

Coating of ZnS phosphor by SiO₂ sol-gel

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Abstract

Silica coating on ZnS particles with buffer solution has been investigated. Diluted sodium silicate in water was used as the precursor material and it was diluted in water. Sodium silicate was added drop-wise in the continuously stirred suspension of ZnS in the buffer solution at room temperature. Smooth and evenly distributed silica coated ZnS phosphors has been obtained when the pH of buffer solution was 10, the concentration of sodium silicate in water was 20 wt%, firing temperature was 500 °C.

1. Introduction

One important class of EL(electro luminescence) phosphors includes the copper- activated zinc sulfide phosphors (ZnS:Cu) which have commercially desirable brightness and color characteristic(1-4). Such phosphors may be blue, green or yellow orange(co-activated with manganese)emitting. These phosphors may also contain other activators and co-activators such as Al,Cl and Br(5-8). EL phosphors have many commercial uses such as for LCD(liquid crystal display) backlight, copy machines, automotive dashboard displays, watch dials etc(9). Their value lies in their long life and high electrical resistance, thus making them very economical to operate. However, these materials are found to be unstable when used in EL device due to moisture and other atmospheric components. Many researchers have tried their best to enhance the stability of ZnS:Cu phosphor by synthesis method to improve crystallinity and increase the size of phosphor particles, using different fluxes and different concentration of activators or co-activators.

The coating of a thin layer on the surface of phosphor particles is a frequently applied technique to enhance the chemical stability of sulfide phosphors .Generally, oxide coating of different metals such as Si, Al, Ti, Zn, etc. is performed to make them stable in water or in moisture. However, it is very important to apply a suitable amount of coating compound. Coating has to be transparent , hard and have high resistance to moisture and chemical deterioration, and the photoluminescence(PL) intensity has to decrease as little as possible.

Literature surveyreveals that the SiO₂ coating on particles can be achieved by using different precursor materials like sodium silicate, ethyl silicate, polysilicate and hexamethyl disiloxane etc.

In this paper , we tried to modify ZnS:Cu phosphor by coating a silicon oxide layer on phosphor particles, when these are dispersed in the a aqueous buffer solution of appropriate pH. It is expected the constant pH not only inhibits the precipitation of solid particles of SiO₂ separately but as the charges on the

coated ZnS particles are constant in sign and magnitude (due to constant pH) therefore, completely dispersed and evenly coated particles should be obtained.(10) The enhancement of chemical stability of phosphor by adhering layer of SiO₂ coating is discussed.

2. Experimental

The green emitting ZnS:Cu,Cl phosphor with average 20 μ m particle size was used as a base material for coating. In the 0.4m Boric acid + 0.4m KCl solution, 0.4m NaOH solution was added to attain a particular value of pH(between 9 to 10). To this 50 ml. solution, 3g phosphor particles were dispersed with constant stirring. 10% sodium silicate solution was added drop-wise to the buffer solution of constant pH value. The solution was further stirred for an hour after the addition of sodium silicate. The solution containing phosphor was repeatedly washed with decantation while adding distilled water to remove electrolytes. The final washing was given with methanol. The solid was recovered by filtration then dried at 60°C and further heated to 500°C for 1 hour in the furnace. The experiments were performed at different pH(9, 9.5, 10), temperature (25, 50, 75) and amount of sodium silicate. Scanning electron microscopy(philips XL-30), EDAX(PV99) and XRD were employed to characterize the coating. The photoluminescence was measured using spectro radiometer(Minolta CS-100).

3. Results and Discussion

The coating of silicon oxide by sodium silicate has many variables that can affect the surface morphology of the coatings. Among them, the concentration of precursor material, pH and temperature of solution are the most important parameters on which the smooth, evenly thick and transparent film of silica on phosphor particles can be formed. In order to investigate the effect of sodium

silicate concentration, the phosphor was treated with 10% to 40% by weight with respect to ZnS. Always 10% aqueous solution of sodium silicate was added drop-wise to the suspension of ZnS. In our first experiment, the pH of the solution was kept 9 and temperature was maintained at 25°C. It can be observed from Fig.1(a), the smooth and clear surface of uncoated ZnS:Cu phosphor becomes rough and adhere with different amount of silicon oxide particles when treated with sodium silicate. The amount of SiO₂ particles deposited on the surface increases with the increase of sodium silicate amount added to the phosphor suspension Fig.1(b-e). With 10 % sodium silicate amount, the coating is partial, but with 40% sodium silicate amount, small particles of SiO₂ are formed separately, 20% sodium silicate amount seems to be the adequate amount for coating on the phosphor particles. It may be observed that the surface morphology of coating is not smooth and film-like but small particles of SiO₂ are formed on the whole surface Fig. 1(c). In brief, the surface coverage is generally proportional to the quantity of sodium silicate added.

When we carried the experiments at elevated temperatures, the morphology of the coating again changes from film to small particles. It seems that the reaction at high temperature becomes so fast that some of silica is precipitated separately without forming a film.

The EDX pattern of uncoated ZnS:Cu was shown only two peaks corresponding to ZnS are observed. The amount of Cu is so low as compared to Zn and sulfur, that no peak of Cu was detected

The EDX pattern of uncoated ZnS:Cu is shown in Fig.2 Only two peaks corresponding to ZnS are observed. As the amount of Cu is so low as compared to Zn and sulfur, that no peak of Cu is detected. The EDX profile of 20% sodium silicate coated ZnS at pH=10 shows the additional signal corresponding to Si element apart from the uncoated

phosphor signals. Atomic ratios of Zn:S is deviated far from 1:1 for coated phosphor as may be observed from Table 1. This deviation may be due to the hydrolysis of uncoated phosphor surface during the course of coating.

The results of EDX also correspond to those of SEM photographs. Silicate polymerization in dilute solution at pH values up to 10 is sensitive to pH and other factors that generally influence colloidal systems, e.g. ionic strength, dielectric constant and temperature(11). Larger particles grow at the expense of smaller particles, especially at higher pH values. This results from the tendency of smaller particles to condense at the surface of the larger particles.

As the ZnS particles are dispersed in the solution, polymerization takes place at the surface of phosphor particles. The degree of polymerization increases with increase of pH. It seems that for the formation of a continuous, evenly thick polymeric film of silica, the right conditions of pH, temperature and ionic strength are the same as described in the experimental, e.g. pH=10, temp.=25, and the buffer solution of the given ionic strength. In order to check the nature of silica film, the XRD curves of uncoated, coated phosphor and pure silica prepared at pH=10 and at 25 C are recorded in Fig.3 It may be observed that the XRD curves of coated and uncoated phosphors are identical. There is no additional peak corresponding to silica is observed. This is because the film of silica is amorphous as being depicted in the XRD curve of pure silica.

PL intensities of coated and uncoated phosphors were compared for 30 days by keeping them in moisture. It was found that the brightness of the uncoated phosphor reduces to almost half its initial value, on the other hand the coated phosphor showed the almost same PL intensity after 30 days. This clearly indicates that coated phosphor is stable in moisture.

The effect of the firing temperature was also studied. The film coated at pH=10 was fired at the

temperature 130°C, 200°C, 300°C, 400°C, 500°C for 2 hours, and its moisture resistance was tested with AgNO₃ solution. The samples fired at 130°C and 200°C turned brown with in 5 minutes, and the samples at 400°C and 500°C showed no change of color for 2 days. Thus the coating obtained between 400°C to 500°C showed the complete surface coverage and was the most stable. After sintering, it was observed that the phosphor becomes more free flowing as compared to the uncoated phosphor.

4. Conclusion

A continuous, evenly thick and transparent SiO₂ film on ZnS:Cu phosphor with 20 μ m average particle size could be obtained by adding 20% sodium silicate amount by weight with respect to ZnS: Cu phosphor drop-wise to the H₃BO₄-NaOH buffer maintained at pH=10 and 25°C. The hydrous film of silica became transparent, and continuous when sintered at the temperature between 400°C to 500°C. The mechanism of SiO₂ film formation and its stability to moisture and other environmental components have also been discussed.

5. References

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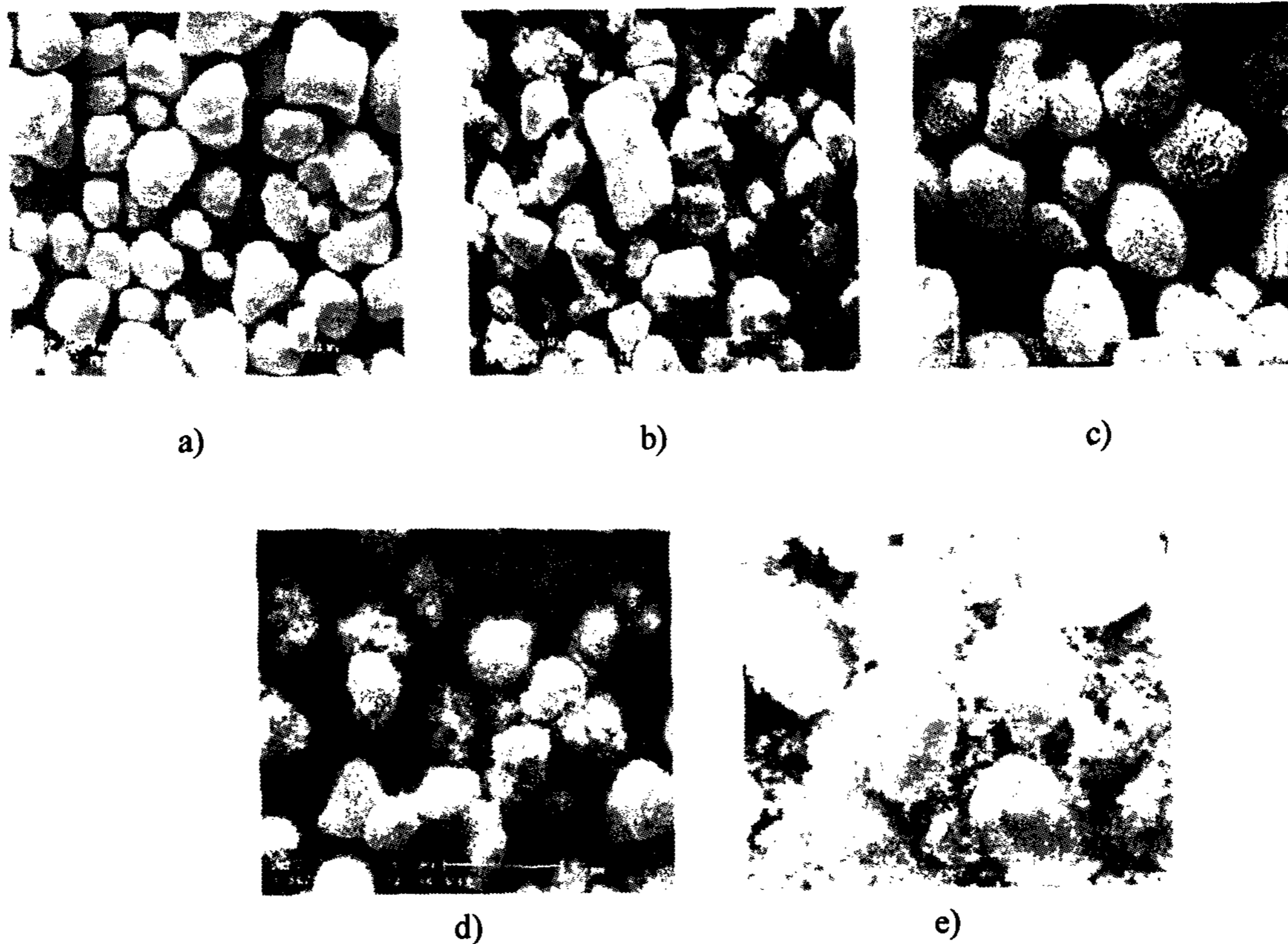


Fig.1 SEM micrographs of ZnS:Cu phosphors coated with different oxides: a) uncoated, b)10%Na-silicate, c) 20% Na-silicate, d) 30% Na-silicate and e) 40% Na-silicate

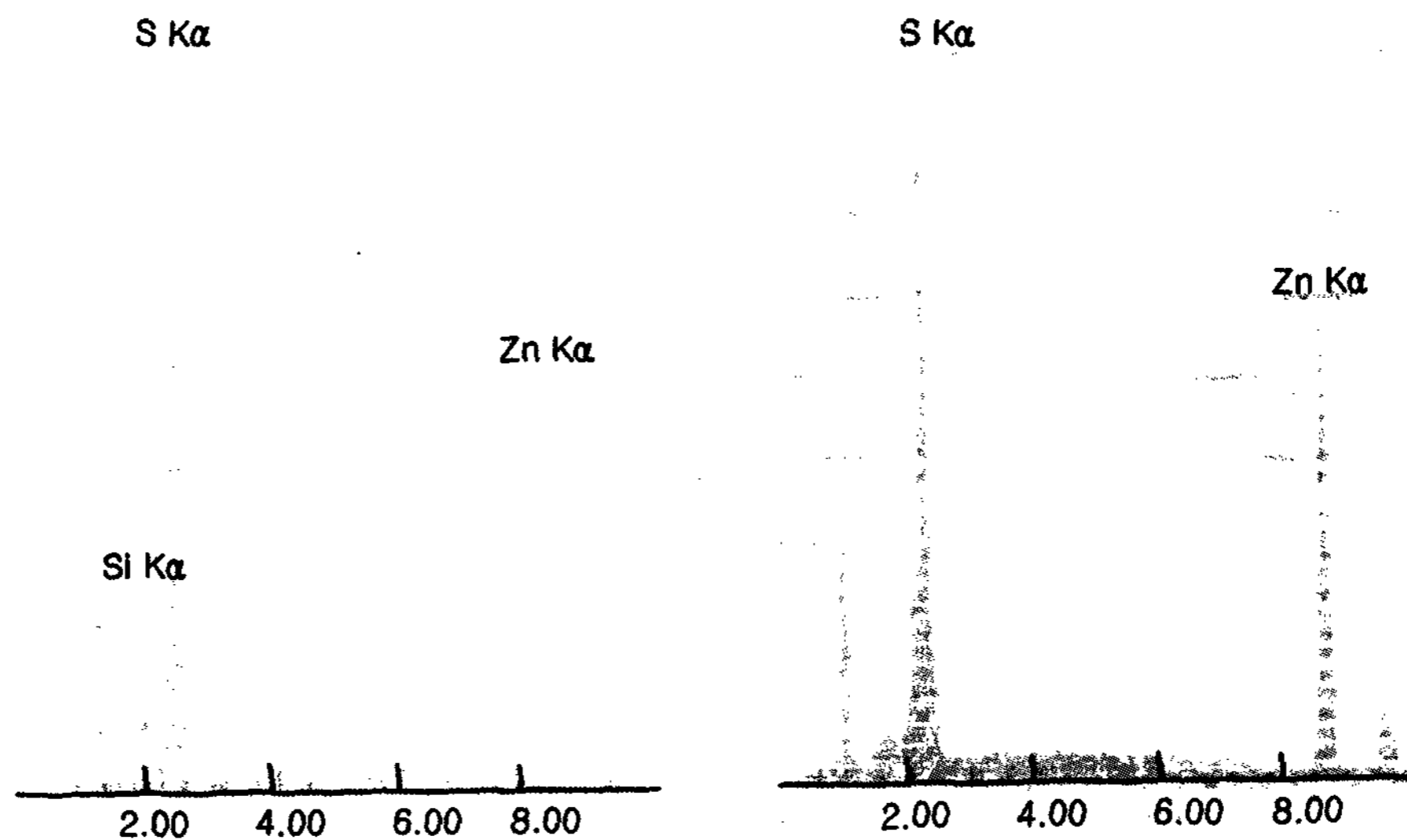


Fig. 2 EDAX profiles a) coated and b) uncoated phosphors

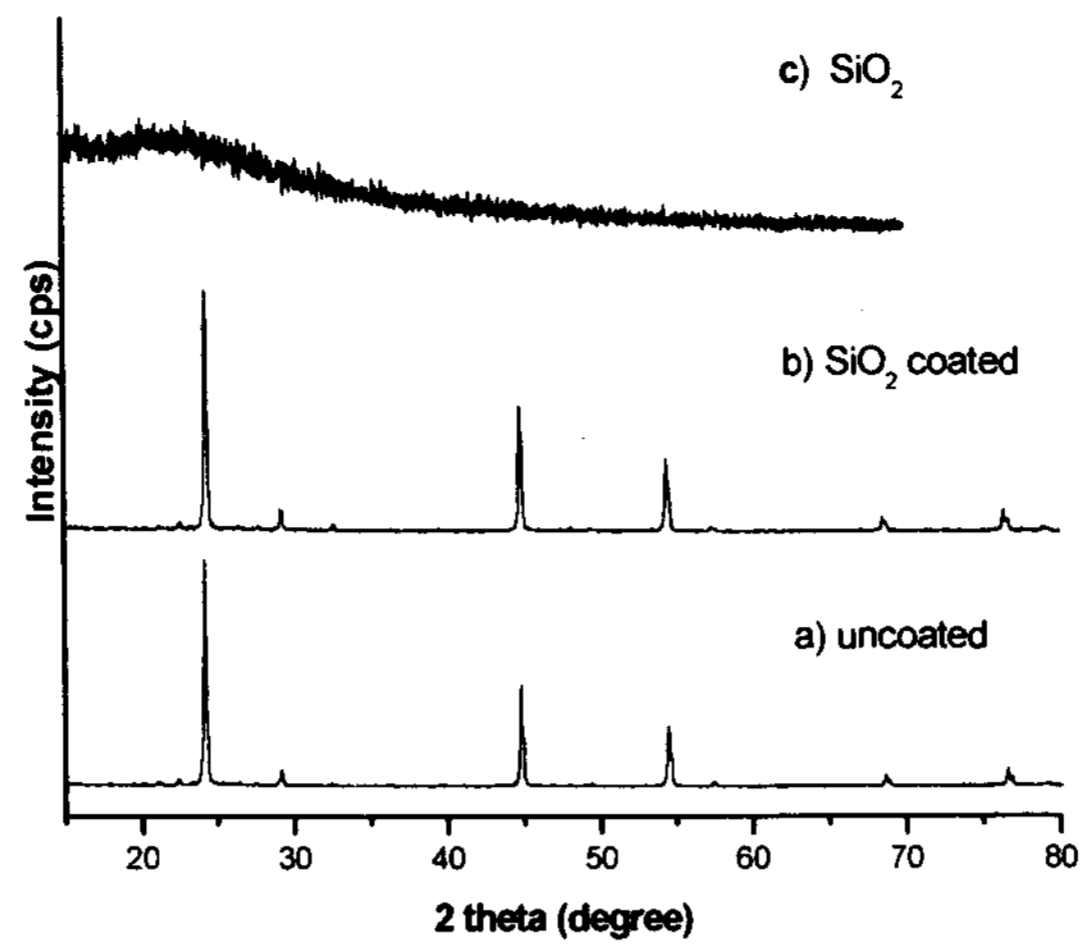


Fig. 3 XRD curves of a) uncoated b) coated and c) SiO_2 powder

Table 1

Phosphor	EDX analysis (At%)		
	Zn	S	Si
Uncoated	53.22	46.78	-
Coated with 10% Na-silicate	52.46	40.24	7.30
Coated with 20% Na-silicate	50.67	38.12	11.21
Coated with 30% Na-silicate	50.28	34.25	15.47
Coated with 40% Na-silicate	48.62	30.35	21.03