Synthesis and luminescence characterization of ZnS:Cu,Al phosphor by combustion method

Young Ho Jeong

Adv. Energy materials & Application Research Dept. Korea Institute of Energy Research (KIER), Yuseong, Daejeon, Korea

Kwang Shik Myung, Jin Won Park[1], Yang Hua[2], Sang Do Han

[1]Dept. of Chemical Engineering, Yonsei University, Shinchon, Korea

[2]Department of Chemistry, Jilin University, Changchun, China

Abstract

A novel powder processing technique for the preparation of copper activated zinc sulfide (ZnS:Cu,Al) phosphor by combustion process has been proposed. Exothermic reaction between dissolved copper nitrate and carbohydrazide give small-sized particles in presence of alkali metal halides at lower temperature than the traditional method of preparation. This new route takes less than five minutes and requires much less energy. The optical and luminescence characteristics of ZnS:Cu,Al phosphor thus prepared were found to be enhanced significantly. Carbohydrazide acted as fuel at 500℃ with rapid heating and then the phosphors obtained were heated at 900℃ in an inert atmosphere for 3hrs to get better luminescent properties.

1. Introduction

The visible light generating luminescent materials are called phosphor and these are composed of inert host and optically excited activators. The phosphors used for practical applications must have high luminescence efficiency, high resistance to current saturation, good chromaticity and chemical/thermal stability. Many researchers have devoted their efforts in creating new materials and processes for better phosphor properties. Small amounts of metal ions are called activators, while aluminium as co-activator added in the firing process (usually 900-1200℃) not only facilitate the crystal growth, but also particulate in ZnS lattice in the formation of luminescence centers. Introduction of Cl^- ions also showed a similar effect with Al^{3+} ions. The ZnS:Cu,Al has been investigated for a long time because it has many practical applications for CRT and the potential to be used in the FED as a fluorescent material. 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 ㎛. The small-sized particles are only possible when the larger particles are grinded and milled. The final product generally contains additional defects and unreacted precursors, which change the morphology of the particles and 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 minutes. The objectives of this paper is to present a simplified process for the synthesis of ZnS:Cu,Al phosphor having uniform small particles.

2. Experimental

All chemicals except ZnS, used were of high purity procured from Aldrich Chemicals. High purity commercially available zinc sulfide (Korea Zinc Co.) was taken as a base material. 1.0 mole of zinc sulfide, 0.00-0.12mole% of copper in the form of copper nitrate, NaCl in 2 wt% of zinc sulfide as flux was taken in aqueous solution. The appropriate amount of this compound was mixed in a beaker with calculated carbohydrazide as a fuel. A homogeneous paste of above mixture was prepared in water and then fired at 500℃ in a preheated furnace for about 15 min. The material undergoes rapid dehydration and foaming followed by decomposition generating combustible gases such as oxides of nitrogen, HNCO and ammonia. The resultant compound was white, foamy and crisp due to spontaneous ignition at 500℃. The powder was cooled, milled and then fired at 900℃ 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 distilled water. The PL and color coordinates were measured using spectroradiometer Minolta CS-1000. XRD patterns were obtained with a Rigaku RINT Dmax 2000 powder diffractometer using Cu Kα radiation generated at 30kV/20mA. The morphology and the size of particles were investigated by SEM and EDAX techniques using Philips XL30 and PV99 models respectively.

3. Results and Discussion

Combustion method is a novel technique to synthesize phosphor materials. It is a highly exothermic redox reaction between metal nitrate and organic fuel such as carbohydrazide. The volatile combustible gases ignite with a flame producing voluminous fine powder. In our experiments, the resulting powders were again fired at varying temperature between 900-1200℃ in an inert atmosphere and their emission spectra were compared at each step. It was observed that the phosphors samples made by facile combustion method when heated at 900℃ for 3hours had better luminescence intensity. Fig 1. shows emission intensity of the ZnS phosphors doped with varying amounts of copper ions in presence of Al^{3+} when fired at 900℃. The optimum concentration of copper for maximum luminescence intensity is found to be 0.06 mol% of copper. Fig 2, 3 show the emission spectra and chromaticity of ZnS phosphors obtained at 500℃ and 900℃. It can be observed that the emission spectra of samples at 900℃ has about 20% more luminescence intensity than those of at 500℃. The strongest peak at 463nm is ascribed to a transition from anion vacancy to the d-level of copper. An additional peak at 520nm of increased intensity in 900℃ spectra is also observed. The color coordinates for maximum emission intensity indicated x:0.1975, y:0.3334 on display. Fig. 4a,b) shows the SEM micrograph of the ZnS:Cu,Al (0.06mole% Cu concentration) phosphor produced using combustion synthesis by firing at 500℃ and 900℃. Fig. 4c) shows the SEM of the same phosphor powder obtained by solid-state reaction. Fig. 4a,c) have irregular and low crystallinity while

Fig. 4b) is more regular and completely crystalline having zinc blende structure in the range 1-2 ㎛.
XRD patterns for the phosphor prepared at 500℃ post-reacted at 900℃ are shown in Fig 5.

4. Conclusion

ZnS:Cu,Al powder phosphors have been prepared employing facile combustion method. The combustion involves a low temperature, self-propagating ignition route that is safe, simple and rapid for the synthesis of fine and homogeneous powders displaying bright luminescent blue color.

5. References

[1] J. J. Kingsley and L. R. Pederson, Energetic materials in ceramics synthesis, Mat. Res. Soc. Symp. Proc., 1993; 296: 361-366.

[2] Tao Ye, Zhao Guiwen, Zhang Weiping and Zia Shangda, Materials Research Bulletin, 1997; 32(5): 501-506.

[3] L. R. Pederson, G. D. Maupin, W. J. Weber, D. J. McReady and R. W. Stephens, Mater. Lett., 1990; 10: 437.

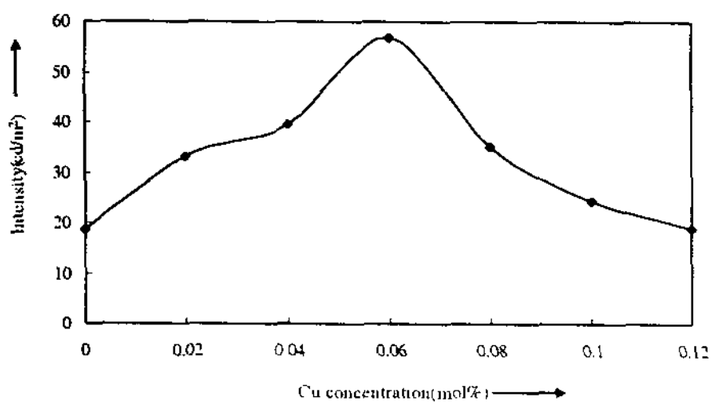
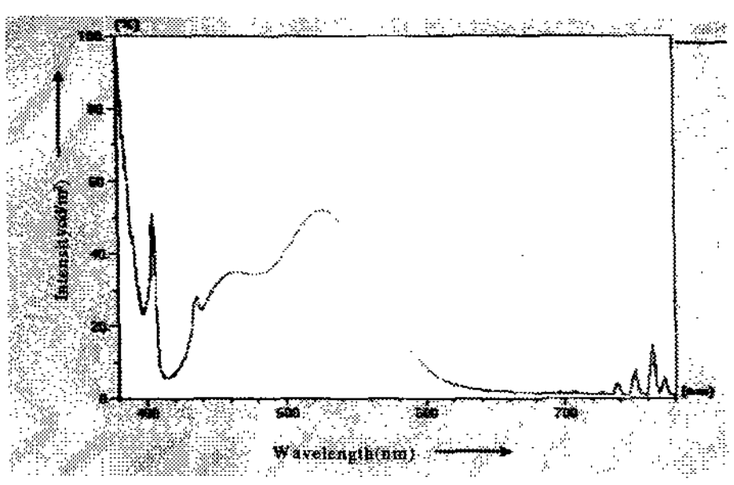
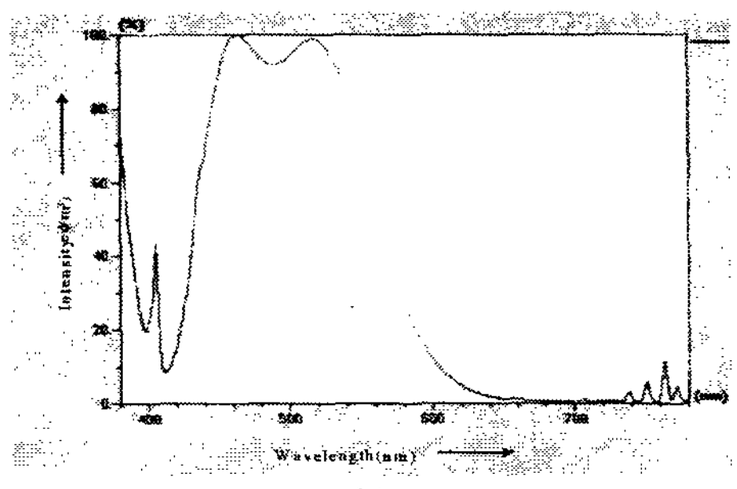


Fig 1. Luminescence intensity and concentration quenching of ZnS:Cu,Al phosphor made by combustion method.

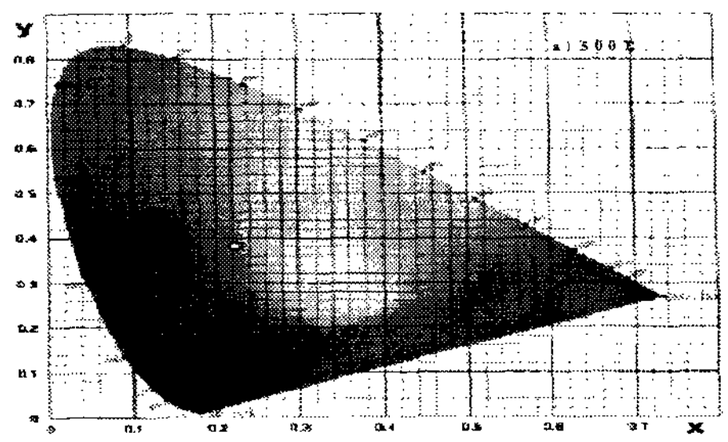


a)

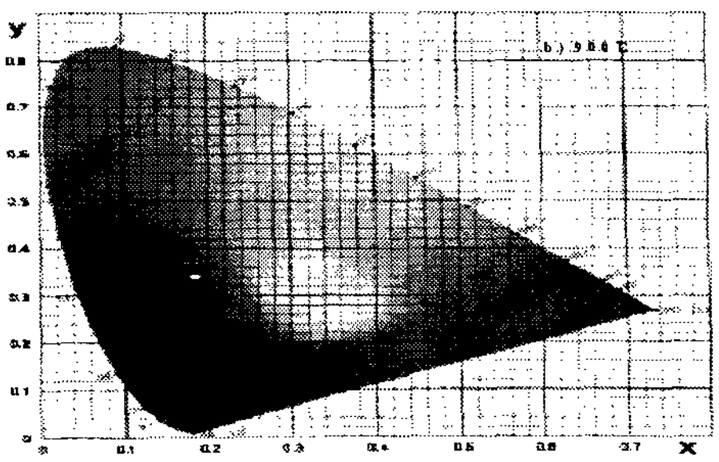


b)

Fig 2. Emission spectra of the ZnS:Cu,Al phosphor.
a) Pre-heated at 500℃. (Lv=9.26cd/m^2)
b) Post-heated at 900℃. (Lv=56.73cd/m^2)

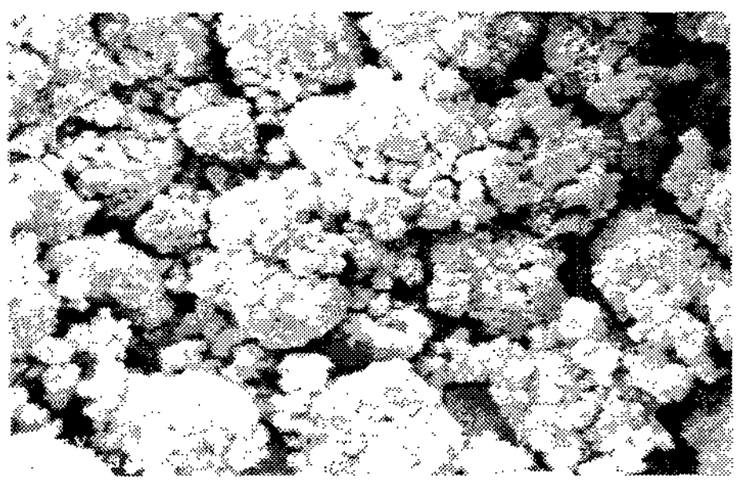


a)

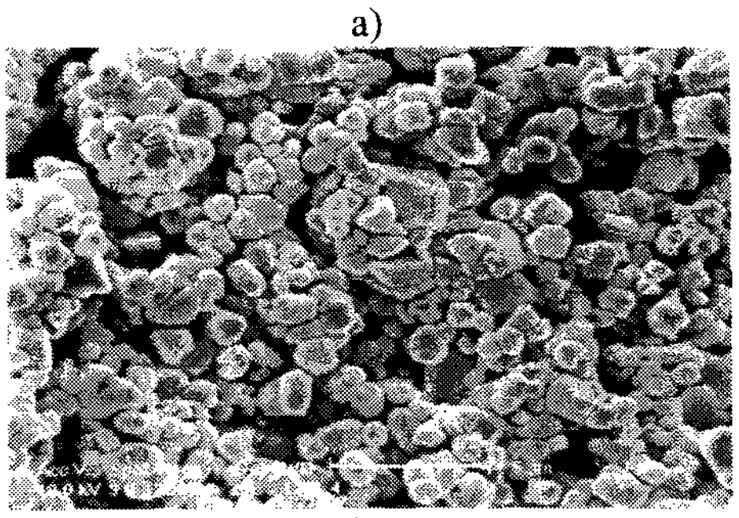


b)

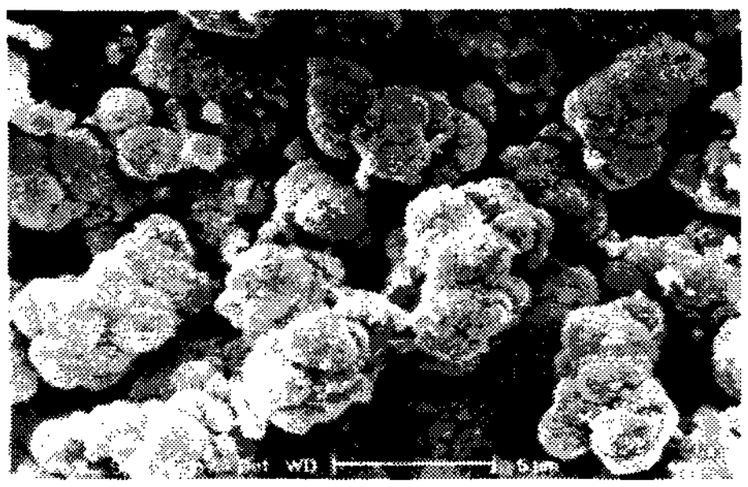
Fig 3. Color coordinates of the ZnS:Cu,Al phosphor.
a) Pre-heated at 500℃. (x=0.2259, y=0.3935)
b) Post-heated at 900℃. (x=0.1975, y=0.3338)

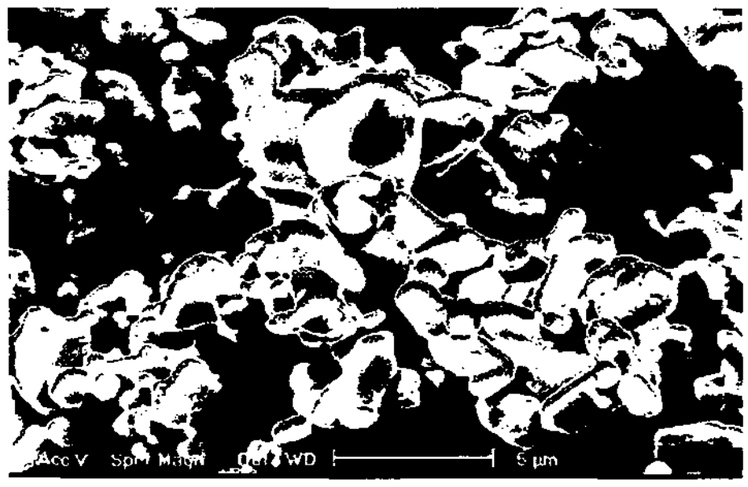


a)



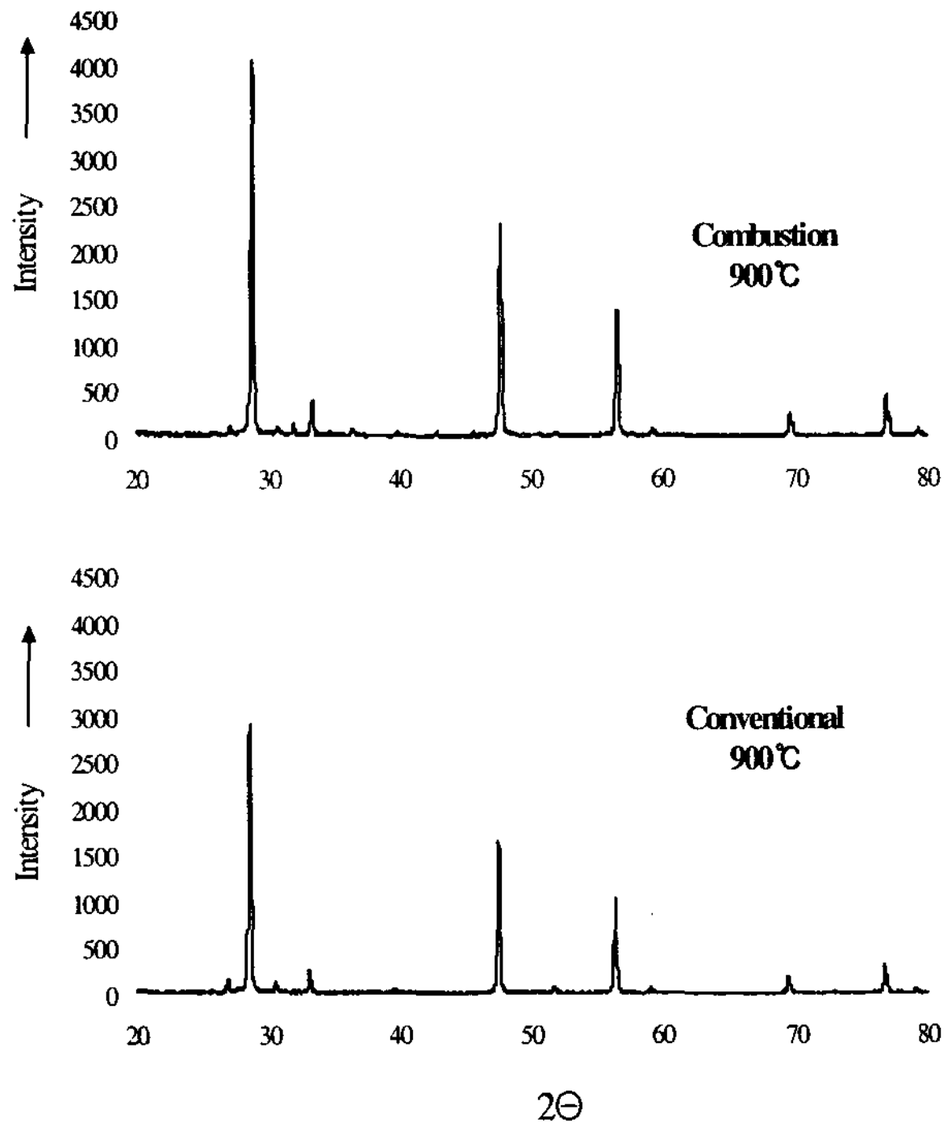
b)





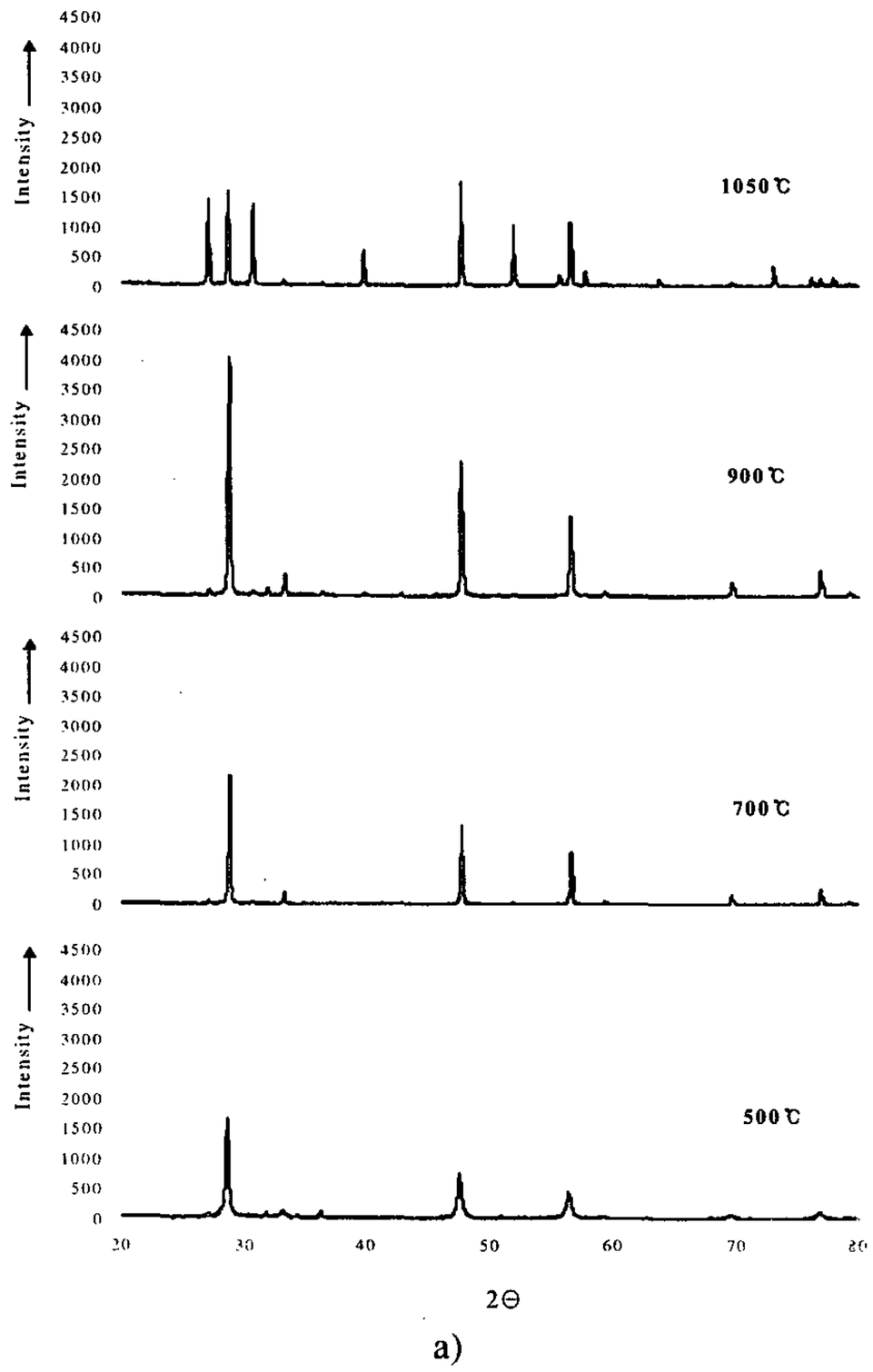
c)

Fig 4. SEM micrograph of the ZnS:Cu,Al phosphor.
(a) Pre-heated at 500℃
(b) Post-heated at 900℃
(c) Heat-treated at 500℃ and 900℃ by conventional method



b)

Fig 5. XRD patterns of ZnS:Cu,Al phosphor
a) according to different temperatures
b) compared with conventional method



a)