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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF ZnSe SEMICONDUCTOR NANOPARTICLES

MOHD. SHAKIR[a, b*], SIDDHARTHA[a], G. BHAGAVANNARAYANA[b], M.A. WAHAB[a]

[a]*Crystal Growth Laboratory, Dept. of physics, Jamia Millia Islamia, New Delhi-110025, India.*

[b]*X-Ray and crystal growth section, National Physical Laboratory, New Delhi-110012, India.*

Zinc Selenide nanoparticles were synthesized by a microwave irradiation technique at 2.8 GHz using 7N purity Zn and Se powder in stoichiometric ratio as the starting materials. The crystal system and phase was confirmed by powder X-ray diffraction, the crystallite size was calculated using Scherer's formula and found to be ~ 35 nm. Scanning electron microscope (SEM) also used to determine the size and shape of the nanoparticles which shows average particle size ~50 nm in agreement with PXRD and spherical in shape. The fluorescence study of ZnSe nanoparticles has been done and shows that the material is highly fluorescent. The broad emission peak at 401 nm (3.1 eV) has been observed in the fluorescence spectra this value is highly blue shifted towards the lower wavelength from the bulk value, which shows confinement effect. The temperature dependent electrical measurements on the synthesized nanoparticles were carried out. An anomaly in electrical studies was observed near ~ 488 K, which may be due to the glass phase transition. The resistivity of the synthesized nanoparticles was also calculated and found to be ~ $>10^9$ Ωcm.

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1. Introduction

Zinc Selenide is an attractive II-VI semiconducting material having a large band gap of 2.7 eV at room temperature, which attracted considerable attention owing to its wide applications in laser diodes, green-blue light-emitting diodes and solar cells [1]. ZnSe is also a promising material for windows, lenses, output couplers, beam expanders, and optically controlled switching due to its low absorptivity at infrared wavelength, visible transmission and giant photoresistivity [2]. A nanometer-sized semiconductor particle belongs to a state of matter in the transition regions between molecules and solids. From last two-three decades the research on quantum size semiconductor particles has increased enormously due to their exciting novel properties. Now-a-days, semiconductor nanocrystals/nanoparticles are very important materials due to their crystallite/particle size dependent electronic structure, which lead to give tunable electrical as well as optical properties [3–9]. The nanoparticles of ZnSe have been prepared by different methods like sol-gel method, melt quenched method, aqueous colloidal method, reverse miscell method, surfactant-assisted chemistry methods, sonochemical method, solvothermal routes, and vapor-phase synthesis [10-13, 14-16] etc. The naoparticles of many materials already have been synthesized by using microwave rapid heating process using chemical route [17,18].

*Corresponding author: shkirphysics@gmail.com

Generally, the semiconducting nanoparticles were synthesized by chemical methods and the particle size is controlled by using matrices or ligand shells which also prevents agglomeration of the nanometer size particles. However, these matrices or ligand shells might influence the electronic as well as optical properties of the material therefore it is more favorable to synthesize semiconductor nanoparticles free from these matrices or ligand shells. In the present investigation we have synthesized ZnSe nanoparticles with a homogeneous crystallite size within a short time from Zn and Se elements by a cost effective method known as microwave irradiation-[19]. The synthesized nanoparticles were subjected to powder X-ray diffraction to check the crystalline structure, lattice parameters and to calculate the crystallite size. The scanning electron microscopy study (SEM) was used to determine the particle size and shape. The fluorescence study has been done in the range of 320-800 nm. The DC electrical (dark, light) studies have been carried out by using Kiethely electrometer at various temperatures.

2. Experimental

The multimode vacuum able microwave furnace of 8.8 kW and 2.8 GHz was used for microwave synthesis of ZnSe nanoparticles. The high quality zinc and selenium powders (SIGMA ALDRICH) were used for the synthesis of ZnSe nanoparticles. The sample was loaded in the good quality quartz ampoule and vacuum sealed at 10^{-6} torr after sealing, the crucible was placed on the center of a thermal insulation package made of light and porous fiberfrax. We have made some modifications in the furnace, as the center was made moveable continuously for proper aging and mixing. The heating process was programmed through the Eurotherm controller. The content of the crucible become reddish yellow within 30 min. The yellow color of the material confirms the synthesis of ZnSe. The synthesized material was taken outside from the ampoule which was in sponge form.

The synthesize nanoparticles were subjected to powder X-ray diffraction to know the crystalline phase presents in the synthesized compound using PW3710 based Philips Analytical powder X-ray diffractometer with nickel filtered, CuKα radiation (35 kV, 30 mA). The specimen was scanned for the angular range 5–60 $^{\circ}$ of 2-theta with the scan rate of 0.001°/s. The scanning electron microscope (SEM) has been used to find out the morphology and size of the synthesized nanoparticles of the titled material. The fluorescence study was carried out on the synthesized nanoparticles by using Perkin Elmer LS-55, Fluorescence spectrofluoremeter in the wavelength range of 330 to 600 nm. To study the electrical properties of the synthesized nanoparticles of ZnSe, a pallet of diameter 12 mm and thickness 1 mm have been prepared using a hydraulic press machine. Dark conductivity was measured in the temperature range of 300–533 K under high vacuum more than 10^{-5} Torr by Keithley electrometer (Model 4200-SCS) using a coplanar Al contact geometry with a gap of 0.07 cm. Photoconductivity was also measured under the illumination of ~100 mW/cm^2 at above said temperatures.

3. Results and discussion

The powder X–ray diffraction pattern as shown in Fig.1 was recorded of the synthesized nanoparticles of ZnSe. The room temperature PXRD data is analyzed using “X'Pert HighScore Plus” and Chekcell software for calculating cell parameters and refined the obtained cell parameters, respectively. The refined values were found to be of cubic phase with cell parameter a=b=c=5.6609 Å and$\alpha=\beta=\gamma=90^{0}$, which is in good agreement with the earlier reported value [19,20]. The crystallite size of the synthesized ZnSe nanoparticle was calculated using Scherer’s formula $D = 0.9\lambda / \beta\cos\theta$; where, D is the average crystallite size, λ is the X-ray wavelength (1.54056 Å) and β is full width at half maximum in radian. The average crystallite size for (111) planes was found to be ~35 nm. The sharpness of the powder XRD peaks also shows good crystallinity of nanoparticles.

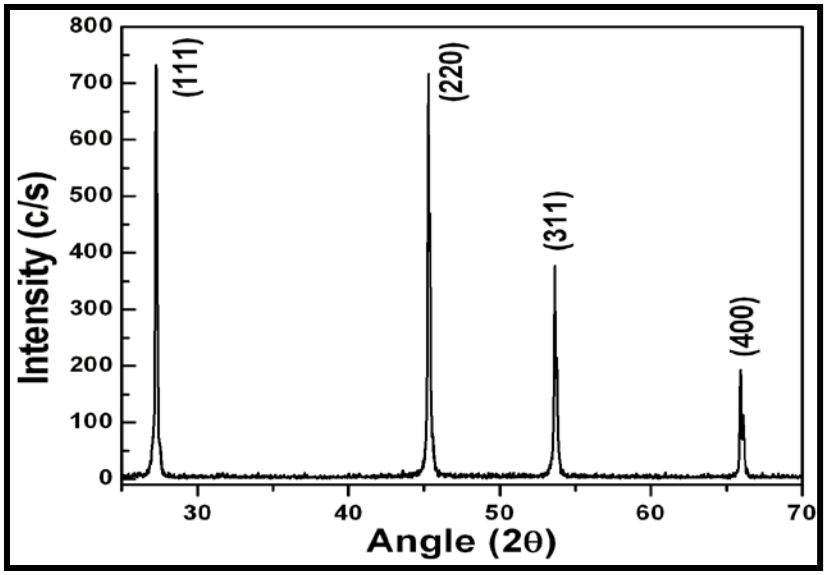

Figure 1 Powder XRD pattern of synthesized ZnSe nanoparticles.

Fig. 2 shows the micrograph of the synthesized ZnSe nanopowder investigated by SEM at magnification 10,000 which shows that the highly dense and homogeneous distribution of the nanoparticles over a wide range of samples. The average particle size was found to be ~50 nm which is in good agreement with the XRD results.

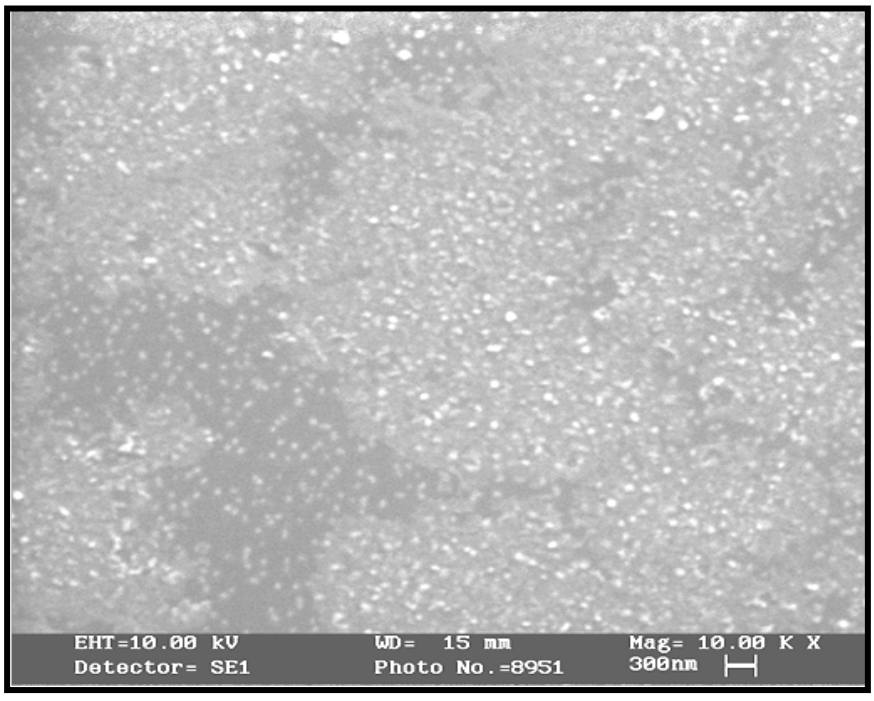

Figure 2 SEM micrograph for ZnSe nanoparticles.

Fig. 3 shows a typical room temperature fluorescence spectrum of ZnSe nanoparticles excited at 327 nm, which exhibits a very broad and stable emission peak centered at 401 nm (3.1 eV), which can be attributed to the excitonic emission [21]. In fact that the PL of ZnSe crystals or

thin films is usually reported to occurred at 442 nm for band gap emission or 500-600 nm for doped ion emission [22,23]. The broadening and blue shifting in the emission peaks towards the lower wavelength and high band gap (3.1 eV) reveals that the particle size is very small. As a result, such type of blue shift and broadening of the band gap will occur [24] due to confinement effect.

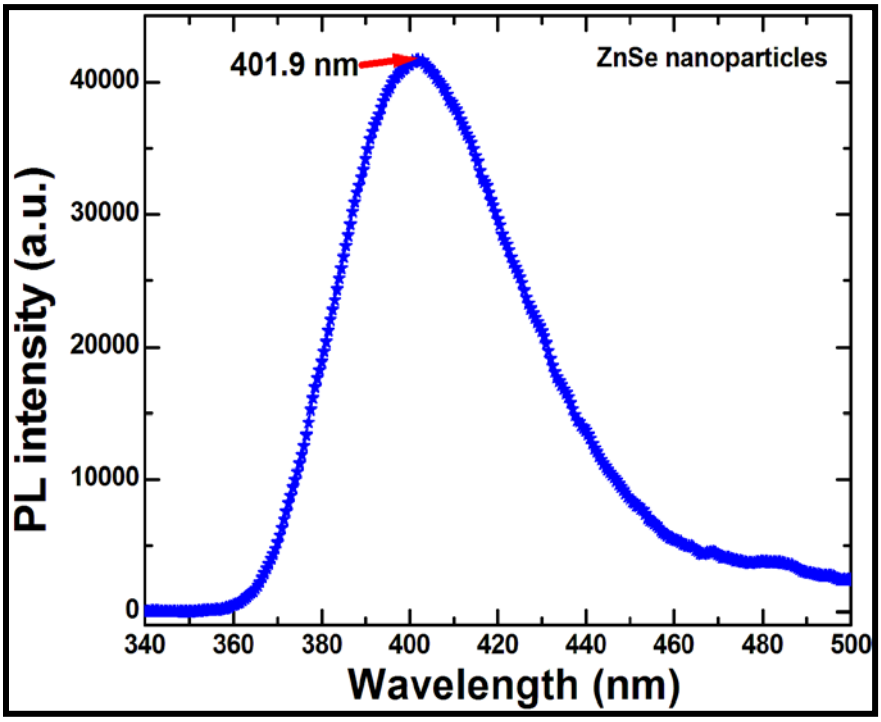

Figure 3 Fluorescence spectra for ZnSe nanoparticles.

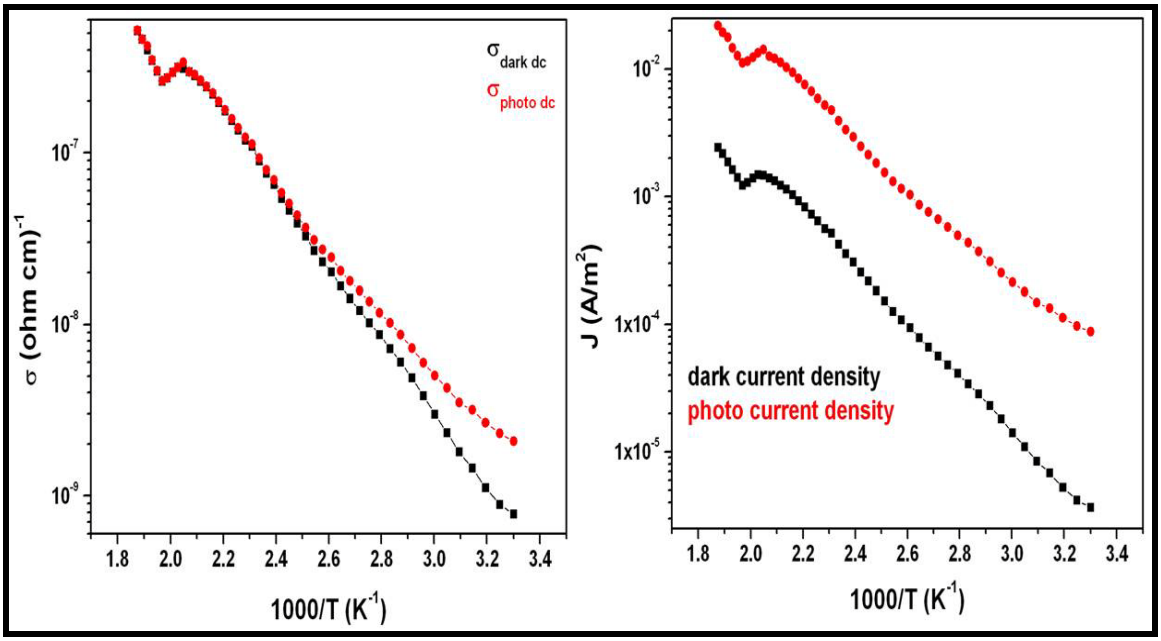

Figure 4 (a) Electrical conductivity and (b) electrical current density graphs for the synthesized ZnSe nanoparticles.

The electrical conductivity and current density (dark and photo) with temperature of the synthesized nanoparticles are shown in Fig. 4 (a) & (b). The dark and photo conductivity is increasing with temperature in the ZnSe nanoparticles as shown in Fig 4 (a). The I region of the graph from 301 to 371K is the impurity exhaustion temperature. This region is identified with the extrinsic conductivity of ZnSe semiconductor nanoparticles due to the ionization of impurity atoms [25,26]. In this region, all the 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 impurty concentration. Therefore, the temperature dependence of the conductivity of the semiconductor is decided by that of the carrier mobility. On the other hand, if the main scattering mechanism is scattered by ionized impurities, the conductivity within the intermediate region will also increase with rising temperature. The II region region from 371K to 485K is identified with the transition to intrinsic conduction in semiconductor. Within this region, the density of carriers is equal to that of intrinsic carriers [27]. After 485 K an anomaly was observed at 488 K as shown in Fig 4 (a), which indicates to the glass phase transition as observed in the dielectric study of ZnSe nanoparticles [20]. It is also clear from the figure that the photoconductivity is higher than the dark conductivity from 300 to 383 K but after this it's having similar trend [Fig. 4 (a)]. The resistivity of the synthesized nanoparticles was calculated and found to be ~ $>10^9$ Ωcm at room temperature this value is very high then the reported value of bulk and thin film of ZnSe [28,29]. The current densities were also calculated as shown in Fig. 2 (b). From figure it is clear that the photo current density is higher than the dark current density. The variation in electrical properties may be due to the change in size of nanoparticles with temperature.

4. Conclusions

In the present investigation we have observed high resistivity (~$>10^9$ Ωcm) of ZnSe nanoparticles synthesized by microwave heating process. The X-ray diffraction study confirms that there is no phase of Zn or Se separately in the synthesized ZnSe nanoparticles. The calculated crystallite size was found ~35 nm while the particle size obtained by SEM was ~50 nm. The optical band gap of the synthesized nanoparticles was found ~3.1 eV which is higher than bulk material and shows the blue shifting due to the crystallite size. The observed broadness, high intensity and blue shifts in the emission peak of PL spectra indicate the confinement effect which may be due to the wide distribution of the nanoparticle/crystallite size. The dark and photo conductivity are increasing with temperature, the value of photo conductivity was found higher than the dark conductivity. The photo current density is also higher than the dark current density. The high band gap, photoconductivity, current density and fluorescence intensity, shows that the synthesized nanoparticles are may be very useful for fabrication of optoelectronic devices.

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