**SYNTHESIS, STRUCTURAL AND ELECTRICAL PARAMETERS OF PURE AND Cu DOPED ZnS NANOPARTICLES**

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**Abstract**

The structural and electrical parameters of pure and copper doped ZnS nanoparticles are reported in this paper. The nanoparticles were prepared by co-precipitation method. The influence of the dopant on the structural behavior was examined by Powder X-ray diffraction analysis. The dielectric constant(εr), dielectric loss factor(tanδ), and the electrical conductivity measurements were carried out for the pure and doped samples.

**Keywords:** Co-precipitation method, Structural behavior, Electical conductivity.

**Introduction**

ZnS is one of the important II-VI semiconductor with a wide direct band gap of 3.77 eV that has shown the remarkable properties and it can be exploited for versatile applications including  optical coating, electro-optic modulator, photoconductors, optical sensors, phosphors, reflector, dielectric filter, window material, the field emission display and other light emitting materials . Compared to bulk ZnS, nano ZnS possess anomalous physical and chemical properties such as enhanced surface to volume ratio, the quantum size effect, surface and volume effect and macroscopic quantum tunneling effect, more optical absorption, chemical activity and thermal resistance, catalysis, and the low melting point [1,2,3]. ZnS is also regarded as a low-cost and non-toxic material with high resistance to photochemical degradation[4] However, the nanostructures of ZnS have not been investigated in much detail compared to ZnO nanostructures[5]. Various routes have been adopted for the synthesis of ZnSnanoparticles such as wet chemical [6-8, 9], micro emulsion

[10], chemical vapor deposition [11], hydrothermal technique [12], etc.

In this chapter, we report the synthesis and characteristics of zinc sulphide nanoparticles obtained by co-precipitation method. Co-precipitation is a simple method for synthesising nanoparticles that can be made in a variety of sizes. The purpose of the study is to synthesize the pure and Cu doped zinc sulphide nanoparticles and the effect of Cu on its structural and electrical properties.

**Experimental Detail**

ZnS nanoparticles were prepared by coprecipitation method. The reactants used for the synthesis of ZnS nanoparticles were sodium sulphide (Na2S.7H2O) and zinc acetate

(Zn (CH3COO)2 · 2H2O). Cupric acetate (Cu (CO2CH3)2 · H2O) was used as a dopant and distilled water was used as a solvent.

In a typical process of pure ZnS nanoparticles, zinc acetate and sodium sulphide were taken in 1:3 molecular ratio and dissolved separately in 200 ml of distilled water. Under stirring condition of zinc acetate solution, sodium sulphide solution was added drop wise. The mixing mode is continued until a precipitate is obtained. The resulting colloidal precipitate was washed several times with distilled water and then with acetone to remove possible organic impurities. Washed samples were dried in atmospheric air and collected. Similar, procedure were carried out for the preparation of Cu (5 and 10 wt%) doped ZnS nanoparticles by using cupric acetate along with the precursors used for the preparation of pure ZnS nanoparticles.

**Characterization**

The crystal structure of pure and doped samples were analyzed by the powder x-ray diffraction. AC electrical measurements were made by the conventional parallel plate capacitor method using an Agilent 4284A LCR meter at various temperatures and frequencies.

**Results & Discussion**

Figure 1 to 3 shows The PXRD pattern of pure and Cu (5 and 10 wt %) doped ZnS nanoparticles. All the diffraction peaks present in the PXRD pattern of pure and Cu doped ZnS nanoparticles can be indexed using the data available in the JCPDS file (05-0566). From the PXRD pattern the average crystallite size and lattice parameters were determined .The average crystallite size was determined by Scherer formula and it is found to be 3-4 nm. The average particle size increase with increase in the addition of dopant. It confirms that the enclosure of dopant into the host matrix. The peaks corresponding to Cu were not indexed in the PXRD pattern of Cu-doped ZnS nanoparticles because only a small amount of copper acetate was added as an impurity.But significant changes in the position of host peaks were noticed in the PXRD pattern of Cu doped ZnS nanoparticles. From the indexed PXRD pattern the structure of prepared pure and Cu (5 and 10 wt %) doped ZnS nanoparticles were found to be cubic with lattice parameter a = 5.368(4) Ǻ. For all samples of ZnS doped with Cu ions, strong absorption peaks were observed corresponding to the lattice planes of (111), (220) and (311) [13,14]. The doping causes the peak broadening and decrease in the intensity of the peaks. The sharpness of the peak exhibits the nanoparticles are perfectly crystallized.

Table 1: Average grain size of pure and Cu doped ZnS nanoparticles

|  |  |
| --- | --- |
| **System(with expected)** | **Grain size(nm)** |
| Pure ZnS | 3.11 |
| 5wt% Cu doped ZnS | 3.86 |
| 10wt% Cu doped ZnS | 4.74 |

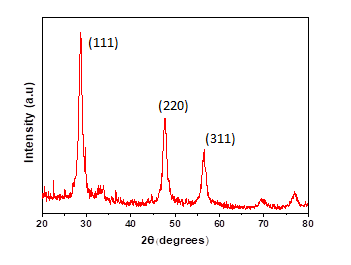


Figure:1 PXRD pattern for pure ZnS nanoparticles

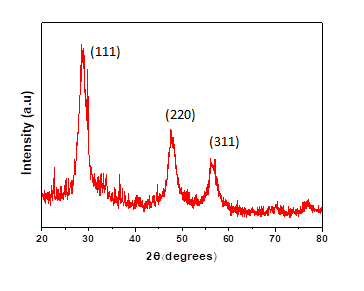


Figure 2: PXRD pattern for 5 wt% Cu doped ZnS nanoparticles

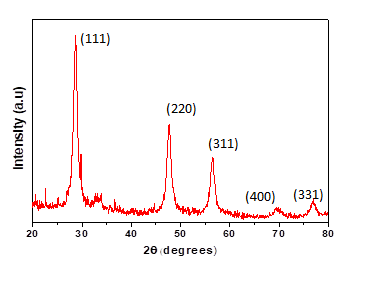


Figure 3: PXRD pattern for 10 wt% Cu doped ZnS nanoparticles

The behavior of electrical parameters such as dielectric constant, dielectric loss factor and AC electrical conductivity in relation to frequency and temperature is shown in Figures 4-12. The variation of the dielectric constant at different frequencies and temperatures is shown in Figures 4-6. The dielectric constant of all prepared samples was found to increase with increasing temperature and decrease with increasing frequency.

The variation of dielectric loss with frequency and temperature is shown in Figures 7 to 9. It was observed that the dielectric loss coefficient increases with increasing temperature and decreases with increasing frequency for all prepared samples. The charge transport relaxation time caused the change in dielectric constant with the applied field. In heterogeneous structures, the polarization of the space charge was dominant and this leads to a decrease in the dielectric constant as the frequency increases.

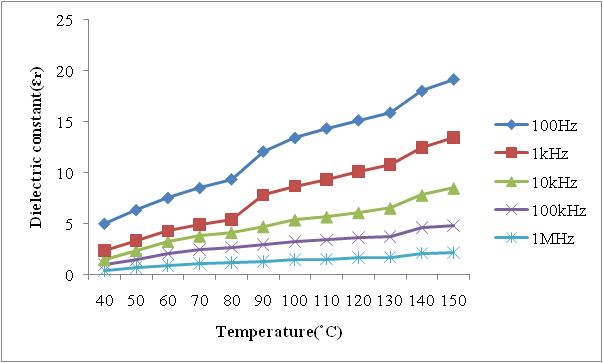
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Figure 4: Dielectric constant for pure ZnS nanoparticles

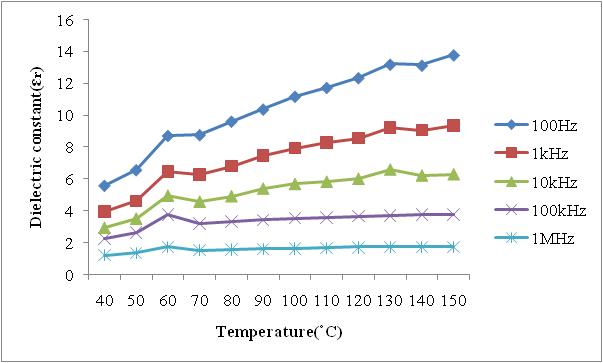
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Figure 5: Dielectric constant for 5wt% Cu doped ZnS nanoparticles

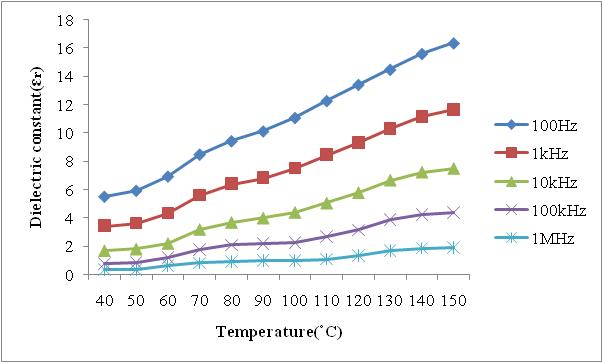


Figure 6: Dielectric constant for 10wt% Cu doped ZnS nanoparticles

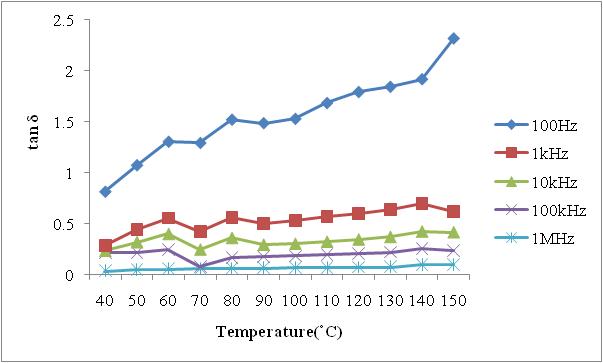


Figure 7: tan δ for pure ZnS nanoparticles

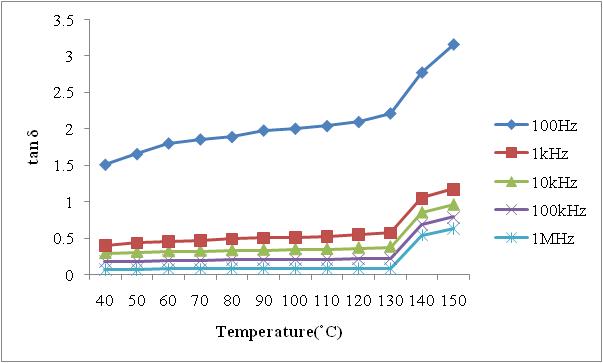


Figure 8: tan δ for for 5wt% Cu doped ZnS nanoparticles

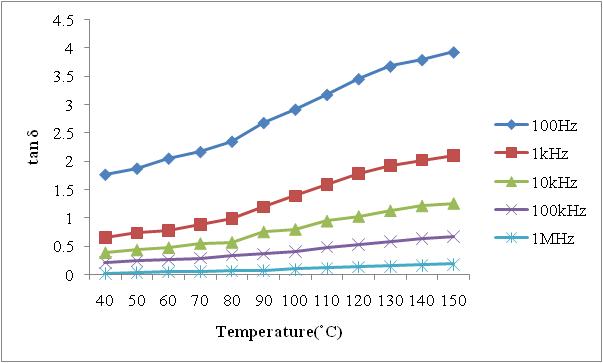


Figure 9: tan δ for 10wt% Cu doped nanoparticles

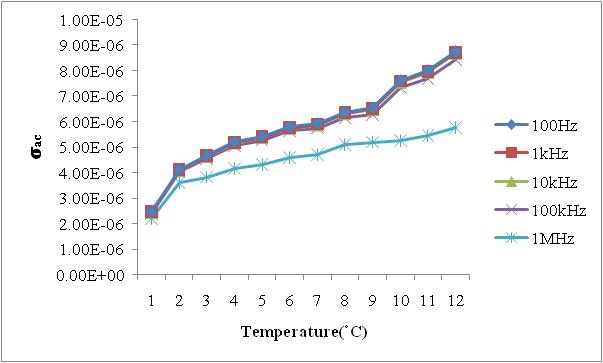


Figure 10: for pure ZnS nanoparticles

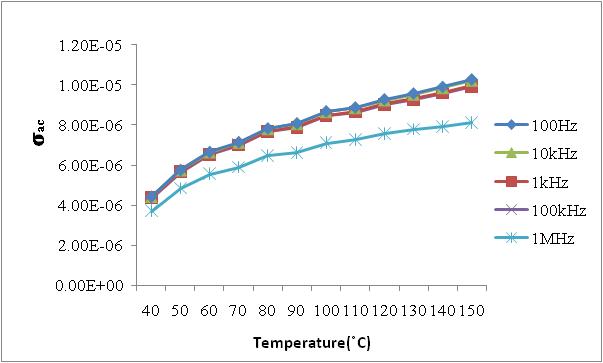


Figure 11: for 5 wt% Cu doped ZnS nanoparticles

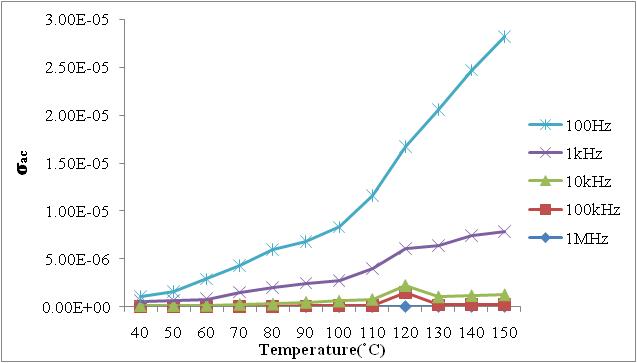


Figure 12: for 10 wt% Cu doped ZnS nanoparticles

The variation of AC electrical conductivity with frequency and temperature is shown in Figures 10 - 12. It was observed that for all the prepared samples, AC electrical conductivity increases with increasing temperature and frequency. Here, the AC electrical conductivity increases with increasing frequency, and thus the conduction mechanism of the fabricated samples is a local conduction mechanism. Also, the conduction process was due to small polaron hopping, as the conduction increases with frequency.The conductivity of the material is low at low temperatures because the mobility of ion is very low at low temperatures. When the temperature increases the mobility of ion increases thereby increasing the space-charge polarization which in turn the value of capacitance [15 ,16].

**Conclusion:**

Pure and Cu-doped ZnS nanoparticles were prepared by a chemical coprecipitation method. X-ray diffraction was used to study the structural properties, the particle sizes increase from 3.1 nm to 4.7 nm with a cubic structure. Dielectric constant and dielectric loss factor increase with increasing temperature and decrease with increasing frequency. AC conductivity values ​​were observed to increase with increasing temperature and frequency. The obtained results showed a good performance of nanostructured materials.

References:

# 1.  Kaur N, Kaur S, Singh J, Rawat M. A ,”Review on Zinc Sulphide Nanoparticles: From Synthesis, Properties to Applications”, J Bioelectron Nanotechnol ,1(1) 5, 2016.

2 . lC.S. Pathak , M.K. Mandal , V. Agarwala ,”Synthesis and characterization of zinc sulphide nanoparticles prepared by mechanochemical route “ [Superlattices and Microstructures](https://www.sciencedirect.com/journal/superlattices-and-microstructures),[Vol 58](https://www.sciencedirect.com/journal/superlattices-and-microstructures/vol/58/suppl/C), Pages 135-143, 2013.

3.Ong HC, Chang, “ RPH. Optical constants of wurtzite ZnS thin films determined by spectroscopic ellipsometry”, Appl Phys Let, 79(22): pages 3612–314,2001.

4.Dilpazir S, Siddiq M, Iqbal , “A. Synthesis of zinc sulphide nanostructures by Co-precipitation: effects of doping on electro-optical properties”. Kenkyu J Nanotechnol Nanosci, 1: 34–9, 2015.

5. X. Fang, T. Zhai, U. K. Gautam, L. Li, L. Wua, Y. Bando and D.Golberg, “ZnS nanostructures: From synthesis to applications,” Progress in Materials Science, vol. 56, pages. 175-287, 2011.

6. A. A. Khosic, M. Kundu, L. Jatwa, S. K. Deshpande, U. A.Bhagwat, M. Sastry and S. K. Kulkarni, “Green luminescence fromcopper doped zinc sulphide quantum particles,” Applied PhysicsLetters, Vol. 67, pages 2702–2704, 1995.

7. N. Dixit, H. Soni, M. Chawda and D. Bodas, “Study of electrical and optical properties of Mn doped ZnS clusters,” Materials Letters, vol. 63, pages 2669-2671, 2009.

8. H. Soni, M. Chawda and D. Bodas, “Electrical and optical characteristics of Ni doped ZnS clusters,” Materials Letters, vol. 63, pages 767-769, 2009.

9. D. Denzler, M. Olschewski and K. Sattler, “Luminescence studiesof localized gap states in colloidal ZnS nanocrystals,” J. Applied Physics, vol. 84, pages. 2841-2845, 1998.

10. J. Zhang, B. Han, J. Liu, X. Zhang, G. Yang and H. Zhao, “Sizetailoring of ZnS nanoparticles synthesized in reverse micelles and recovered by compressed CO2,” The Journal of Supercritical Fluids, vol. 30, pages. 89-95, June 2004.

11. T. Zhai, Z. Gu, Y. Ma, W. Yang, L. Zhao and J. Yao, “Synthesis of ordered ZnS nanotubes by MOCVD-template method,” Materials Chemistry and Physics, vol. 100, pages. 281-284, December 2006.

12. T. T. Q. Hoa, L. V. Vu, T. D. Canh and N. N. Long, “Preparation of ZnS nanoparticles by hydrothermal method,” J. Physics, vol. 187, pages 012081-012087, 2009. [APCTP-ASEAN Workshop on Advanced Materials Science and Nanotechnology

13. M. Navaneethan, J. Archana, K.D. Nisha, Y. Hayakawa, S.Ponnusamy and C.Muthamizhchelvan,“Temperature dependence of morphology, structural and optical properties of ZnS nanostructures synthesized by wet chemical route,” J. Alloys and

Compounds, vol. 506, pages. 249-252, 2010.

14. Tran Thi Quynh Hoa, Le Van Vu, Ta Dinh Canh and Nguyen Ngoc Long, “Preparation of ZnS nanoparticles by hydrothermal method”, Journal of Physics: Conference Series 187 (2009) 012081

15.Y.T.Ravikiran,M.T.Lagare,M.Sairam,N.NMallikarjuna,B.Sreedhr,S.Manohar,A.G.MacDiarmid, andT.M.Aminahavi, “Synthesis, characterization and low frequency AC conduction of polyaniline/niobium pentoxide composites", Synthetic Metals ,156, pages1139-1147, 2006.

16.M.M.Abdullah, M.Ajmal khan,G.Bhagavan narayana,and M.A.Wahab,”Science of advanced materials” vol’,3,1,2011.