

# Novel effect of 100 MeV Ni<sup>+7</sup> ion beam on ZnS quantum dots prepared by chemical method

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## Citation

S Nath, D Chakdar, G Gope, D Avasthi. *Novel effect of 100 MeV Ni<sup>+7</sup> ion beam on ZnS quantum dots prepared by chemical method*. The Internet Journal of Nanotechnology. 2006 Volume 2 Number 1.

## Abstract

We report here the synthesis, optical absorption, luminescence and impedance study of 100 MeV Nickel ion irradiated ZnS quantum dots prepared by chemical method. Ion doses of  $1 \times 10^{11}$ ,  $3 \times 10^{11}$ ,  $1 \times 10^{12}$  and  $3 \times 10^{12}$  ions/cm<sup>2</sup> were selected for irradiation. It has been observed that with higher ion dose the optical absorption spectra of irradiated samples possess red shift of the energy gap parameter with respect to the unirradiated (virgin) samples. Red shifts infer the particle growth under ion irradiation which is confirmed from high resolution transmission electron microscope (HRTEM) images. Photoluminescence spectra show that the luminescence quantum efficiency after irradiation of the samples enhances remarkably. The possible reason for enhancement in luminescence efficiency in irradiated specimen is the creations of Zn<sup>2+</sup> vacancy due to high energy ion irradiation. Impedance analysis also shows that impedance (which is basically capacitive admittance) also changes significantly.

## INTRODUCTION

In the present article, we report the synthesis of ZnS quantum particle by using a chemical method. These samples have been irradiated by 100 MeV Nickel ion (Ni<sup>+7</sup> Swift heavy ion) at four different fluencies  $1 \times 10^{11}$ ,  $3 \times 10^{11}$ ,  $1 \times 10^{12}$  and  $3 \times 10^{12}$  ion/cm<sup>2</sup>. The irradiated samples were analyzed by High resolution transmission electron microscopy (HRTEM), UV/VIS optical absorption spectroscopy, photoluminescence spectroscopy [1,2,3,4,5,6,7,8,9,10,11,12] and Impedance analysis [5, 23]. Optical absorption of 100 MeV Cl<sup>+9</sup> ion irradiated ZnO quantum dots (prepared by quenching method) has been reported elsewhere<sup>18</sup> but optical absorption, photoluminescence study and impedance analysis of ion irradiated ZnS quantum dots (prepared by chemical route) have not been focused earlier. Hence we believe this report is highly important from the view point of quantum dot characterizations<sup>22</sup>.

## SYNTHESIS

5wt% D/D water solution of PVA is prepared by moderate heating and stirring. 1.36wt% aqueous solution of ZnCl<sub>2</sub> and 0.75wt% solution of Na<sub>2</sub>S are prepared so that the molecular weight ratio of ZnCl<sub>2</sub> and Na<sub>2</sub>S becomes 1:1. With this, few drops of HNO<sub>3</sub> is added. The solutions of PVA and ZnCl<sub>2</sub> are mixed in the ratio of 2:1 and then stirred at 250 rpm at 60 C while with dropping funnel, Na<sub>2</sub>S solution is put into it,

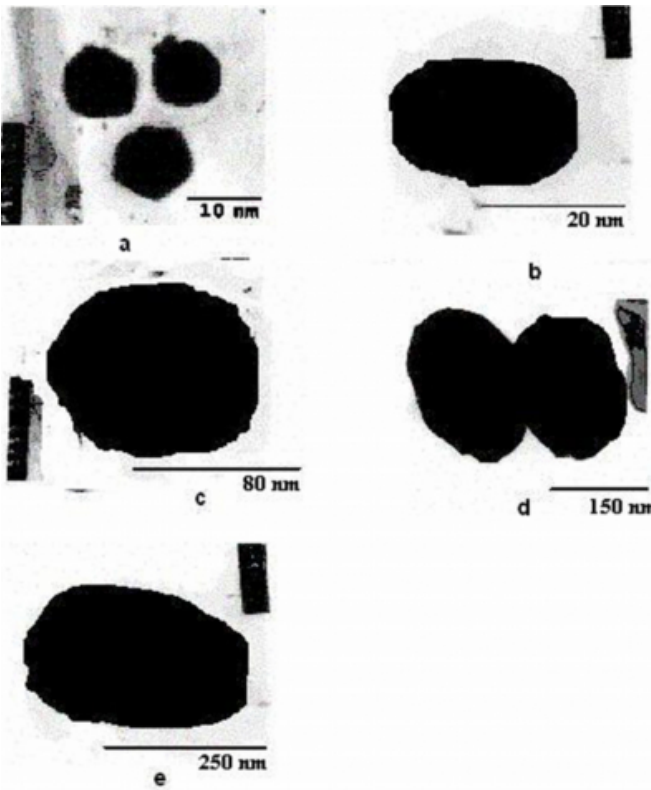
until the whole solution appears completely milky. The prepared solution is kept in dark chamber at room temperature for 12 hours for stabilization. Finally, the solution is cast over laboratory glass substrate and then dried in oven at 40 C. The film over substrate contains the quantum dots of ZnS specimens embedded in PVA matrix. Thus ZnS quantum dot samples were developed. These were irradiated in the Material Science chamber under high vacuum ( $4.6 \times 10^{-6}$  Torr) by using the 100-MeV Ni<sup>+7</sup> ion beam with four ion doses with doses  $1 \times 10^{11}$ ,  $3 \times 10^{11}$ ,  $1 \times 10^{12}$  and  $3 \times 10^{12}$  ions/cm<sup>2</sup>, available from the 15UD tandem pelletron accelerator at IUAC(formerly NSC), New Delhi, India.

## CHARACTERIZATION

High resolution transmission electron microscopy (using JEM 1000 C XII) it is evident that in polyvinyl alcohol (PVA) matrix, the virgin quantum dot samples are orderly distributed [1,2,3,4,5] with very small inter particle distances separated by only a thin wall of polymer matrix as displayed in fig 1.

Figure 1

Figure 1: HRTEM images of ZnS specimens: a, b, c,d and e stand for the virgin sample and the samples irradiated by 1 , 2 , 3 and 4 dose respectively.



When swift heavy ion (SHI) irradiates the sample, it gets heated up resulting in sudden rise in sample temperature that reaches the melting point of the specimen [1,2] . Due to this phenomenon, quantum dots melt and as they start to agglomerate to form bigger particles (fig1). Also, the red shifts (fig 2) in strong absorption edges of irradiated samples in UV/VIS absorption spectra (using Perkin Elmer Lamda 351.24) indicate the formations of bigger particles [6,7,8,9,10,11] . Different sizes also have been estimated form the spectra by using hyperbolic band model [9,22] .These sizes agrees (with little discrepancies) the quantum dot sizes obtained from Transmission Electron Microscopy.

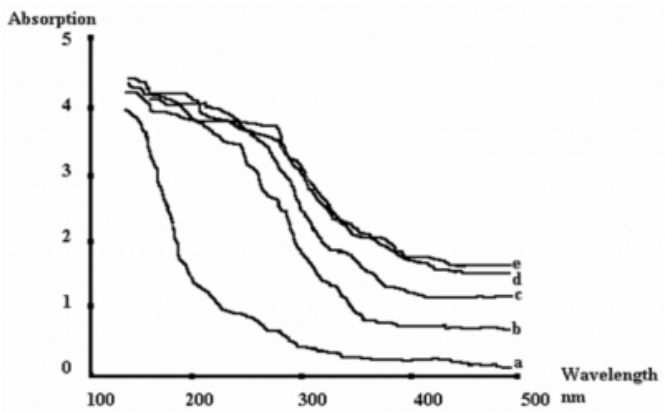
Figure 2

Table 1: Sizes of samples calculated from absorption spectra.

Sample	Strong absorption edge (nm)	Size (nm)
S <sub>2</sub>	200	9
S <sub>2</sub> d <sub>1</sub>	330	40
S <sub>2</sub> d <sub>2</sub>	345	80
S <sub>2</sub> d <sub>3</sub>	350	145
S <sub>2</sub> d <sub>4</sub>	350	160

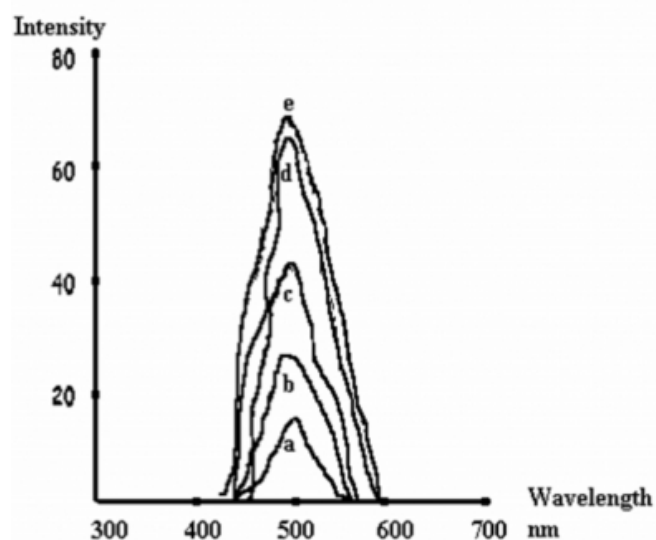
Figure 3

Figure 2: UV/VIS absorption spectra of ZnS specimens: a, stands for virgin sample and b, c, d e for samples irradiated by 1stm 2 , 3 and 4 dose.



**Figure 4**

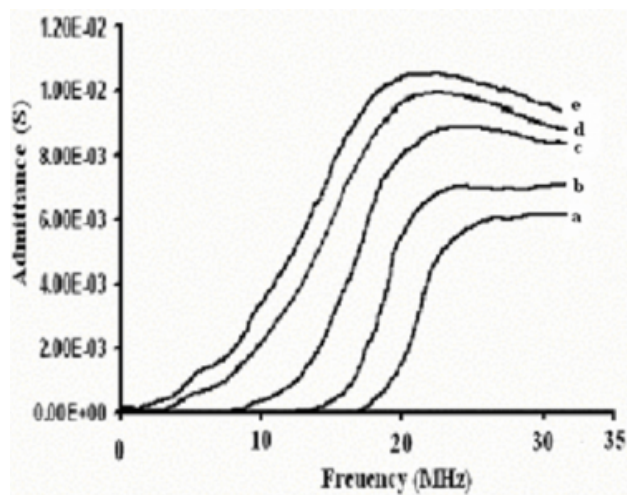
Figure 3: spectra of ZnS samples: a stands for virgin sample and b, c, d e for samples irradiated by 1, 2, 3, and 4 ion dose respectively.



We carried out the photoluminescence study (using HITACHI-F-2005) of the samples. Photoluminescence spectra of ZnS samples excited with 200 nm source (fig.3) reveal that virgin ZnS quantum dots possess the Zn<sup>2+</sup> vacancy related luminescence<sup>23</sup> with peak position at 500 nm. It is observed from the spectra of irradiated samples that emission intensity increases with no shift in emission peak positions with higher ion doses. This infers that the unlike luminescence in virgin quantum dot [14, 23], luminescence in irradiated quantum dot is also due to the Zn<sup>2+</sup> vacancy but we believe that Ni<sup>7+</sup> ion produces more numbers defects in the form of Zn<sup>2+</sup> vacancies in the ZnS specimen resulting in higher intensities of emission out put.

**Figure 5**

Figure 4: Impedance spectra of ZnS sample: a stands for virgin sample and b, c, d e for samples irradiated by 1, 2, 3, and 4 ion dose respectively.



Impedance analysis (Using Solartron SI 1260) of the sample reveals that after ion irradiation admittance Vs frequency curves of the ZnS quantum dot modifies. It is already reported<sup>22</sup> that quantum dot impedance is basically due to capacitance which varies directly with particle size. After ion irradiation, particle agglomerates resulting in formation of bigger particle of larger capacitance<sup>21</sup> (fig 4). Due to this phenomena, quantum dot impedance changes resulting in modification in admittance Vs frequency curves of irradiated samples.

## CONCLUSION

After Ion irradiation bigger particles form. Photoluminescence study infers that luminescence intensity of irradiated specimen becomes higher and Impedance of the sample changes after irradiation, which are our new findings.

## ACKNOWLEDGEMENT

The authors thank Prof. A Choudhury, Vice Chancellor, Gauhati University, Guwahati, Assam, India and Dr. H Chander, Dr S Chawla, LMD Group, Division of Electronic Materials, NPL, New Delhi, India for their suggestions and assistance during the work.

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