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Electroluminescence Studies in Copper Doped Zinc Sulfide Nanocrystalline and Nanocomposite Films for Display Device

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Abstract

Copper doped Zinc Sulfide (ZnS:Cu)) is a known green light emitter. Present paper reports luminescence of ZnS:Cu nanoperticles and nanocomposites. Two different nanostructures: polyvinyl alcohol (PVA) capped ZnS:Cu nanoparticles and ZnS:Cu/PVA nanocomposites have been prepared by chemical route and characterized by XRD and absorption spectra. No effect of doping has been observed on the absorption spectra. The detail of EL characterization and application in display devices of these materials are reported in this paper.

Keywords:Copper doped zinc sulphide, absorption spectra,Polyvinyl Alcohol (PVA), Electroluminescence .

1.0 INTRODUCTION

Semiconductor nanoclusters comprise a burgeoning area of materials science that has great potential for many optoelectronic applications and have attracted much attention in the past few years because of their unique properties such as size quantization,[1] nonlinear optical behaviors[2]. This class of new materials has not only provided many unique opportunities for studying physics in low dimensions but also exhibited novel optical properties which are potentially useful for technological applications. Present studies have been undertaken to synthesize ZnS:Cu/PVA composite and ZnS:Cu nanoparticles, characterize them by absorption spectra and X-ray differaction and investigat their electroluminescence.

2.0 EXPERIMENTAL TEQUNIQE

In the present work, I have prepared copper doped zinc sulphide nanoparticles capped with Polyvinyl alcohol (PVA) and Copper doped zinc sulfide nanocrystals embedded in polyvinyl alcohol matrix. All the samples were prepared by chemical route since it is a cost effective technique and expected to give low size distribution. In all the samples, the Cu doping was kept at the level of 0.01% because it is found to show maximum luminescence [3]. For the synthesis of PVA capped ZnS:Cu nanoprticles, the chemicals used were $ZnSO_4.7H_2O$, $CuCl_2.4H_2O$, polyvinyl alcohol (PVA) and Na_2S. In a typical synthesis procedure, aqueous stock solutions of 1 M of $ZnSO_4.7H_2O$ and different concentrations of PVA were dissolved in 50 ml double distilled water under vigorous stirring, and then 0.01% $CuCl_2.4H_2O$ solution was added to the above solution. Finally, 50 ml of 1 M Na_2S solution was introduced into the above solution under continuous stirring. During the whole reaction process, the reactants were vigorously stirred at 80^0C for 1h. Then the precipitate was cleaned repeatedly with deionized water [16]. The PVA concentration controls the size of nanoparticles. Five different samples, ZnS:Cu-i, ZnS:Cu-ii, ZnS:Cu-iii, ZnS:Cu-iv, and ZnS:Cu-v were prepared by varying PVA concentration at the level of 0 gm, 0.5 gm, 1.0 gm, 1.5 gm and 2.0 gm, respectively. The ZnS:Cu nanocomposites were also prepared by the chemical method. For the synthesis of composite films, 400 mg poly vinyl alcohol (PVA) was dissolved in dimethylformamide (DMF) by constant stirring and heating at 70^oC. Zinc acetate was added to it in appropriate quantity. For doping 0.01% copper acetate was mixed in the initial solution. The resulting solution was stirred for 30 minutes. The solution was refluxed by applying nitrogen and then H_2S gas was passed for a 30 second. The solution immediately turned milky white. Now again the solution was stirred for a few seconds, then caste over glass slides and conducting glass plate also and dried to obtain uniform film of ZnS:Cu/PVA nanocomposite [4-5]. Five different samples ZnS:Cu-1, ZnS:Cu-2, ZnS:Cu-3, ZnS:Cu-4, and ZnS:Cu-5 were prepared by varying loading percentage of ZnS:Cu as 5, 10, 20, 30 and 40 % by weight, respectively. The crystal structures and regularity of atomic arrangements in all the samples were studied by X-ray diffraction technique using Rigaku Rorating Anode (H-3R) diffractometer at UGC-DAE Consortium for Scientific Research Indore. The UV-Vis absorption studies were carried out by Perkin Elimer, Lambda-12 spectrometer in the range 200-600 nm. ZnS:Cu is a well known luminescent material having a band gap of 3.7 eV at 300 K. This corresponds to ultraviolet (UV) radiation for optical inter-band transition with a wavelength of 335 nm. For study of electroluminescence of ZnS:Cu nanostructures, the EL cells were prepared by placing ZnS:Cu nanoparticles/composites between SnO_2 coated conducting glass plate and aluminum foil. The EL cell was connected with low distortion frequency generator coupled with power supply (wide band amplifier). AC voltage of different frequencies was applied and EL brightness at different voltages was measured at each frequency, with the help of photomultiplier tube connected to a picoammeter. The corresponding current was recorded by a microammeter, which is connected in series with the EL cell.

3.0 RESULT AND DISCUSION

The samples prepared with polyvinyl alcohol (PVA) as capping agent were in powder form where as ZnS:Cu/PVA nanocomposites were films on glass slides. All the samples were milky white in color. The XRD patterns give information about the crystal structure. Figures 1, 2 show the XRD patterns of polyvinyl alcohol (PVA) capped ZnS:Cu nanoparticles and ZnS:Cu/PVA nanocomposites respectively. In case of nanocompsites the peaks due to ZnS are superimposed over the pattern due to PVA with major peak at ~ 28^0 (2θ). The crystalline size of PVA capped ZnS:Cu nanoparticles are obtained in the range of 20 nm to 4 nm and the particle size of ZnS:Cu in nanocomposites are obtained in the range of 5 nm to 3 nm. The variations of crystalline size decreases with increasing capping agent or loading percentage.

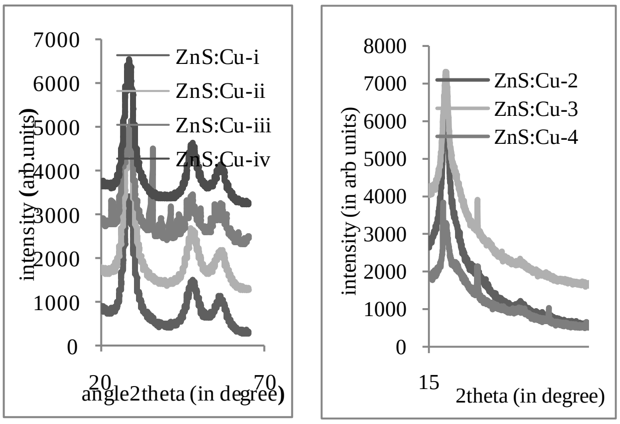

Fig 1 and 2 X-Ray differaction of ZnS:Cu nanocrystals and nanocomposites

The optical absorption spectra of ZnS:Cu samples prepared by different methods are shown in figure 3 and 4. It can be seen from the spectra that there is practically uniform absorption in the visible range (800 nm-390 nm). Absorption increases suddenly in the UV region. No absorption peaks are found. The gradual shift in absorption edge to the shorter wavelength side (blue shift) indicates increased band gap with reducing particle size because of quantum confinement effects.

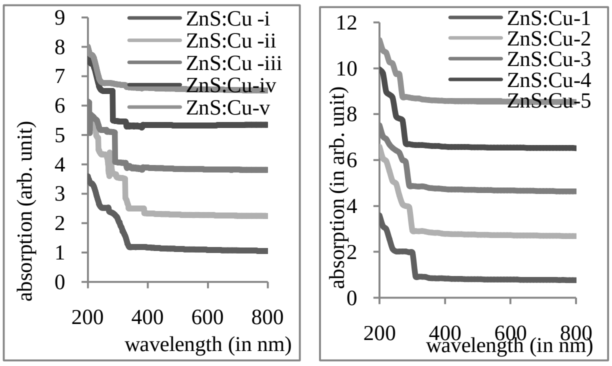

Fig 3 and 4 Optical absorption spectra of ZnS:Cu nanoparticles and nanocomposites

The particle size estimated using the effective mass approximation model is found to be decreases with increasing capping agent concentration or loading percentage of ZnS:Cu in PVA. The estimated particle size is nearly same as obtained by XRD.
The electroluminescence has been investigated both types of nanostructures. Voltage-brightness characteristic shows that, on increasing the input voltage, brightness increases for all samples. Figure 5 and 6 show EL brightness versus voltage curves at 1000 Hz frequency, for various samples. It is observed that EL starts at threshold voltage and then increases with increasing voltage, and lower threshold current is obtained for smaller particles. It can be seen from the figures that for PVA capped samples the threshold voltage is lower and EL intensity increases rapidly with voltage. Similar effect is seen in case of ZnS:Cu/PVA nanocomposites also, but here EL intensity is quite high and increase with voltage is also very fast.

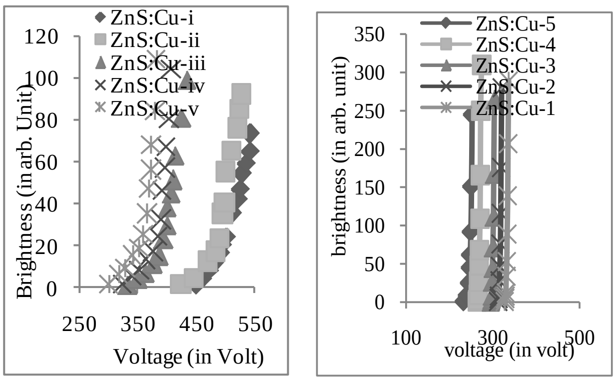

Fig 5 and 6 Brightness-Voltage Characteristics of ZnS:Cu nanoparticles and nanocomposites (at 1000Hz)

Figure 7 shows the voltage-brightness curve, for ZnS:Cu nanoparticles of same size (about 4 nm size) synthesized by different concentration of capping agent and different

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loading percentage of zinc sulfide in PVA matrix at 1200 Hz frequency. It is observed that threshold voltage is nearly same for both samples but the increase in EL brightness with voltage is increases for PVA capping and there is very fast increase in case of nanocomposites. It appears that in case of nanocomposites the charge carrier transportation is easy and hence electron and hole can easily move towards each other and recombine giving high emission.

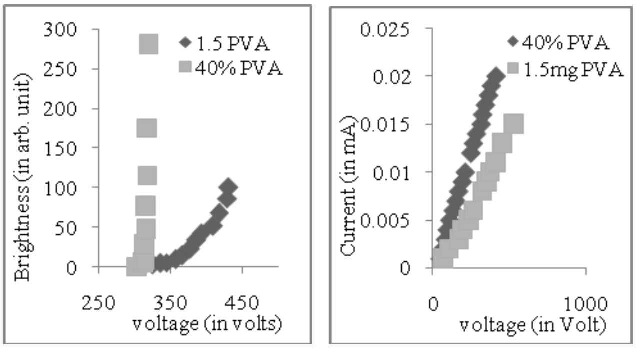

Fig 7 and 8 Brightness-Voltage and Current-Voltage curve for both samples

In both cases, voltage-current (V-I) characteristic shows that, on increasing the voltage, current increases continuously and linear relation is found between them, which indicates ohmic nature. From the slope of line impedance can be estimated. Comparing the V-I characteristics for both types of samples it is found that impedance is minimum for nanocomposites, and maximum for capped nanoparticles indicating easy charge carrier transportation in the composites. (Fig. 8).

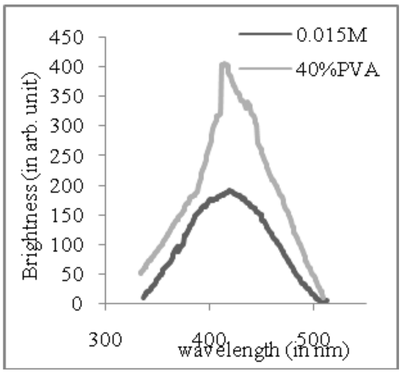

Fig 9 Electroluminescence spectra of three different types of ZnS:Cu nanostructures

The EL spectra of ZnS:Cu nanoparticles of same size (about 4 nm size) prepared by both methods are shown in fig.9. A single broad peak is obtained for both samples at about 420 nm but EL intensity of ZnS:Cu/PVA nanocomposites is much larger than the ZnS:Cu nanoparticles. This shows that the surface states are well passivated in nanocomposites causing the transition to be radiative.

4.0 CONCLUSION

The studies have shown that smaller ZnS:Cu nanocrystals can be prepared by increasing capping agent concentration and smaller size ZnS:Cu nanocomposites with PVA matrix can be prepared by increasing loading percentage of ZnS:Cu. X-ray diffraction (XRD) has revealed cubic zinc blend structure of ZnS:Cu nanocrystals of size below 20 nm. Optical absorption spectra show blue shift in the absorption edge indicating increase in effective band gap due to quantum size effect. Electroluminescence studies have shown that light emission starts at a threshold and then increases rapidly with voltage. Higher EL intensity and lower threshold voltage is obtained in case of smaller particles. The EL spectra of all the sample is found to be broad with peak at about 420 nm. The EL intensity of ZnS:Cu/PVA nanocomposites is much larger than the ZnS:Cu nanoparticles. The high efficiency EL devices for display and lighting can be fabricated using ZnS:Cu nanocomposites with PVA matrix giving violet emission.

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