

# OPTICAL ABSORPTION AND TRANSMISSION IN CuZnS ALLOYS

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## ABSTRACT

Varieties of pellets of the alloy of copper (Cu) and zinc sulphide (ZnS) have been produced by pressing mechanically together fine ground powders of Cu and ZnS alloys prepared by the chemical reaction between the aqueous solution of copper II nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) and ZnS powder. The optical absorption and transmission in these alloys were investigated in the spectral range 200nm –750nm at room temperature to examine their potential for use in optoelectronic devices. The investigation showed that the alloys are transparent over the ultraviolet (UV) spectrum but with increasing dopant mole fraction the absorption edge moves into the visible region. However, a gradual decrease in the energy gaps of the samples with a corresponding gradual shift in the absorption edge towards the visible spectrum, as the concentration of the copper impurity increases leads to an improvement in conductivity of the alloys examined. The location of the band gaps of CuZnS alloys (3.58 – 3.82eV) within the UV spectrum suggests that all the samples are very valuable in optoelectronic devices that utilize wide band gap materials.

## 1. INTRODUCTION

Over the years, zinc sulphide has been of great interest for its application in optoelectronic devices such as light emitting diodes (Sze, S. M., 1985) and electroluminescent devices (Thomas, D. G., 1982). Some of its properties which make it an attractive material for optoelectronic device applications include low cost, feasibility of crystal growth, excellent luminescent property (Berg, A. A. and Dean, P. J., 1976) and it is transparent over a wide range of the visible spectrum (Thomas, D. G., 1982). Also, ZnS can be used as a cathodoluminescent material for coating the screens of cathode ray tubes (Berg, A. A. and Dean, P. J., 1976; Sybil, P., 1982). Furthermore, it is used in the production of fluorescent and luminous paints (Berg, A. A. and Dean, P. J., 1976). In addition, it is a prospective material for the passivation of the surfaces of some semiconductors and for the modulation of optoelectronic device (Osasona, O., Djebah, A., Ojo, A., Eleruja, A., Adedeji, A., Jeynes, C., and Ajayi, O., 1997). The present work was therefore, partly inspired by these applications and the need to search for more applications for ZnS and CuZnS alloys.

Copper is an important impurity in wide band gap zinc chalcogenides. In ZnS and ZnSe the incorporation of copper results in a variety of characteristic visible bands (Stringfellow, G. B. and Bube, R. H., 1968; Satoh, S. and Igaki, K., 1983). However, there is a long-standing uncertainty about the role of copper in the afore-mentioned materials. Hence, there is need to develop new experimental techniques for incorporating copper into zinc chalcogenides in order to provide additional information on the behaviour of this important impurity. It is necessary to gain a clear understanding of the role of copper in zinc

chalcogenides because copper is the most efficient known activator of luminescence in these compounds (Robbins, D. J., Dean, P. J., Summots, P. E. and Tews H., 1986) and secondly because of the high diffusion rate of copper in the II – VI compound semiconductors (Shaw, D., 1992).

Little attention has been paid to CuZnS alloys. Hence only a few papers dealing with the electronic and electrical properties of ZnS have been published (Yoichiro, N., Hiromichi, Y. and Goro, S., 1981; Richard, S. and Frank, H., 1985; Hiroshi, F. and Koji, M., 1985; Fernandez, A. M. and Sebastian, P. J., 1993). However, valuable information on the optical properties of CuZnS which may be useful in the field of photoluminescence is still lacking. Hence, the present investigation was undertaken to provide some of the relevant information on the optical properties of CuZnS alloys. In the present work controlled amounts of copper were incorporated into ZnS by chemical reaction process. Thereafter, the ultraviolet – visible transmittance and spectral analyses of the samples under investigation were performed. Also, the effect of incorporating copper in ZnS on the band structure of ZnS has been studied.

## 1. EXPERIMENTAL PROCEDURE

### 1.1 MATERIALS AND METHOD

The materials used in this investigation were 99.99% pure  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and ZnS powder obtained from the British Drug House (BDH). 5ml of different concentrations of aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were prepared and added drop by drop to 100ml of ZnS suspension prepared in four different beakers and the stoichiometric composition of the samples is presented in Table 1.

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**Table 1:** Stoichiometric composition of the samples and the Energy gaps of ZnS and the various samples of CuZnS alloys

Sample	Mole Fraction of Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Energy gaps (eV)
Pure ZnS	0.00	3.91
A	0.05	3.82
B	0.10	3.74
C	0.20	3.60
D	0.40	3.58

Thereafter, the mixture was stirred continuously and precipitates were observed to form and the colour of the ZnS suspension changed from white to dark brown. The precipitates obtained were then filtered and air-dried overnight. The samples were later annealed in a stream of argon gas at a temperature of 300°C for 5 hours and at an argon flow rate of 20mlmin<sup>-1</sup>. After the annealing, the samples were cooled in an argon gas to room temperature.

Thereafter, they were crushed with a mortar and pestle and sieved through a mesh to obtain fine ground powders. Then thin pellets of the samples were formed from the finely ground powder of the synthesized materials by powder compression method using a vacuum pump aided powder presser. The pellets were then sintered at a temperature of 300°C for 4 hours in an electric furnace to correct the imperfections that might have resulted from voids in the materials. The prepared pellet has a diameter of 10mm and thickness of 0.38mm. The samples were used to carry out subsequent measurements. Optical absorbance and transmittance spectra of the samples were recorded using a phamacia LKB Biochron 4060 spectrophotometer in the spectra range of 200nm – 750nm at room temperature.

### 1.1 DATA ANALYSIS

From the optical data, the transmittance (T) was determined from the expression (Adegboyega, G. A., 1989).

$$T = I/I_0 = \exp(-\alpha d) \quad (1)$$

Where I and I<sub>0</sub> are the intensities of the transmitted and incident optical radiations respectively, d is the thickness of the sample under investigation and α is the absorption coefficient.

Absorbance (A) is related to the transmittance (T) according to the following expression (Adegboyega, G. A., 1989):

$$T = 10^{-A} \quad (2)$$

From equation (1) the coefficient of absorption can be re-written as

$$\alpha = 1/d \ln(1/T) \quad (3)$$

substituting equation (2) in (3), we have

$$\alpha = \frac{2.303A}{d} \quad (4)$$

The energy gap is determined from the expression (Omar, A. M., 1975; Smith, R. A., 1978):

$$\alpha = (h\nu - E_g)^{1/2} \quad (5)$$

where hν is photon energy and E<sub>g</sub> is the energy gap. By plotting α<sup>2</sup> against hν, the energy gap is obtained when α<sup>2</sup> = 0.

## 2. RESULTS

The variation in transmittance and absorbance with wavelength for pure ZnS and the various samples of CuZnS alloys are illustrated in Figures 1 to 5. Figure 6 shows the graph of energy gap versus the mole fraction of CuZnS alloys. The variation of α<sup>2</sup> with photon energy (hν) for pure ZnS and the various samples of CuZnS is summarized in Figure 7. The intercepts of Figure 7 obtained by extrapolating the linear portion of the plots on the photon energy axis, give the energy gaps of the various samples investigated and it is presented in Table 1. The energy gap of 3.91eV obtained for ZnS in this investigation differs slightly from 3.67eV reported by Osasona et al., 1997. for ZnS thin film prepared by metalorganic chemical vapour deposition (MOCVD) and 3.68 eV reported by Sze, S. M., 1985). The slight variation in energy gap could be due to the difference in the preparation techniques.

From Figure 7, it is observed that as the concentration of copper impurity increases, the absorption curves shift to lower energies.

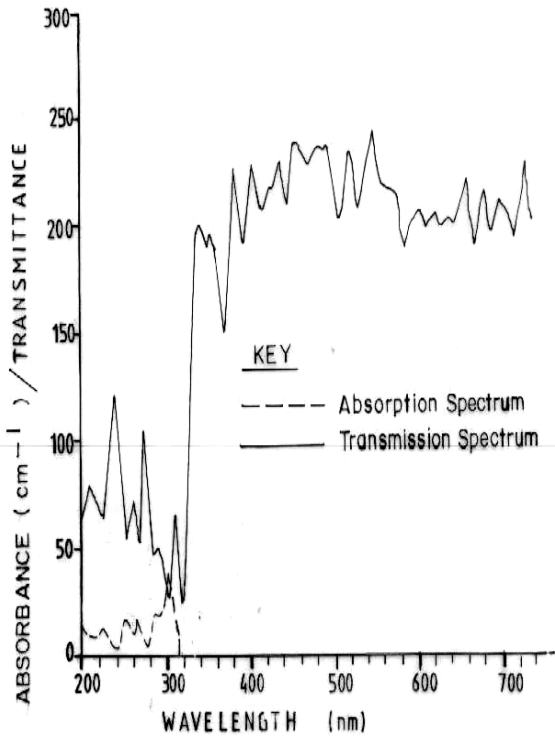


Fig.1. Variation of transmittance (T) and absorbance (A) with wavelength at room temperature for pure ZnS.

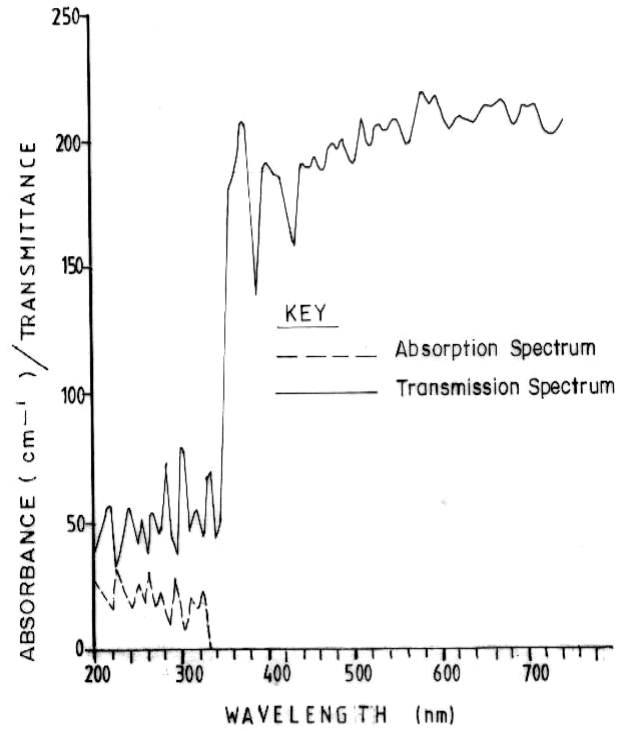


Fig.3. Variation of transmittance (T) and absorbance (A) with wavelength at room temperature for sample B.

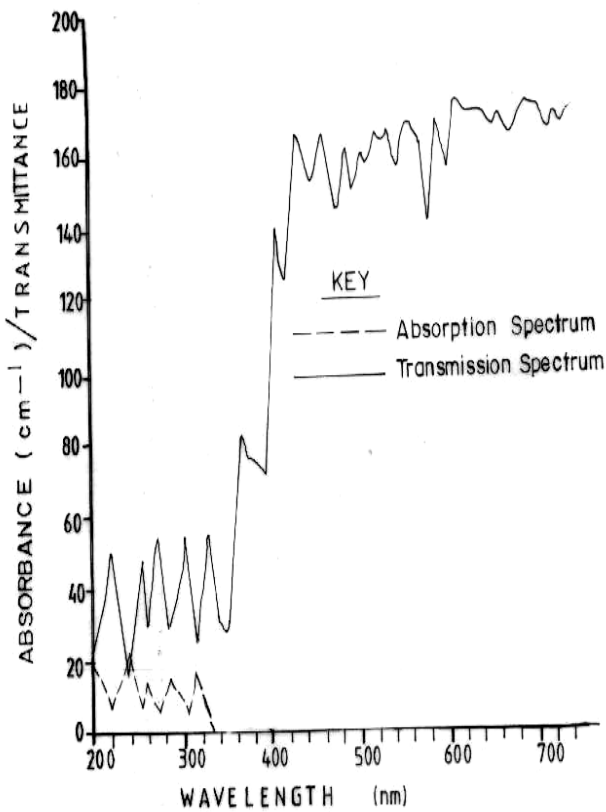


Fig.2. Variation of transmittance (T) and absorbance (A) with wavelength at room temperature for sample A.

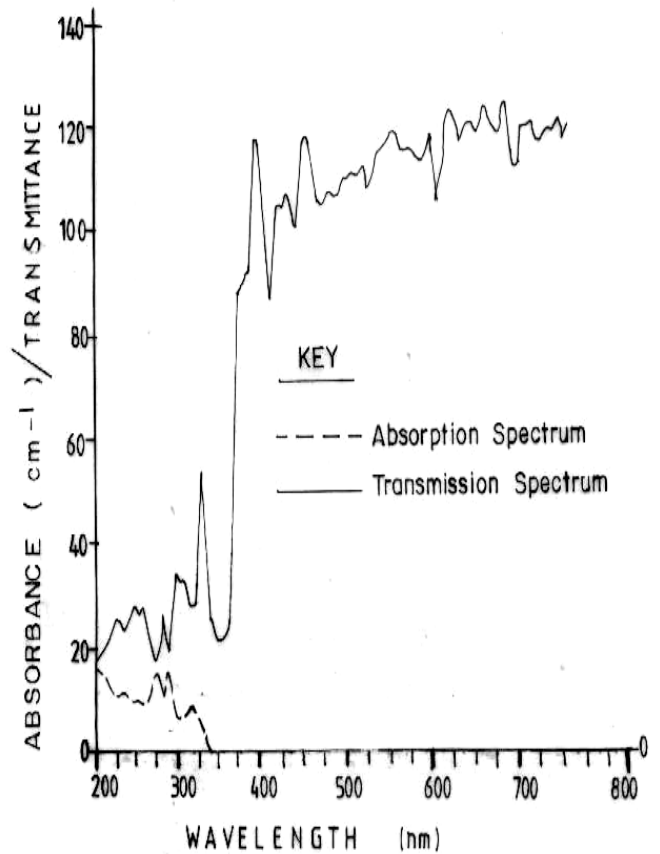


Fig.4. Variation of transmittance (T) and absorbance (A) with wavelength at room temperature for sample C.

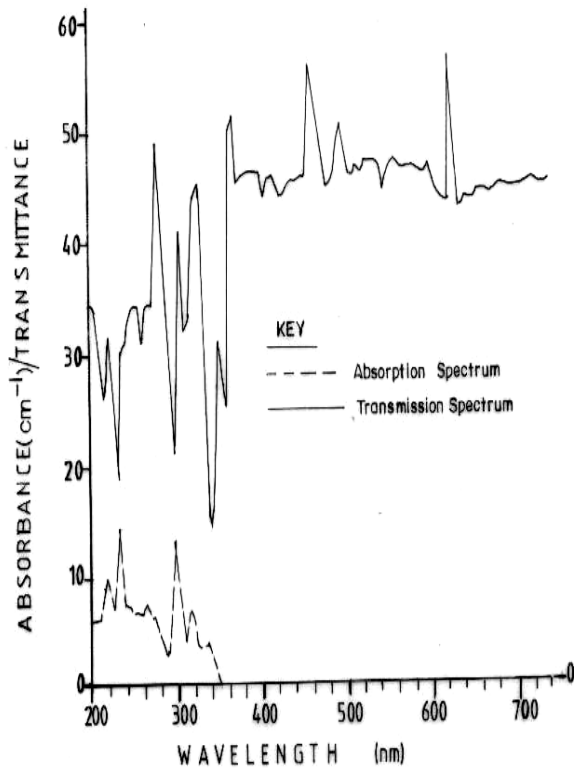


Fig. 5. Variation of transmittance (T) and absorbance (A) with wavelength at room temperature for sample D.

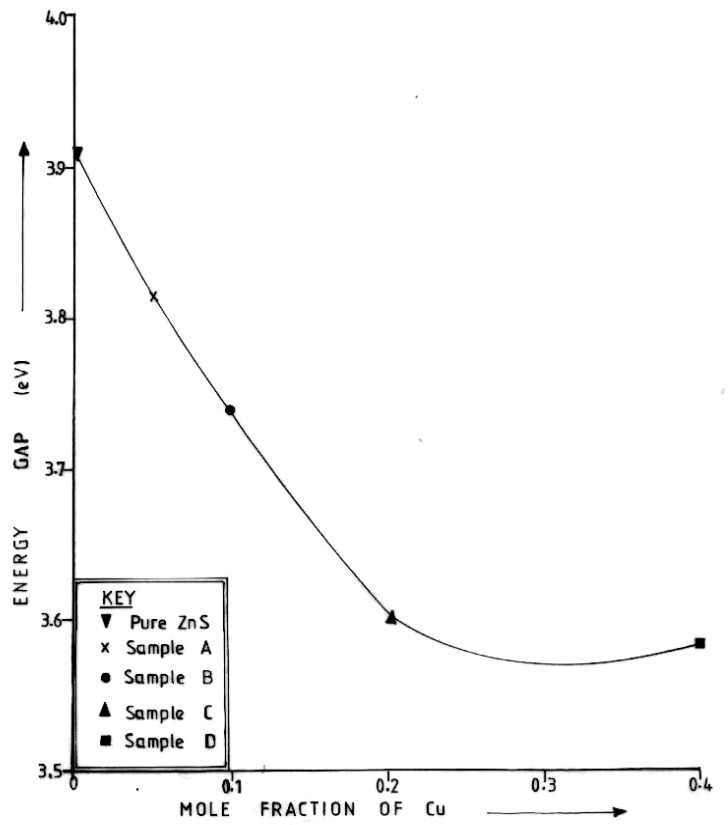


Fig. 6. Energy gap versus the mole fraction of Cu in CuZnS alloys.

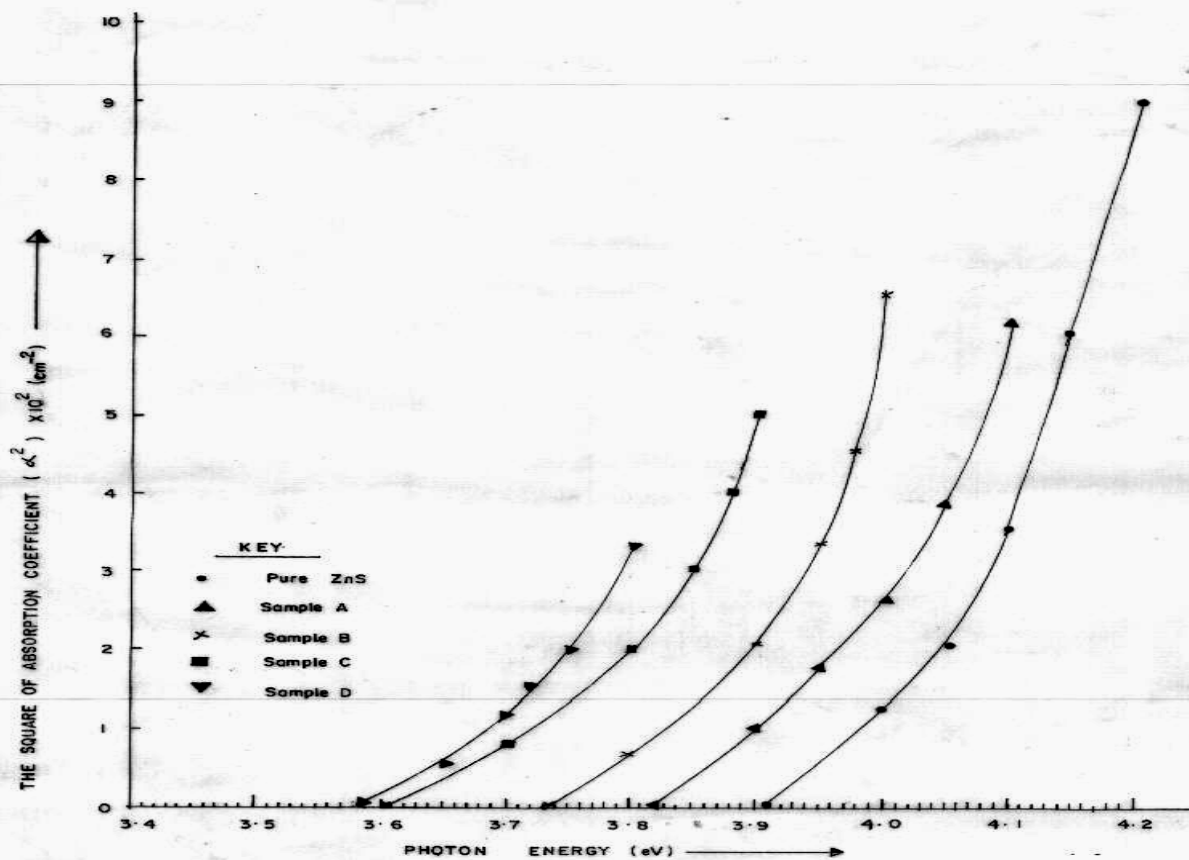


Fig. 7. The Variation of the square of Absorption Coefficient with Photon Energy for pure ZnS and the various samples

### 3. DISCUSSION

For all the samples of the CuZnS alloys examined, the transmittance is high over most of the visible region but with increasing dopant mole fraction the absorption edge moves into the visible spectrum.

The introduction of acceptor levels above the valence band of the ZnS band gap by the incorporation of copper impurity is indicated by the noticeable shift in the optical absorption edges as the impurity concentration increases. This suggests the ease of electron transition to the conduction band leading to an improvement in the conductivity of the materials.

Furthermore, a spread (increase in width) of the irregular zig-zag feature which extends into the visible range as the dopant concentration increases can be attributed to the introduction of free carriers into the host lattice. These undergo intraband transition in the excitation process. The linear decrease in the direct band gaps with increase in dopant concentration corresponds to the shift in the optical absorption edges from pure ZnS to CuZnS alloys, thus improving the conductivity of the materials.

In Figure 7,  $\alpha^2 = 0$  for  $h\nu \leq E_g$  and increases as  $h\nu$  increases above  $E_g$  in accordance with the expression given in equation 5. The region of  $h\nu > E_g$  is due to transitions from the extended states at the top of the valence band to the localized states at the bottom of the conduction band and also it is as a result of transitions from the localized states of the top of the valence band to extended states in the conduction band (Smith, R. A., 1978).

### 4. CONCLUSIONS

The following conclusions can be made from the present study:

- i. The behaviour of CuZnS alloys indicates that the transmittance is high over most of the visible region but with increasing dopant mole fraction the absorption edge moves into the visible region. Hence they can be used for coating in optics and as transparent conductors or electrodes.
- ii. The location of the energy gaps of the samples within the ultraviolet spectrum makes them attractive materials for optoelectronic devices that utilize wide energy gap materials.
- iii. The linear decrease in bandgaps with increase in mole fraction of copper observed in the CuZnS alloys up to the range (0.25 – 0.30) moles of Cu, suggests that there is a limit to the amount of copper that could be incorporated interstitial into ZnS lattice. This implies that excess Cu impurity may not have much effect on the band gap of ZnS.

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