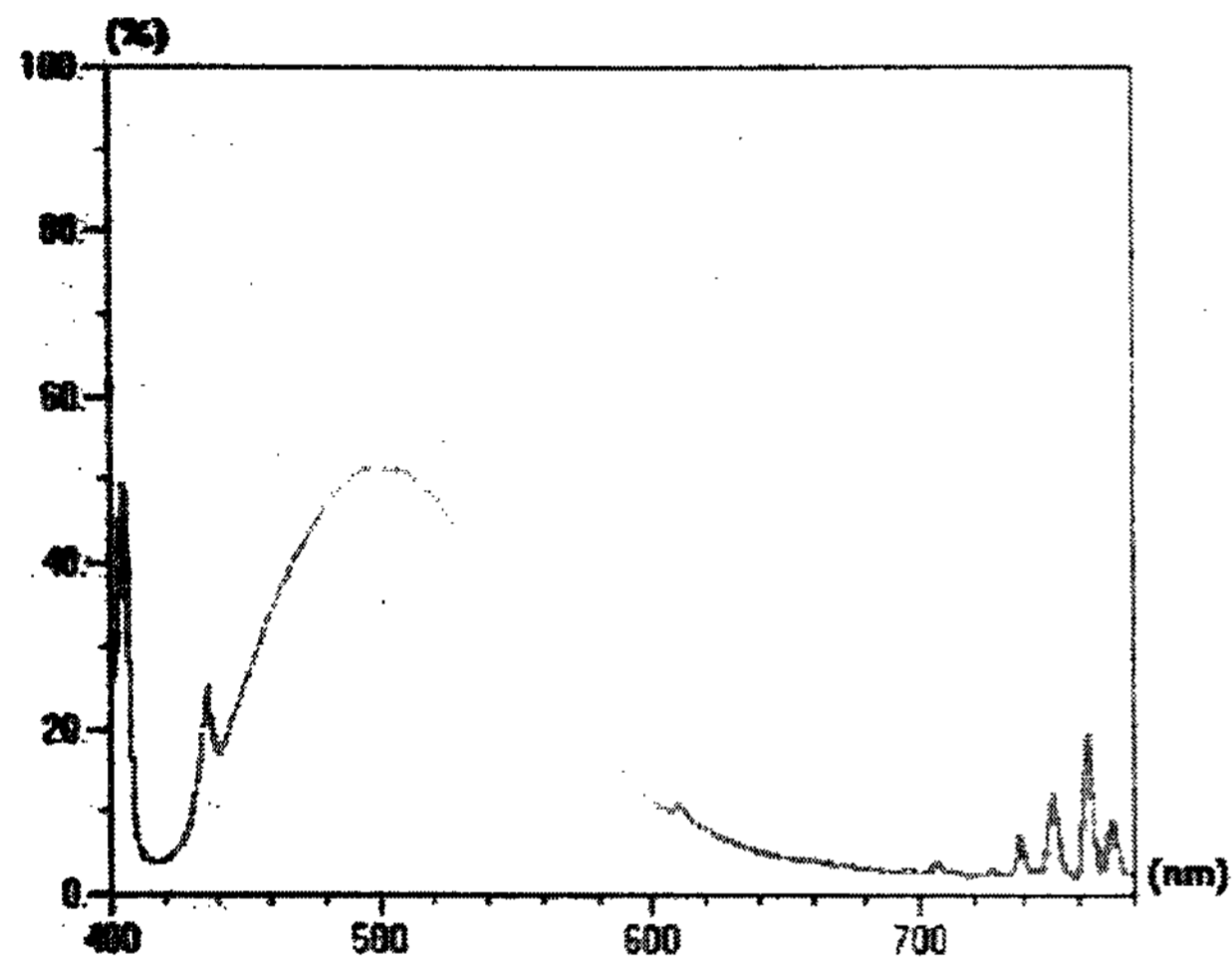
The ZnS activated with Cu ions is the most efficient cathodoluminescence phosphor. There has been a steady market for CRT application, because of their stability against physical and chemical treatments during CRT operation processes. Moreover, ZnS based phosphors are extensively used in many display systems such as plasma display panel(PDP), field emission display(FED) and electron luminescence(EL). Specially green emitting ZnS:Cu,Cl phosphor used in CRT is a well-known phosphor. We have presented a simplified method for the preparation of ZnS:Cu,MX using a facile combustion process.

### 5. References

- [1] Shionoya, S., and Yen, W.M.,(eds.) Phosphor Handbook, CRC Press. Boca Raton (1999).
- [2] Kawai,H., Abe, T., and Hoshina, T., Jap. J. Appl. Phys. 20, 313 (1981).
- [3] Tabei, M., Shionoya, S., and Ohmatsu, H., Jap. J. Appl.Phys. 14, 240 (1975).
- [4] Ekambaram, S., and Patil, K.C., J. Alloys and Compd. 248, 7 (1997).
- [5] Chen,Y.Y., Duh,J.G., Chiou, B.S., and Peng, C.G., Thin Solid Films, 392, 50-55(2001).

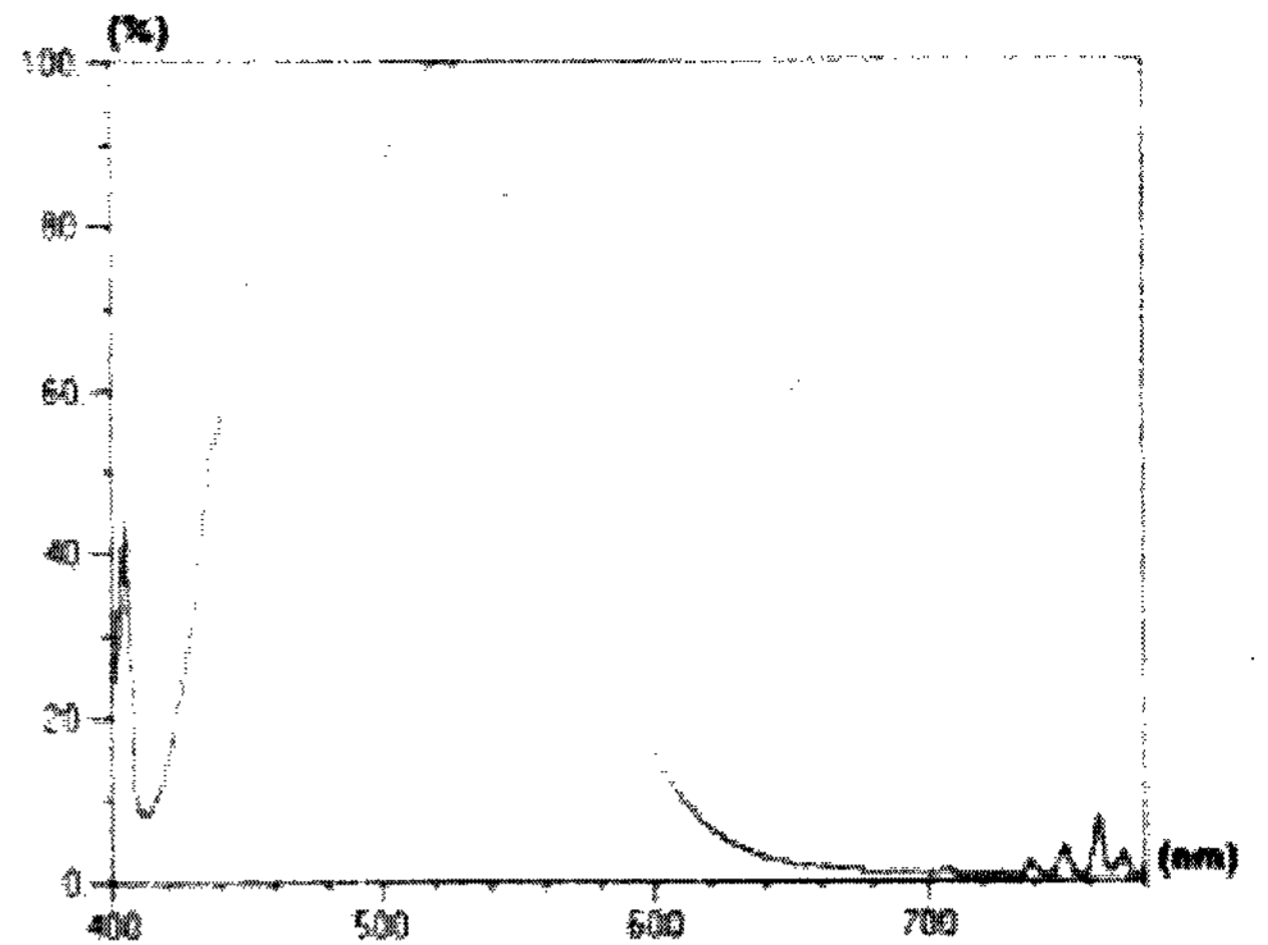


a)

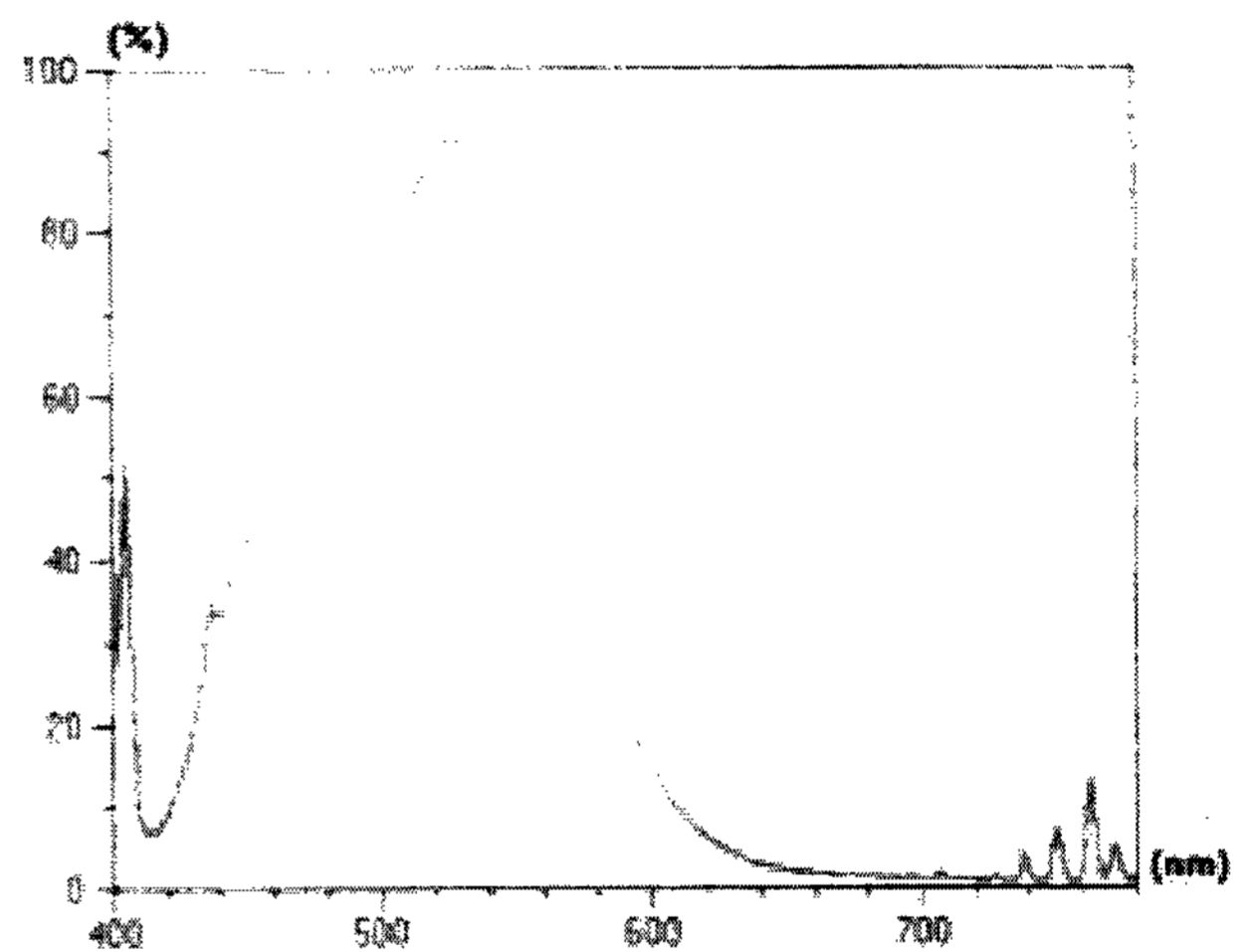


b)

Figure 1. Emission spectra of ZnS:Cu,Cl (a) with 416ppm copper ( $L_v=24.6\text{cd/m}^2$ ), (b) with 175ppm of copper ( $L_v=19.7\text{cd/m}^2$ ) when prepared at  $500^\circ\text{C}$ .



a)



b)

Figure 2. Emission spectra of ZnS:Cu,Cl made first at  $500^\circ\text{C}$  and then fired at  $900^\circ\text{C}$  in inert atmosphere (a) with 416ppm copper ( $L_v=63.1\text{cd/m}^2$ ), (b) with 175ppm of copper ( $L_v=58.7\text{cd/m}^2$ ).