Chapter VII

THERMAL PROPERTIES OF ZnS:Cu NANOPARTICLES

7.1 INTRODUCTION

Annealing process is effective for reproducible size control of nanoparticles and also it can be used to improve the crystal quality and stability which are required for device purposes (Wang et al., 1991b; Kuzuya et al., 2005 and Motlan et al., 2007). However, Motlan et al. (2007) reported that there was no phase transition of the ZnS nanoparticles. In this chapter, the synthesized sample (ZnS:Cu$^{2+}$) was annealed for 1hr at different temperatures lying in the range 200–900˚C and then cooled down (furnace cooling) to room temperature. Then the samples were characterized by TG-DTA, FTIR and XRD.

7.2 RESULTS AND DISCUSSION

7.2.1 TG - DTA analysis

The TG-DTA thermogram were recorded for ZnS:Cu$^{2+}$ nanoparticles in the temperature range, room temperature (RT) to 1000˚C with an increment of 10˚C/min in an air atmosphere. Fig. 7.1 shows combined plots of TG and DTA. From, the TGA data plots, it is noticed that the weight loss of the nanoparticles are found to take place upto 850˚C. In DTA curve, first endothermic peak is found at 65˚C. This peak is attributed to the evapouration of the water and organics. The first exothermic peak at around 290˚C probably corresponds to the lattice deformation of ZnS, which is in good agreement with the results of Mu et al., 2005 and Motlan et al., 2007. The composition does not
vary in the annealing range from 100 to 200˚C, where as, beyond 300˚C, most of the Cu$^{2+}$ ions are released.

Fig. 7.1. TG and DTA curve of ZnS:Cu$^{2+}$ (0.4%) nanoparticles
from the ZnS matrix. The observed endothermic peak at 320°C is believed to be the beginning of phase transition. A broad exothermic peak appeared at around 400°C is implying the improvement of the crystallinity of the sample. Additionally, above 400°C, there is a smooth downward trend in DTA curve with significant weight loss. This may be due to the release of residual sulfur ions from the sample. At around 900°C, much weight loss is observed. This may be due to complete removal of sulfur ions.

7.2.2 FTIR analysis

For this analysis, the samples (ZnS:Cu$^{2+}$) were heated in an electrical furnace from 200° to 900°C at an optimum interval. Then the samples were subjected to FTIR analysis. The spectra were recorded and are shown in Fig. 7.2. The spectra obtained from RT to 350°C show characteristic peaks at 612, 1010, 1116 cm$^{-1}$ along with some other minor peaks (Fig. 7.2a, b, c and d). As seen in the figure, the bands at 1010 and 612 cm$^{-1}$ were strongly present with broadness, due to Zn–S vibration. There is no change in the peak position while the temperature of the ZnS:Cu was increased from 200°C to 350°C. However, the relative intensity is varied. When the samples are heated above 350°C, the vibration properties of ZnO nanocrystals are observed. Increasing of annealing temperature from 400°C to 650°C yields the shifting of peak positions (935, 1010 and 612 cm$^{-1}$) to lower wavenumber side with decreasing in intensity, which may be due to oxidation of the sulfur from samples and also transformation of the ZnS to ZnO. However, a strong new peak appeared at around 900 cm$^{-1}$.
(400 °C). This may be due to oxidation of the ZnS and starting nature of the formation of ZnO. When the temperature was further increased at 700°C (Fig. 7.2j) the peaks at 935, 612 and 1010 cm\(^{-1}\) were almost disappeared and some new peaks were appeared in the range 430 to 496 cm\(^{-1}\). The observed peaks are due to stretching vibration of the Zn-O.
Fig. 7.2. FTIR spectra of (a) annealed (RT) and unannealed (b) – (m): 200, 250, 300, 350, 400, 450, 500, 650, 700, 800, 850 and 900°C) ZnS:Cu$^{2+}$ nanoparticles.
This indicates the continuous formation of ZnO by oxidation of ZnS (Gondal et al., 2009). When the annealing temperature was further increased from 700˚C to 800˚C, the intensity of the stretching vibration of ZnO peak (1100cm⁻¹) strongly appeared which indicate the crystalline nature of ZnO at higher temperature. At 850˚C, more number of new peaks appeared in the region 500 – 1650cm⁻¹. These are the characteristic peaks for ZnO. This shows the complete formation of ZnO at 850˚C. At 900˚C it retains its form as ZnO. This is a reversed reaction reported in the literature regarding to the conversion from ZnO to ZnS nanoparticles in the hydrogen sulfide atmosphere at the same temperature (Peng et al., 2005). However, both ZnS as well as ZnO are observed upto 650˚C.

The broad absorption peaks in the range of 3410–3465cm⁻¹ corresponds to –OH group indicate the existence of water absorbed in the surface of nanocrystals. The presence of this band can be clearly attributed to the adsorption of same atmospheric water during FTIR measurements. The bands at 1500–1650 and at 2370cm⁻¹ are due to the C=O stretching mode arising from the absorption of atmospheric CO₂ on the surface of the nanoparticles (Qadri et al., 1999). FTIR spectrum of the annealed sample reveals that moisture is now completely removed from the sample, as intensity and width of O–H modes has drastically reduced. However, ZnO configuration is not affected due to annealing (<650˚C), as vibrations of metal – oxygen are still observed at 420cm⁻¹ (Nyquist, 1997). Bands observed in the region 900–1500cm⁻¹ are due to the oxygen stretching and bending frequency.
The additional weak bands and shoulders at 2931, 2847, 1425 and 1402 cm\(^{-1}\) are due to the microstructural formation of the sample. Bands around 1200 and 1100 cm\(^{-1}\) are due to the characteristic frequency of inorganic ions.

7.2.3 XRD analysis

Fig. 7.3 shows the XRD pattern of surfactant-free ZnS:Cu\(^{2+}\) nanoparticles annealed at different temperatures from 200°C to 900°C at an optimum interval. All the diffractograms show a significant amount of line broadening, a characteristic of nano-phase materials. For unannealed (RT) (Fig. 3.1 in chapter - III) ZnS:Cu\(^{2+}\) nanoparticles, the peaks appeared at diffraction angles (2θ) a 28.4°, 47.6° and 57.6° corresponding to 111, 220 and 311 planes, respectively. It indicates that the ZnS:Cu\(^{2+}\) nanoparticles are in stable cubic phase at room temperature. Annealing the particles at 200°C for 1 hr has produced a slight change in the lattice parameters; moreover there is an increase in the average crystalline size from 5.3 to 6.1 nm. Further, annealing of ZnS:Cu\(^{2+}\) at 400°C for 1 h, two structures of ZnS and ZnO are noticed. At this temperature Cu may be released from ZnS:Cu\(^{2+}\). In Fig. 7.3, it is clear that at 400°C, the sample is still mostly at its cubic phase with broadened XRD peak and with some additional small peaks corresponding to hexagonal ZnO phase. For the annealing temperatures between 400°C to 650°C, both structures are formed. From 650°C to 800°C, there is no change in the peak position (not shown in figure 7.3). When the samples were further heated to a temperature of 850°C, pure ZnO nanoparticles were obtained with
hexagonal structure (Fig. 7.3). This result reveals that the temperature above 850°C is essential for the complete conversion of ZnS to ZnO nanoparticles in an air atmosphere. This is the reversed reaction reported in the literature regarding to the conversion, from ZnO to ZnS nanoparticles in an atmosphere of hydrogen sulfide at same temperature by Tang et al., 1996. It is likely that at 700°C and above, the ZnS is completely oxidized to ZnO in an atmospheric air as shown by the following equation (Peng et al., 2005). In present study, ZnS is completely transformed to ZnO at 850°C.

$$2\text{ZnS} \, (s) + 3\text{O}_2 \, (g) = 2\text{ZnO} \, (s) + 2\text{SO}_2 \, (g)$$
Fig. 7.3. XRD patterns of ZnS:Cu$^{2+}$ nanoparticles annealed at different temperatures.
Fig 7.4 shows temperatures versus particle sizes. When annealing temperature is increased from 200˚C to 900˚C, the particle size is also increased from 6.1 to 42.3nm. The increasing particles sizes may be due to agglomeration of the particles at higher temperature.

7.3 CONCLUSION

On the basis of oxidization of ZnS nanoparticles, pure well-crystallized ZnO nanopowders were obtained from ZnS:Cu\(^{2+}\) by heat treatment. From thermal study, the stability of cubic ZnS:Cu\(^{2+}\) was found at around 200˚C. The drastic weight loss at around 850˚C indicates the formation of ZnO and significant removal of sulfur. The complete transformation of ZnS and ZnO was clearly identified by the observation of stretching vibration (Zn-O) in the range 430–496 cm\(^{-1}\) in FTIR spectrum at around 850˚C. From XRD study, the formation of hexagonal ZnO was started at 400˚C and completed at around 850˚C. The particle size of ZnS:Cu\(^{2+}\) is increased from 6.1 to 42.3nm by increasing of annealing temperature from 200˚C to 900˚C. The stability of ZnO particles was found upto 900˚C. The changes observed from both FTIR and XRD very well match with each other. From this one can conclude that the temperature 850˚C is essential for the conversion of ZnS to ZnO nanoparticles in an air atmosphere.
Fig. 7.4. A plot for temperature versus particle size