Study of electric conduction mechanisms, dielectric relaxation behaviour and density of states in zinc sulphide nanoparticles

Raja Yasir Mehmood, M. F. Afsar, A. Jamil, S. Fareed, F. Siddique, M. H. Bhatti, M. Ali and M. A. Rafiq
Department of Physics and Applied Mathematics, Pakistan Institute of Engineering and Applied Sciences Nilore, Islamabad, Pakistan

ABSTRACT
Zinc Sulfide (ZnS) nanoparticles were synthesized by solid-state reaction method at 190°C. Dielectric, electrical properties, and conduction mechanism of ZnS nanoparticles were investigated. Average crystallite size and interplanar spacing of ZnS nanoparticles were approximately 4.47 nm and 1.92 Å respectively. The nanoparticles were spherical with size range of 10–20 nm. Complex impedance spectroscopy (CIS) of ZnS nanoparticles was performed at 20 Hz to 2 MHz and 236–320 K. The ZnS nanoparticles have negative temperature coefficient of resistance (NTCR). The AC measurements of ZnS nanoparticles from 236 K to 320 K revealed that the conduction in ZnS nanoparticles is due to correlated barrier hopping (CBH). The density of states (DOS) of ZnS nanoparticles have been calculated by CBH model as a function of temperature using photon frequency (fo) 10^13 Hz and localized wave function (α) 1010 m^−1 which ratified hopping as dominant conduction mechanism in ZnS nanoparticles.

Introduction
Zinc sulphide (ZnS) is an important non-toxic, chemically stable II–VI semiconductor with a direct bandgap of 3.5–3.7 eV in the cubical form and 3.7–3.8 eV in the hexagonal form [1,2]. Due to its wide bandgap, it has been extensively studied and explored for different applications such as photoluminescence, electroluminescent displays, photo-catalysis, solar cells and blue light diodes [3]. Zinc sulphide has structural and chemical properties as those of Zinc Oxide (ZnO) [4], however, its wider bandgap has an advantage over ZnO (∼ 3.4 eV). The wider bandgap makes it suitable for visible-blind ultraviolet-light-based devices such as sensors and photodetectors [5]. Due to the innate defects in ZnS, it is difficult to grow ZnS in thin films and single crystals with high conductivity. Different dopants, such as Al, Cd, In, Ag, Mn, Cu, etc. are used to improve the properties of ZnS. It can be doped easily with Mn^2+ atoms [6]. Different techniques, such as the Sol–gel method [7], the co-precipitation method, chemical vapour deposition [8], the solid-state reaction method [9], the wet chemical method [10], the hydrothermal method [11], microwave-assisted synthesis [12], etc., are used for the synthesis of ZnS nanoparticles. Each of the above techniques has its own benefits and limitations. Among them the solid-state reaction method is easy, economical, and fast for the synthesis of ZnS nanoparticles.

ZnS has a negative temperature coefficient of resistance (NTCR) and exhibits semiconducting behaviour. Therefore, the investigation of temperature-dependent properties of ZnS nanoparticles at higher and lower temperatures is of prime importance. To the best of our knowledge, frequency and temperature-dependent density of states (DOS), hopping distance (R_min), binding energy (W_m), detailed CBH conduction mechanism and calculations of experimental data by applying the CBH model have not been reported for ZnS nanoparticles. These parameters have great potential in electrical devices. Therefore, we report a one-step synthesis of ZnS nanoparticles without using surfactants. Different relevant characterizations confirm the physical features, purity and chemical composition of ZnS nanoparticles. Low-temperature (236–320 K) and frequency (20 Hz to 2 MHz)-dependent ac electrical measurements were carried out to determine ac conductivity, dielectric, modulus properties and the dominant conduction mechanism of ZnS nanoparticles.

Experimental work
Solid-state reaction method
ZnS nanoparticles were synthesized by the solid-state reaction method. The Zinc acetate dihydrate (Zn(CH₃OO)₂·2H₂O) and thiourea (NH₂CSNH₂) were used as precursors. The precursors were mixed in stoichiometric ratios and ground with a mortar pestle for half an hour. The grinding of the mixture released heat to start the reaction immediately. The ground mixture was placed in a box furnace and kept under heating at

CONTACT M. A. Rafiq afortab@cantab.net  Department of Physics and Applied Mathematics, Pakistan Institute of Engineering and Applied Sciences Nilore, Islamabad 45650, Pakistan

© 2022 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group
This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
190°C for 4 h. The temperature was increased gradually in steps of 10°C/min to minimize the thermal stresses and the cooling to room temperature was carried out with a cooling rate of 10°C/min heat loss. The mixture was kept in the oven for 24 h to avoid moisture.

Pellet formation

The mixture was ground to prepare pellets of ZnS nanoparticles. The pellets were prepared in a uniaxial hydraulic press with a dye of 10 mm diameter and a pressure of 700 bar was applied. The thickness of the prepared pellets was 2 mm. The pellets were sintered at 170°C for two hours to enhance their strength then, they were removed from the furnace and cooled naturally before applying the contacts on the pellets. The contacts were made on the pellets with copper wires using silver paste.

Characterizations

The X-ray diffraction (XRD) pattern of ZnS nanoparticles was obtained using a “Bruker D8 advance powder” X-ray diffractometer with monochromatic X-rays of wavelength 1.5418 Å (CuKα). The XRD pattern was taken in Bragg’s angle (2θ) range 25°–80° in steps of 0.013°. The field emission scanning electron microscopy (FESEM) “JEOL JSM-6340F” and the transmission electron microscopy (TEM) “TEM JEOL 2100F” were carried out for the morphological analysis of the sample. Energy-dispersive spectroscopy (EDS) “JEOL JSM-6340F” was used for the elemental and composition analysis.

Impedance spectroscopy

The impedance analysis was carried out in the frequency and temperature range of 20 Hz to 2 MHz and 236–320 K, respectively, with a complex impedance analyzer “Agilent E4980A LCA”.

Results and discussion

XRD analysis

The crystallographic structure of the prepared ZnS was investigated using a Bruker D8 advance X-ray diffractometer operated at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5418 Å). The XRD pattern of ZnS nanoparticles matched with JCPDS card number 00-005-0566, as illustrated in Figure 1, which shows the sphalerite or zinc blende cubical structure. The interplanar distance (d) was calculated by Bragg’s formula [14] $2d\sin\theta = n\lambda$ for n = 1 is ∼1.92 Å. The lattice constants calculated by relation $d^2 = \frac{k^2 + \ell^2 + m^2}{a^2}$ are $a = b = c = 5.40$ Å which matched with lattice constants given in JCPDS card number 00-005-0566. The average lattice strain calculated by the Stokes–Wilson equation ($\varepsilon = \frac{\beta}{\tan\beta}$) is ∼3.45 × 10⁻², while the average dislocation density calculated by relation $\delta = \frac{15\varepsilon}{2\pi}$ is ∼2.38 × 10¹⁷ lines/m². Texture coefficients along different planes in the XRD pattern are calculated by the relation $(T_c = \frac{I_c}{\sum I_k})$ [15], where “n” is the measuring intensity of a peak, while “I” is the reference intensity along that plane obtained from JCPDS card and “k” is number of peaks. Texture coefficients along different planes are listed in Table 1. Texture coefficient has a maximum value along plane (200) which is 2.30. Hence the preferred direction of growth of ZnS nanoparticles is along plane (200).

FESEM and TEM analysis

FESEM “JEOL JSM-6340F” and TEM “TEM JEOL 2100F” were used for the morphological analysis of ZnS nanoparticles. FESEM and TEM images of ZnS nanoparticles are shown in Figure 2(a, b). The ZnS nanoparticles are spherical with particle sizes in the range of 10–20 nm.

Table 1. Texture coefficient for different orientations.

| No. | Hkl | I (%) | $I_c$ (%) | $T_c$ |
|-----|-----|-------|---------|-------|
| 1   | 111 | 100   | 100     | 1.11  |
| 2   | 200 | 20.75 | 10.0    | 2.30  |
| 3   | 220 | 94.12 | 51      | 1.18  |
| 4   | 311 | 33.22 | 30      | 1.23  |
| 5   | 400 | 9.12  | 6       | 1.69  |
| 6   | 331 | 11.74 | 9       | 1.45  |
Figure 2. (A) FESEM image (B) TEM image of ZnS nanoparticles.

**EDS analysis**

Figure 3 confirms the presence of zinc and sulphur in the EDS analysis of ZnS nanoparticles. No other peak for any impurity has been observed. The peak at 0 keV is caused by the noise of the electronics detector of the EDS spectrometer, mainly the electron shot noise in the preamplifier behind the silicon drift detector. The inset of Figure 3 shows the atomic and weight percentages of zinc and sulphur in ZnS nanoparticles.

**Impedance analysis**

Complex impedance spectroscopy was performed to investigate electrical, dielectric properties, conduction mechanism and DOS of the ZnS nanoparticles. The measurements were carried out in the frequency range from 20 Hz to 2 MHz and the temperature range from 236 to 320 K using an Agilent E4980A LCR meter. The complex impedance is mathematically expressed as follows:

\[ Z^*(\omega, T) = Z' + iZ'' \]  

(1)

where \( Z' \) and \( Z'' \) are the real and imaginary parts of impedance, respectively. In Figure 4 (a), \( Z' \) was plotted as a function of frequency at various temperatures. Initially, the \( Z' \) decreases as the frequency increases and a frequency-independent region is observed at a higher frequency. Hence, the emission of space charges reduces the impedance of the ZnS nanoparticles. The \( Z' \) decreases with the increase in temperature from 236 K to 320 K indicating the NTCR in ZnS nanoparticles. This exhibits the semiconducting behaviour in ZnS nanoparticles. Thus, the overall actual impedance of ZnS nanoparticles decreases with an increase in frequency and temperature. ZnS nanoparticles synthesized by the co-precipitation method at 400°C also show the decrease in \( Z' \) with the increase in temperature and frequency [16]. The variation of \(-Z''\) as a function of frequency and temperature is shown in Figure 4(b). The imaginary part of the impedance is minimum at lower frequencies and increases with an increase in frequency. As actual impedance corresponds to resistive behaviour, while imaginary impedance corresponds to capacitive behaviour of a material. Hence, ZnS nanoparticles exhibit resistive impedance at lower frequencies and capacitive impedance at higher frequencies [17].

Nyquist plot of ZnS nanoparticles in the temperature range 280–320 K in steps of 10 K has been plotted further to investigate impedance and conduction mechanism of ZnS nanoparticles, as shown in Figure 4(c). The impedance spectrum is in the form of semicircles. The radius of semicircles gives the magnitude of the impedance of the circuit. The radius of semicircles decreases with an increase in temperature, which shows that the impedance offered to the mobility of charge carriers varies inversely with an increase in temperature, which confirms NTCR behaviour in ZnS nanoparticles. A decrease in impedance with a rise in temperature is due to thermally activated hopping and the release of charge carriers from trapped states. In this case, the Nyquist plot is a single depressed semicircle. Depressed semicircular arcs represent the presence of multiple relaxation phenomena in the sample. The semicircles in the impedance spectrum are modelled with an equivalent circuit \((R_gC_g)(R_{gb}Q_{gb})\), where \( R_g \) and \( C_g \) represent grain resistance and grain capacitance, respectively. At the same time, \( R_{gb} \) and \( Q_{gb} \) represent resistance and constant phase element (CPE) for grain boundaries, respectively. CPE is used to compensate non-ideal capacitive behaviour arising from non-uniform grain boundaries and the presence of more than one relaxation phenomenon. The value of capacitance can be estimated by \( C = (R^{1-m}Q)^{1/m} \), where \( m \) is an exponent and its value depends upon the temperature and nature of a material. It is 1 for a pure capacitor and 0 for a pure resistor. Physically, it varies from ideal Debye behaviour. The total resistance \( (R_t) \) of the sample is the sum of grain and grain boundary resistances. The values of \( R_g, R_{gb}, C_g, C_{gb} \) and \( R_t \) in the temperature range 246–320 K are listed in Table 2. The values of \( R_g, R_{gb}, \) and \( R_t \) decrease with temperature due to the release
Figure 3. EDS spectrum of ZnS nanoparticles.

Figure 4. Variation of impedance with frequency (a) real part, (b) imaginary part and (c) cole–cole plots of ZnS nanoparticles.
of trapped charge carriers and thermally activated hopping. The value of $C_g$ first decreases with the increase in temperature from 246 K to 266 K and increases after 266 K. The value of $C_{gb}$ increases with an increase in temperature. The increase in $C_{gb}$ is due to an increase in charge carrier hopping from bulk to interfaces and piling up of charges at interfaces. Piling up of charges gives rise to polarization that results in an increase in grain boundary capacitance [18,19].

**Modulus analysis**

Complex electric modulus ($M^*$) is the inverse of complex relative permittivity. Mathematically,

$$M^*(\omega, T) = M' + iM''$$

and

$$M^*(\omega, T) = 1/\varepsilon^*$$

By simplifying, we have

$$M' = -\omega C_0 Z''$$

$$M' = \omega C_0 Z'$$

here $\omega = 2\pi f$ is the angular frequency of the applied electric field, $\varepsilon^*$ is the complex relative permittivity, $Z''$ is the complex impedance and $C_0 = \varepsilon_0 A/t$ is geometric, where $\varepsilon_0$ is the permittivity of free space, $A$ is the area of electrode and $t$ is the thickness of the pellets. The variation of the actual part of electric modulus with frequency and temperature is shown in Figure 5(a). At lower frequencies actual electric modulus is approximately zero that increases with the increase in frequency at all temperatures. The increase in actual electric modulus is due to the short-range mobility of charge carriers [17]. As the frequency increases, polarization at grain boundaries decreases and dielectric permittivity also decreases. Therefore, from Equation (3), the increase in actual electric modulus with increased frequency is associated with a decrease in electric polarization and permittivity.

Table 2. Values of $R_g$, $R_{gb}$, $C_g$, $C_{gb}$ and $R_t$ at different temperatures.

| No. | T (K) | $R_g$ (Ω) | $C_g$ (F) | $R_{gb}$ (Ω) | $C_{gb}$ (F) | $R_t$ (Ω) |
|-----|-------|----------|----------|--------------|-------------|----------|
| 1   | 246   | $7.5 \times 10^6$ | $1.2 \times 10^{-11}$ | $3.7 \times 10^7$ | $4.5 \times 10^{-12}$ | $4.5 \times 10^7$ |
| 2   | 256   | $8.2 \times 10^5$ | $1.1 \times 10^{-11}$ | $2.4 \times 10^7$ | $6.6 \times 10^{-12}$ | $2.5 \times 10^7$ |
| 3   | 266   | $8.1 \times 10^5$ | $9.9 \times 10^{-12}$ | $1.5 \times 10^7$ | $1.5 \times 10^{-11}$ | $1.6 \times 10^7$ |
| 4   | 280   | $2.6 \times 10^5$ | $2.7 \times 10^{-11}$ | $7.2 \times 10^7$ | $1.7 \times 10^{-10}$ | $7.4 \times 10^4$ |
| 5   | 290   | $1.9 \times 10^5$ | $1.7 \times 10^{-11}$ | $2.4 \times 10^7$ | $6.9 \times 10^{-11}$ | $2.6 \times 10^4$ |
| 6   | 300   | $7.2 \times 10^4$ | $2.1 \times 10^{-11}$ | $6.8 \times 10^6$ | $9.3 \times 10^{-11}$ | $7.5 \times 10^3$ |
| 7   | 320   | $1.6 \times 10^4$ | $3.8 \times 10^{-11}$ | $1.3 \times 10^5$ | $9.6 \times 10^{-11}$ | $1.5 \times 10^5$ |

Dielectric relaxation occurs when polarization lags the frequency of the applied AC. Due to this lagging dielectric permittivity decreases to its minimum and hence electric modulus increases to its maximum. The time for which dielectric relaxation occurs is called relaxation time ($\tau_r$). The increase in temperature shifts the relaxation peak to a higher value of frequency, as shown in Figure 5(b). The imaginary part of electric modulus was fitted with the Kohlrausch–Williams–Watts function (Figure 5(b)) as:

$$M''(\omega) = \frac{M''_{gbmax}}{(1 - \beta_{gb}) + \beta_{gb} \left(\frac{\omega_{gbmax}}{\omega} + \frac{\omega}{\omega_{gbmax}}\right) \beta_{gb}}$$

$$M''_{gbmax} = \frac{M''_{gmax}}{(1 - \beta_{g}) + \beta_{g} \left(\frac{\omega_{gmax}}{\omega} + \frac{\omega}{\omega_{gmax}}\right) \beta_{g}}$$

where $M''_{gmax}$ and $M''_{gbmax}$ are the peak maxima due to grain and grain boundary relaxation, respectively, both are mutually dependent on each other and difficult to differentiate individually from $M''$ spectra [20]. The height and broadening of the peak increase with temperature. The increase in height, broadening and shifting of peaks predict the dielectric relaxation phenomenon in ZnS nanoparticles is temperature-dependent. The distribution of dielectric relaxation is consistent with the condition $\omega\tau_r \times \tau_r = 1$. The values of relaxation frequencies ($\omega_r$) and relaxation times ($\tau_r = 1/\omega_r$) at different temperatures are listed in Table 3. The variation of relaxation frequency with temperature obeys Arrhenius relation:

$$f_r = f_0 e^{(-E_{am}/k_BT)}$$

where $E_{am}$ is the activation energy of the relaxation process, $k_B$ is the Boltzmann constant and $f_0$ is the pre-exponential factor. The value of activation energy for
relaxation phenomenon is 0.524 eV calculated from the slope of $\ln(f_r)$ versus $1000/T$ graph, as shown in Figure 5(c).

Figure 5(d) shows the cole–cole ($M’$ vs $M’’$) plots of electric modulus for ZnS nanoparticles to investigate grain and grain boundary contribution in the relaxation process. The graph shows two depressed adjoint semicircular arcs that tend to enlarge with the decrease in temperature. The tiny relaxation arcs at the lower frequency side correspond to the poor grain boundary effect and significant relaxation arcs at the higher frequency zone are related to the dominant bulk or grain effect [20].

Dielectric analysis

The dielectric analysis is the first tool to study various electrical properties such as permittivity, conductivity, and conduction mechanisms in materials. It is also used to understand the dynamics of complex materials and quantify their response to an applied electric field. The complex permittivity or dielectric constant is a function of frequency and physical conditions like temperature etc. It is defined as [21]

$$\varepsilon^*(\omega, T) = \varepsilon’ - i\varepsilon’’$$  \hspace{1cm} (9)

here “$\varepsilon’$” is the actual part of permittivity and “$\varepsilon’’$” is the imaginary part of permittivity. The real part of permittivity represents the alignment of dipoles, and it corresponds to energy storage. While imaginary permittivity represents ionic conduction and corresponds to energy loss. Permittivity is calculated by the following relations:

$$\varepsilon^*(\omega, T) = \frac{1}{iC_0\omega Z^*}$$  \hspace{1cm} (10)

To investigate dielectric response and energy loss in ZnS nanoparticles, real permittivity, and loss tangent (Tanδ) are plotted as a function of frequency (20 Hz to 2 MHz) and temperature (236–320 K). The $\varepsilon’$ decreases with an increase in frequency, as shown in Figure 6. At lower frequencies permittivity is maximum. However, with an increase in frequency, permittivity decreases quickly to a minimum value. At higher frequencies (greater than $10^6$ Hz) real permittivity is approximately zero. It can be attributed to the
polarization in the ZnS nanoparticles. Different polarizations, such as ionic, space charge, dipolar, electronic and atomic polarization, are expected at different temperature and frequency regimes [22,23]. At lower frequencies, space charges are accumulated at the inner boundary layers separating dielectric components and interface between the sample and electrode. This accumulation of space charges gives rise to a strong Maxwell–Wagner–Sillars (MWS) interfacial polarization [21]. According to this model, the dielectric structure is visualized as well-conducting magnet grains separated by deficient conducting grain boundaries [22]. At lower frequencies MWS interfacial polarization mainly contributes to \( \varepsilon' \). Also, ionic polarization and dipoles at the sample-electrode interface contribute to the permittivity. Therefore, at lower frequencies, \( \varepsilon' \) is maximum. With an increase in frequency \( \varepsilon' \) decreases because at higher frequencies electric dipoles are incompatible with aligning themselves, according to the varying electric fields. At higher frequencies AC field changes quickly and dipoles relax to nonaligned positions. This results in a decrease in electric polarization and real permittivity. The \( \varepsilon' \) increases with the temperature, as depicted in Figure 6. The increase in \( \varepsilon' \) with temperature is due to an increase in the thermal energy of space charges. The space charges hop from bulk to interfaces, and are accumulated on the interfaces of grains due to the increase in thermal energy with temperature. This accumulation also results in an increase in polarization and hence \( \varepsilon' \). The \( \varepsilon' \) merges at higher frequencies for all temperatures. Real permittivity represents the alignment of dipoles that is the energy storage component. In conclusion, the dielectric and energy storage ability of ZnS nanoparticles decreases with an increase in frequency but increases with an increase in temperature. The capacitance of ZnS nanoparticles is given by the following relation [24]:

\[
C(\omega, T) = \frac{\varepsilon_0 \varepsilon' A}{t}
\]  

(11)

Variation of the capacitance of ZnS nanoparticles with frequency and temperature is shown in Figure 7. At lower frequencies different types of electric dipoles are aligned completely in the direction of the applied AC field. Therefore, at lower frequencies ZnS nanoparticles have maximum permittivity and capacitance and store maximum possible energy. At higher frequencies due to dielectric relaxation phenomenon, a small number of dipoles are aligned in the direction of the applied AC field, and energy storage is minimum. Due to this fact, at higher frequencies ZnS nanoparticles have minimum dielectric constant and capacitance.

The capacitance of ZnS is also temperature-dependent. At lower frequencies the value of capacitance of ZnS nanoparticles at 320 K is almost 100 times the capacitance at 236 K. At higher frequencies capacitance curves are merged and become almost
frequency independent. Temperature-dependent permittivity and capacitance make ZnS nanoparticles an important material for technologically critical dielectric applications.

Variation of loss tangent (Tan\(\delta = \frac{\varepsilon''}{\varepsilon'}\)) as a function of frequency at temperature range 236–320 K is shown in Figure 8. Tan\(\delta\) of ZnS nanoparticles is frequency- and temperature-dependent. As the frequency increases Tan\(\delta\), decreases, and at higher frequencies, it becomes approximately frequency independent. However, Tan\(\delta\) increases with an increase in temperature. Frequency and temperature dependence of Tan\(\delta\) can be explained by Koop’s theory that considers a dielectric system as an inhomogeneous medium of two layers of the Maxwell–Wagner type [25]. According to this model, the dielectric system consists of semiconducting grains that are separated by insulating layers. Through hopping, charges reach grain boundaries and pile up due to the insulating layer separating grains. This piling up of charges gives rise to electric polarization. As the frequency of the applied field increases, charges reverse their direction more often before reaching the grains boundaries. As a result, the piling up of charges and electric polarization decrease and hence Tan\(\delta\) decreases with an increase in frequency. On the other hand, with the increase in temperature the thermal energy of the charge carrier increases hence increasing the probability of reaching charges on grain boundaries. This gives rise to the piling of charges, and consequently, electric polarization increases. As a result, Tan\(\delta\) increases with an increase in temperature.

Electrical conductivity analysis

The conduction mechanism in ZnS nanoparticles was investigated as a function of frequency at 236–320 K temperature range as shown in Figure 9 (a) linear and (b) log–log scale. It can be observed in Figure 9(a) that each AC conductivity curve has two regions, the first region is frequency independent, and the second region is frequency-dependent. Direct leakage current may lead to direct conductivity in the frequency-independent region, while the conductivity increases with the increase in frequency in the second region. This behaviour shows that the conductivity follows Jonscher’s power [26]:

\[
\sigma_{ac}(\omega, T) = \sigma_{dc} + A\omega^n
\]

“\(\sigma_{dc}\)” is the DC conductivity, “\(A\)” is a pre-factor, “\(\omega\)” is the hopping frequency at which the slope of curves changes and “\(n\)” is the slope of conductivity curves. Jonscher’s power law deals with the mobility of charge carriers and is based on hopping between energy states near-Fermi level. Variation of \(n\) as a function of temperature determines the type of carriers hopping and conduction mechanism in a material. Based on the variation of \(n\) with temperature, different theoretical hopping models have been reported for conduction in materials: Firstly, if \(n\) increases with an increase in temperature, then conduction is due to small polaron hopping (SPH) [27]; secondly, if \(n\) decreases with an increase in temperature, then conduction is due to correlated barrier hopping (CBH) [28]. Thirdly, if \(n\) decreases to a minimum value with temperature and increases with further increase in temperature, then conduction is due to overlapping large polaron hopping [29] and fourthly if the value of \(n\) remains approximately constant and its value remains about 0.8, then conduction is due to quantum mechanical tunnelling [30]. Values of \(\sigma_{dc}\), pre-factor \(A\) and slope \(n\) for conductivity curves of ZnS nanoparticles at different temperatures obtained by nonlinear curve fitting are listed in Table 4. The variation of \(\sigma_{dc}\) as a function of temperature is shown in Figure 10(a). It increases with an increase in temperature. Below room temperature (300 K) there is a slight increase in \(\sigma_{dc}\) with temperature, while there is significant increase above room temperature. This variation of dc conductivity
Table 4. Value of $\sigma_{dc}$, $n$ and $A$ at different temperatures.

| No. | $T$ (K) | $\sigma_{dc}$ (S/m) | $n$ | $A$ |
|-----|---------|-------------------|-----|-----|
| 1   | 236     | $1.4 \times 10^{-10}$ | 0.66 | $1.7 \times 10^{-10}$ |
| 2   | 246     | $2.2 \times 10^{-8}$  | 0.65 | $3.2 \times 10^{-10}$ |
| 3   | 256     | $5.8 \times 10^{-8}$  | 0.62 | $7.9 \times 10^{-10}$ |
| 4   | 266     | $2.1 \times 10^{-7}$  | 0.60 | $1.8 \times 10^{-9}$  |
| 5   | 280     | $8.2 \times 10^{-7}$  | 0.54 | $8.5 \times 10^{-9}$  |
| 6   | 290     | $2.0 \times 10^{-6}$  | 0.51 | $2.1 \times 10^{-8}$  |
| 7   | 300     | $7.2 \times 10^{-6}$  | 0.48 | $5.7 \times 10^{-8}$  |
| 8   | 320     | $3.9 \times 10^{-5}$  | 0.46 | $1.5 \times 10^{-7}$  |

with temperature indicates thermally activated transport in ZnS nanoparticles. The variation of dc conductivity with temperature is according to the Arrhenius equation:

$$\sigma_{dc} = \sigma_o e^{(-E_{dc}/K_BT)}$$  \hspace{1cm} (13)

where “$\sigma_o$” is the pre-exponential factor, “$E_{dc}$” is the activation energy for dc conductivity, “$K_B$” is the Boltzmann constant and “$T$” is the temperature in kelvin. The value of activation energy for dc conductivity has been determined from the slope of $\ln(\sigma_{dc})$ versus 1000/T graph, as shown in Figure 10(b) is 0.69 eV.

Variation of slope $n$ of the conductivity curves with temperature is shown in Figure 11(a). With the increase in temperature $n$ decreases. $A$ decreases in $n$ with temperature indicates conduction in ZnS nanoparticles is according to the “correlated barrier hopping (CBH)” model. Consequently, an increase in AC conductivity with temperature is due to the increase in hopping between localized states. The pre-factor $A$ is temperature-dependent. Its variation with temperature is shown in Figure 11(b). At temperature below room temperature, variation in $A$ is approximately independent of temperature, but above room temperature, $A$ increases rapidly with an increase in temperature.

In the CBH model conduction of charges occurs from localized states created from barriers separating.

According to the CBH model [31]

$$n = 1 - \frac{6K_B T}{W_m - K_B T \ln \left( \frac{1}{\omega \tau_0} \right)}$$  \hspace{1cm} (14)

where “$K_B$” is the Boltzmann constant, “$W_m$” is the binding energy and “$\tau_0$” is the characteristic time constant. For $W_m > > K_B T \ln(1/\omega \tau_0)$, Equation (14) becomes:

$$n = 1 - \frac{6K_B T}{W_m}$$  \hspace{1cm} (15)

Variation of $W_m$ with temperature is shown in Figure 12(a). It can be observed, the binding energy of ZnS nanoparticles decreases with an increase in temperature. In other words, the number of free charge carriers increases with temperature. Therefore, conduction in ZnS nanoparticles increases with a rise in temperature.

Based on the CBH model the minimum hopping distance $R_{min}$ is [32]

$$R_{min} = \frac{2e^2}{\pi \varepsilon_0 \varepsilon'' W_m}$$  \hspace{1cm} (16)

here “$e$” is the charge of an electron, “$\varepsilon''$” is the real dielectric permittivity, “$\varepsilon_0$” is the permittivity of free space and “$W_m$” is the binding energy. The variation of $R_{min}$ with the temperature at 632.5 Hz frequency is shown in Figure 12(b). The minimum hopping distance decreases with an increase in temperature. The variation of minimum hopping distance as a function of frequency at all temperatures (246–320 K) is shown in Figure 13. At lower frequencies $R_{min}$ is minimum and its value is a few nanometers. As the frequency increases $R_{min}$ increases continuously. This dispersion in $R_{min}$ with frequency is associated with conduction due to short-range carrier hopping. At higher frequencies $R_{min}$ approaches to a saturation value, which is associated with long-range carrier hopping.

Figure 10. (a) Variation of $\sigma_{dc}$ with temperature and (b) $\ln(\sigma_{dc})$ vs. 1000/T of ZnS nanoparticles.
Figure 11. (a) Variation of $n$ with temperature and (b) variation of pre-factor $A$ with the temperature of ZnS nanoparticles.

Figure 12. (a) Variation of $W_m$ with $T$ and (b) variation of $R_{\text{min}}$ with $T$ of ZnS nanoparticles.

Figure 13. Variation of $R_{\text{min}}$ with the frequency of ZnS nanoparticles.

Figure 14. Variation of $N(E_f)$ with $T$ of ZnS nanoparticles.

AC conductivity can be used to calculate the DOS. In the CBH model $\sigma_{ac}$ and DOS ($N(E_f)$) are related as [32]

$$\sigma_{ac} = \frac{\pi}{3\alpha^2} e^2 \omega K_B T [N(E_f)]^2 [\ln(f_0/\omega)]^4$$  \hspace{1cm} (17)

here “$\alpha$” is the localized wave function and “$f_0$” is the frequency of the photon. Values of $\alpha$ and $f_0$ used to calculate DOS are $10^{10}$ m$^{-1}$ and $10^{13}$ Hz, respectively [26].
The variation of DOS as a function of temperature at different frequencies is shown in Figure 14. DOS decreases with an increase in frequency, while it increases with an increase in temperature. The calculated value of DOS was of the order of $10^{21}$. Higher values of DOS indicate that the dominant conduction mechanism in ZnS nanoparticles is hopping between pairs of localized states.

Conclusions

ZnS nanoparticles were synthesized by the solid-state reaction method. XRD confirmed the zinc blende or sphalerite structure with the space group F-43 m of prepared ZnS nanoparticles. ZnS nanoparticles have an average crystallite size of $\sim 4.47$ nm, average interplanar spacing $\sim 1.92$ Å, average lattice strain of $\sim 3.45 \times 10^{-2}$ due to lattice distortion and the average dislocation density of $\sim 1.73 \times 10^{17}$ lines/m$^2$. FESEM and TEM revealed that ZnS nanoparticles have a spherical morphology with the size range 10–20 nm. The EDS analysis confirmed the purity of ZnS nanoparticles with the presence of Zn and S peaks only. The impedance, dielectric, and electrical properties of ZnS nanoparticles were studied as a function of frequency (20 Hz to 2 MHz) and temperature (236–320 K). The impedance of ZnS nanoparticles decreases with an increase in frequency and temperature. ZnS nanoparticles have a NTCR and hence showed semiconducting behaviour in the temperature range 236–320 K. The dielectric behaviour of ZnS nanoparticles decreases with an increase in frequency but increases with an increase in temperature. AC conductivity of ZnS nanoparticles obeys Jonscher’s power law. Conduction in ZnS nanoparticles is according to the CBH model. The binding energy of ZnS nanoparticles is much less than 1 eV, and it decreases with increase in temperature. The minimum distance for hopping ($R_{\text{min}}$) in ZnS nanoparticles is in nanometers, and it decreases with an increase in temperature while increasing with the increase in frequency. At lower frequencies, a small range of charge carrier mobility dominates at all temperatures, while at higher frequencies long-range charge carrier mobility dominates. The DOS of ZnS nanoparticles shows an increase with an increase in temperature while it decreases with an increase in frequency. The calculated values of DOS lie in the range of $10^{21}$; higher values of DOS confirmed hopping as the dominant conduction mechanism in ZnS nanoparticles.

Acknowledgements

We would like to acknowledge the financial support from Higher Education Commission Islamabad through research grant no NRPU 3662.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

We would like to acknowledge the financial support from Higher Education Commission Islamabad, Pakistan through research [grant number NRPU 3662].

References

[1] Dizaji HR, Zavaraki AJ, Ehsani MH. Effect of thickness on the structural and optical properties of ZnS thin films prepared by flash evaporation technique equipped with modified feeder. Chalcogenide Letters. 2011;8(4):231–237.

[2] Lok SK, et al. Growth temperature dependence of the structural and photoluminescence properties of MBE-grown ZnS nanowires. J Cryst Growth. 2009;311(9):2630–2634.

[3] Shanmugam N, Cholan S, Kannadasan N, et al. Effect of annealing on the ZnS nanocrystals prepared by chemical precipitation method. J Nanomater. 2013;2013:351798.

[4] Azpiroz JM, Mosconi E, Angelis FD. Modeling ZnS and ZnO nanostructures: structural, electronic, and optical properties. J Phys Chem C. 2011;115(51):25219–25226.

[5] Yang H, Holloway PH, Ratna BB. Photoluminescent and electroluminescent properties of Mn-doped ZnS nanocrystals. J Appl Phys. 2003;93(1):586–592.

[6] Denzler D, Olschewski M, Sattler K. Luminescence studies of localized gap states in colloidal ZnS nanocrystals. J Appl Phys. 1998;84(5):2841–2845.

[7] Kovtyukhova NI, Buzaneva EV, Waraksa CC, et al. Ultrathin nanoparticle ZnS and ZnS: Mn films: surface sol–gel synthesis, morphology, photophysical properties. Mater Sci Eng B. 2000;69-70:411–417.

[8] Kryshتاب T, Adame A, Zavyalova LV. Preparation and properties of thin ZnS: Cu films phosphors. Thin Solid Films. 2006;515(2):513–516.

[9] Lan C, Hong K, Wang W, et al. Synthesis of ZnS nanorods by annealing precursor ZnS nanoparticles in NaCl flux. Solid State Commun. 2003;125(9):455–458.

[10] Maity R, Chattopadhyay KK. Synthesis and optical characterization of ZnS and ZnS: Mn nanocrystalline thin films by chemical route. Nanotechnology. 2004;15(7):812–816.

[11] Liu J, et al. Synthesis of ZnS nanoparticles via hydrothermal process assisted by microemulsion technique. J Alloys Compd. 2009;486(1-2):L40–L43.

[12] La Porta FA, et al. Synthesis of wurtzite ZnS nanoparticles using the microwave assisted solvothermal method. J Alloys Compd. 2013;556:153–159.

[13] John R, Florence S. Structural and optical properties of ZnS nanoparticles synthesized by solid state reaction method. Chalcogenide Lett. 2009;6:10.

[14] Theivasanthi T, Alagar M. (2010). X-ray diffraction studies of copper nanopowder. arXiv preprint arXiv:1003.6068.

[15] Chandrasekar LB, Chandramohan R, Vijayalakshmi R, et al. Preparation and characterization of Mn-doped ZnS nanoparticles. Int Nano Lett. 2015;5(2):71–75.

[16] Ali H, et al. Electrical conduction mechanism in ZnS nanoparticles. J Alloys Compd. 2014;612:64–68.

[17] Khatri P, Behera B, Srinivas V, et al. Complex impedance spectroscopic properties of Ba3 V2 O8 ceramics. Adv Mater Sci Eng. 2008;2008.

[18] Karmakar S, Varma S, Behera D. Investigation of structural and electrical transport properties of nano-flower shaped NiCo2O4 supercapacitor electrode materials. J Alloys Compd. 2018;757:49–59.
[19] Karmakar S, Behera D. Non-overlapping small polaron tunneling conduction coupled dielectric relaxation in weak ferromagnetic NiAl$_2$O$_4$. J Phys Condens Matter. 2019;31(24):245701–248984.

[20] Karmakar S, Tyagi H, Mohapatra DP, et al. Dielectric relaxation behavior and overlapping large polaron tunneling conduction mechanism in NiO–PbO $\mu$-cauliflower composites. J Alloys Compd. 2021;851:156789–158388.

[21] Ali H, et al. Temperature dependent dielectric and electric modulus properties of ZnS nano particles. Semicond Sci Technol. 2017;32(3):035008.

[22] Karmakar S, Behera D. Small polaron hopping conduction in NiMnO$_3$/NiMn$_2$O$_4$ nano-cotton and its emerging energy application with MWCNT. Ceram Int. 2019;45(10):13052–13066.

[23] Karmakar S, Manna AK, Varma S, et al. Investigation of optical, electrical and magnetic properties of hexagonal NiTiO$_3$ nanoparticles prepared via ultrasonic dispersion techniques for high power applications. Mater Res Express. 2018;5(5):055037.

[24] Lvovich VF. Impedance spectroscopy: applications to electrochemical and dielectric phenomena. Hoboken (NJ): John Wiley & Sons; 2012.

[25] Kambale RC, Shaikh PA, Bhosale CH, et al. Dielectric properties and complex impedance spectroscopy studies of mixed Ni–Co ferrites. Smart Mater Struct. 2009;18(8):085014.

[26] Imran Z, Rafeq MA, Hasan MM. Charge carrier transport mechanisms in perovskite CdTiO$_3$ fibers. AIP Adv. 2014;4(6):067137.

[27] Schmidt R, Basu A, Brinkman AW. Small polaron hopping in spinel manganates. Phys Rev B. 2005;72(11):115101.

[28] Ata-Allah SS, Sayedahmed FM, Kaiser M, et al. Crystallographic and low frequency conductivity studies of the spinel systems CuFe$_2$O$_4$ and Cu $1-x$ Zn $x$ Ga 0.1 Fe 1.9 O 4;($0.0 \leq x \leq 0.5$). J Mater Sci. 2005;40(11):2923–2930.

[29] Megdiche M, Perrin-Pellegrino C, Gargouri M. Conduction mechanism study by overlapping large-polaron tunnelling model in SrNiP$_2$O$_7$ ceramic compound. J Alloys Compd. 2014;584:209–215.

[30] Gopalan EV, Joy PA, Al-Omari IA, et al. On the structural, magnetic and electrical properties of sol–gel derived nanosized cobalt ferrite. J Alloys Compd. 2009;485(1-2):711–717.

[31] Okutan M, Basaran E, Bakan H, et al. AC conductivity and dielectric properties of Co-doped TiO$_2$. Phys B. 2005;364(1-4):300–305.

[32] Jamil A, et al. Effect of titanium doping on conductivity, density of states and conduction mechanism in ZnO thin film. Appl Phys A. 2019;125:4.