Single step synthesis of ZnS quantum dots and their microstructure characterization and electrical transport below room temperature

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Abstract
Low dimensional cubic phase ZnS quantum dots (QDs) are formed by mechanical alloying the stoichiometric mixture of Zn and S powders at room temperature. During milling process the primary mixed phase ZnS is formed at about 3.5 h of milling and strain less single phase cubic ZnS QDs are formed with ≈4.5 nm in size after 20 h of milling. Detailed microstructure study has been done by both Rietveld analysis of x-ray diffraction pattern and high resolution transmission electron microscope images. Dc resistivity decreases with increasing temperature which can be explained by three-dimensional hopping conduction mechanisms. Observed negative magnetoconductivity has been analyzed by wave function shrinkage model. Alternating current conductivity can be described by the correlated barrier hopping conduction mechanism. Analysis of complex impedance indicates that the grain boundary resistance is found to be dominating over the grain resistance. Relaxation behavior has been explained by the analysis of the electric modulus.

Keywords: nanostructures, x-ray diffraction, impedance spectroscopy, electrical properties, dielectric properties

Classification numbers: 5.10

1. Introduction

Synthesis of quantum dots (QDs) and their various applications is now seen one of the potential areas of modern day research [1–3] due to their novel electrical and optical properties obtaining from quantum confinement. ZnS has drawn much attention due to its excellent properties such as direct recombination, and resistance to high electric field [4–7]. ZnS QDs are also potentially used in optoelectronic and electroluminescence devices, solar cells and infrared windows. Due to high luminescence phosphorence properties ZnS QDs are utilized in the field of laser, sensors and displays [8–10]. Though various chemical and physical paths had been adopted to synthesize semiconductor QDs but there are very few report on mechanosynthesis of QDs by mechanical alloying the elemental powders in a single step at room temperature.

In zinc-blende structure (77090-ICSD, Sp. Gr. F-43m, a: 5.434 Å) the cubic ZnS is stable in nanocrystalline form and it converts to hexagonal wurtzite (67453-ICSD, Sp. Gr. P6₃mc, a: 3.8227 Å, c: 6.260 Å) structure at ~1020 °C [11]. It is reported in the earlier cases that whatever the methods of preparation are, ZnS QDs always belong to the cubic structure [12, 13]. From the x-ray diffraction (XRD) pattern of ZnS QDs, it is very much difficult to identify the presence of...
minor hexagonal phase, though the existence of hexagonal phase in small quantity may affect several properties of QDs to a great extent. It is possible to determine the presence as well as quantitative phase estimation of the trivial hexagonal phase in a precise way by considering all its reflections and adopting Rietveld method [14–16] of profile fitting of x-ray powder diffraction spectra based on crystal structure and microstructure refinement methodology. In addition to that, extensive and in-depth study of the XRD pattern of the ZnS QDs by Rietveld method revealed the existence of different kinds of stacking faults, small particle size, change in lattice parameter, residual strain etc [17–19].

Due to large surface to volume ratio and quantum confinement effects, the nanomaterials exhibit novel electrical, magnetic and optical properties as compared to their bulk counterparts. Recently, nanostructures viz., nanoparticles, nanofibers, nanotubes, QD etc have received remarkable attention among the scientific community owing to their potential applications [20–24]. Despite the remarkable progress in the field of nanostructures, both in terms of fundamental and technological viewpoints, charge transport mechanism in such disordered low dimensional structures has not been fully understood. DC resistivity and magnetoresistivity are the primary tool to understand the charge transport mechanism in a material. Impedance spectroscopy is a non-destructive technique to characterize the electrical and charge carrier relaxation behavior of materials under the application of an alternating electric field. The charge transport and charge carrier relaxation behavior are the two fundamental aspects for designing electronic devices. In the present work, we report an in-depth analysis of the dc resistivity, magnetoresistivity, ac conductivity and impedance spectroscopic study of the ZnS QDs in the temperature range $77 \, \text{K} \leq T \leq 300 \, \text{K}$.

2. Experimental procedure

Mechanical alloying (MA) of pure zinc (purity 99.5%, Loba Chem.) and sulphur powders (purity 99.5%, Merck) were carried out at room temperature under Ar atmosphere using a planetary ball mill (model-P5, M/S Fritsch, GmbH, Germany). The progress of milling was monitored at different intervals of time, and changes are noticed in x-ray powder diffraction pattern of ball-milled samples. The x-ray powder diffraction profiles of the unmilled mixture and ball milled samples were recorded using Ni-filtered CuKα radiation from a highly stabilized and automated Philips x-ray generator (PW 1830). All the samples were dispersed in ethanol, sonicated and subsequently, a drop of it was put on a copper grid for microstructural analysis using high resolution transmission electron microscope (HRTEM) operated at 200 kV.

The electrical conductivity of the samples was measured by a standard four probe method after good contact was ensured with highly conducting graphite adhesive (Electrodag 5513, Acheson, Williston, VT) and fine copper wires as the connecting wires. The dc conductivity was measured with an 8½-digit Agilente 3458A multimeter. The temperature dependence of the conductivity was studied with a liquid nitrogen cryostat. For the control and measurement of the temperature, an ITC 502S Oxford temperature controller was used. To measure the dc response, pellets of 1 cm in diameter of the samples was made by pressing the powder under a hydraulic pressure of 500 MPa. The magnetoresistivity was measured in the same manner by the variation of the transverse magnetic field ($B < 1 \, \text{T}$) with an electromagnet.

To obtain the optimized structural parameters and microstructure parameters such as particle size, rms lattice strain and stacking faults, we have adopted the Rietveld’s software MAUD 2.14 [17] for powder structure refinement analysis of XRD pattern. The simulation was done using cubic ZnS and hexagonal ZnS phases in a single pattern as the patterns are composed of reflections from these phases. Considering the combined intensity of the peaks as a function of structural and microstructural parameters, the Marquardt least-squares procedures were adopted for optimization and the minimization of the difference between the observed and simulated powder diffraction patterns was monitored using the value of goodness of fit (GoF). Refinements of all parameters like particle size, lattice strain values, lattice parameters (including zero-shift error) and stacking fault were continued till convergence is reached with the value of the quality factor, GoF very close to 1 (varies between 1.1 and 1.3), which confirms the goodness of refinement. The more detail analysis of microstructure has been reported in the previous work [25].

3. Results and discussion

All x-ray powder diffraction (XRD) patterns of Zn and S stoichiometric powder mixture prepared at different milling time are shown in figure 1. It clearly shows that the unmilled (0h) mixture is composed of Zn (JCPDF # 04-0831; hexagonal, Sp. Gr. P63/mmc, $a$: 2.665 Å, $c$: 4.947 Å) and sulphur (C171, Sp. Gr. P63/mmc, $a$: 3.239 Å, $c$: 5.426 Å) and the milling process results in the formation of a new phase (ZnS (H)) which shows the hexagonal structure (JCPDF # 04-0831).

Figure 1. X-ray powder diffraction patterns of unmilled and ball-milled stoichiometric mixture of elemental Zn and sulphur powders (1:1 molar ratio) for different durations under argon medium. ZnS (C) denotes the cubic ZnS phase and ZnS (H) denotes the hexagonal ZnS phase.
Experimental XRD patterns. The residual of the GoFs in all cases lie in between 1.1 and 1.3 which signify that structure parameters of respective simulated patterns. The simulated XRD patterns for Rietveld analysis are generated with the following phases: ZnS (cubic), and ZnS (hexagonal). Experimental XRD patterns (figure 2) of ball-milled samples are fitted very well by refining the structural and microstructure parameters of respective simulated patterns. The GoFs in all cases lie in between 1.1 and 1.3 which signify that the fitting qualities are good enough for all experimental patterns. The residual of fittings \((I_{o}-I_{c})\) between observed \((I_{o})\) and calculated \((I_{c})\) intensities of each fitting is plotted under respective XRD patterns. Peak positions of all reflections of ZnS phases are marked \((l)\) and shown at the bottom of the plot. It is clear from the figures 1 and 2 that the degree of overlapping between two phases of ZnS is very high. As the contribution of hexagonal phase is quite small it is therefore very difficult to notice its presence in the XRD patterns. However, the Rietveld analysis of XRD data clearly reveals the simultaneous presence of both cubic and hexagonal ZnS phases and estimates the phase content and other structural/microstructure parameters of this phase which was not possible by any simple technique of XRD data analysis or even by HRTEM alone. The Rietveld analysis of ball-milled samples up to 10 h detects the presence of hexagonal phase and confirms the presence of single cubic ZnS phase after 20 h of milling.

The occurrence of different kinds of stacking faults is clearly evidenced in the HRTEM images of 20 h milled sample. The atomic layer shown in the figure 3 is identified as \((111)\) plane of cubic ZnS phase with inter planer spacing \(d = 3.05 \text{ Å}\). This HRTEM image authenticates the existence of different kinds of stacking faults in the ball-milled samples. However, HRTEM image fails to give their concentrations because this image is extremely localized. The concentrations of all three types of stacking faults, intrinsic \((\alpha')\), extrinsic \((\alpha'')\) and twin \((\beta)\) among \(10^{5}\) atomic layers have been worked out employing the peak-shift analysis as proposed by Warren and Averbach [18] and adopting the Rietveld software MAUD 2.14 [17] and are given in table 1. The variation in relative phase abundances of ball-milled samples are taken from the Rietveld analysis of XRD data of respective samples and are reported in table 1. It is interesting to note that after the instant formation of both the phases at 3.5 h of milling and after 20 h of milling only single cubic phase is formed. The rapid reduction in particle sizes of all phases in ball-milled sample with increasing milled time is reported in table 1. Initially, after 3.5 h of milling particle sizes of cubic and hexagonal ZnS phases are almost equal and decrease with same manner and size of cubic ZnS phase reduces to ~4.5 nm after 20 h of milling. It is evident from table 1 that the ball milled sample contains lattice strains. The rms lattice strain produced in both the ZnS phases during the milling has been obtained from the Rietveld analysis. The stable cubic phase is initiated with a less amount of lattice strain and the strain in cubic lattice reduces rapidly almost to zero within 20 h of milling.

The dc resistivity variation with temperature has been studied in the temperature range 77–300 K for different samples. Resistivity of the samples decreases with increasing temperature; such behavior indicates the prevalence of hopping type charge transport and resistivity variation with temperature can be expressed as [26]

\[
\rho(T) = \rho_0 \exp\left(\frac{T_{\text{Mot}}}{T}\right),
\]

where \(\rho_0\) is the resistivity at infinite temperature, \(\gamma\) is an exponent and its value depends on the sample dimension. Its value is 1/2 for one-dimension, 1/3 for two-dimensions and 1/4 for three-dimensions. \(T_{\text{Mot}}\) is the Mott characteristic...
The LTT increasing magnetic have measured magnetoconductivity which is decreasing with different samples. 

\[ \gamma \] lines in dimensional pellet of the samples for electrical measurement, 

\[ k \] where temperature, which depends on the localization length \( L_{\text{loc}} \) and density of states \( N(E_F) \) at Fermi surface and can be given by the relation

\[ T_{\text{Mott}} = \frac{16}{k_B N(E_F)L_{\text{loc}}^3}, \]  

where \( k_B \) is the Boltzmann constant. We have used the three-dimensional pellet of the samples for electrical measurement, \( \gamma = 1/4 \) has been useful for analysis the experimental data. In figure 4, the logarithmic resistivity variation with \( T^{-1/4} \) has been shown. A straight line variation has been calculated from the slope of the straight lines in figure 4 and listed in table 2. The value of \( T_{\text{Mott}} \) of the zones samples increases with increasing milling time from 3.5 to 20 h.

Magnetotransport property of the zones QD samples have been studied within the temperature range \( 77 \text{ K} \leq T \leq 300 \text{ K} \) in presence of transverse magnetic field \( B \leq 1 \text{ T} \). We have measured magnetoconductivity which is decreasing with increasing magnetic field i.e. negative magnetoconductivity has been observed for all samples. At magnetic field \( B = 0.8 \text{ T} \) and temperature \( T = 300 \text{ K} \) the maximum percentage changes of conductivity \( \frac{\sigma(B, T) - \sigma(0, T)}{\sigma(0, T)} \times 100 \) varies from \(-1.72\% \) to \(-5.76\% \). Figure 5 shows the variation of room temperature magneto conductivity with magnetic field for different samples. Generally, the dc magnetoconductivity of the investigated samples can be analyzed by two simultaneously acting hopping conduction processes like (i) the wave function shrinkage model [27, 28] and (ii) the forward interference model [29–31]. According to wave function shrinkage model, in presence of magnetic field the wave functions of conduction electrons are contracted, which reduces the average hopping length. Hence the conductivity decreases with increasing magnetic field and the magnetoconductivity ratio can be presented by the relation [27]

\[ \ln \left( \frac{\sigma(B, T)}{\sigma(0, T)} \right) = -t_1 \frac{e^2 L_{\text{loc}}^4}{h^2} \left( \frac{T_{\text{Mott}}}{T} \right)^{3/4} B^2, \]  

where \( t_1 = 5/1600 \) and \( L_{\text{loc}} \) is the localization length. On the other hand, in case of forward interference model, the forward interference among random paths between two sites has been observed in the hopping conduction processes and resulting the positive magnetoconductivity. Hence the magnetoconductivity ratio can be expressed as

\[ \frac{\sigma(B, T)}{\sigma(0, T)} = 1 + \frac{C_{\text{sat}} B / B_{\text{sat}}}{1 + B / B_{\text{sat}}}, \]  

where \( C_{\text{sat}} \) is a temperature independent parameter and \( B_{\text{sat}} = 0.7(\hbar/\varepsilon)(8/3)^{1/2}(1/L_{\text{loc}}^2)^2(T/T_{\text{Mott}})^{3/8} \). Therefore, due to the competition between the wave function shrinkage effects and the quantum interference effects, the sign and magnitude of magnetoconductivity of the investigated samples will be changed. In our observation the negative magnetoconductivity of the investigated samples suggested that the wave function shrinkage effect is predominant over forward interference effect. Therefore, the experimental data have been analyzed by using the wave function shrinkage model. In figure 5 a linear variation of \( \ln(\sigma(B, T)/\sigma(0, T)) \) with \( B^2 \) for different samples at room temperature are shown. Different points in the figure represent the measured data and the solid straight lines represent the theoretical best fits according to the wave function shrinkage model. From this fitting we may presume that the experimental data are

| Milling time (hour) | Phases | Mol fraction % | Intrinsic stacking fault | Extrinsic stacking fault | Twin fault | Particle size (nm) | rms strain \( \times 10^3 \) |
|-------------------|--------|---------------|--------------------------|-------------------------|------------|------------------|------------------|
| 3.5               | ZnS(C) | 0.875         | 62.27                    | 0.0809                  | 10.47      | 41.15            | 10.87            |
|                   | ZnS(H) | 0.125         | —                        | —                       | —          | 48.675           | 24.6             |
| 6                 | ZnS(C) | 0.88          | 62.52                    | 0.4265                  | 19.36      | 17.104           | 8.724            |
|                   | ZnS(H) | 0.12          | —                        | —                       | —          | 10.152           | 11.18            |
| 10                | ZnS(C) | 0.905         | 38.62                    | 0.9297                  | 19.55      | 11.938           | 8.15             |
|                   | ZnS(H) | 0.095         | —                        | —                       | —          | 8.11             | 7.04             |
| 20                | ZnS(C) | 1             | 11.56                    | 1.0194                  | 28.31      | 4.557            | 1.98             |
|                   | ZnS(H) | 0             | —                        | —                       | —          | —                | —                |

Figure 4. Variation of the dc conductivity \( \sigma_{dc} \) with temperature of different samples.

Table 1. Variation of different microstructure parameters with increasing milling time obtained from Rietveld analysis for both ZnS cubic [ZnS(C)] and Zn hexagonal [ZnS(H)] phases. Stacking faults are associated among thousand atomic layers.
Table 2. Values of relevant physical parameters for different milled samples. $\rho_{300 \text{K}}$ is the resistivity at 300 K, $T_{\text{Mott}}$ is Mott characteristic temperature, $L_{\text{loc}}$ is the localization length, $R_{\text{hop}}$ is the hopping range, $W_{H}$ is the effective barrier height and $\tau_{0}$ is the characteristic relaxation time.

| Parameters                     | 0      | 3.5    | 6      | 10     | 20     |
|--------------------------------|--------|--------|--------|--------|--------|
| $\rho_{300 \text{K}}$ (Ωm)    | $5.40 \times 10^{7}$ | $8.08 \times 10^{7}$ | $9.33 \times 10^{7}$ | $2.38 \times 10^{7}$ | $1.26 \times 10^{7}$ |
| $T_{\text{Mott}}$ (K)         | $11.60 \times 10^{7}$ | $1.63 \times 10^{7}$ | $3.88 \times 10^{7}$ | $4.57 \times 10^{7}$ | $8.50 \times 10^{7}$ |
| $L_{\text{loc}}$ (nm)         | 4.14   | 7.93   | 6.94   | 7.15   | 6.91   |
| $R_{\text{hop}}$ (nm)         | 0.06   | 0.19   | 0.14   | 0.14   | 0.11   |
| $W_{H}$ (eV)                  | 0.54   | 0.65   | 0.77   | 0.89   | 1.04   |
| $\tau_{0}$ (s)                | $5.63 \times 10^{-8}$ | $4.52 \times 10^{-8}$ | $2.10 \times 10^{-8}$ | $7.53 \times 10^{-9}$ | $6.56 \times 10^{-9}$ |

Figure 5. Variation of the dc magnetoconductivity with perpendicular magnetic field of different samples at 300 K.

Figure 6. Variation of the dc magnetoconductivity with perpendicular magnetic field of the S5 sample at different temperatures.

The total frequency dependent conductivity has been measured at constant temperatures of all the samples. At a particular temperature, the total frequency dependent conductivity shows two distinct behaviors like a weak frequency dependent behavior due to dominant dc conductivity at lower frequency. On the other hand at higher frequency conductivity strongly depends on frequency and follows the power law of frequency. In this case the total frequency dependent conductivity can be expressed as the sum of the ac ($\sigma_{ac}$) as well as dc ($\sigma_{dc}$) conductivity [26, 32, 33] and can be written as

$$\sigma'(f) = \sigma_{dc} + \sigma_{ac}(f) = \sigma_{dc} + \alpha f^s,$$  \hspace{1cm} (5)

where $\alpha$ is the temperature dependent constant and $s$ is the frequency exponent. In figure 7 we have plotted $\ln[\sigma_{ac}(f)]$ with $\ln(f)$ which shows the straight line variation. For different temperatures the values of $s'$ have been calculated from the slope of each straight line. The variation of $s'$ with temperature for different samples has been shown in figure 8. It is observed that the values of $s'$ decreases with increasing temperature. In case of amorphous semiconductors, the temperature dependence of $s'$ has been reported by different theoretical models [32–34] where the functional form of $s'$ with temperature is different for different conduction models. Considering all the models and comparing with the observed
temperature variation of ‘s’, correlated barrier hoping (CBH) model is suitable conduction processes. According to this model, the charge carriers hop over the potential barrier between two charged defect states and the variation of ‘s’ with temperature can be expressed as

$$s = 1 - \frac{6k_B T}{W_H - k_B T \ln (1/\omega \tau_0)} , \tag{6}$$

where $W_H$, $\omega$ and $\tau_0$ are the effective barrier height, angular frequency and characteristic relaxation time respectively. The variation of ‘s’ with temperature for different sample has been shown in figure 8, where the different points are the experimental data and the solid lines are the theoretical best fit with the equation (6) taking $W_H$ and $\omega \tau_0$ as fitting parameters. Hence the experimental data are well fitted with the theoretical prediction obtained from CBH model. The best fitted values of the parameters $W_H$ and $\tau_0$ at 10 KHz are lying in the range 0.54–1.05 eV and 5.63 $\times$ 10$^{-8}$–0.66 $\times$ 10$^{-8}$ s, respectively, for different samples. It is observed from the analysis that the value of effective barrier height increases with increasing milling time, whereas the characteristic relaxation time decreases with increasing milling time. Considering all the above facts, we may conclude that the ac conduction mechanism of all investigated samples is corroborated by the CBH model.

For a particular frequency, the temperature dependence of real part of dielectric permittivity of $\varepsilon'(f)$ for the 20 h milled sample has been shown in figure 9, where no sharp peak has been observed within the maximum possible investigation temperature range. It is observed from the figure that the real part of dielectric permittivity increases monotonically with temperature and follows a power law behavior $\varepsilon'(f) \propto T^n$. Different points are the experimental data at different frequencies and the solid lines are the theoretical best fitted values in accordance with the power law. The fitting yields the values of temperature exponent $n$ which depends strongly on the frequency (its value decreases with increasing frequency). According to the figure the variation of the $\varepsilon'(f)$ with temperature at lower frequency is dominating over the variation at higher frequency. In disordered semiconductor, interfacial polarization has been observed due to structural inhomogenities. Hence the hopping electron may be trapped by the inhomogenities at low frequencies. However by increasing temperature, the resistance of the composites decreases and electron hopping is promoted by the low resistance. As a result an enhanced polarizibility or larger $\varepsilon'(f)$ has been observed with temperature for a particular frequency.

In order to find out the grain and grain boundary contribution of such inhomogeneous system, the complex impedance can be analyzed by an equivalent circuit containing grain and interfacial grain boundary resistances and capacitances and can be expressed as [35, 36]

$$Z = \frac{1}{i \omega C_0 \varepsilon(\omega)} = Z' - iZ'' , \tag{7}$$
The real part of the complex impedance versus frequency of different samples at 300 K.

\[
Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2},
\]

where \(C_0\) is free space capacitance, \(R_g\), \(R_{gb}\), \(C_g\) and \(C_{gb}\) are grain and interfacial grain boundary resistance and capacitance, respectively. By using the real \(\varepsilon'(f)\) and imaginary \(\varepsilon''(f)\) part of dielectric constant, the real part of the complex impedance can be calculated by using the relation

\[
Z'(f) = \frac{\varepsilon''(f)}{\omega C_0 (\varepsilon'(f)^2 + \varepsilon''(f)^2)}.
\]

At room temperature, the variation of real part of complex impedance has been shown in figure 10 for different samples. The grain and grain boundary resistance and capacitance have been calculated by least square fitting of experimental data with equation (10) taking \(R_g\), \(R_{gb}\), \(C_g\) and \(C_{gb}\) as fitting parameters. In figure different points are the experimental data whereas the best fitting is represented by solid lines. The best fitted values of the parameters are lying in the range 2.23–280.93 kΩ for \(R_g\), 0.14–0.48 nF for \(C_g\), 7.28 KΩ–5.68 MΩ for \(R_{gb}\) and 0.22–5.67 nF for \(C_{gb}\) for different samples. It is observed that the values of \(C_{gb}\) and \(C_g\) have the same order of magnitude, however the values of \(R_{gb}\) for different samples are greater than the values of \(R_g\). This implies that the grain boundary contribution dominates over the grain contribution. In figure 11, variation of real part of complex impedance with frequency in presence and in absence of magnetic field at different temperature has been shown. It is observed from the figure that below the 10 kHz frequency the impedance of the sample is greater than the values obtained without magnetic field. This is because at lower frequency long range conduction are favorable, so the applied magnetic field may influence more on the carrier motion which results more positive impedance by application of magnetic field at lower frequencies. From analysis of the real part of complex impedance data with equation (8) we have calculated the grain and grain boundary contribution in presence of constant magnetic field \(B = 0.8\ T\). It is observed from the calculation that the total contribution due to grain and grain boundary resistances \((R = R_g + R_{gb})\) increases from 5.83 to 25.80 MΩ at 300 K and 24.96 to 53.77 MΩ at 77 K in absence and in presence of magnetic field 0.8 T, respectively. So we may presume that the influence of the magnetic field on the impedance is due to the change of grain and grain boundary resistances by the applied magnetic field.

Analysis of the dielectric properties of the samples by the complex electric modulus formalism has been done to avoid the electrode effect [37]. The complex electric modulus \(M'(f)\) can be described by the relation

\[
M'(f) = M'(f) + jM''(f) = \frac{\varepsilon'(f)}{\varepsilon'(f)^2 + \varepsilon''(f)^2} + j\frac{\varepsilon''(f)}{\varepsilon'(f)^2 + \varepsilon''(f)^2},
\]

where \(M'(f)\) and \(M''(f)\) represent the real and imaginary components of the complex electric modulus respectively. The variation of real and imaginary components of complex electric modulus with frequency is shown in figure 12 for different samples. From the figure it is noticed that the value of \(M'(f)\) increases with increasing frequency and undergoes a step like change. It is also observed in figure 12 that the step like change in \(M'(f)\) versus \(f\) curve is accompanied by a relaxation peaks in \(M''(f)\) versus \(f\) curve. The relaxation peaks are not observed for temperature \(T < 300\ K\). The peak frequency has an importance because the charge carriers freely move below the peak frequency and are confined above this frequency [38, 39]. It is observed in figure 12 that for a particular temperature, the peak position is shifted to higher frequency due to increase of milling time. With increasing milling time the hexagonal phase ZnS is converted to cubic phase and the sample is fully cubic phase after 20 h of...
ZnS QDs with cubic phase can be prepared by top-down physical method of MA at room temperature. Initially along with major cubic ZnS phase the amorphous like minor hexagonal ZnS phase is formed and in the course of milling up to 20h, the single phase cubic ZnS is formed with ~4.5 nm in size and almost free from lattice strain. The existence of different kinds of stacking faults in ball-milled samples are estimated by the Rietveld method which is also approved by the HRTEM images and thereby an well rationalization of the Microstructure of Materials (Berlin: Springer)

4. Conclusion

ZnS QDs with cubic phase can be prepared by top-down physical method of MA at room temperature. Initially along with major cubic ZnS phase the amorphous like minor hexagonal ZnS phase is formed and in the course of milling up to 20h, the single phase cubic ZnS is formed with ~4.5 nm in size and almost free from lattice strain. The existence of different kinds of stacking faults in ball-milled samples are estimated by the Rietveld method which is also approved by the HRTEM images and thereby an well rationalization between direct and indirect observation techniques is noticed. Resistivity of the samples decreases with increasing temperature, which indicates the prevalence of three-dimensional hopping type charge transport. The negative magnetococonductivity of the investigated samples suggested that the wave function shrinkage effect is predominant over forward interference effect. The localization length increases from 3.62 to 6.52 nm with increasing temperature. At higher frequency conductivity strongly depends on frequency and follows the power law of frequency. Hence the ac conduction mechanism of all investigated samples is corroborated by the CBH model. Relaxation properties of the samples have been described by the analysis of the electric modulus. Analysis of the complex impedance by an equivalent circuit containing grain and interfacial grain boundary resistances and capacitances implies that the grain boundary contribution dominates over the grain contribution.

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