

Luminescence studies of 120 MeV Fe³⁺ ions Irradiated Cu Doped ZnTe Quantum Dots

Lalit Baruah^{1,2}, B. I. Sharma² and Siddhartha S. Nath^{3,*}

¹*Department of Physics, Biswanath College, Chariali, Assam.*

²*Department of Physics, Assam University, Silchar, India*

³*Central Instrumentation Laboratory, Assam University, Silchar, India.*

Abstract

Efficient Cu-doped ZnTe quantum dots (ZnTe:Cu QDs) have been successfully synthesized by chemical route at a moderate temperature. Prepared samples were irradiated with 120 MeV Fe³⁺ Swift Heavy Ions (SHIs). Irradiated samples cover the important green window for nano light emitting devices at 560 to 569 nm. X-ray diffraction (XRD), high resolution transmission electron microscope (HRTEM) and Scanning electron microscope (SEM) studies have been carried out on the unirradiated and irradiated samples of ZnTe:Cu. UV-Vis absorption spectra of irradiated samples show a slight shift of absorption edge towards higher wavelength with the increase of fluence. Moreover, intense luminescent peaks (FL & EL) are observed at green region for the irradiated samples. Significantly better luminescent peaks are achieved at the same wave length for the irradiated samples.

Keywords: Electroluminescence, SHI irradiation, Fluence, Copper doped.

INTRODUCTION

Synthesis of doped semiconductor nanoparticles have recently become an attractive subject in the field of material science for their peculiar electronic, optical and magnetic properties (1-6). By introducing transition metal dopants, quantum size effect and atomic band transition (2,3) are quite different from undoped nanoparticles.

Swift heavy ion (SHI) irradiation plays a crucial role in modifying the properties of thin films, foils, and surfaces of bulk solids. SHI penetrate deep into the material and produce a long and narrow disordered zone along their trajectory (6,7). Effect of the ion beam on the materials depends on the ion energy, fluence, temperature, and ion species (8). The irradiation effects in semiconductor materials are known to be manifested as changes in the physical, optical, and electrical properties (9). The synthesis of highly monodisperse quantum dots (QDs) over a range of chemical composition is still a challenge in material science. Several manufacturing techniques that usually employ molecular processing in vacuum or liquid medium are in use (10). Most of the techniques are expensive, as well as inefficient in materials and energy use. Hence, there is an ever-growing need to develop cheap and nontoxic synthesis procedures. But only few reports are available about the preparation of ZnTe QDs. Dwivedi et al. (11) prepared ZnTe nanoparticles of 2.6 nm based on the chemical replacement reaction among the chemical compounds.

This study concerns the preparation of copper doped zinc telluride (ZnTe:Cu) quantum dots through chemical route and irradiated with Fe^{3+} ions with 120 MeV at different fluence. The effect of SHI irradiation on luminescence (FL & EL) of ZnTe:Cu quantum dots is completely a piece of novel work that has been explored by the investigators. These studies demonstrated a significant enhancement of luminescence in case of irradiated samples at a fluence of 3×10^{12} ions/cm². X-ray diffraction, HRTEM and SEM and UV-vis absorbance analysis of pre and post irradiated samples are also presented and discussed.

EXPERIMENTAL

Zinc acetate and tellurium powder are obtained from Merck (India) chemicals. Ethylene glycol, hydrazine hydrate and anhydrous ethanol are purchased from SRL (India) chemicals. All of them are used without any further purification. De-ionized water has been used throughout the experiment.

To prepare Copper doped ZnTe QDs, hydrazine hydrate, ethylene glycol and de-ionised water are mixed in the volume ratio of 1:3:6 respectively. Then, 0.6 g zinc acetate and 0.638 g tellurium powder are poured into the conical flask. The solution is refluxed under vigorous stirring at 300 °C and Copper Chloride is poured with the solution and stirred for 6 h. When the reaction is over the greenish brown precipitate is collected and washed with anhydrous ethanol and hot distilled water for several times. Then it dried in vacuum at 50 °C for 6 h.

Copper doped zinc telluride thin films are grown on glass substrate and irradiated at room temperature with 120 MeV Fe^{3+} ions with fluence of 1×10^{11} (BS1), 3×10^{11} (BS2), 1×10^{12} (BS3) and 3×10^{12} (BS4) ions/cm². The ion beam current was kept

as 1 pA ($\sim 6 \cdot 25 \times 10^9$ ions/s) to avoid any heating effect. The ion beam was scanned over an area of 10×10 mm² using electrostatic scanner to uniformly irradiate the whole sample. The crystalline phase of the ZnTe:Cu thin films are characterized using an X-ray powder diffractometer (Bruker, $\lambda=1.5418$ Å). The surface morphology was examined using scanning electron microscopy (JSM 6390LV). HRTEM observations are performed by using a Jeol JEM-2100 transmission electron microscope, operating at 200 kV accelerating voltage, with an interpretable resolution limit of 0.16 nm. UV–visible absorption spectra are recorded using a Perkin Elmer Lambda-35 UV–visible spectrophotometer. Fluorescence (FL) spectra of the samples are recorded with Perkin Elmer LS-45 Fluorescence spectrometer. Optical measurements are carried out at room temperature under ambient condition.

RESULTS AND DISCUSSION

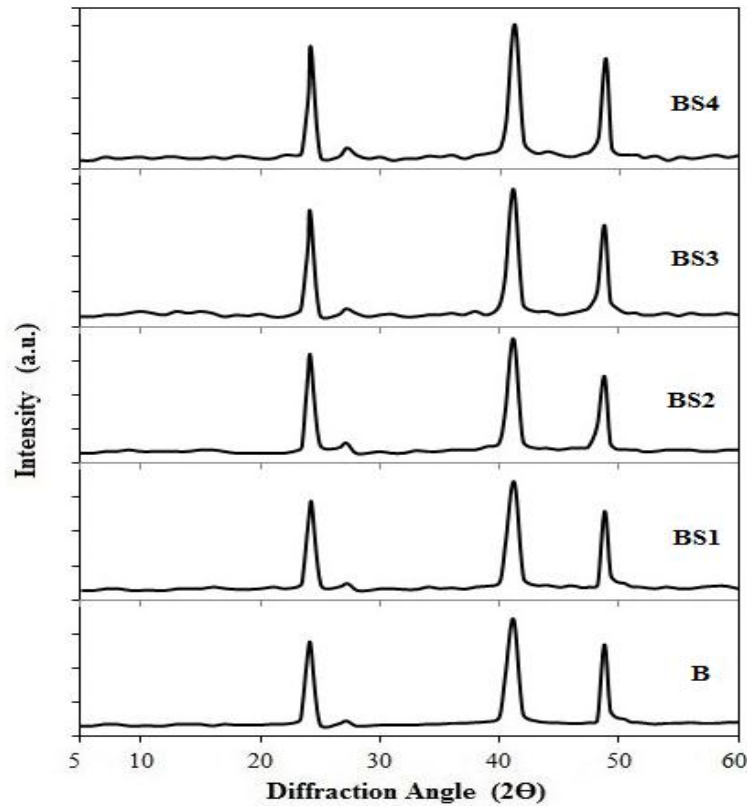


Fig-1 X-ray diffraction patterns of ZnTe:Cu samples with different fluence.

Fig. 1 presents the X-ray diffraction patterns of the unirradiated and irradiated ZnTe:Cu samples with 120 MeV Fe^{3+} ions for the fluence of 1×10^{11} , 3×10^{11} , 1×10^{12} and 3×10^{12} ions/cm². All unirradiated and irradiated samples exhibited peaks at

$2\theta = 24.2^\circ$, 41.2° , and 48.8° respectively, which correspond to the lattice planes $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 200 \rangle$ confirming the formation of cubic structure of ZnTe:Cu. No change in the phase of ZnTe:Cu was observed after ion irradiation. The average particle diameters of the sample were calculated using Debye-Scherrer's formula (12,13). The average particle size 'd' is found to be 8.8 nm for unirradiated samples remain unaltered 8.8 nm and 9 nm with ion fluence 1×10^{11} (BS1), 3×10^{11} (BS2) and 1×10^{12} ions/cm² (BS3) respectively, but slightly increased upto 11.4 nm at higher fluence 3×10^{12} ions/cm², BS4.

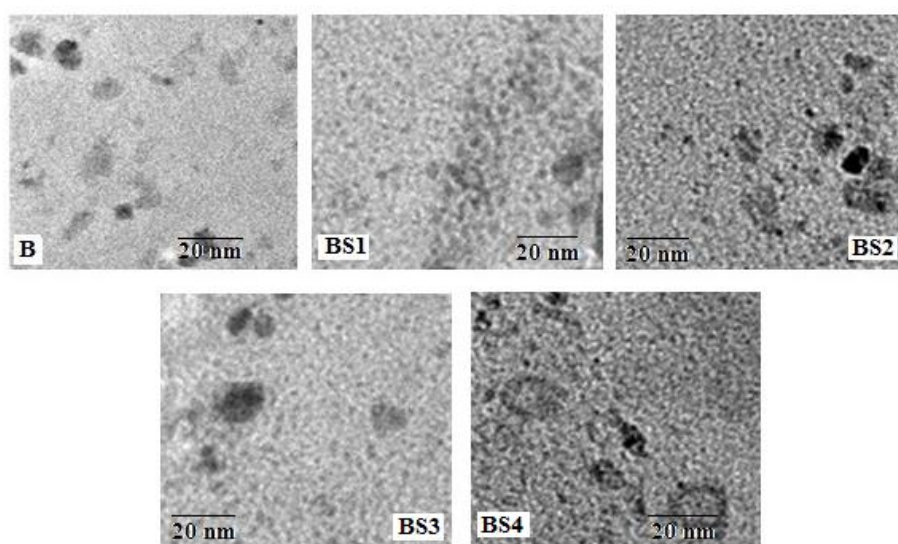


Fig-2 High-resolution (HR) TEM images of unirradiated and irradiated samples ZnTe:Cu QDs.

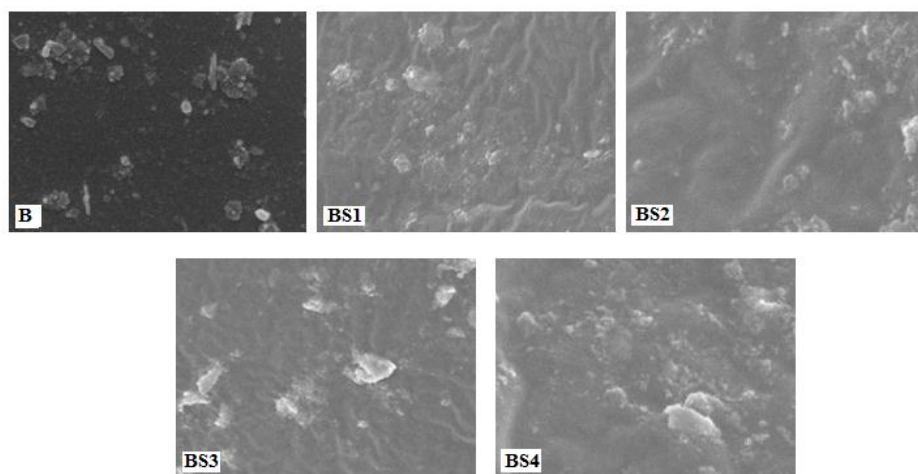


Fig-3 SEM images of unirradiated and irradiated samples ZnTe:Cu QDs at different fluence.

The Morphology of the ZnTe:Cu QDs are observed by TEM and SEM as shown in fig. 2 and fig. 3. It is evident from the TEM (HR) micrographs that the average size of particles as directly measured from the ruler of the image is 2-14 nm. The micrograph show clearly endorses the formation of well-separated and crystalline nanoparticles of ZnTe:Cu. The sizes of particles remain unchanged for the samples irradiated at lower fluence. At higher fluence (BS4), size of particles slightly large, which are probably due to dispersion of the particles in the sample. The SEM images of irradiated samples reveals the rough surfaces of ZnTe:Cu QDs. With the increase of fluence, the surface roughness increases but agglomeration of particles has not been observed.

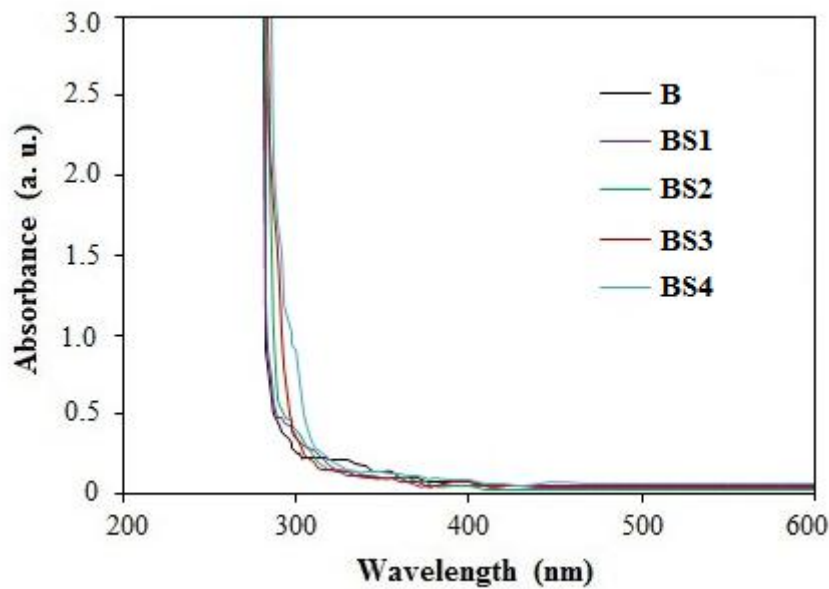


Fig-4 Optical absorption spectra of unirradiated and irradiated ZnTe:Cu samples.

Fig. 4 compares the optical absorption spectra of unirradiated ZnTe:Cu QDs with irradiated ZnTe:Cu QDs using different fluence. The absorption spectra have been observed at room temperature. Blue shifted absorption edges are observed at 298 nm for unirradiated ZnTe:Cu samples (B) with energy band gap 4.15 eV (14) which may be caused due to the quantum confinement (15). The absorption edges are appeared at 299 nm, 302 nm and 314 nm for irradiated samples. Absorption edges for the irradiated samples are observed at nearly same wavelength range. It's slightly shifted to higher wavelength (314 nm) at higher fluence (3×10^{12} ions/cm²). The sharp absorption peaks reveals that the size of the ZnTe:Cu QDs could be close to monodisperse (16). The values of the particle sizes are calculated (14) to be 12.44 nm for samples B, BS1, and BS2 respectively. And it's slightly differ to 12.54 nm and

12.88 nm for BS3 and BS4 respectively. Size of the QDs, remain unaltered during irradiation.

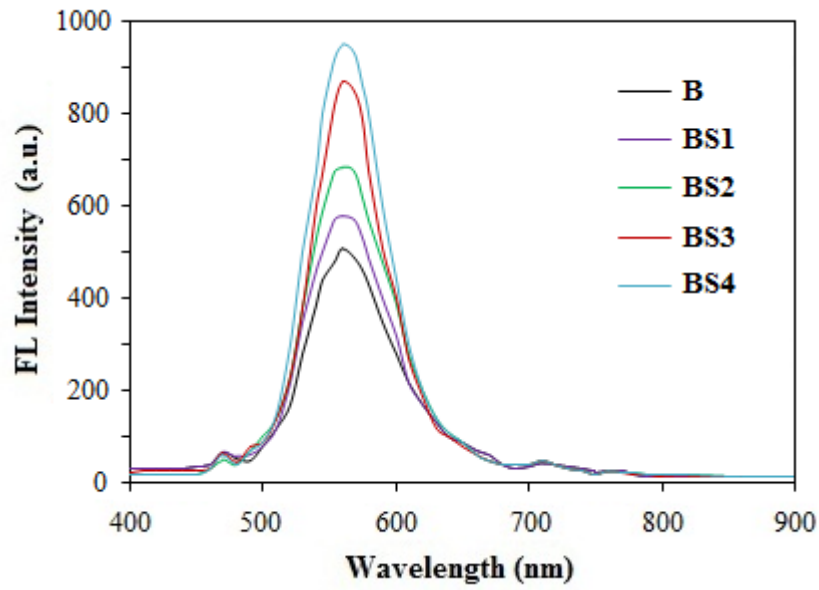


Fig-5 FL spectra of unirradiated and irradiated ZnTe:Cu samples

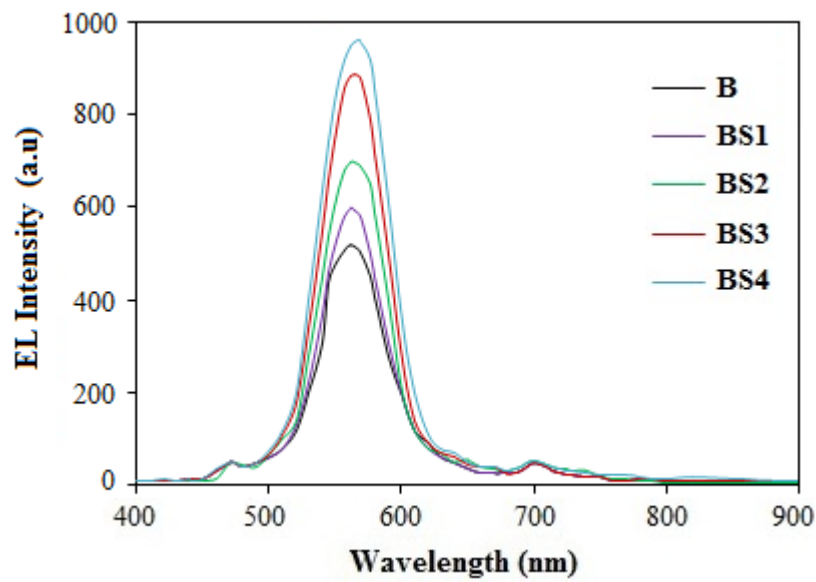


Fig-6 EL spectra of unirradiated and irradiated ZnTe:Cu samples

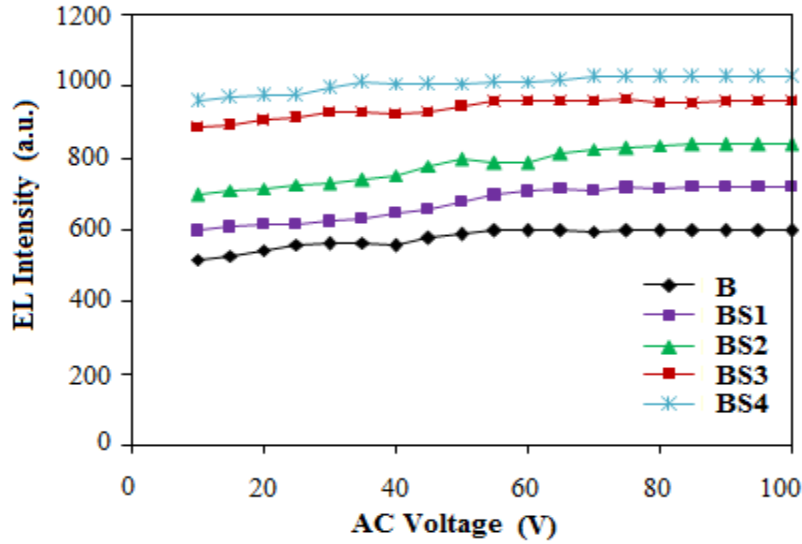


Fig- 7 Intensity variation spectra of unirradiated and irradiated ZnTe:Cu samples

Fig. 5 displays fluorescence spectra recorded at room temperature for unirradiated and ion irradiated ZnTe:Cu sample. It has been observed that for an excitation wavelength at 400 nm, emission peak are appeared at 560 nm for unirradiated ZnTe:Cu QDs along with two shoulder peaks at 482 nm and 702 nm. The ion irradiated samples also show broad emission peaks at 560 nm, 565 nm and 568 nm with different fluence of Fe^{3+} ions along with the shoulder peaks. Emission peaks observed at 560 to 568 nm region for different fluence are attributed to the incorporation of doped Cu^{2+} ions in ZnTe:Cu QDs (17). When Cu^{2+} ions are doped into ZnTe nanoparticles more defect states will be introduced. And the Fe^{3+} ions irradiation enhanced the Cu^{2+} ions vacancies in ZnTe:Cu QDs. Probably, due to this reason intensity of peaks gradually increases with the increase of fluence and the intensity tends to become saturation for higher fluence with the saturation value of Cu^{2+} ions. Besides this green emission peak, the shoulder peak observed at blue region (at 482 nm) is responsible for Zn^{2+} vacancies (18). The shoulder peak observed at 702 nm is still unknown reason. Electroluminescence (EL) spectra of unirradiated and Fe^{3+} ions irradiated ZnTe:Cu samples are shown in fig. 6. The EL emission peaks follow the FL emission peaks. Comparatively narrow and sharp EL emission peaks are observed at same wave length range (562-569 nm) for different fluence of Fe^{3+} ions along with low intense shoulder peaks (at 480 nm & 705nm). Variation of EL emission peak intensity with applied voltage has been shown in fig. 7. Peak intensity initially increases with the increase of applied voltage and become saturates at higher voltage. Consequently, Fe^{3+} ions irradiated ZnTe:Cu QDs are applicable for producing Light Emitting devices (LEDs) in green region.

CONCLUSION

In summary, we have synthesized Copper doped ZnTe quantum dots of size less than 15 nm by a simple chemical route. Prepared samples are irradiated with Fe^{3+} ions at 120 MeV. The XRD patterns exhibited the cubic structure for all the samples and no other crystalline phase is detected after ion irradiation. Sharp absorption edge is observed for the unirradiated samples at 298nm. Irradiated samples also show similar absorption edge at the same wavelength range. Sharp absorption edge reveals the quantum confinement of particles. Intense luminescence peaks are observed at 560 nm to 569 nm for the ion irradiated samples. It reveals the probable application of ion irradiated ZnTe:Cu QDs as nano light emitting device.

ACKNOWLEDGEMENT

We are grateful to Dr B. Dkhar (Scientific Officer, SAIF, North Eastern Hill University, Shillong, India), Dr R Baruah (S.O., Dept of Physics, Tezpur University, Assam, India), Dr. G. Gope (S.O., CIL, Assam University, Silchar, India) and IUAC New Delhi for fruitful discussions and the instrumentation facility provided during this work.

REFERENCES

- [1] Xie, R., Peng, X, 2009, "Synthesis of Cudoped InP nanocrystals with ZnSe diffusion barrier as efficient and colour tunable NIR emitter", *J. Am. Chem. Soc.*, 131,10645-10651.
- [2] Chin, P. T. C., Stouwdam, J. W., and Janseen, R. A. J., 2009, "Highly luminescent ultra narrow Mn doped ZnSe nanowire", *Nano letters*, 9(2).
- [3] Dey, S.C., Nath, S.S., and Bhattacharjee, R., 2011, "Optical properties of colloidal CdSe quantum dots", *Micro & Nano Letters*, 6: 113–115.
- [4] Dmitri, V., Talapin, C., and Murray, B., 2005, *Science*, 86:316.
- [5] Sustro, K., 2005, *Current Appl. Phys.*, 5:156.
- [6] Amekura, H., N., Okubo, Tsuya, N. I, Mitsuishi, D., K., Nakayama, Y. Singh, U. B. S. Khan, A., Mohapatra, S., and Avasthi, D. K., 2013, "Swift heavy ion irradiation of ZnO nanoparticles embedded in silica: Radiation-induced deoxidation and shape elongation", *Applied Physics Letter*, 103, 203106.
- [7] Kanjilal, D., 2001, "Swift heavy ion-induced modification and track formation in materials" *Curr. Sci.*, 80, 1560–1566.
- [8] Benyagoub, A., Levesque, F., Couvreur, F., Gibert-Mougel, C., Dufour, C., and Paumier, E., 2000, *Appl. Phys. Lett.*, 77, 3197–3199.
- [9] Jiang, W.; Weber, W. J.; Thevuthasan, S.; Exarhas, G. J.; Bozlee, B. J. (1999) *Int. J. Nitride Semicond. Res.*, 1–6.

- [10] Daniel, M.C., and Astruc, D. (2004) Chem Rev., 104:293-346.
- [11] Dwivedi, D.K., Dayashankar, A., and Dubey, M., 2009, Journal of Ovonic Research, 5:35-41.
- [12] Singh, A. P., Kumari, S, Tripathi, A., Singh, F., Gaskell, K. J., Shrivastav, R., Dass S., Ehrman, and Satsangi S. H., 2011, “Improved Photoelectrochemical Response of Titanium Dioxide Irradiated with 120 MeV Ag⁹⁺” J. Phys. Chem. C, 114, 622–626
- [13] Nath, S.S.; Chakdar, D.; Gope, G.; and Avasthi, D.K., 2008, “Characterisation of CdS and ZnS Quantum dots Prepared via Chemical Method on SBR Latex”, AZojono- Journal of Nanotechnology, 4:34.
- [14] Baruah, L., Nath, S.S., 2017, “Electroluminescence of Copper doped ZnTe Quantum Dots”, J. Res.Insp., 2(2): 345-353.
- [15] Nath, S.S., Chakdar, D., and Gope, G., Avasthi D, K., 2008, “Novel effect of Swift Heavy Ion on ZnO quantum dots prepared by quenching method”, J. of Nanotechnology, 2:1.
- [16] Deng, Z., Li C., Tang, F., and Zou, B., 2005, J. Phys. Chem. B, 109:16671-16675.
- [17] Sharma, K. P., Kumar, M., and Pandey A.C., 2011, J. of Nano Research, 13:1629-1637.
- [18] Nath, S.S.; Chakdar, D.; Gope, G.; Kakati, J.; Kalita, B.; Talukdar, A.; and Avasthi, D.K., 2009, Green luminescence of ZnS and ZnS:Cu quantum dots embedded in zeolite matrix J. of Appl. Phy., 105: 094305

