



PHYSICS

STUDIES OF CADMIUM SELENIDE (CdSe) NANOPARTICLES SYNTHESIZED BY SOLVO-THERMAL ROUTE

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Abstract

Synthesis of nanoparticles of Cadmium Selenide(CdSe) was carried out by using a microwave oven. Cadmium chloride and sodium selenite were used as the precursor materials to prepare CdSe nanoparticles. Ethylene glycol was used as the capping agent to control the size of the nanoparticles. Powder XRD pattern reveals the crystal structure of the prepared CdSe nanoparticles. The average particle size of the sample was found to be 54 nm. The morphology of the sample was studied by a SEM. UV-vis absorption spectrum for prepared CdSe sample was recorded. Dielectric studies were carried out for the pelletized sample of CdSe nanoparticles and AC conductivity and DC conductivity values have been measured. The obtained results are discussed.

Keywords: Nanomaterials; CdSe; X-ray diffraction; SEM; Microwave-assisted solution method; Electrical studies

Introduction

During the last two decades, there has been an enormous interest in nanomaterials due to their novel physical and chemical properties that differ markedly from those of bulk materials. The novel properties of nanomaterials are due to quantum confinement of charge carriers in these materials. Most physico-chemical properties of these nanomaterials are sensitively dependent on their size and shape and researchers are now focusing on developing simple and effective methods for the preparation of nanomaterials of controlled size and morphology[1-5]. Recently, there are many extensive studies on semiconductor nanocrystals because they exhibit strongly size dependent optical properties and from the viewpoint of fundamental physics, semiconductor nanocrystals provide us with an excellent stage for experimental studies of many-body effects in strongly photoexcited semiconductors[6-9]. Semiconductor nanocrystals are already commercially marketed for application as luminescent biolabels and have been demonstrated as components in regenerative solar cells, optical gain devices, and electroluminescent devices[10-16]. Cadmium selenide (CdSe) is a useful semiconductor that is a binary compound of cadmium and selenium. It has common names such as cadmium(II) selenide, cadmium selenide and cadmoselite. Three crystalline forms of cadmium selenide viz. wurtzite (hexagonal), sphalerite (cubic)

and rock-salt (cubic) are available. Many researchers have reported their works on semiconducting nanocrystals [17-19]. The nanopowder of CdSe provides excellent and unique properties and these properties depend upon shape and size of nanostructures[20,21]. Various methods such as hydrothermal, sol-gel approach and surfactant-assisted approach etc had been utilized for the synthesis of nanomaterials[22,23]. In this work, nanoparticles of CdSe was synthesized by solvo-thermal route using a microwave oven. Microwaves are the electromagnetic waves with frequency range of 0.3-300 GHz and corresponding wavelength from 1 mm to 1000 mm. In the microwave irradiation region, the frequency of the applied irradiation is low enough so that the dipoles have time to respond to the alternating electric field and therefore respond to rotation. This method has been successfully applied for the preparation of a variety of nano-sized inorganic materials [24-26]. Compared with conventional heating, microwave heating has an advantage of high efficiency and rapid formation of nanoparticles with a nano-size distribution and less agglomeration. The fundamental mechanism of microwave heating involves agitation of polar molecules or ions that oscillate under the effect of an oscillating electric field. In the presence of an oscillating field, particles try to orient themselves. This constant re-orientation creates friction and collisions between molecules, thus producing heat[27]. The synthesized CdSe nanoparticles using the microwave oven were characterized by XRD method, SEM

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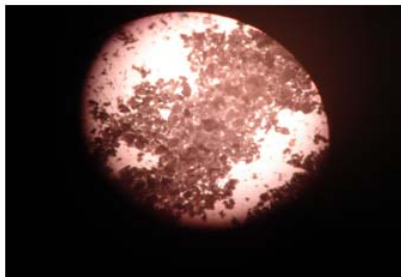
method, UV-visible absorption technique, dielectric studies and conductivity studies and results are reported.

Experimental Methods

Synthesis

Nanoparticles of CdSe was synthesized by microwave-assisted solution method. The chemicals such as cadmium chloride and sodium selenite were used as the precursor materials to prepare CdSe nanoparticles. Cadmium chloride and sodium selenite in 1:1 molar ratio were dissolved in de-ionized water and stirred well using a magnetic stirrer for 30 minutes. During stirring 20 %volume of ethylene glycol was added to the solution. This solution mixture was kept in a microwave oven for 45 minutes (ON for 4 minutes and OFF for 4 minutes). Then the solution was centrifuged, filtered and washed. The precipitate formed was collected and dried at 50 °C for 1 hour. The photograph of the prepared CdSe nanoparticles is displayed in the figure 1.

Fig.1: Photograph of CdSe nanoparticles



Instrumentation

Powder X-ray diffraction measurement was taken using an automated X-ray powder diffractometer (PANalytical) with nickel filtered, monochromated CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). The morphology of the nanoparticles was examined by Scanning Electron Microscopy and the SEM image of the synthesized CdSe nanoparticles was recorded using a Hitachi Scanning Electron Microscope. A Perkin Elmer UV-visible Spectrophotometer was used to carry out absorption spectrum in the 200-1000 nm wavelength range at room temperature. The pelletized samples of the synthesized nanoparticles were subjected to dielectric and DC conductivity measurements. The dielectric constant and loss of the samples was measured using an LCR meter and a two probe arrangement [28]. The measurements were taken at fixed frequency of 1000 Hz and at different

temperatures ranging from 30 to 100 °C. AC conductivity of the pellet form of the prepared CdSe nanoparticles was determined using the measured values of dielectric constant and loss. AC conductivity of the sample was determined using the $\sigma_{ac} = 2\pi f \epsilon_r \epsilon_0 \tan \delta$ where f is the frequency of a.c. signal ϵ_r is the dielectric constant, ϵ_0 is the permittivity of free space or vacuum and $\tan \delta$ is the dielectric loss. DC electrical conductivity of the pelletized nanoparticles was calculated using a two-probe arrangement and a megohm digital meter. The resistance (R) of the sample was measured in the temperature range 30-100 °C and the conductivity was determined using the relation $\sigma_{dc} = d/(RA)$ where d is the thickness of the pellet, A is the area of cross section the pellet.

Results and Discussion

X-ray diffraction (XRD) studies

Figure 2 shows the XRD pattern of the CdSe sample. From this figure, the characteristic peaks located at $2\theta = 23.45, 25.56, 27.23, 41.21$ and 49.87° are corresponding to (100), (002), (101), (110) and (112) planes respectively. These peaks match well with the peaks of hexagonal(wurtzite) crystal structure. The particle size of nanoparticles was determined using the Scherrer's relation $d = (0.9 \lambda) / (\beta \cos \theta)$ where β is the full width at half maximum in radians, λ is the wavelength of X-rays used and θ is the Bragg's angle. For the various reflection peaks of the XRD pattern, the particle size was estimated and the average size of nanoparticles of the sample was found to be around 54 nm. The indexing of the diffraction peaks has been carried out using the software "INDEXING" and the unit cell parameters have been found using the software "UNITCELL" [29] and these values are found to be $a = 4.231 \text{ \AA}$ and $b = 7.0153 \text{ \AA}$. The values of 2θ (degrees), Full Width at Half Maximum(FWHM), hkl and particle size are provided in the table 1.

Fig.2: Powder XRD pattern for the prepared CdSe sample

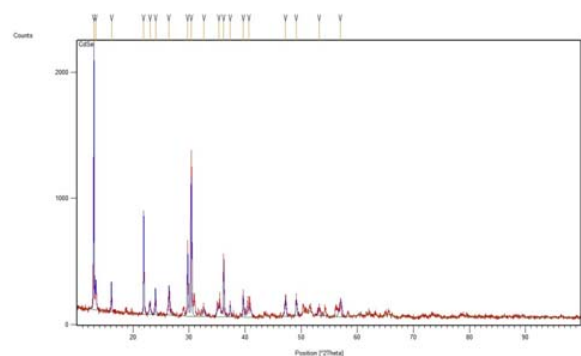


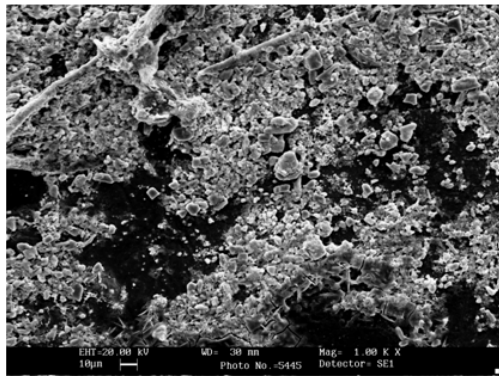
Table 1: Values of XRD data and particle size

| Peak No. | 2 θ (degrees) | FWHM (degrees) | hkl | Particle size (nm) |
|----------|----------------------|----------------|-----|--------------------|
| 1. | 23.45235 | 0.02617 | 100 | 54.16 |
| 2. | 25.56412 | 0.02442 | 002 | 58.23 |
| 3. | 27.23674 | 0.02960 | 101 | 48.31 |
| 4. | 41.21453 | 0.02250 | 110 | 58.83 |
| 5. | 49.87341 | 0.02967 | 112 | 51.52 |

SEM studies

The SEM image of the synthesized CdSe nanoparticles is displayed in the figure 3. It is observed that different structures have been formed when microwave oven was used to prepare the particles of CdSe and in this case most of the particles are agglomerated.

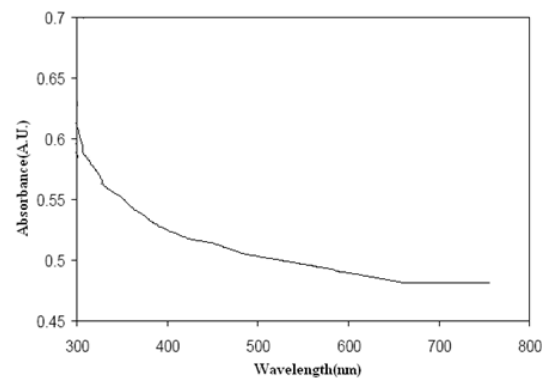
Fig. 3: SEM image of CdSe nanoparticles



UV-visible absorption studies

UV-Visible-absorption spectrum of CdSe nanoparticles in the wavelength range 300-750 nm is shown in figure 4. The spectrum consists of an absorption shoulder at 606 nm and an absorption edge at 668 nm for the CdSe sample. This spectral study may be assisted in understanding electronic structure of the optical band gap of the material. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. The study of the absorption edge is important especially in connection with the theory of electronic structure, which predicts that the band structure is mostly affected near the band extreme. A major objective of this study is to determine the magnitude of the optical energy band gap. The broadness of the absorption shoulder is attributed to the self-assembly of the nanoparticles and the formation of elongated particles

Fig.4: UV-vis absorption spectrum for the prepared CdSe sample



Electrical studies

Temperature dependence of dielectric constant, AC conductivity and DC conductivity of the disc form of CdSe nanoparticles are shown in the figures 5, 6 and 7. It is observed from results that dielectric constant, AC conductivity and DC conductivity of CdSe nanoparticles increase with increase in temperature. The measured values of the dielectric parameters are observed to be larger than those of conventional CdSe material.

Fig.5: Temperature dependence of dielectric constant for pellet form of CdSe nanoparticles

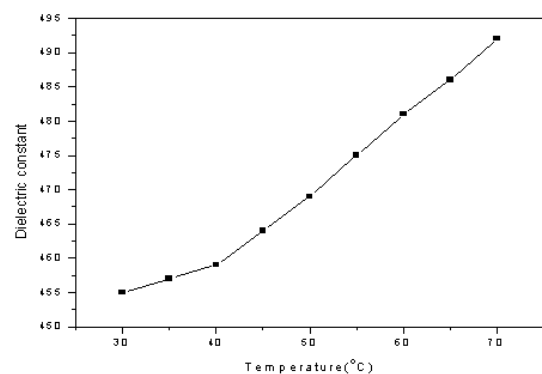


Fig.6: Temperature dependence of AC conductivity for pellet form of CdSe nanoparticles

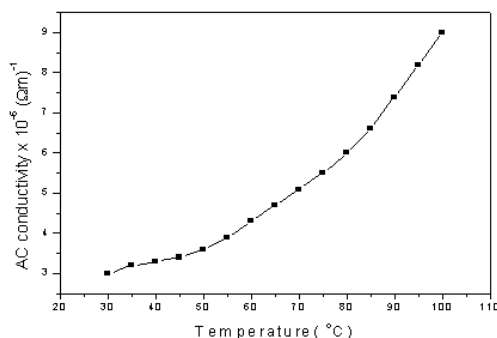
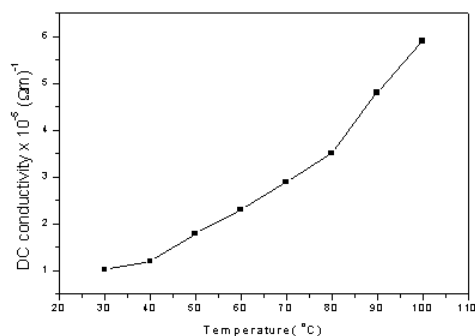


Fig.7: Variation of DC conductivity with temperature for pellet form of CdSe particles



The increase in AC and DC conductivity values with temperature shows the semiconducting nature of the sample. Due to thermionic emission and tunneling of charge carriers across the barrier, the conductivity increases with temperature. Because of small size of the particles, the charge carriers reach the surface of the particles more and easily enabling easy electron transfer by thermionic emission or tunneling to enhance the conductivity [30]. The conductivity values are fitted in the equation

$$\sigma_{ac \text{ or } dc} = \sigma_0 e^{-E/KT}$$

where σ_0 is the constant which depends upon the type of material and K is the Boltzmann's constant, T is the absolute temperature and E is the activation energy.

Taking natural logarithm on both side of the above equation,

$$\ln \sigma_{ac \text{ or } dc} = \ln \sigma_0 - E/KT$$

This is an equation of a straight line with a slope E/K . The activation energies of the synthesized nanoparticles of CdSe for AC and DC conduction processes were obtained to be 0.112 and 0.165 eV respectively.

Conclusion

Nanoparticles of CdSe were synthesized by using a domestic microwave oven. The synthesized sample was observed to be consisting of agglomeration of nanoparticles and nanorods. The crystal structure and the size of nanoparticles were found by XRD studies. AC and DC conductivities of the

pellet form of CdSe nanoparticles were determined and observed that they increase in increase with temperature. The activation energies for AC and DC conduction processes for the prepared CdSe sample were found. From UV-visible absorption spectrum, the absorption edge of the prepared CdSe sample was found to be 668 nm.

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References

1. M. Artemyev, D. Kisiel, S. Abmiotko, et al., J. Am. Chem. Soc. 126,10594 (2004)
2. D.J. Pena, J.K. Mbindyo, E.M. Thomas, et al., J. Phys. Chem., B 106 ,7458(2002)
3. Y. Xie, Z.P. Qiao, M. Chen, X.M. Liu, Y.T. Qian, Adv. Mater. 11 (1999) 1512.
4. Y.Lu, Y.Yin , B.T.Mayers, Y.Xia , Nano Lett. 2,183(2002).
5. M. Brightson, P. Selvarajan, John Kennady Vethanathan, T.H. Freeda, S. Meenakshi Sundar, Rec. Res. Sci. Tech. 2(6), 29(2010).
6. L. E. Brus, Al. Efros, and T. Itoh, J. Lumin. 76, 1 (1996).
7. R. Heitz, F. Guffarth, I. Mukhametzhanov, M. Grundmann, A. Madhukara, and D. Bimberg, Phys. Rev. B 62, 16881(2000).
8. S. Raymond, S. Fafard, P. J. Poole, A.Wojs, P. Hawrylak, S. Charbonneau, D. Leonard, R. Leon, P. M. Petroff, J. L. Merz, Phys. Rev. B 54, 11548 (1996).
9. S. Raymond, K. Hinzer, S. Fafard, and J. L. Merz, Phys. Rev. B 61,R16331 (2000).
10. W. C. W. Chan and S. Nie, Science, 281, 2016 (1998).
11. M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, Science, 281, 2013 (1998).
12. Zaban, O. I. Micic, B. A. Gregg, and A. J. Nozik, Langmuir, 14, 3153 (1998).
13. W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, Science, 295, 2425 (2002).
14. V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H.J.Eisler, and M. G. Bawendi, Science, 290, 314 (2000).
15. V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, Nature (London), 370, 354 (1994).
16. B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, and M. F. Rubner, Appl. Phys. Lett., 66, 1316 (1995).

17. S.K. Haram, B.M. Quinn, A.J. Bard, J. Am. Chem. Soc. 123 (2001)8860.
18. Z.L.Wang, X.Y.Kong , Y.Ding et al, Adv. Funct. Mater., 14, 943(2004).
19. S.Datta and B.Das, Appl.Phys.Lett., 56, 6651(1990)
20. Rajeev R. Prabhu and M. Abdul Khadar, Pramana-J. Phys., 65, 5, 801(2005).
21. X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich, A.P. Alivisatos, Nature 404,59 (2000).
22. K.B. Tang, Y.T. Qian, J.H. Zeng, X.G. Yang, Adv. Mater. 15,448 (2003).
23. B.D. Busbee, S.O. Obare, C.J. Murphy, Adv. Mater. 15,414 (2003).
24. W.X. Tu, H.F. Liu, J. Mater. Chem. 10, 2207(2000).
25. H. Wang, J. Z.Xu, J.J. Zhu, H.Y. Chen, J. Cryst. Growth 244, 88(2002).
26. C. Gabriel, S. Gabriel, E.H. Grant, B.S.J. Halstead, D.M.P. Mingos, Chem.Soc. Rev. 27, 213 (1998).
27. Hung-Yi Chang, Huey-Ing Chen, J. Crystal Growth 283,457 (2005).
28. P. Selvarajan, J. Glorium Arulraj , S. Perumal, Physica B, 405,738 (2010).
29. B. Sivasankari and P. Selvarajan J. Experimental Sci. 1(3), 1 (2010).
30. P. Mechant and C. Elbarum. Solid State Commun. 26,73(1978).