

Vibrational Spectroscopy of ZnO-ZnS Nanoparticles

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Abstract: A Fourier Transform Infrared spectrum represents the finger-print of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. This paper reports the FT-IR spectroscopy of ZnO-ZnS nanoparticles synthesised via a simple solvothermal method. Five samples of $ZnS_xO_{(1-x)}$ nanoparticles with $x = 0.0, 0.25, 0.5, 0.75$ and 1.0 have been synthesised. The FTIR spectrum was recorded on a Shimadzu FTIR-8400S, Prestige-21 spectrophotometer in a KBr matrix. The finger print region peaks observed around 550 and 650 cm^{-1} explain the distinct vibration of zinc oxide and the same around $570 - 680\text{ cm}^{-1}$ show the stretching vibration of zinc sulphide. The FT-IR spectra of other three mixed samples show a mixture of peaks both corresponding to ZnO and ZnS. This result gives a way for us to confirm that the synthesised ZnO-ZnS nanoparticles form hetero-structured zinc oxide and zinc sulphide. Peaks observed around 3500 cm^{-1} is assigned to O-H vibration and that around $1500 - 1650\text{ cm}^{-1}$ and at 2370 cm^{-1} are due to C=O stretching mode, arising from the absorption of atmospheric water and CO_2 on the surface of the nanoparticles respectively.

Keywords: FT-IR spectroscopy, solvothermal method, stretching vibration, ZnO-ZnS nanoparticles

1. Introduction

The vibrational spectrum of a molecule is considered to be a unique physical property and is one of the most powerful attributes of this diverse and versatile analytical technique. The fundamental absorption frequencies (also known as group frequencies) are the key in unlocking the structure-spectral relationships of the associated molecular vibrations¹. In infrared spectroscopy we study the interaction of infrared light with matter and the spectrum, which is a plot of measured infrared intensity versus wavelength (or frequency) of light. It was stated that the fundamental infrared absorption frequencies are not the only component to be evaluated in a spectral interpretation, they are the essence and foundation of the art.

Nanoparticles or quantum dots are defined as small particles with 1-100 nm in diameter at least in one dimension. As the diameters of the particles approach their Bohr diameter, the optical properties begin to change and quantum confinement effect begins to play a much more important role. It brings a great difference in physical and electronic properties of the nanometer scale particles compared to bulk materials. Among the family of semiconductors, II-VI group semiconductor compounds have immense technological importance in various applied fields of science and technology. For instance, $ZnS^{2,3}$, ZnO^4 and $CdTe^5$ are important because of their excellent electronic and optical properties for optoelectronic applications.

ZnO and ZnS are widely used in photo-catalysis, solar cell, etc due to their high electrochemical stability and high electron mobility. Special morphologies^{6,7} such as nanorods, nanowires, or nanoflowers have been synthesized by thermal evaporation techniques, chemical route and physical methods. ZnO-ZnS nanoparticles with shapes like nanocables, nanoribbons and nanocombs have also been fabricated using the sulfidization or oxidation.

In our present study we have synthesised ZnO-ZnS nanocomposites by a simple solvothermal method using the microwave irradiation technique. Five samples of ZnS-ZnO ($ZnS_xO_{(1-x)}$) with $x = 0.0, 0.25, 0.5, 0.75$ and 1.0 have been synthesised. Fourier transform infrared spectroscopy (FT-IR), was performed to study the absorbance properties of the prepared samples and hence to deduce the nature of bonds present. The peaks give a way for us to confirm whether the synthesised ZnO-ZnS nanoparticles form hetero-structured zinc oxide and zinc sulphide.

2. Experimental

Five samples of $ZnS_xO_{(1-x)}$ nanoparticles with $x = 0.0, 0.25, 0.5, 0.75$ and 1.0 have been synthesised using a simple solvothermal method. Zinc chloride, urea and thiourea were mixed thoroughly in a molecular ratio of 1:3. The solvent used is ethylene glycol. Then the mixture was placed under microwave (IFB model number 17PG1S operated with frequency 2.25 GHz and power 800W) irradiation for about 35 to 40 minutes. The precipitate formed was washed with distilled water and then with acetone to remove the impurities. The dried samples were annealed at 200°C for about 1 hour and cooled naturally to room temperature and used for further characterization.

FT-IR-spectroscopic analysis was done by a Shimadzu FTIR-8400S, Prestige-21 spectrophotometer in a KBr matrix operating in the $4000 - 400\text{ cm}^{-1}$ wavenumber range. The samples were mixed with KBr, and then pressed into pellets before recording the spectra. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis and to determine what chemical groups are in

aspecific compound. The spectra were interpreted with the known data for analysis.

3. Result and Discussion

One way to begin analyzing an IR spectrum is to start at the high wavenumber end of the spectrum (typically 4000 cm^{-1}) and look for the presence and absence of characteristic absorptions as we move toward lower wavenumbers. The absorption wavenumber for a stretching vibration is related to both the force constant between the two atoms (k) and the

mass of the two atoms (m_1 and m_2) by the Hooke's Law equation:

$$\bar{\nu} = \frac{1}{2\pi c} \left[k \left(\frac{m_1 + m_2}{m_1 \cdot m_2} \right) \right]^{1/2}$$

From this relationship, two important trends in the wavenumber for stretching vibrations can be deduced.

1) As the bond strength increases, the wavenumber increases. For example:

Bond stretch	C—C	C=C	C≡C	C—H	=C—H	≡C—H
Wavenumber of Absorption (cm^{-1})	1200	1650	2150	2900	3100	3300
	CC stretch			CH stretch		

2) As the mass of one of the two atoms in the bond increases, the wavenumber decreases (assuming the change in bond strength is relatively small). For example:

Bond stretch	C—H	C—D	C—C	C—O	C—Cl	C—Br	C—I
Wavenumber of Absorption (cm^{-1})	3000	2100	1200	1100	800	550	500

The intensity of an absorption in the IR spectrum is related to the change in dipole that occurs during the vibration. Consequently, vibrations that produce a large change in dipole (e.g. C=O stretch) result in a more intense absorption than those that result in a relatively modest change in dipole

(e.g. C=C). Vibrations that do not result in a change in dipole moment (e.g., a symmetrical alkyne C triple bond C stretch) will show little or no absorption for this vibration.

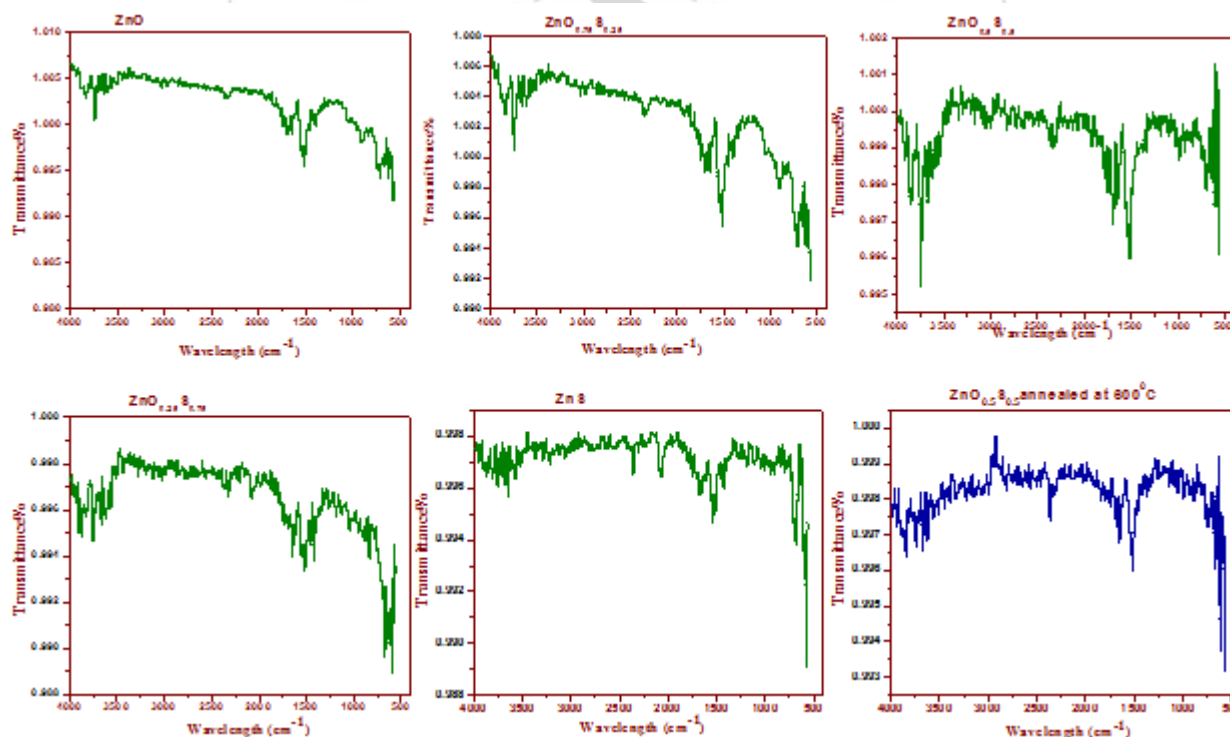


Figure 1: The observed FT-IR spectra

The FT-IR spectra observed for all the five $\text{ZnS}_x\text{O}_{(1-x)}$ nanoparticless with $x = 0.0, 0.25, 0.5, 0.75$ and 1.0 are shown in Figure 1. The finger print region peaks observed around 550 and 650 cm^{-1} in Figure 1 (except that for ZnS) explain the distinct vibration of zinc oxide. The peaks observed around 570 - 680 cm^{-1} in Figure 1 (except that for ZnO) show the stretching vibration of zinc sulphide. The FT-IR spectra of

the mixed samples (Figure 1) show a mixture of the peaks corresponding to both ZnO and ZnS. This result gives a way for us to confirm that the synthesised ZnO-ZnS nanoparticles form hetero-structured zinc oxide and zinc sulphide. Peaks observed around 3500 - 3900 cm^{-1} are assigned to the hydroxyl (-OH) group vibration and that around 1500 - 1650 cm^{-1} and at 2370 cm^{-1} are due to C=O

stretching mode, arising from the absorption of atmospheric water and CO₂ on the surface of the nanoparticles respectively.

4. Conclusion

ZnO-ZnS nanoparticles were synthesised using a simple solvothermal method and characterised using the FT-IR spectroscopy technique. Additional peaks appeared in the finger print region of the spectra observed for the prepared mixed systems indicate the presence of both zinc oxide and zinc sulphide and thereby the formation of hetro- structured ZnO-ZnS nanoparticles.

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