

SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF ZnTe NANOPARTICLES

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ZnTe nanoparticles have been synthesized by chemical synthesis method, which is based on the chemical replacement reaction between the chemical compounds. Structural analysis of ZnTe nanoparticles has been performed by using x-ray diffraction techniques. It has been found that the average particle size is 2.6 nm using uv-vis spectroscopy. DC and AC electrical conductivities of ZnTe nanoparticles have been studied. Conduction mechanism is described in brief. The activation energies have also been determined. The results indicate that ZnTe behaves as a semiconducting material.

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1. Introduction

Nanometer-sized semiconductor particles belong to a state of matter in the transition region between molecules and solids. During the last two decades, research on quantum size semiconductor particles has increased enormously due to their exciting novel properties [1-4]. II - VI semiconductor nanoparticles are currently of great interest for their practical applications such as zero dimensional quantum confined materials, and in optoelectronics and photonics. Numerous reports are available in the literature on synthesis techniques as well as potential applications of nano-sized semiconductor particles [5-9]. In the present paper the characterization of ZnTe nanoparticles have been studied at 300°C, 500 °C, 700°C for 4 hours using various concentration of capping agent (i.e. ethylenediamine). ZnTe nanoparticles have been synthesized by using chemical synthesis method. X-ray powder diffraction and transmission electron microscope were employed to characterize the size, morphology, and crystalline structure of the as prepared sample. The Formation process was discussed and it revealed a uniform hexagonal shape of ZnTe nanoparticles with good dispersion, average particle size is found to be 2.6 nm [10-13]. DC and AC electrical conductivities were studied and the activation energies have been determined [14-15]. The results indicate that ZnTe behaves as a semiconductor material. The dielectric properties were measured, as a function of temperature at different frequency range from 100 Hz to 100 KHz. The increase of dielectric constant with increasing frequency is attributed to the dielectric dispersion [16-17]. In ZnTe, structural phase change from hexagonal to face centered cubic is also observed, when the particle size becomes 2.6 nm. This phase transition may occur due to correlation between the structure, size and the surface properties of these nanoparticles [18]. Various methods, such as pyrolysis, chemical synthesis, plasma deposition technique and magnetron sputtering etc had been utilized for the synthesis of nanoparticles. In this work we limit ourselves to use of chemical synthesis technique for the preparation of ZnTe nanoparticles. Most physical and chemical properties of these nanomaterials are sensitively dependent on their size and shape, and scientists are still focusing on developing of simple and effective methods for fabrication of nanomaterials of control size and morphology. In order to obtain crystalline non dispersive nanoparticels, it is

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usually necessary to work at relatively high temperature [19]. The electrical behaviour has been studied for electrical applications.

2. Experimental

2.1 Synthesis of ZnTe nanoparticles

ZnTe nanoparticles have been prepared by chemical synthesis method, because it is very common method for II-VI compound of the periodic table. This method is based on the chemical replacement reaction [20] between chemical compounds providing metal ions (Zn^{2+}) and those containing chalcogenide ions (Te^{2-}). Materials which have been used for making zinc telluride (ZnTe) are zinc acetate [$Zn(OCOCH_3)_2$] and sodium telluride (Na_2Te) as the source of Zn^{2+} and Te^{2-} ion respectively. To make ZnTe nanoparticle, freshly prepared 100 ml solution of zinc acetate [$Zn(OCOCH_3)_2$] (0.2M) is taken in magnetic stirrer. Then 100 ml solution of sodium telluride [Na_2Te] (0.1M) in 50% methanol and 50% water (i.e. 25 ml methanol & 25 ml water) was added while stirring constantly. The cream coloured precipitate was formed instantaneously. To remove any type of unreacted chemicals or impurities, precipitate has been washed three times with methanol and dried it by evaporation method. The particle size of the nanoclusters can be changed by zinc acetate, sodium telluride and ethylenediamine solution [21].

2.2 Characterization Techniques

There are variety of different techniques for the characterization of nanoparticles, mainly drawn from the material science. Common techniques are electron microscopy [Transmission Electron Microscopy, Scanning Electron Microscopy], atomic force microscopy [AFM], and X-ray diffractometry [XRD][17-18]. The microscopic characterization and spectroscopic analysis method has been carried out by using the stable dispersions. X-ray diffraction analysis has been done using the dried powders obtained from precipitation by means of ionic strength. For measuring X-ray data we have used X-ray diffractometer (made by Diano Corporation, USA equipped with $Co K_{\alpha}$ radiation, $\lambda=1.790 \text{ \AA}$). Transmission electron microscope (TEM) type ZEISS, EM10, West Germany power 30 kV was used to study the morphology of the sample. DC conductivity was carried out over the range room temperature to 421 K and measured using Keithley electrometer type 6517A. AC conductivity and dielectric measurements were carried out in frequency range 100 Hz to 100 kHz by using LCR meter types AG-411 B (Ando electric Ltd., Japan).

3. Results and discussion

3.1 Structural properties

Fig. 1 shows the X-ray diffraction (XRD) pattern of zinc telluride. From this figure it is clear that the sample exhibits crystalline nature. Analysis of the XRD patterns prove that the formed crystals belong to hexagonal phase. The particle size has been estimated using Scherer's equation [22]

$$D = K\lambda / \beta \cos \theta, \quad (1)$$

where D is the mean dimension of the crystallites, β the broadening at half band width, λ the wavelength, and K is a constant approximately equal to unity and related to both the crystallite shape and the way in which β and D are defined. The crystallite size is about 2.6 nm, as estimated according to the (1, 1, 0) reflection by Scherer's equation.

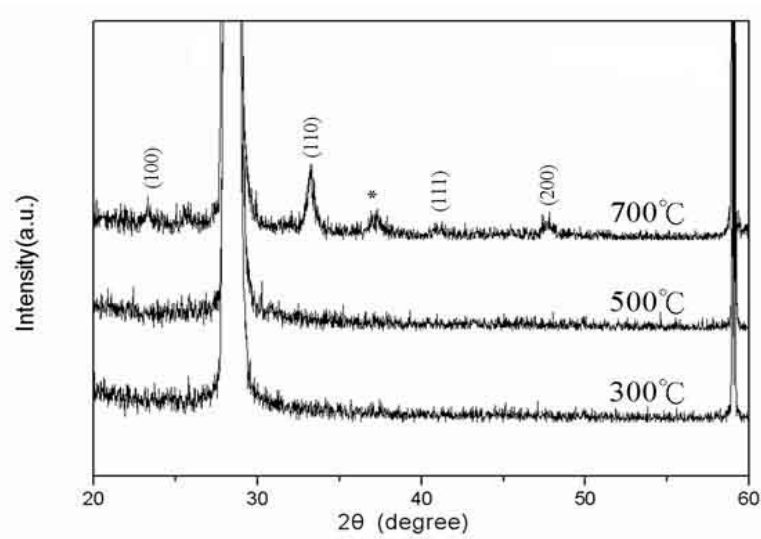


Fig. 1. X-ray diffraction pattern of ZnTe nanoparticle prepared at (300 °C, 500 °C, 700 °C).

The particle distribution and the microstructure of ZnTe investigated by TEM, is shown in Fig. 2. From Fig.2 it can be noticed that, a homogeneous distribution of the nanoparticles prevails over a wide range of the sample. Also, it is made up of small spheres or faceted particles. The diameters of the particles were measured by a millimeter scale, and the number of the particles within a bin of 5 nm with different value of average diameters was counted.

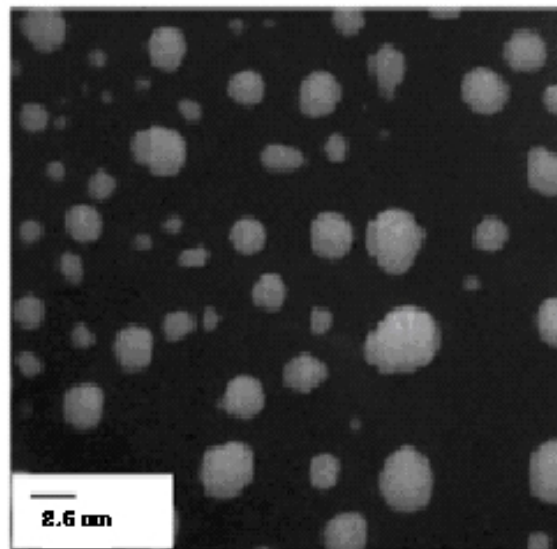


Fig. 2. Transmission electron microscope of ZnTe nanoparticles prepared at 300 °C

The particle size was calculated and the data were fitted to a log-normal distribution function [20]. The numbers were plotted as a function of different average particle diameters to obtain the histogram [23] as shown in Fig.3.

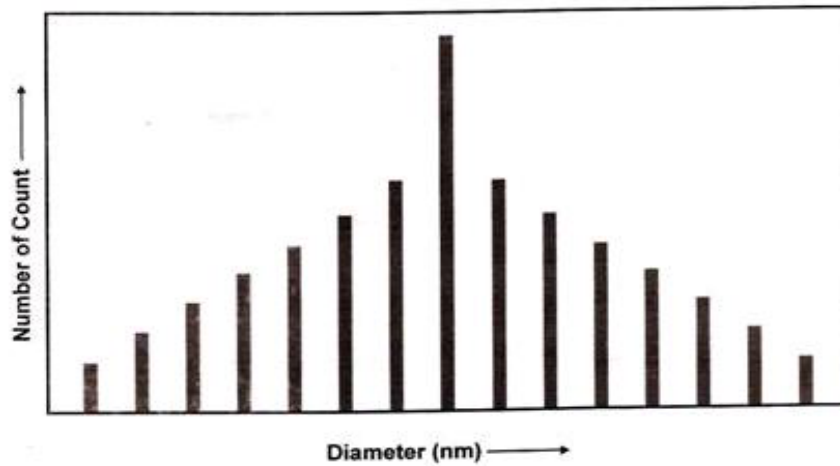


Fig. 3. Relation between number of grains (n) and average particle diameter

From these figures, the mean diameter obtained from TEM picture was about 2.6 nm with hexagonal phase.

3.2 Electrical properties

DC electrical conductivity of the ZnTe as a function of temperature is shown in Fig. 4

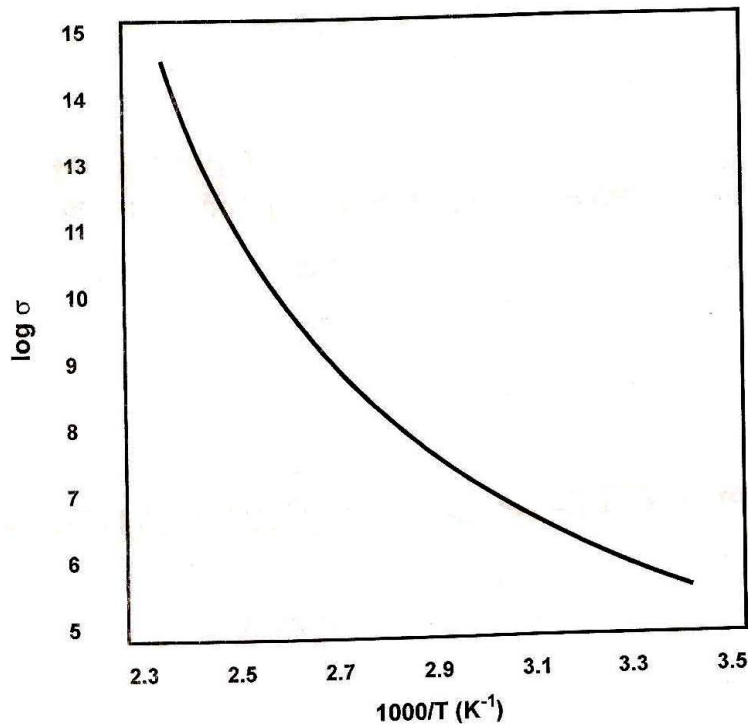


Fig. 4. Variation of $\log \sigma$ with $1000/T(K^{-1})$ for ZnTe nanoparticles prepared at 300°C

From the Fig. 4, the variation of $\log \sigma$ with $1000/T(K^{-1})$ indicates that there are three distinct temperature zones with three characteristic regions. The first region from room temperature up to 333K is identified with low temperature and extends upwards up to the impurity exhaustion temperature. This region is identified with the extrinsic conductivity of semiconductor due to the ionization of impurity atoms [24-25]. The intermediate region from 333K up to 363K

extends from the impurity exhaustion temperature to the intrinsic temperature. In this region, all impurity atoms are ionized, but the intrinsic carrier are not yet excited to a marked degree because the density of carriers remains approximately constant and equal to the impurity concentration. Therefore, the temperature dependence of the conductivity of the semiconductor is decided by that of the carrier mobility. If the main scattering mechanism in this region is scattering by thermal vibrations of the lattice for which the mobility decreases with rising temperature, the conductivity will decrease within this region. On the other hand, if the main scattering mechanism is scattering by ionized impurities, the conductivity within the intermediate region will increase with rising temperature. The third region from 363K up to 421K is identified with the transition to intrinsic conduction in semiconductor. Within this region, the density of carriers is equal to that of intrinsic carriers [26]. The activation energies from DC and AC conductivities were calculated using the Arrhenius relation in high and low temperature regions and are found to be equal to 0.234 eV and 0.09 eV, respectively [23]. The values of the activation energy indicate that the prepared samples are semiconductors. The frequency dependence of AC conductance was measured for ZnTe in the frequency range 100Hz–100kHz at different temperatures as shown in Fig.5

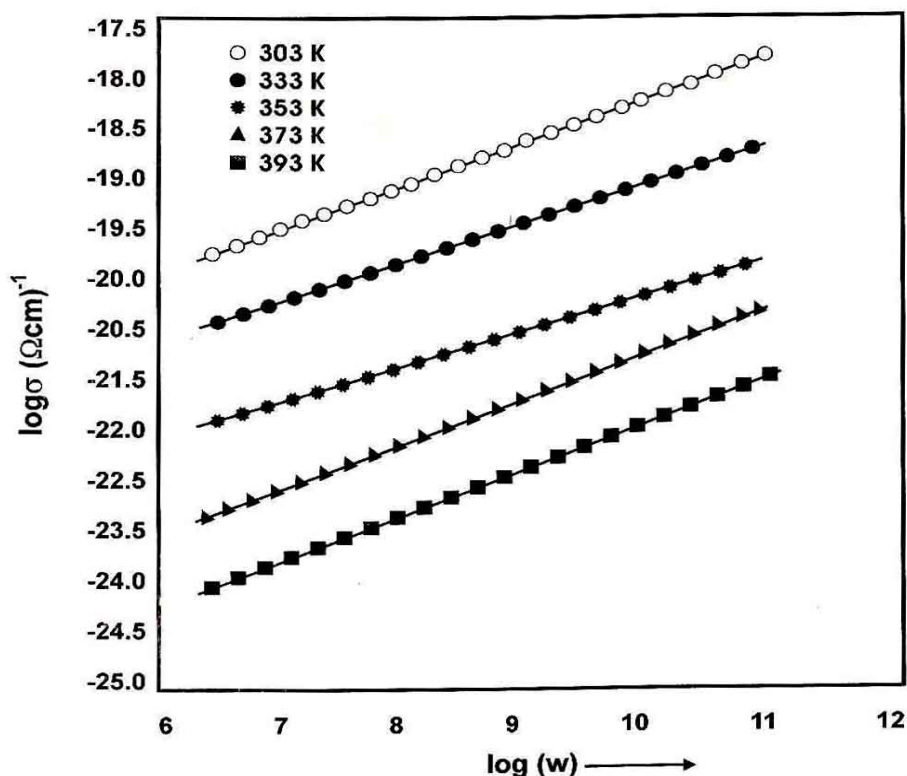


Fig. 5. Variation of $\log(\sigma)$ with $\log w$ measured at different temperature for ZnTe nanoparticles prepared at 300°C.

From the Fig.5 it is clear that, the variation of the AC conductance, $\log \sigma$, with frequency, $\log(\omega)$ may be expressed as [11-27]

$$S = d \log(\sigma) / d \log(\omega) \quad (2)$$

where S is the frequency exponent, which is temperature dependent parameter. The correlated barrier-hopping model (CBH) proposed by Elliott [24] is used to describe the behavior of conduction mechanism. According to this model, single electron transfer by thermal activation occurs over the barrier between two defects. Generally, the exponent S in Eq. (2) is related to both frequency and temperature by the following equation [28]

$$S = 1 - [6kT / \{W_M - kT \ln(1/\omega T)\}] \quad (3)$$

where W_M is the binding energy of electrons and k is the Boltzman's constant. When S is near unity, it is almost frequency independent and decreases approximately linearly with increasing temperature. Thus Eq. (3) is then reduced to

$$S=1- 6kT/ W_M \quad (4)$$

The study of exponent frequency S as a function of temperature allows us to determine the AC conductance mechanisms, the change of exponent S with temperature is shown in Fig.6. The values of S decrease with increasing temperature, this implies the assumption that CBH model is the dominant conduction mechanism [29]. The value of binding energy W_M (eV) was calculated from Fig.6 using Eq. (4) and it is found to be equal to 0.16 eV.

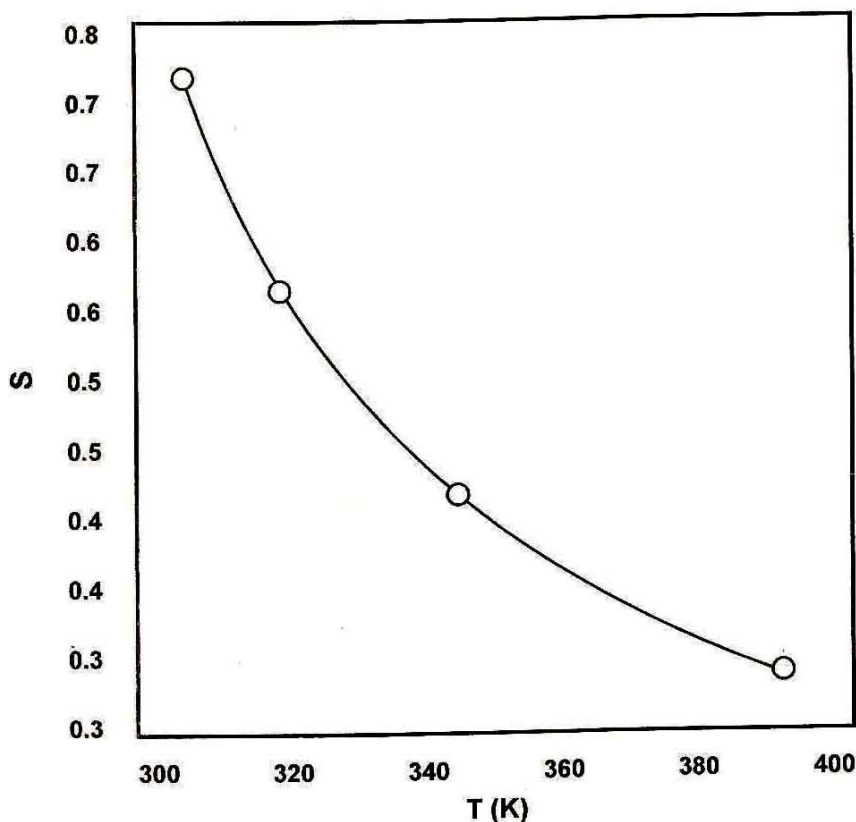


Fig. 6. Variation of frequency exponent with temperature T .

4. Conclusions

Synthesis and characterization of ZnTe nanoparticles prepared by chemical synthesis method using ethylenediamine as a capping agent at 300°C, 500°C, 700°C have been described. The XRD and TEM indicate that the particle size was 2.6 nm. The activation energies calculated from DC and AC conductivities are found to be 0.234 eV and 0.09 eV respectively. The conduction mechanisms were studied and the data obtained indicates that the sample behaves as semiconductor material.

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References

- [1] L. Brus, *J. Phys. Chem.* **90**, 2555 (1986).
- [2] A. Henglein, *Chem. Rev.* **89**, 1861 (1989).
- [3] H. Weller, *Adv. Mater.* **5**, 88 (1993).
- [4] A. P. Alivisatos, *Science* **271**, 933 (1996).
- [5] M. Tamborra, M. Striccoli, R. Comparelli, M. L. Curri, A. Petrella, A. Agostiano, *Nanotechnology* **15**, 5240 (2004).
- [6] N. Tessler, V. Medvedev, M. Kazes, S. Kan, U. Banin, *Science* **295**, 1506 (2002).
- [7] V. L. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, *Science* **290**, 340 (2000).
- [8] D. Battaglia, X Peng, *Nano Lett.* **2**, 1027 (2002).
- [9] M Abdulkhadar, Binny Thomas, *Nanostruct. Mater.* **5**, 289 (1995).
- [10] S.K. Haram, B.M. Quinn, A.J. Bard, *J. Am. Chem. Soc.* **123**, 8860 (2001).
- [11] K.B. Tang, Y.T. Qian, J.H. Zeng, X.G. Yang, *Adv. Mater.* **15**, 448 (2003).
- [12] B.D. Busbee, S.O. Obare, C.J. Murphy, *Adv. Mater.* **15**, 414 (2003).
- [13] G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lacaze, F. Fievet-Vincent, F. Fievet, *Chem. Mater.* **15**, 486 (2003).
- [14] M. Rajamathi, R. Seshadri, *Curr. Opin. Solid State Mater. Sci.* **6**, 337(2002).
- [15] C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).
- [16] T.J. Trentler, T.E. Denler, J.F. Bertone, A. Agrawal, V.L. Colvin, *J. Am. Chem. Soc.* **121**, 1613 (1999).
- [17] M. Green, P. O'Brien, *J. Chem. Soc. Chem. Commun.* **3**, 183 (2000).
- [18] S.H. Yu, *J. Ceram. Soc. Japan* **109**, 565 (2001).
- [19] Nirmal, L. Brus, *Acc. Chem. Res.* **32**, 407 (1999).
- [20] V.I. Klimov, A.A. Mikhailovsky, S. Xu, A. Malko, J.A. Hollingsworth, C.A. Leatherdale, H.J. Eisler, M.G. Bawendi, *Science* **314**, 290 (2000).
- [21] G.W. Stewart, R.M. Morrow, *Phys. Rev.* **30**, 232 (1927).
- [22] B. Li, Y. Xie, J. Huang, H. Su, Y.T. Qian, *Nanostruct. Mater.* **11(8)**, 1067 (1999).
- [23] A.N. Shipway, E. Katz, I. Williner, *Chem. Phys. Chem.* **1**, 18 (2000).
- [24] J. Phillips, *J. Appl. Phys.* **91**, 4590 (2002).
- [25] T.J. McCarthy, M.G. Kanatzidis, *Inorg. Chem.* **34**, 1257 (1995).
- [26] K. Chondroudis, M.G. Kanatzidis, *J. Am. Chem. Soc.* **119**, 2574 (1997).
- [27] J. Yang, X.L. Yang, S.H. Yu, X.M. Liu, Y.T. Qian, *Mater. Res. Bull.* **35**, 1509 (2000).
- [28] P.K. Basu, *Theory of Optical Processes in Semiconductors Bulk and Microstructure*, Clarendon Press, Oxford (1997).
- [29] B.K. Rai, H.D. Bist, R.S. Katiyar, M.T.S. Nair, P.K. Nair, A. Manivannan, *J. Appl. Phys.* **82**, 1310 (1997).