Synthesis and luminescence of silver doped zinc sulfide phosphor

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Abstract

A new route for the synthesis of silver doped of zinc sulfide phosphor by combustion method has been investigated. Silver nitrate was decomposed with urea or carbohydrazide to give small size particles in presence of alkali metal halides at low temperature compared to the conventional method. The high temperature inherent to the highly exothermic nature of redox reaction leads to well-crystallized powder in short time. The phosphors thus obtained were further heated at 1050℃ in an inert atmosphere for 3hrs to get better luminescence properties.

1. Introduction

The visible light generating luminescent materials are called phosphor and these are made of inert host and optically excited activators. Small amounts of metal ions viz. Ag^{+}, Cu^{2+} etc when added to host matrix are called activators. Halide fluxes added in the firing process (usually 1200℃) not only facilitate the crystal growth, but also particulate in ZnS lattice in the formation of luminescence centers. The phosphors used for practical applications must have high luminescence efficiency, high resistance to current saturation, good chromaticity and chemical/thermal stability. The ZnS:Ag,Cl as blue emitting phosphor has been studied for a long time because of many practical purposes. Generally, ZnS phosphors prepared by solid state reaction above 1100℃ have the wurtzite structure, while those prepared below this temperature have zinc blende structure. The particle size of the phosphors prepared by conventional high temperature solid state technique is of the order of 5-20 ㎛. Phosphors of small particles must be obtained by grinding and milling the larger phosphor particles. These processes introduce additional defects, and change the morphology of the particles as a result reduce luminescence efficiency. For practical application of phosphors, it is desirable to have a fine particle size for high resolution and chemical purity for optimum chromaticity and brightness. Recently, with the development of scientific technologies on phosphors several chemical synthesis techniques have received great attention. The routes for the preparation of phosphors by sol-gel and co-precipitation are complicated and time consuming. However, the combustion process to prepare phosphor is quite simple and reaction time is only a few seconds[1,2]. The objectives of this paper is to present a simplified process for the preparation of ZnS:Ag,Cl phosphor having uniform small particles by combustion synthesis method.

2. Experimental

All chemicals except ZnS, used were of high purity procured from Aldrich Chemicals. High purity commercially available ZnS (Korea Zinc Co.) was taken as a base material. 1.0 mole of zinc sulfide, 0-0.18mole% of silver in the form of silver nitrate, varying mixtures of NaCl, $MgCl_2$, $BaCl_2$ in 2 wt% of zinc sulfide as flux[3]. Calculated amounts of urea or carbohydrazide to act as decomposing agents were mixed. A homogeneous paste was prepared and then fired at 500℃ in a preheated furnace for about 15 min. This process involves the dissolution of corresponding metal nitrate and fuel in water, evaporation of water, and exothermically self-sustained redox reaction with gases. The resultant compound was white, foamy and crisp due to spontaneous ignition at 500℃. The powder was cooled, milled to a fine powder and then fired at 1050℃ for 3hrs in an inert atmosphere to crystallize completely. The cooled mixture was treated with very dilute mineral acid to remove the excess fluxes and then finally washed 3 times with pure water. The PL and CIE were measured using spectroradiometer Minolta CS-1000. XRD patterns were obtained with a Rigaku RINT Dmax 2000 powder diffractometer using Cu Kα(λ=1.5418Å) radiation generated at 30kV/20mA. The morphology and size of particles were investigated by SEM and EDAX techniques using Philips XL30 and PV99 models respectively.

3. Results and Discussion

Conventional methods presented till date for the synthesis of ZnS phosphors are based on the firing of appropriate amounts of ZnS with typically 3d or 4f electron metals as activators at temperatures between 900-1200℃. One of the contributory factors 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 ignited with an organic fuel at a temperature of 500℃, produced a large amount of heat due to evolution of combustible gases those burnt to produce a high enthalpy of reaction in about 3-5min. Thus heat produced by facile combustion process was sufficient to produce a phosphor and the resultant product was a voluminous, foamy powder. Pure ZnS with little $AgNO_3$ when heated with stoichiometric amounts of fuel (i.e.equivalent amount to silver) produced little amount of heat and was not sufficient to dope silver ions homogeneously. However, when appropriate amount of NH_4NO_3 was added as reactant to produce more heat with organic fuel, the mixture melted and homogeneous doping of silver occurred. This is because chemical energy released from the exothermic reaction between metal nitrates and fuel can rapidly heat the system to high temperatures without an external heat source. One of the advantages using NH_4NO_3 is that it completely decomposes at high temperature around 500℃ producing sufficient heat to make the phosphor. These gases break up large agglomerates and yield a porous mass of powder that fills the volume of the reaction container. The surface area to volume ratio of combustion-synthesized powder is usually very large due to the large porosity individual particles exhibit after reaction. Additional small amounts of alkali halides in 2-3% of ZnS also act as co-activators. Fig 1 (a, b) shows the emission intensity of ZnS phosphors doped with varying amounts of silver ions and prepared by solid state and combustion method with two different fuels i.e. urea and carbohydrazide at temperature 500℃ and then heated at 1050℃ for 3hours in inert atmosphere. It

may be observed from Fig 1(b) that phosphor prepared by conventional method (solid state method) has very less luminescence intensity as compare to those prepared by combustion method. However, the luminescence intensities of phosphors prepared at 1050℃ by solid state technique are comparable with the phosphor prepared by combustion method at the same temperature(Fig 1(a)). The maximum luminescence intensity is obtained to 0.04 mol% of Ag^+ doping. Both urea and carbohydrazide are the efficient fuels for the preparation of phosphors. Both produce the final products of almost same intensities at 1050℃. Fig. 2 shows the emission spectra of zinc sulfide phosphors doped with silver ion (0.04mol%) prepared at different temperature. Emission spectra of these phosphors showed less intensity (about 20%) in comparison to phosphors made by direct firing method at 1050℃. However, the phosphors obtained at 500℃ were milled to a small powder and again fired at 1050℃ for 3hrs in an inert atmosphere. This step gave very bright phosphors, as shown by emission spectrum and color coordinates in Fig. 2,3. It was noticed that when silver concentration was equivalent to 0.04mol% in the phosphor, the strong blue emission peak at 455nm, which was ascribed to a transition from a donor level such as anion vacancy to the levels of the silver impurities, was dominating under ultraviolet excitation. With increasing temperature, it was observed that the additional peak at 525nm appeared and relative intensity increased. The color coordinates (CIE) for maximum emission intensity indicate x=0.2029, y=0.2729 (blue area) on display. Fig. 4 shows the SEM micrograph of the ZnS:Ag,Cl (0.04mole% Ag concentration) phosphor obtained by sintering at 500℃ and 1050℃. Fig. 4a) have irregular and low crystalline while Fig. 4b) are more regular and complete crystalline having cubic structure in the range 1-2 ㎛. XRD patterns for the phosphor prepared at 500℃ and post-reacted at 1050℃ are shown in Fig. 5.

4. Conclusion

Combustion method is a simple and efficient method to produce homogeneous and fine sized particles of phosphors. These phosphors when synthesized at 500℃ did not show full luminescence intensity. However, when these were fired further at 1050℃ in inert atmosphere for 3 hours produced bright emission spectra. Maximum luminescence is obtained with 0.04mol% of Ag^+ in ZnS matrixes. Both urea and carbohydrazide are efficient fuels to produce the fine particles of phosphor almost of same luminescence intensity.

5. Reference

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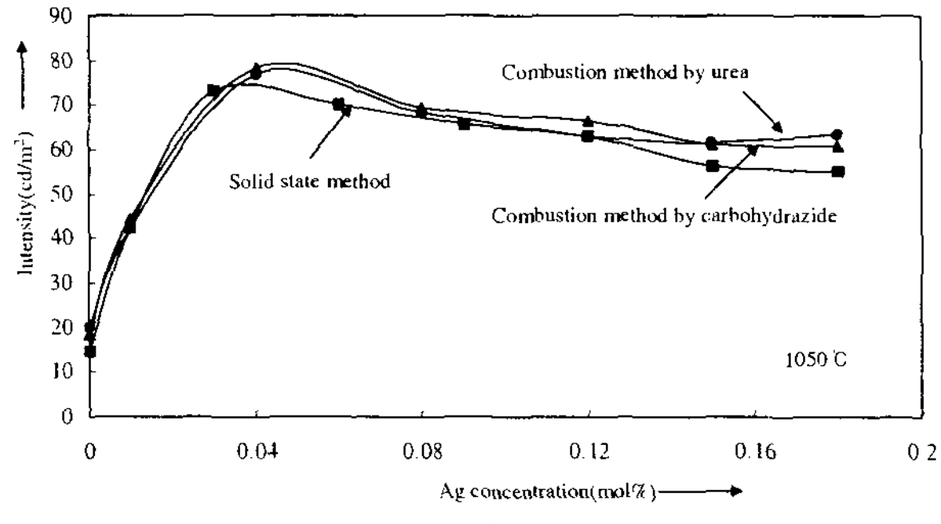
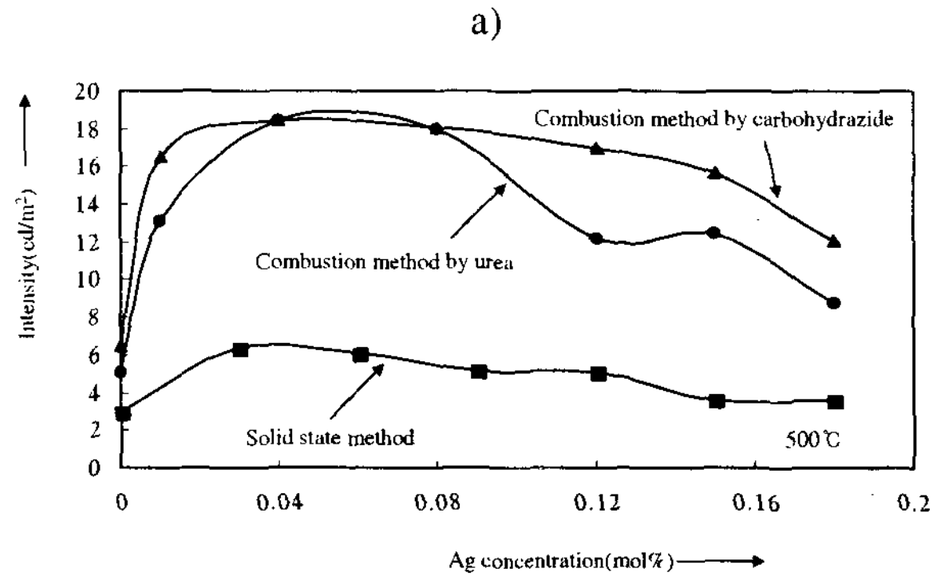
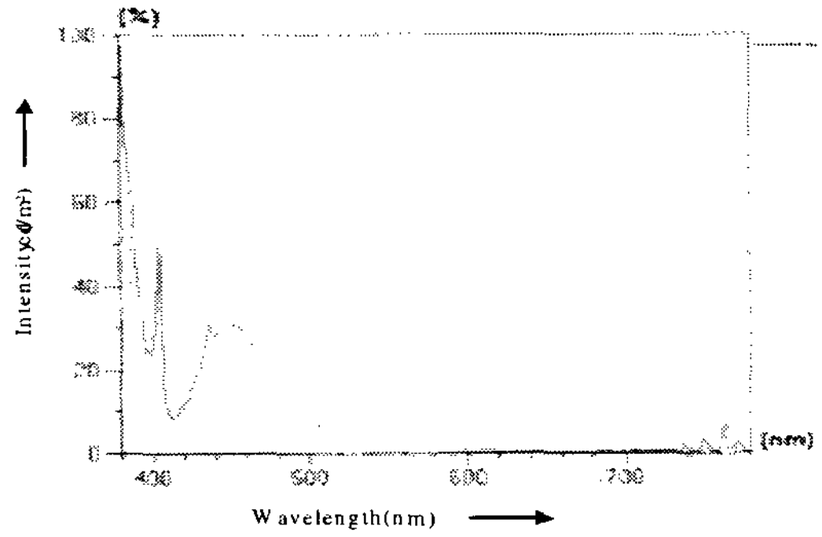


a)

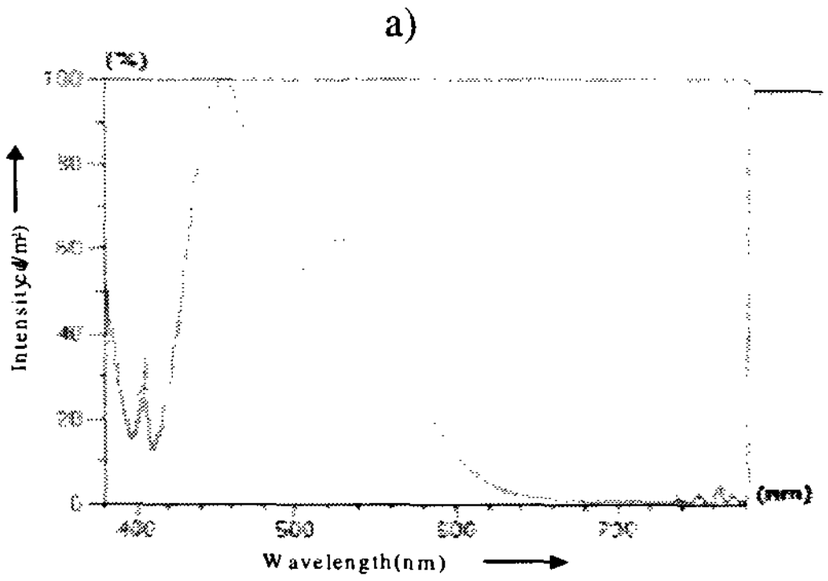


b)

Fig 1. Luminescence intensity and concentration quenching of ZnS:Ag,Cl phosphor made by combustion method

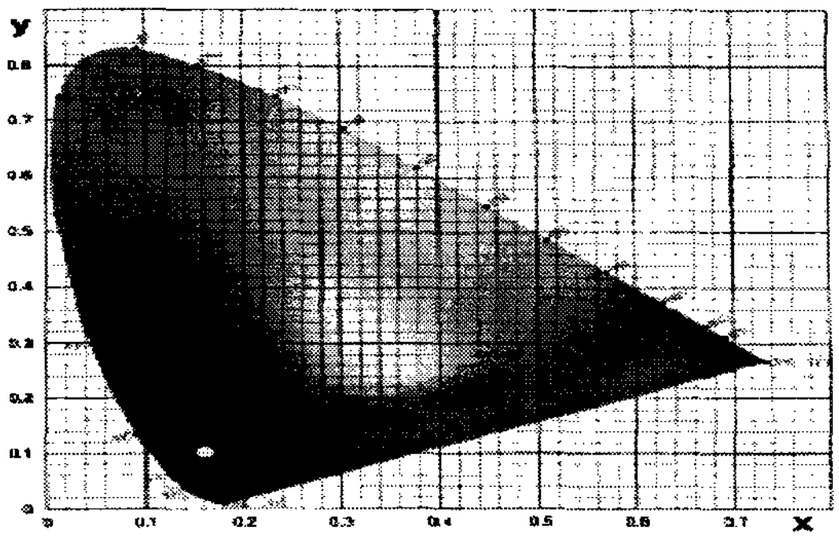


a)

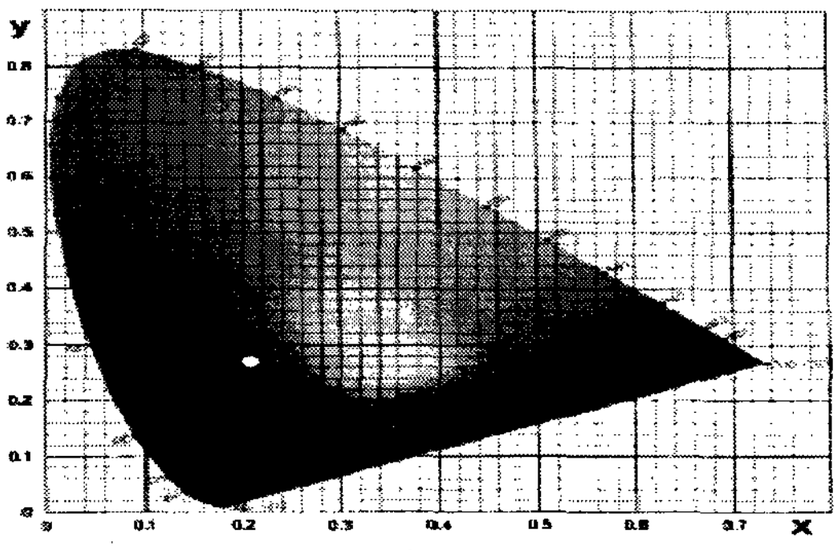


b)

Fig 2. Emission spectra of the ZnS:Ag,Cl phosphor
a) Pre-heated at 500℃. (Lv=14.99cd/m^2)
b) Post-heated at 1050℃. (Lv=78.52cd/m^2)

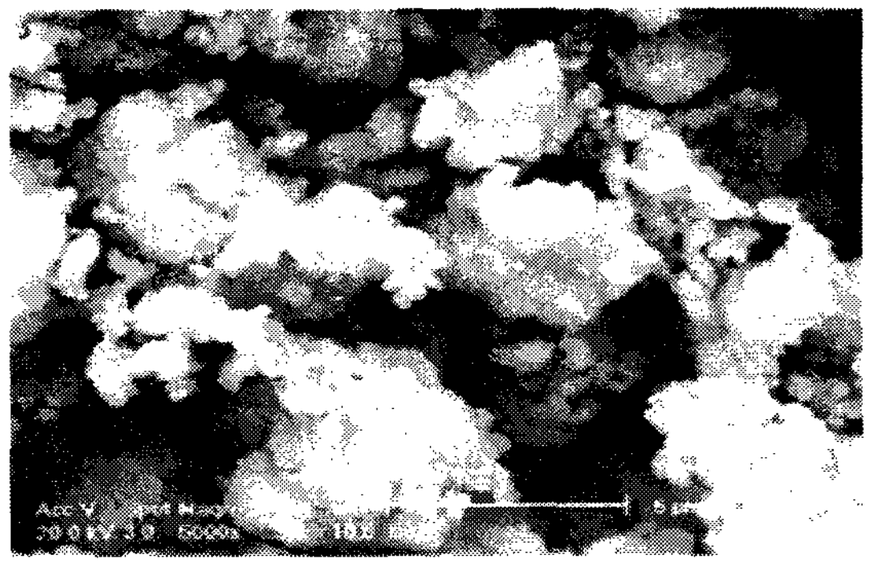


a)



b)

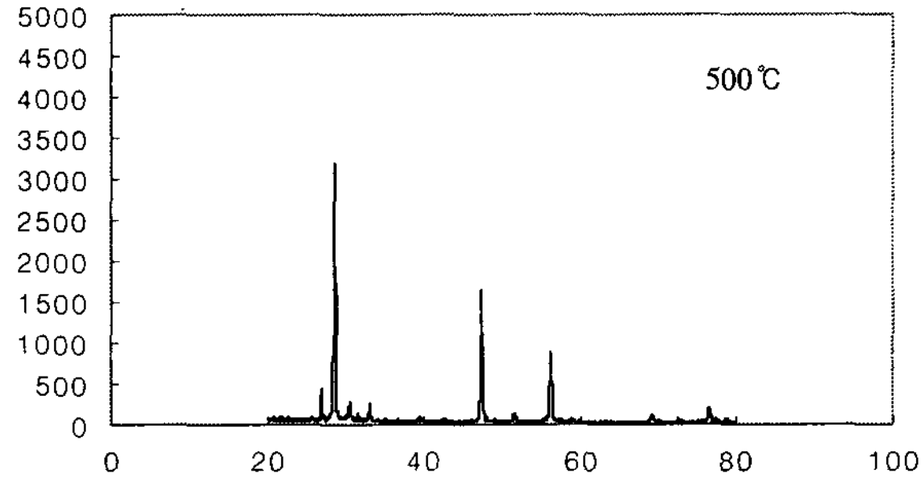
Fig 3. Color coordinates of the ZnS:Ag,Cl phosphor
a) Pre-heated at 500℃.(x=0.1613 y=0.1061)
b) Post-heated at 1050℃.(x=0.2029 y=0.2729)



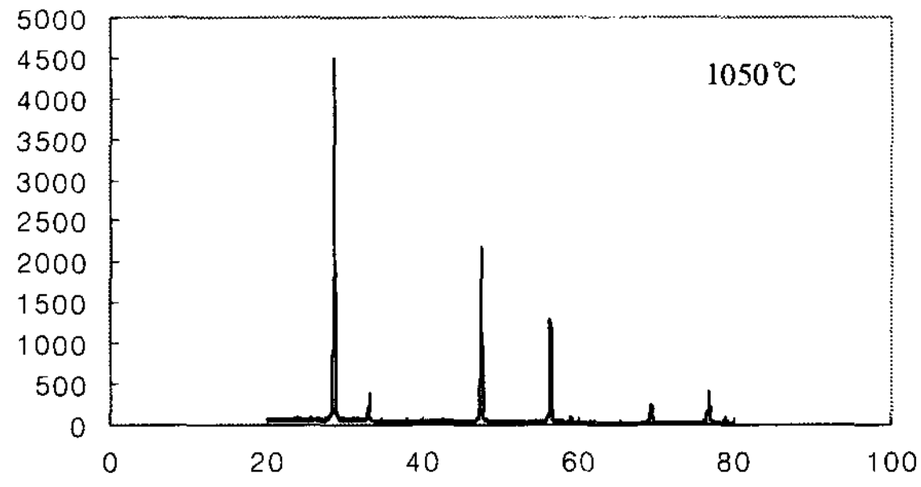
a)

b)

Fig 4. SEM micrograph of the ZnS:Ag,Cl phosphor.
(a) pre-heated at 500℃
(b) post-heated at 1050℃



a)



b)

Fig 5. XRD patterns of ZnS:Ag,Cl phosphor
(a) pre-heated at 500℃
(b) post-heated at 1050℃