Effect of calcination temperature on the structural and morphological properties of zinc sulphide nanomaterials

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Abstract. Metal sulfide nanomaterials have emerged an important material in recent times due to its potential applications in optical devices, nanoelectronics and nano-optoelectronics. In current research work, zinc sulfide (ZnS) nanoparticles were synthesis by simple chemical co-precipitation method and effect of calcination temperature on the structural and morphological properties of the nanomaterials have been investigated. It was observed that when temperature rises to 500 °C, cubic structure of ZnS transformed into hexagonal phase. Further increase in temperature oxidize the sulfide and ZnS changes into zinc oxide at 750 °C. This temperature rise was also evident in the SEM images where nanoparticles transformed into rod like morphology at 750 °C. Oxidation of the ZnS to ZnO also confirmed by FTIR spectrum which shows Zn-O bonds presence. These studies show that temperature variation can affect the structure and ultimately their relevant technological applications.

1. Introduction
Nanomaterials demonstrate distinguished characteristics as compared to those bulk materials. Nanomaterials based on semiconductor properties is an important class which shows excellent applications in many fields such as gas sensing [1], photocatalysis [2], LEDs [3], capacitors [4] etc. Metal sulfides become very popular inorganic nanomaterials during the last decade as a potential candidate to replace metal oxide-based materials due to their certain limitations [5]. ZnS is a type of metal sulfide belong to the II-IV group but with wider band gap from other materials of the family. Due to some exclusive and beneficial properties of ZnS, it becomes more popular as compared to ZnO. These properties include wide band gap, bond energy of exciton, high refractive index, luminescent characteristic, optical absorption and many others [6].

ZnS found in two crystalline forms i.e. zinc blende and wurtzite. Zinc blende, also known as sphalerite, has cubic crystal structure [7]. This phase shows more stability at low temperature than other form of ZnS. Sphalerite also occurs naturally in our environment. The range of energy band gap of Zinc blende is 3.5 eV to 3.7 eV. Wurtzite is the hexagonal structure of ZnS, stable at high temperature. Usually, this phase of ZnS obtained synthetically. The range of energy band gap of wurtzite is 3.7 eV to 3.9 eV [1].

It is essential task to prepare ZnS nanoparticles having small dimensions, specifically in the nanosized. The arrangement and size of nanoparticles affect the characteristics associated with various uses. This is the reason why size and structure of nanoparticles should be controlled during preparation.
In the production and development of nanotechnology, there are a number of techniques used for the fabrication of ZnS nanoparticles such as green synthesis [8], microwave assisted [9], hydrothermal [10] and chemical co-precipitation method [11]. The chemical co-precipitation is a very simple technique [12]. Co-precipitation is a technique in which solute is frequently dissolve in the solvent. Both solute and solvent are mixed together by adjusting pH of the mixture. These reactions can perform at normal temperature and pressure conditions. There are very few studies have been reported on the temperature effect on the ZnS nanomaterials. In this research work, ZnS nanoparticles have been prepared by using chemical co-precipitation method and effect of different calcination temperature has been investigated.

2. Experimental set up

All the chemicals were of analytical grade and used without any further purification. Experiment details are as follows: ZnSO$_4$·5H$_2$O and Na$_2$S·7H$_2$O were used as starting materials, dissolved separately in de-ionized water to make one molar solution and stirred at room temperature for 30 minutes. Then Na$_2$S solution was added in ZnSO$_4$ solution dropwise using burette while stirring. The reaction was completed in 2 hours. Then obtained solution was filtered. In order to remove the sodium impurities, the precipitates were washed with distilled water three times. The collected precipitates were dried at 80 °C for 16 hours in the oven. After drying, the resultant precipitates were ground in fine powder form with the help of pestle and mortar. Then sample was divided into four parts and treated at different temperatures i.e. as synthesized, 250, 500 and 750 °C. Schematic of the synthesis scheme is shown in figure 1. Samples were characterized by using X-ray diffraction, SEM, and FTIR.

![Figure 1. Schematic illustration of ZnS synthesis scheme.](image_url)

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction (XRD) is a useful technique for the determination of crystal structure. XRD pattern of the synthesized ZnS nanostructures treated at different temperature is shown in figure 2. As synthesized and treated at 250 °C nanostructures have presented typical XRD spectrum as it is observed in many studies with signature peaks present at 2 theta values of 28.53°, 47.45° and 56.3°. These 2 theta values correspond to (111), (222) and (311) planes of cubic zinc blend structure. XRD pattern of ZnS nanomaterials treated at 500 °C exhibits many additional peaks as compare to synthesized and heated 250 °C. The 2 theta values and corresponding diffraction planes are listed in table 1. While analysing and comparing with standard data, it is observed that ZnS at 500 °C actually has hexagonal crystal structure, indicating stretching in lattice parameter and angle. When
nanomaterials are further heated up to 750 °C, 2 theta positions of the diffraction peaks are shifted and by matching with standard data. These peaks show ZnO structure with hexagonal crystal structure. The 2 theta values and corresponding diffraction planes are presented in Table 1. This shows that at elevated temperature, oxidation of ZnS produce ZnO. In conclusion, current study shows that cubic phase of ZnS is stable till 250 °C. More heat changes the cubic phase into hexagonal phase with increased crystallinity. Further increase in temperature, may change the metal sulphide into metal oxide by oxidation of the sulphide nanomaterial.

Further investigation of the effect on crystallite size, Scherrer formula was used to calculate the crystalline size as tabulated in Table 2. Scherrer equation can be written as equation (1).

\[ Dp = \frac{K \lambda}{\beta \cos \theta} \]  

Where, \( Dp \) is Average crystalline size, \( K \) is Shape factor (typically value about 0.94), \( \lambda \) is X-ray wavelength, \( \beta \) is Full width at half maximum of highest intensity diffraction peak, \( \theta \) represents Bragg’s angle.

![Figure 2. XRD pattern of ZnS nanomaterials calcinated at different temperatures (a) as synthesized, (b) 250 °C, (c) 500 °C and (d) 750 °C.](image)

The crystalline size of as-synthesized and heated at 250 °C powder 3.72 nm broader peaks in the XRD pattern of these two samples indicates higher amorphous nature of material which result smaller grain size as it was calculated by Scherrer formula. Particle size at 500 °C is 42.47 nm which indicating heating effect and high crystalline order in the structure (also more diffraction peaks observation). Finally, at 750 °C, crystallite size increased to 47.47 nm, can be attributed to the heating effect.
### Table 1. Peak analysis of samples.

| Sample | Peak position \(2\theta\) | Planes (hkl) | Compound |
|--------|--------------------------|--------------|----------|
| 1      | 28.53                    | (111)        | ZnS      |
|        | 47.45                    | (220)        | ZnS      |
|        | 56.30                    | (311)        | ZnS      |
| 2      | 28.53                    | (111)        | ZnS      |
|        | 47.45                    | (220)        | ZnS      |
|        | 56.30                    | (311)        | ZnS      |
| 3      | 26.88                    | (100)        | ZnS      |
|        | 28.50                    | (002)        | ZnS      |
|        | 30.43                    | (101)        | ZnS      |
|        | 39.39                    | (102)        | ZnS      |
|        | 47.31                    | (110)        | ZnS      |
|        | 51.41                    | (103)        | ZnS      |
|        | 55.97                    | (200)        | ZnS      |
| 4      | 27.16                    | (100)        | ZnS      |
|        | 32.02                    | (100)        | ZnO      |
|        | 34.50                    | (002)        | ZnO      |
|        | 36.51                    | (101)        | ZnO      |
|        | 47.80                    | (110)/(102)  | ZnS/ZnO  |
|        | 56.81                    | (112)/(110)  | ZnS/ZnO  |
|        | 63.06                    | (103)        | ZnO      |
|        | 69.27                    | (201)        | ZnO      |

### Table 2. Particle size calculated by Scherrer formula.

| Sample | Temperature | Crystallite size (nm) |
|--------|-------------|-----------------------|
| S-1    | As-synthesized | 3.72                  |
| S-2    | 250°C        | 3.72                  |
| S-3    | 500°C        | 42.47                 |
| S-4    | 750°C        | 47.47                 |

### 3.2. SEM analysis

Scanning electron microscopy provides information about shape and morphology of the nanomaterials. SEM images have taken for samples calcinated at temperature of 500 °C and 750 °C as shown in figure 3 and figure 4, respectively. In figure 3, images are taken at magnification 300x, 495x, 718x and 1440x. Low magnification images present high yield of ZnS nanomaterials with hexagonal crystal structure. There are smaller spherical particles are observed along with large irregular aggregates of the nanomaterials. Whereas when sample is heated at 750 °C, these aggregates are reorganized and formed rod like morphologies as shown in figure 4. These results show that nanomaterials not only change from zinc sulphide to zinc oxide, there is also change in morphology with the increase in temperature.
Figure 3. SEM images of ZnS nanoparticles calcinated at 500 °C at different magnifications. (a) 300x, (b) 495x, (c) 718x and (d) 1440x.
3.3. FTIR analysis
Fourier transform infrared spectroscopy provides information about impurity and functional groups attached with the nanomaterials. In this study, we have obtained FTIR spectrum of sample treated at 750 °C to confirm about the transformation of ZnS into ZnO form. FTIR spectrum of the sample is shown in figure 5. There is one visible band is observed at 605 cm$^{-1}$ which is related to the stretching vibrations of ZnO bonds [13]. This spectrum confirms XRD results where we have observed ZnO diffraction peaks at 750 °C.

Figure 4. SEM images of nanomaterials heated at 750 °C at different magnifications (a) 2210x, (b) 3150x, (c) 4800x.

Figure 5. FTIR spectrum of ZnS nanomaterials heated at 750 °C.

4. Conclusion
ZnS nanomaterials have been synthesized successfully by using chemical co-precipitation method. Synthesized nanomaterials were subjected to different calcination temperatures i.e. 250 °C, 500 °C and 750 °C. Then these samples have been investigated by XRD, SEM and FTIR. XRD analysis shows
changes in crystal structure with temperature and also showed oxidation of ZnS into ZnO nanomaterials at 750 °C. SEM images presented variation in morphology with temperature. FTIR spectrum confirms the formation of ZnO nanomaterials at elevated temperatures.

References
[1] Zhao Y, Zhang Y, Zhu H, Hadjipanayis G C and Xiao J Q 2004 *Journal of the American Chemical Society* **126** 6874
[2] Lai C-H, Lu M-Y and Chen L-J 2012 *Journal of Materials Chemistry* **22** 19
[3] Wang K-H, Zhu B-S, Yao J-S and Yao H-B 2018 *Science China Chemistry* **61** 1047
[4] Raj C J, Kim B C, Cho W-J, Lee W-G, Seo Y and Yu K-H 2014 *Journal of Alloys and Compounds* **586** 191
[5] Sadovnikov S I, Rempel A A and Gusev A I 2018 *Russian Chemical Reviews* **87** 303
[6] Shakil A, Das S, Rahman A, Akther U S, Hassan K and Rahman K 2018 *Materials Sciences and Applications* **9** 751
[7] Bai H-J, Zhang Z-M and Gong J 2006 *Biotechnology letters* **28** 1135
[8] Aljani H Q, Pourseyedi S, Mahani M T and Khatami M 2019 *Journal of Molecular Structure* **1175** 214
[9] Sousa D M, Alves L C, Marques A, Gaspar G, Lima J C and Ferreira I 2018 *Scientific Reports* **8** 15992
[10] Sabaghi V, Davar F and Fereshteh Z 2018 *Ceramics International* **44** 7545
[11] Parvaneh I, Samira S and Mohsen N 2015 *Chinese Physics B* **24** 046104
[12] Ayodhya D and Veerabhadram G 2018 *Materials today energy* **9** 83
[13] Bodke M, Purushotham Y and Dole B 2018 *Cerâmica* **64** 91