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Structural, Optical and Thermal Studies on Luminescent Cadmium Selinide Nanoparticles

S. Nima Jessieba Daniel[1], N. Joseph John[2]
[1]Department of Physics, Govt. Arts College, Udhagamandalam,Tamilnadu, India.
[2]Department of Physics, Kamarajar Govt. Arts College, Surandai, Tamilnadu, India.

Abstract: ***The microwave assisted solvothermal synthesis has been explored for the preparation of CdSe semiconductor nanoparticles. The precursors used were cadmium acetate dihydrate and sodium selenite. A mixture of ethylene glycol and waterwas used as solvent to control the size of the nanoparticles. XRD study shows that the average size of CdSe nanocrystallite is found to be 10 nm with hexagonal wurtzite structure.XRD, SEM, EDX and FTIR studies confirm the morphology and composition of CdSe nanocrystals. The optical band gap energy of the material was estimated to be 3eV from UV-Visible spectrum. Uniform absorbance is observed throughout the UV region, and visible region up to 600nm.A sharp intense blue emission peak is observed in the Photoluminescence spectrum at 425nm. Thermogravimetric analysis (TGA) shows that the prepared CdSe nanoparticles are very stable up to 650^{0}C.***

Keywords: **Solvothermal, Semiconductor, Wurtzite, Photoluminescence, Thermogravimetry**

I. INTRODUCTION

Nanoscale materials having the size in between molecules and micromaterials exhibit peculiar properties different from the properties of the bulk materials and the molecules.

As the size of the material decreases, the quantum size effect becomes prominent where the electronic properties of solids are altered in turn increases the surface area to volume ratio which changes the mechanical, thermal and optical properties of materials significantly. The nanoparticles frequently display photoluminescence and sometimes display electroluminescence [1-6]. Semiconductor nanocrystals, also called quantum dots (QDs), are fluorescent inorganic particles with typical diameters ranging from 1 to 10 nm[6-12]. Such materials have electronic properties intermediate between those of bulk semiconductors and those of discrete molecules.

At this dimension, the surface area to volume ratio of the particles is amplified and the surface atoms become dominant contribution to the physical and chemical properties [13,14]. So the properties of nanomaterials become very different from those of their corresponding bulk materials or isolated atoms and molecules[15,16]. Among semiconductor nanomaterials CdSe QDs have wide band gap and probably the most extensively investigated II-VI semiconductor nanoparticles because of their luminescence to be tuned across the visible spectrum by changing their size [9,17].

CdSe nanocrystals show unique and fascinating optical properties that are useful in the fields of photovoltaic devices, light emitting diodes, laser diodes, biological imaging and bio diagnostics [12]. Cadmium selenide (CdSe) can exist either in solid hexagonal or cubic crystal structures [12]. CdSe have been considered as n-type semiconductor material with a direct band gap ~1.74eV at room temperature [12,17].

A variety of techniques have been developed to synthesize CdSe nanoparticles. Most methods currently used to synthesize nanomaterials are complex, require specific equipment and produce small amounts of nanomaterials. The objective of this work is to combine both advantages of the robust solvothemal synthesis and the rapid and efficient microwave heating for the fast preparation of nanometerials. Therefore microwave-assisted solvothermal methods are eminently suited for the synthesis of nanometals of controlled size and shape[18,31].

In order to obtain small and uniform particles, organic additives are often used to stabilize the particles in solution and control particle growth. In microwave heating the effect of heating is created by the interaction of the permanent dipole moment of the molecule with the high frequency (2.45 GHz) electromagnetic radiation. Polyol solvents like ethylene glycol are verymuch suitable for microwave reactions because of their relatively high dipole moment. Another advantage of using ethylene glycol as a solvent is its reducing power. [19] .In this work the microwave assisted solvothermal synthesis has been explored for the preparation of cadmium selenide semiconductor nanoparticles.

II. EXPERIMENTAL

1) *Synthesis of CdSe Nanoparticles:* The precursors used were cadmium acetate dihydrate and sodium selenite. A mixture of ethylene glycol and distilled water was used as solvent. All the chemicals were analytical grade and were used without any further purification[20,21]. Cadmium acetate dihydrate and sodium selenite in the molar ratio 2:1 were dissolved in ethylene glycol and water and stirred well using a magnetic stirrer till it dissolves completely. This solution mixture is kept in a microwave oven and heated until the solvent got evaporated. The colloidal precipitate formed was collected and cooled to room temperature. Then the product obtained was washed several times with doubly distilled water and acetone and filtered. The precipitate thus formed is collected and dried. The dried sample is annealed for 1 hour at 100^0C. The total product mass was measured for the sample to find the yield percentage.
2) *Instrumentation:* The powder XRD pattern for the as prepared sample was done using Bruker AXS D8 Advance diffractometer with Copper target and Cu-Kα (λ=1.5406 Å) radiation. Scanning electron microscope (SEM) was employed for morphological study using Hitachi S-3400 N operated at 3kV. Energy Dispersive X-ray EDX analysis was done using Oxford XMX N EDX analyzer. The UV-Vis absorption spectral studies were carried out using VARIAN 5000 UV-Vis-NIR Spectrophotometer in the spectral region of 200 and 800 nm. The photoluminescence spectra of the samples were recorded with a VARIAN ECLIPSE Fluorescence Spectrophotometer. Thermogravimetric (TG) and Differential thermo gravimetric analysis (DTG) for the air dried sample was performed on a Q600 SDT Thermal analyzer at a heating rate of 20 °C min-1

III. RESULTS AND DISCUSSION

A. Powder X-Ray Diffraction Measurements

Powder X-Ray Diffraction Analysis (XRD) is the major tool for determining the structure of crystalline materials and imperfections. X-ray diffraction data were collected from powder samples of nanoparticles using an automated X-ray diffractometer. The reflections were indexed and lattice parameters were determined. Also the sizes of the samples were calculated by Debye-Scherrer formula. [22-25]

$$D = 0.9\lambda / \beta \cos\theta \qquad \text{\_ (1)}$$

Where D is the mean size (diameter) of the crystallite, β is the full width at half maximum of intensity (in radians), λ is the wavelength of the X- ray radiation used (1.5406 AU), and θ is half the angle at which maximum intensity was observed

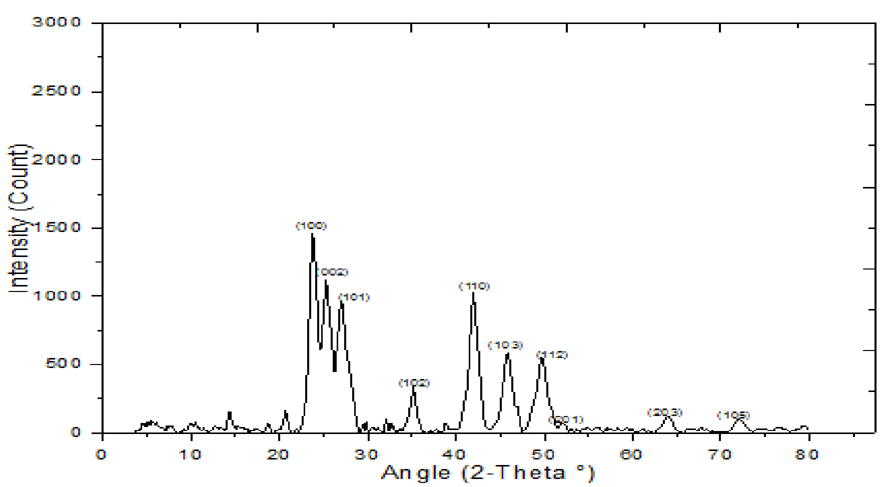

Fig.1 XRD pattern of CdSe nanoparicles

The phase compositions and structural properties of the material was studied using X-ray diffractometer (XRD), Bruker AXS D8 Advance with CuKα radiation, having λ= 1.5406 Å. The broadened diffraction peaks indicate the nanocrystalline nature. The intensity of the peaks shows that the CdSe nanoparticles are highly crystalline. All the observed peaks match with the pattern of crystalline phase of hexagonal wurtzite structure of CdSe (ICSD PDF-008-0459) with space group $P63_{mc}$(186) and unit cell parameters a=b=4.299A^o , c=7.01A^o.and z = 2. The strong and sharp diffraction peaks at angles(2θ) are located at 23.7, 25.3, 27.02,35.15,41.98,45.8 and 49.69 corresponding to (100), (002), (101), (102), (110),(103), and (112) crystal planes. The average crystallite size calculated using Debye-Scherrer formula is 10nm. The size of the particles ranges from 6nm to 20nm

B. Energy Dispersive X-Ray Spectroscopy (EDX)

EDX is an important technique to analyse the composition of elements quantitatively and to find the chemical identity of materials. The EDX studies on the as prepared nanoparticles confirm the presence of Cd and Se. No trace of other elements are observed. From the EDX analysis, it is clear that the obtained products are cadmium selenide nanoparticles.

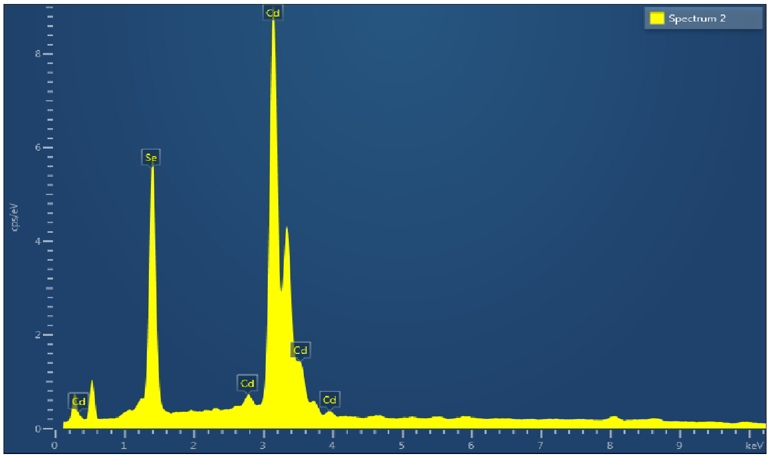

Fig.2 EDX spectrum of CdSe nanoparticles

C. Scanning Electron Microscope (SEM)

Scanning electron microscopy (SEM) was carried out to analyze the morphology and the growth features of the particles of the as prepared nanoparticles. SEM images of as prepared Cadmium selenide nanoparticles are shown in Fig 3, which shows the absence of agglomeration. A close observation of the SEM image suggests that the surfaces of the nanospheres are relatively smooth and there are few prolated spheres as well and this could be attributed to the solvent Ethylene glycol in microwave heating. The pictures confirm the formation of spherical cadmium selenide quantumdots.

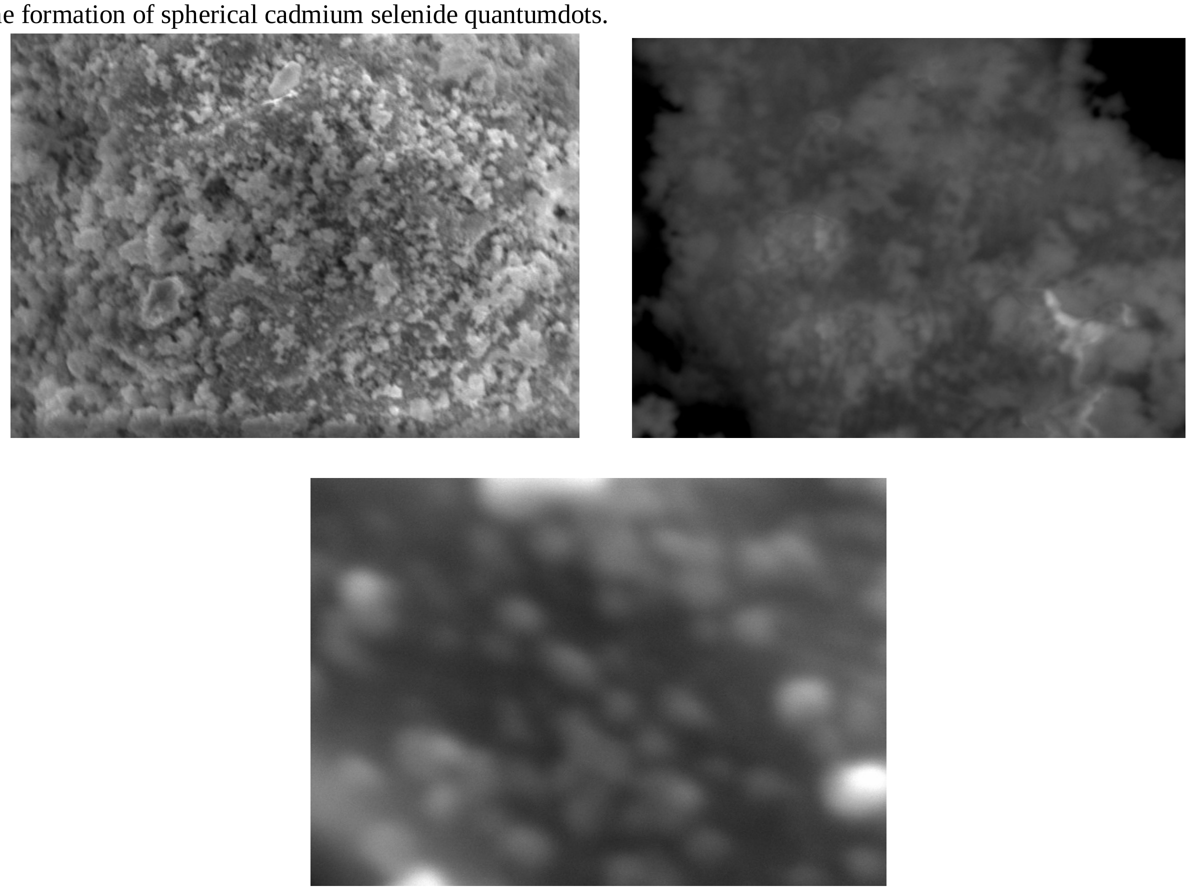

Fig.3 SEM micrograph of CdSe nanoparticles

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D. UV-Vis Absorption Spectroscopy

Ultraviolet-visible (UV-Vis) absorption spectroscopy involves the spectroscopy of absorption of photons in the UV-visible region. This means it uses light in the visible, adjacent (near ultraviolet (UV) and near infrared (NIR)) region. Fig. 4(a) shows the absorption spectrum of Cadmium Selenide nanparticles synthesized by microwave assisted solvothermal process in the wavelength range 200- 800 nm. An absorption peak at 214 nm is observed in the absorption spectrum.. It can be seen from the spectrum that there is uniform absorption in the UV and visible region. The absorption spectroscopy is very useful to calculate the optical band gap (Eg). From the classical relationship of near edge optical absorption of semiconductors[26]:

$$A = k\,(h\nu - E_g)^{n/2} / h\nu \qquad \text{\_ (2)}$$

Where k is constant, Eg is the optical band gap and n is a constant equal to 1 for direct band-gap semiconductors. The plot of $(\alpha h\nu)^2$ vs. hν is shown in Fig. 4(b). Extrapolating the straight line of this plot for zero absorption coefficient it gives the direct band gap of nanoparticles which is shown in Fig. 4(b). The direct band gap energy (Eg) of CdSe nanoparticle was found to be

3eV that represent the 'blue shift' of 1.26 eV from standard bulk band gap (Eg = 1.74 eV).[27,28] The blue shift might be caused by quantum confinement and structural defects of nanocrystals[26]. Fig 4(c) shows the diffused reflectance spectrum of as prepared CdSe nanoparticles.

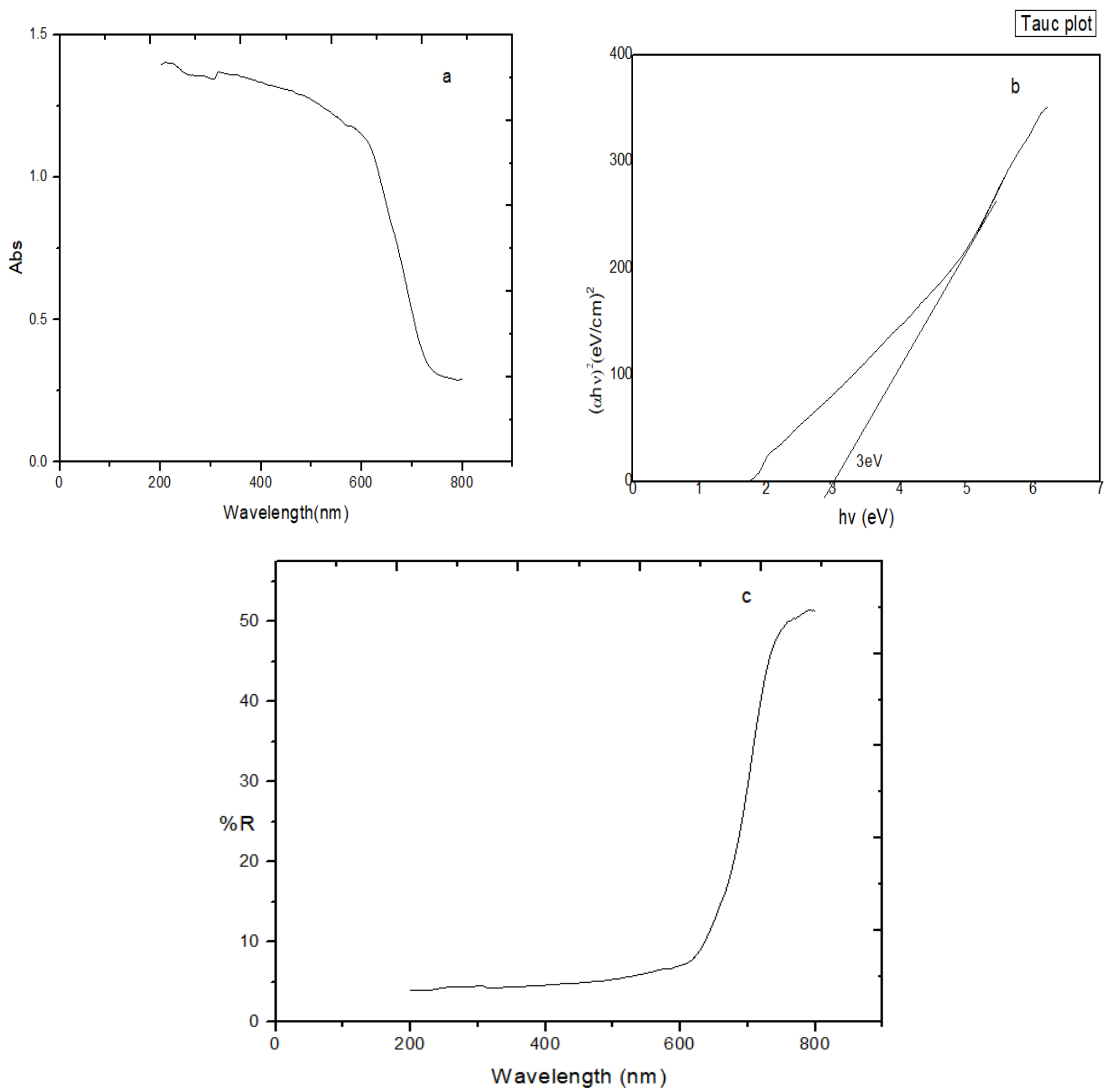

Fig. 4 (a) UV-VIS-IR Absorption spectrum of CdSe nanoparticles (b) Taucplot of CdSe nanoparticles (c) Diffused reflection spectrum of CdSe nanoparticles

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E. FTIR Spectroscopy

The surface morphology of the as synthesized material was investigated using FT-IR spectroscopy of the particles. FTIR spectra of CdSe nanoparticles prepared by solvothermal process is shown in fig5. The charecteristic vibrational peaks at 493 cm-1, and 763 cm-1confirms the presence of Cd-Se band stretching[17,29-30]. In the higher energy region the peak at 3427cm-1 is assigned to O-H stretching of absorbed water on the surface of CdSe nanoparticles[29]. The weak peak at 1455cm-1 and medium peak at 1309cm-1 is assigned to O-H bending. The strong peak at 1622cm-1 is assigned to C=C bending represents the presence of alkene. This may be due to capping of ethylene glycol.

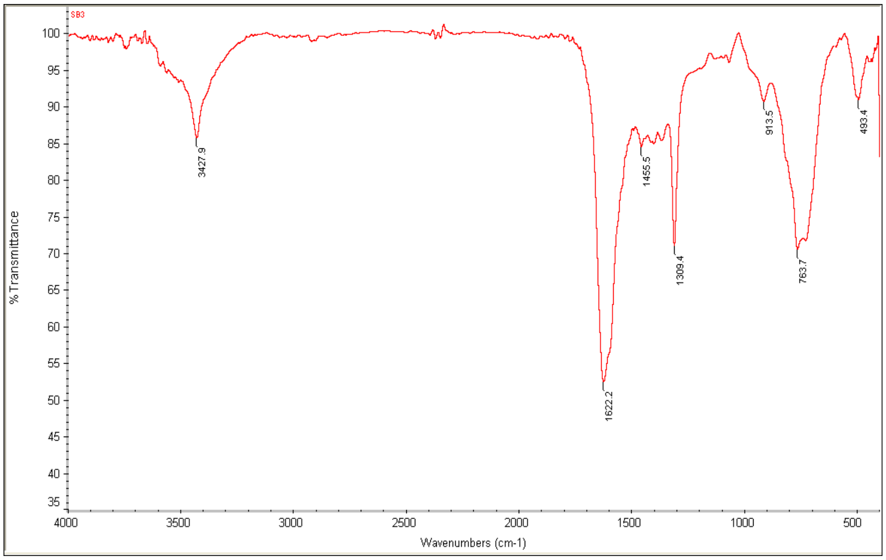

Fig. 5 The FTIR spectrum of CdSe nanoparticles

F. Photoluminescence (PL) studies

Photoluminescence is the measure of photo absorption in direct band gap material, from which the light emission of the material of particular wavelength can be determined. To investigate the luminescence property of as synthesized CdSe nanoparticles, the PL spectral analysis have been performed. The photoluminescence spectra was recorded in the range of 400 - 800 nm as shown in fig 6. It is observed that the photoluminescence spectrum consist of a highly intense band centered at 425nm and less intense peak at 466nm at excitation wave length 380 nm whereas PL peak of bulk CdSe is 720 nm. [19] Usually for semiconductor nanomaterials, two emission peaks can be observed due to exciton and trapped luminescence, among which the exciton emission peak is sharp and trapped emission is broad. The luminescence is produced when the valence electron is excited with certain energy, they emit energy in the form of photons as the excited electron returns to the ground state.[5]

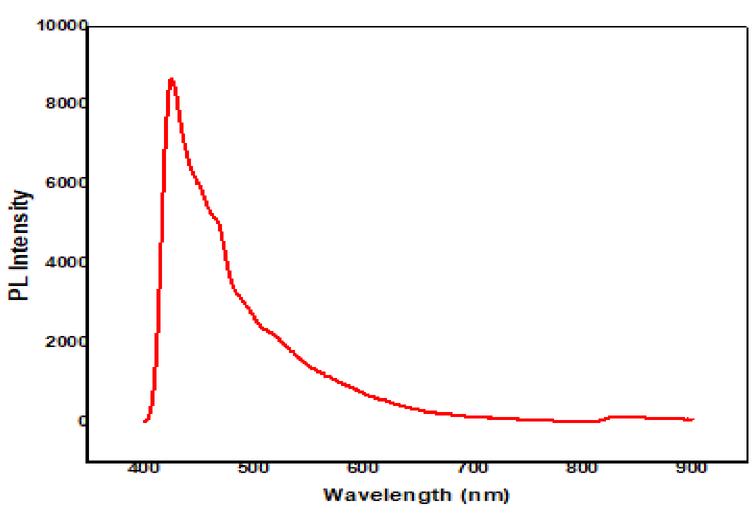

Fig. 6 The photoluminescence spectrum of CdSe nanoparticles

G. Thermal Measurements (TGA)

The thermogravimetric curve of as prepared Cadmium Selenide nanoparticles by solvothermal process shows two major weight losses. It is observed from the thermogram that the material is stable up to 650^{0}C indicating good stability of the material. From 650^{0}C to 675^{0}C a small mass loss of 6.7 % is observed due to endothermic effect. From 675^{0}C to 750^{0}C mass loss of 18% is observed due to exothermic effect. It is observed that the decomposing of the material started from 850^{0}C.

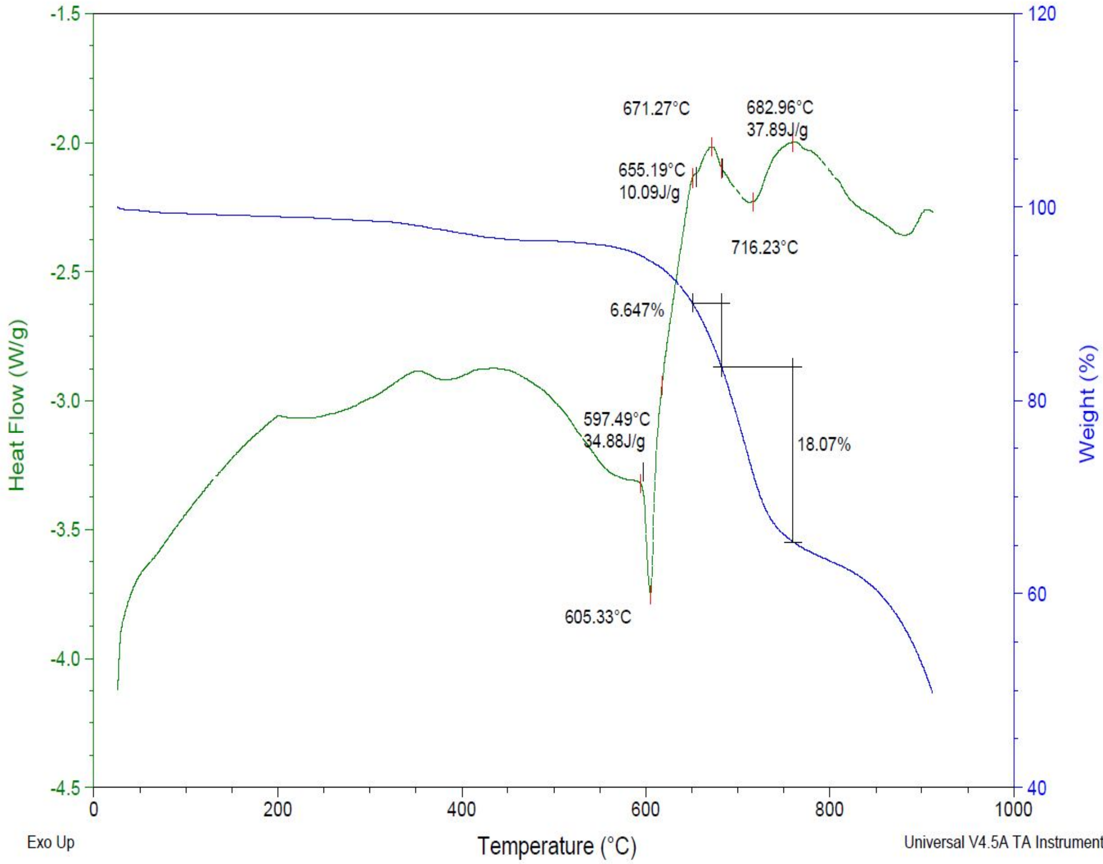

Fig. 7 TGA curve of Cadmium Selenide nanoparticles

H. Yield percentage

The yield percentage was calculated using the relation [31].

Yield Percentage = (Total product mass / Sum of the mass of the reactants) ×100% _(3)

The color of the sample prepared by solvothermal method is Brown and the yield percentage is found to be 46%.

IV. CONCLUSION

The nano structured Hexagonal Cadmium Selenide nanoparticles were prepared by a simple method using domestic microwave oven. The prepared materials were characterized and confirmed that the size were in nanoscale by XRD analysis. The optical band gap energy of the material was estimated to be 3eV by microwave assisted solvothermal method using UV-Visible spectrum. Uniform absorbance is observed throughout the UV and visible region. EDX analysis results confirm the presence of Cd and Se in the prepared samples. PL spectrum of the samples exhibits a sharp, intense peak at 425 nm and 466nm. From the results obtained it is evident that this material has good optical qualities and is well suited for optoelectronic devices.

V. ACKNOWLEDGMENT

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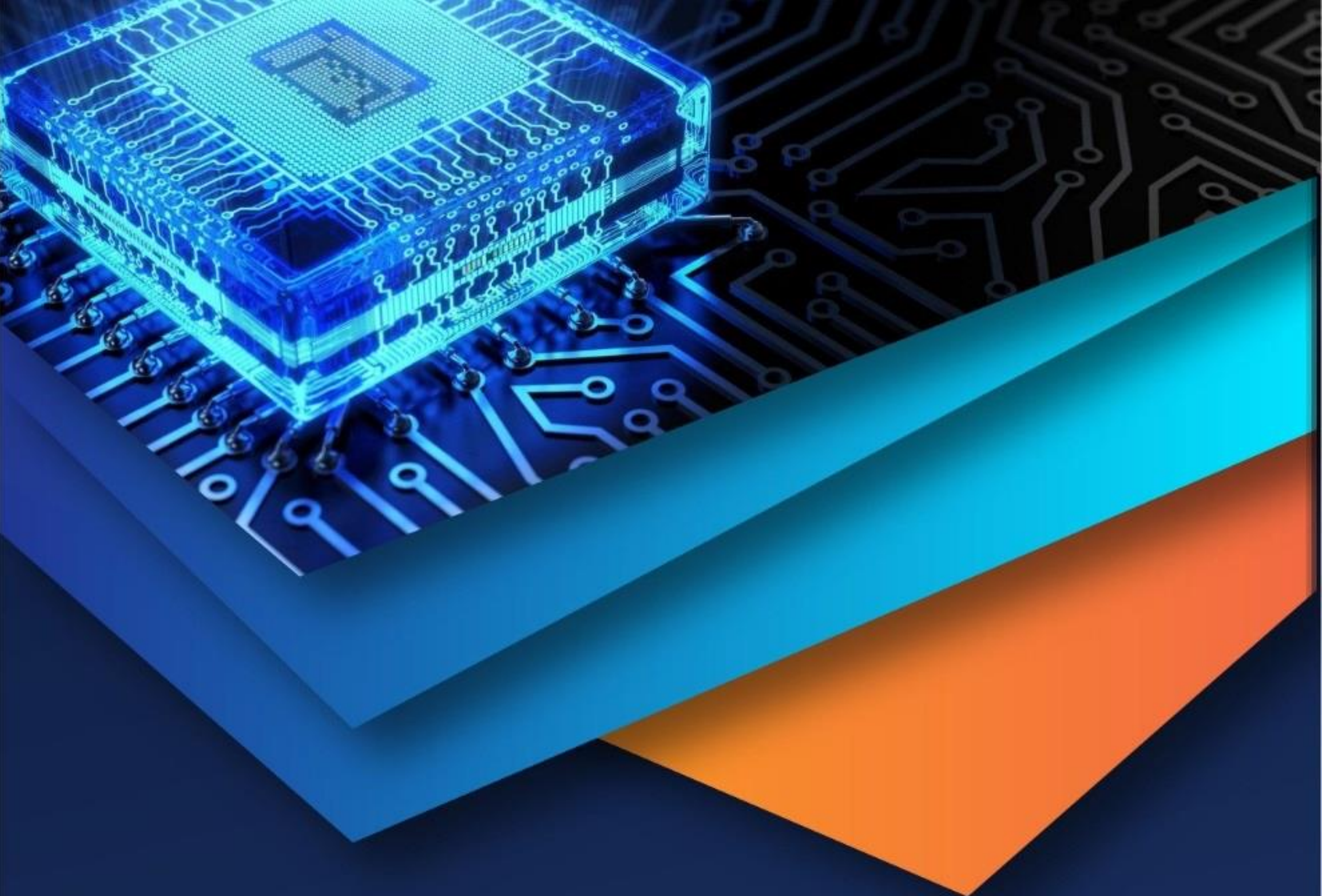

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