

## IMPROVED LUMINESCENCE OF CU DOPED ZNTE QUANTUM DOTS IRRADIATED WITH 120 MEV $Fe^{3+}$ IONS

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### ABSTRACT

Cu-doped ZnTe quantum dots (ZnTe: Cu QDs) have been irradiated with 120 MeV  $Fe^{3+}$  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 SHI irradiated ZnTe: Cu quantum dots. UV-Vis absorption spectroscopy reveals that absorption edges of irradiated samples are little bit red shifted with respect to the unirradiated sample. Moreover, intense luminescent peaks (FL & EL) are observed at green region for the irradiated samples. Significantly, better luminescent peaks are achieved at the same wavelength for the irradiated samples.

**KEYWORDS:** SHI Irradiation, Copper Doped, Fluence, Electroluminescence

### INTRODUCTION

Irradiation of materials by very high energy (typically in MeV or GeV) accelerating particles of heavy ions is referred to swift heavy ions (SHI) irradiation (1- 23). It plays a remarkable role in modifying the properties (1-5). SHI penetrate deep into the material and produce a long and narrow disordered zone along their trajectory (6,7). The 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). For fast ions with higher kinetic energies, i.e., in the MeV range, the energy intensity ( $dE/dx$ )<sub>e</sub> which is imparted to the electronic system is several times higher than that of the energy imparted to the nuclear system of the quantum dots (QDs). Due to the high rate of energy transfer to the electronic system, the role of electronic excitations enhances in generating structural defects, track formations, creation of extraordinary phase and destruction of materials (9). In recent years, a lot of attention has been devoted towards the SHI irradiation induced defect creation and modifications in the bulk and thin films (1-11). But no any study is available on the effect of SHI irradiation of ZnTe: Cu QDs.

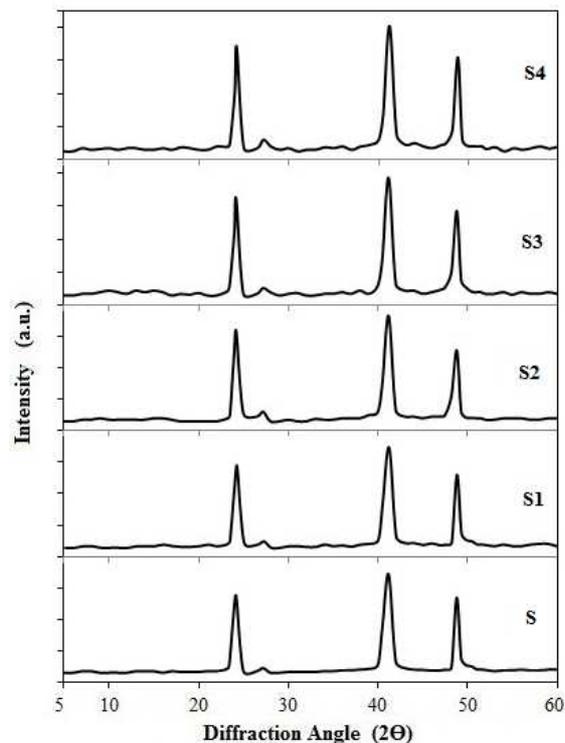
In this study, we investigate the 120 MeV  $Fe^{3+}$  ions irradiated luminescence (FL & EL) of ZnTe: Cu quantum dots at different fluence. The effect of SHI irradiation on luminescence of ZnTe: Cu quantum dots are completely a piece of novel work that has been explored by the investigators. Detailed studies on fluence dependent luminescence are reported here. These studies demonstrated a significant enhancement of luminescence in case of irradiated samples at a fluence of  $3 \times 10^{12}$  ions/cm<sup>2</sup>. X-ray diffraction, HRTEM and SEM and UV-vis absorption analysis of pre and post irradiated samples are also presented and discussed.

## EXPERIMENTAL

Preparation of ZnTe: Cu quantum dots through chemical route have been reported in our earlier report (12). To prepare ZnTe: Cu QDs hydrazine hydrate, ethylene glycol, zinc acetate, tellurium powder, de-ionized water and copper chloride are the required chemicals. The sample has been prepared at around 300 °C under vigorous stirring for 6 hours.

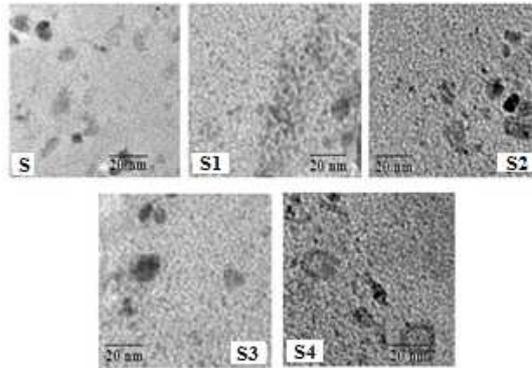
Prepared samples grow on glass substrate, having 1 x 1 cm<sup>2</sup> areas. Fe<sup>3+</sup> ions having 120 MeV are used to irradiate the as prepared samples with four different fluence of 1 × 10<sup>11</sup> (S1), 3 × 10<sup>11</sup> (S2), 1 × 10<sup>12</sup> (S3) and 3 × 10<sup>12</sup> (S4) ions/cm<sup>2</sup>. The ion irradiated samples are characterized with X-ray diffract meter (Bruker, λ=1.5418 Å), SEM (JSM 6390LV) and HRTEM (Jeol JEM-2100) to investigate the crystalline structure and morphological change. UV–visible absorption spectrometer (Perkin Elmer Lambda-35) and Fluorescence (FL) spectrometer (Perkin Elmer LS-45) are used to study the optical behavior of the irradiated samples (QDs).

## RESULTS AND DISCUSSIONS

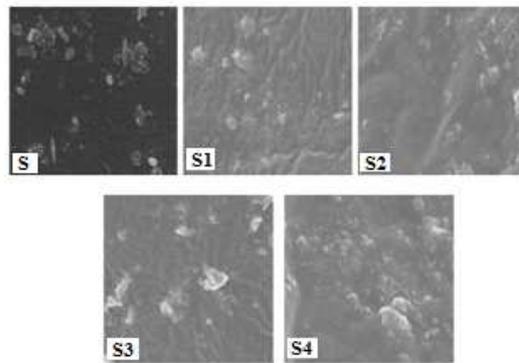


**Figure 1: X-Ray Diffractograms of ZnTe: Cu QDs at Different Fluence.**  
 ‘S’ is Unirradiate Samples and S1, S2, S3 & S4 are Ion Irradiated Samples at Different Fluence

X-ray diffraction patterns of the 120 MeV Fe<sup>3+</sup> ions irradiated ZnTe: Cu samples are shown in Figure 1 at the fluence of 1 × 10<sup>11</sup>, 3 × 10<sup>11</sup>, 1 × 10<sup>12</sup> and 3 × 10<sup>12</sup> ions/cm<sup>2</sup> along with the unirradiated sample. Diffractions peaks appeared for the unirradiated samples at 24.2°, 41.2°, and 48.8° (12) and it remains same after irradiation. Thus, remained responding in crystalline planes <100>, <111>, and <200> remain unaltered, resulting in no crystalline phase change after irradiations. The average sizes of the ion irradiated QDs are 8.8 nm and 9 nm at the fluence from 1 × 10<sup>11</sup> (S1) to 1 × 10<sup>12</sup> ions/cm<sup>2</sup> (S3) respectively. It reveals that size of QDs remains same with unirradiated QDs (8.8 nm) at a lower ion fluence. But, at higher fluence (3 × 10<sup>12</sup> ions/cm<sup>2</sup>), QDs sizes to enhance negligibly, up to 11.4 nm.

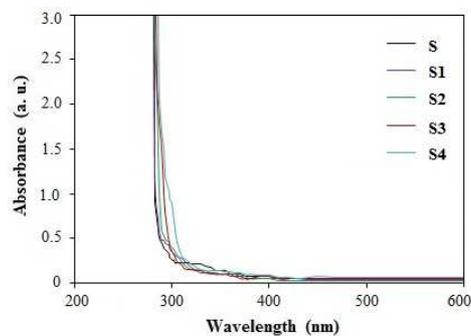


**Figure 2: HRTEM Images of ZnTe: Cu QDs at Different Fluence. Here, 'S' Stands for Unirradiated Samples and 'S1, S2, S3 and S4' are Ion Irradiated Samples with Enhanced Ion Fluence**



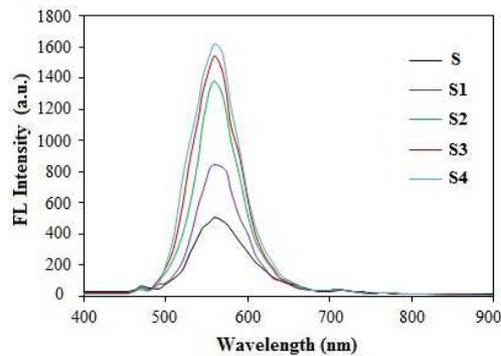
**Figure 3: SEM ZnTe: Cu QDs Samples at Different Fluence. Here, 'S' Stands for Unirradiated Samples and 'S1, S2, S3 and S4' are Ion Irradiated Samples with Enhanced Ion Fluence**

High resolution transmission electron micrographs (HRTEM) and SEM micrographs of ZnTe: Cu QDs are shown in Figure 2 and Figure. 3 respectively. The HRTEM images reveal that the size of the QDs is laying within the range 2-14 nm. Well-separated and crystalline spherical and elliptical shaped QDs are observed in the HRTEM images for all the samples after ion irradiation. QDs size remains same as lower fluence. A little bit larger particles of ZnTe: Cu has been observed at higher fluence (S4) which may be due to the dispersion of the particles in the sample. From the SEM images it has been observed that the surface roughness increases gradually with enhanced ion fluence. That is, higher the fluence, higher surface roughness.

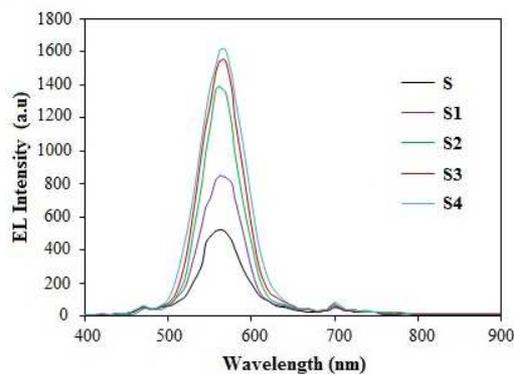


**Figure 4: UV-Vis Absorption Spectra of ZnTe: Cu QDs at Different Fluence. Here, 'S' Stands For Unirradiated Samples and 'S1, S2, S3 and S4' are Ion Irradiated Samples with Enhanced Ion Fluence**

UV-Vis absorption spectra of ZnTe: Cu QDs are displayed in Figure 4 at different fluence. For unirradiated ZnTe: Cu sample, sharp blue shifted absorption edge is observed at 298 nm. The absorption edge is slightly red shifted for the ion irradiated QDs with respect to the unirradiated ZnTe: Cu sample and appeared at 299 nm to 314 nm with enhanced fluence. The Size of the QDs is assessed by using the effective mass approximation method (16) and it has been found 12.44 nm for unirradiated samples and 12.88 nm at highest fluence. It reveals that the size of the QDs remains almost unaltered during ion irradiation.



**Figure 5: FL Spectra of SHI Irradiated ZnTe: Cu Samples at Different Fluence**



**Figure 6: EL Spectra of SHI Irradiated ZnTe: Cu Sample at Different Fluence**

Fluorescence spectra of SHI irradiated ZnTe: Cu sample at different fluence are shown at an excitation wavelength 350 nm in Figure 5. Unirradiated ZnTe: Cu QDs shows luminescence emission peak at 560 nm. The emission peak intensity increases remarkably with enhanced ion fluence. This is attributed due to the fact that SHI raises the temperature of the QDs to a great extent at around 2000 °C which further increases with higher fluence (20, 21). As a result, more Cu<sup>2+</sup> ions (19-23) which remains undoped during the doping process (by chemical) process due to non availability of high temperature, are now incorporated in ZnTe: Cu QDs. The intense emission peaks attribute the incorporation of doped Cu<sup>2+</sup> ions in ZnTe: Cu QDs increases, causing more copper center with enhanced ion fluence. Thus, more copper centres were appeared in the irradiated quantum dots resulting in enhanced luminescence. The intensity tends to saturate at higher ion fluence. Figure 6 displays the electroluminescence (EL) spectra of SHI irradiated ZnTe: Cu QDs. The EL emission follows the FL emission spectra and emission peaks appears at around 562-569 nm for different fluence of Fe<sup>3+</sup> ions. The EL emission peaks was caused due to the same reason as that of FL emission peaks and comparatively EL emission peaks are sharper and narrower than the FL emission peaks.

The EL emission peaks also tend to saturate at higher ion fluence. It has been observed that, luminescence enhances for the SHI irradiated copper doped ZnTe QDs and it provides green luminescence (562-569 nm) resulting probable application as nano light emitting devices (nano-LEDs).

## CONCLUSIONS

In summary, we have synthesized copper doped ZnTe quantum dots of size less than 14 nm by a simple chemical route. Prepared samples are irradiated with Fe<sup>3+</sup> 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. Absorption edge is red shifted a little bit with respect to the unirradiated ZnTe: Cu QDs. The size of the QDs is remaining unaltered during SHI irradiation. Further, the luminescence intensity enhances remarkably for the ion irradiated QDs and provides green emission (562-569 nm).

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## REFERENCES

1. Kumar, R., Sharma, S. K., Dogra, A., Kumar, V. V. S., Dolia, S.N., Gupta, A., Knobel, M., Singh, M., 2005, *Hiperfine interaction*, 160, 143-156.
2. Xie, R., Peng, X, 2009, *J. Am. Chem. Soc.*, 131,10645-10651.
3. Chin, P. T. C., Stouwdam, J. W., Janseen, R. A. J., 2009, *Nano letters*, 9 (2).
4. Dey, S.C., Nath, S.S., Bhattacharjee, R., 2011, *Micro & Nano Letters*, 6: 113–115.
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., Avasthi, D. K., 2013, *Applied Physics Letter*, 103, 203106.
7. Kanjilal, D., 2001, *Curr. Sci.*, 80, 1560–1566.
8. Benyagoub, A., Levesque, F., Couvreur, F., Gibert-Mougel, C., Dufour, C., Paumier, E., 2000, *Appl. Phys. Lett.*, 77, 3197–3199.
9. Komarov, F., F., 2003, *Phy-Uspekhi*, 46 (12), 1253-1282.
10. D'Orleans, C., Stoquert, J.P., Estournes, C., Ceruti, C., Grob, J.J., Guille, J.L., Haas, F., Mullar, D., 2003, *Physical Rev. B*, 67, 220101.
11. Plaksin, O., Takeda, Y., Amekura, H., Kisimoto, N., 2006, *J. of app. Phy.*, 99 (9044307).
12. Baruah, L., Sharma, B. I., Nath, S. S., 2017, *Inter. J. of Nanotechnology and Applications*, 11, 2, 247-253.
13. Singh, A. P., Kumari, S, Tripathi, A., Singh, F., Gaskell, K. J., Shrivastav, R., Dass S., Satsangi. S. H., 2011, *J. Phys. Chem. C*, 114, 622–626.

14. Nath, S.S.; Chakdar, D.; Gope, G.; Avasthi, D.K., 2008, AZojono- Journal of Nanotechnology, 4:34.
15. Nath, S.S., Chakdar, D., and Gope, G., Avasthi D, K., 2008, J. of Nanotechnology, 2:1.
16. Deng, Z., Li C., Tang, F., Zou, B., 2005, J. Phys. Chem. B, 109:16671-16675.
17. Sahay, P. P.; Nath, R. K.; Tewari, S. Crystal Research and Technology 2007, 42, 275.
18. Sharma, K. P., Kumar, M., Pandey A.C., 2011, J. of Nano Research, 13:1629-1637.
19. Nath, S.S.; Chakdar, D.; Gope, G.; Kakati, J.; Kalita, B.; Talukdar, A.; Avasthi, D.K., 2009, J. of Appl. Phy., 105: 094305.
20. Avasthi, D. K., 2000, Current Science, 78 (11), 1297-1303.
21. Agarwal, D. C., Chauhan, R. S., Avasthi, D. K., Khan, S. A.; Kabiraj, D.; Sulania, I., 2008, Journal of Applied Physics, 104, 024304.
22. Tang, A., Yi, L., Han, W., Teng, F., Wang, Y., Hou, Y., Gao, M., 2010, Applied Physics Letters, 97, 033112.
23. Yang, H., Santra, S., Holloway, P. H., 2005, J Nanosci Nanotechnol., 5, 9, 1364-75.