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Study of low dose Gamma irradiation on CuO and PANI-CuO nano particle

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***Abstract*: We have studied the effect of low dose gamma irradiation on CuO have been prepared by sol gel method and the Polyaniline (PANI) - CuO composites can be synthesized by the method of polymerization. The obtained CuO and PANI-CuO composite powders were irradiated with energetic gamma ray of dose rate 11 Gray per minute at room temperature. The radiation induced changes in the structural, morphological and optical properties of CuO and polymer composite were analyzed with X-ray diffraction (XRD), Scanning electron microscope (SEM), Ultra violet -Visible spectroscope (UV-Vis), and Fourier transform infrared spectroscope (FT-IR). The XRD spectrum shows that the crystalline nature of sample is still present after irradiation and the corresponding 2θ values are shifted to higher side and the particle size will be increased. The morphological changes due to the gamma irradiation were confirmed by SEM images. The UV absorption spectra revealed the absorption edge and the corresponding band gap values were correlated. The FTIR spectrum shows the vibrational modes are changing as a result of irradiation.**

***Keywords:* CuO, sol gel method, polymerization, gamma irradiation, optical properties, dosimeter.**

1. INTRODUCTION

On basis of their property, (structural and optical) the nano materials are much different from bulk materials. So we study the materials in the scale of nano range. By the development of nano material, the oxides of metals are quite interest, because the metal oxide nano particles are very much useful in industry and technology. We need some metal oxide for our day to day life such as ZnO, CuO and so on. By this way CuO is a very useful metal oxide in different areas such that coolant materials, gas sensors, optical switch, magnetic storage media, electronic and optoelectronic devices, solar cell fabrication, catalysts, super capacitors etc [1].

The surface to volume ratio of nano materials are very high compared with bulk materials so that we increase their property of materials and the size was reduced to nano scale. In nano level the optical study and calculating the band gap of the material is very important. The direct band gap study was very challenging because of their quantum confinement effects. CuO is a p-type metal oxide semiconductor. Compare to ZnO the CuO has the wide band gap, which is useful for solar energy conversion [2].

According to conductivity, PANI is a good conductor and has wide potential applications, such as sensors, anticorrosion coatings, and good environmental stability [3]. The precipitation polymerization method is a very useful and easiest preparation method of PANI. The conducting polymers are known as good hole conducting materials. When PANI combined with metal oxide, they act as a stabilizer or surface capping agents.

In media, the inorganic nano particles are very easy to agglomerate. The combination of polymers and metal oxide nano particles is usually accomplished by surface modification to prevent agglomeration. It can significantly enhance the stability of nano particles dispersing in polymer solvents by increasing the affinity of the surface for organic substance.

In the present study the effect of gamma irradiation on the structural, optical properties of CuO and the PANI- CuO composites. It shows that distinct structural, vibrational bonding and optical characteristics. It may be change the properties of materials in the applications of different fields in radiation science.

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2. EXPERIMENTAL DETAILS

2.1 Synthesis on CuO Nano particle:

The CuO Nano powders were prepared by Sol-gel method. The aqueous solution of $CuCl_2.6H_2O$ (0.2 M) is prepared in cleaned beaker and heated to 100^0C with constant stirring. 8 M NaOH is added to above heated solution till pH reaches to 7. The color of the solution turned from blue to black and a large amount of black precipitate is formed. It is centrifuged and washed 3-4 times with deionized water, ethanol and acetone. The obtained precipitate was dried in air for 24 h. This powder is further used for the characterization of CuO nano particles [4].

2.2 Synthesis of PANI-CuO nano composites:

The nano-composite sample of PANI-CuO was prepared by Polymerization method: The known weight of CuO was added to the mixture of aniline and the hydrochloric acid and stirred for one hour. Then ammonium per sulfate was added to the prepared mixture and stirred at low temperature (approximately 0^oC) for six hours. The solution was then filtered and the green paste was first washed with acetone and then by distilled water. The paste was then dried in air for two days and the resultant sample was dark green powder, collected in a bottle for further process. [5]

The powder of CuO and PANI-CuO were exposed to gamma radiation from ^{60}Co source at a constant dose rate of 11 Gy/min at room temperature. As prepared sample was named as CuO – A, (PANI-CuO) – PC- A and the irradiated sample named as CuO – B, (PANI-CuO) - PC – B. The crystalline phase and particle size were determined by (XRD) using CuKα as radiation source. The morphology of the prepared and irradiated nano particles was confirmed by SEM. The optical characteristics are studied using UV-Vis and FTIR spectroscope.

3. RESULTS AND DISCUSSION

3.1 Analysis of Crystal Structure:

The synthesized Copper oxide and PANI-CuO nano particles were characterized by X-ray powder diffraction using CuKα (λ=1.54056Å) radiation at Alagappa University, Karaikudi. The XRD data were taken over the angles 0° to 90° in 2θ steps at room temperature. The combined XRD patterns obtained before and after irradiation of CuO and PANI-CuO particles are as shown in Figure 1 and 2 respectively. The XRD patterns were compared with Joint Committee Powder Standard value (JCPDS) which confirmed JCPDS NO [45-0937] and [02-1067]. The synthesized samples exhibit monoclinic structure only and there are no additional phases detected. The lattice parameters were calculated from XRD data. The average particle size calculated by using the Debye-Scherrer formula for particle size, which is as follows:

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where β is full width half maxima of the peak in XRD pattern, θ is peak obtained angle and λ is X- ray wavelength.

The average particle sizes calculated by using above formula are approximately for CuO 28.42nm and 51.03 nm and for PANI-CuO are approximately 17.80 nm and 47.62 nm before and after irradiation, respectively. From XRD, lattice parameters are calculated to be a=0.46nm, b=0.34nm, c=0.51nm [6].

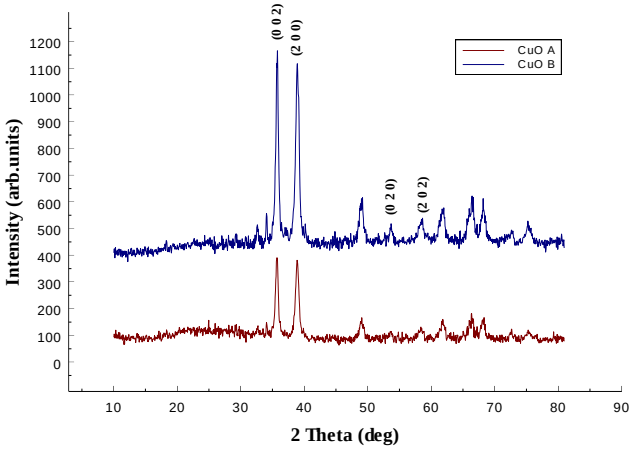

Fig 1: XRD Pattern of before and after irradiation on CuO Nano particle

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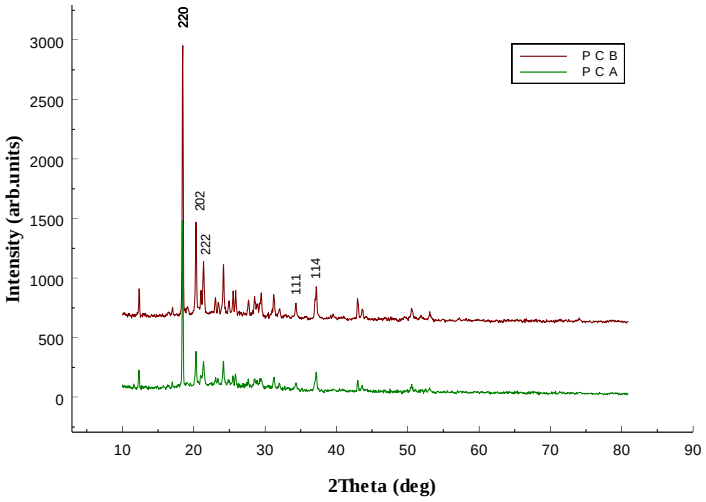

Fig 2: XRD Pattern of before and after irradiation on PANI-CuO particle

From Figure 2 we conclude that both PANI and CuO existed before and after irradiation and their particle size are increased due to absorbing the radiation. From the XRD result, the particle size is increased due to increase of irradiation when compared with as prepared sample.

3.2 Morphology Studies:

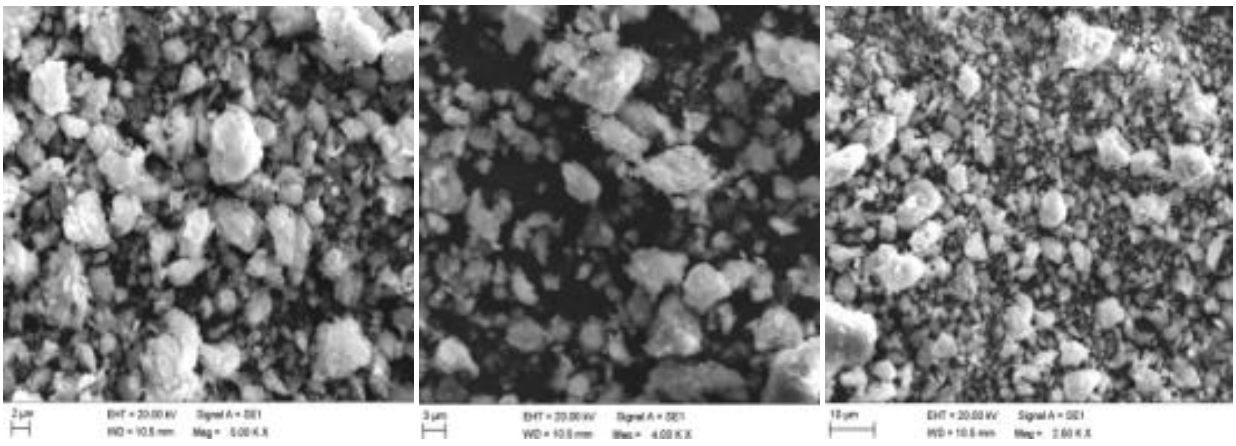

Fig 3: SEM image of as prepared sample- (CuO- A)

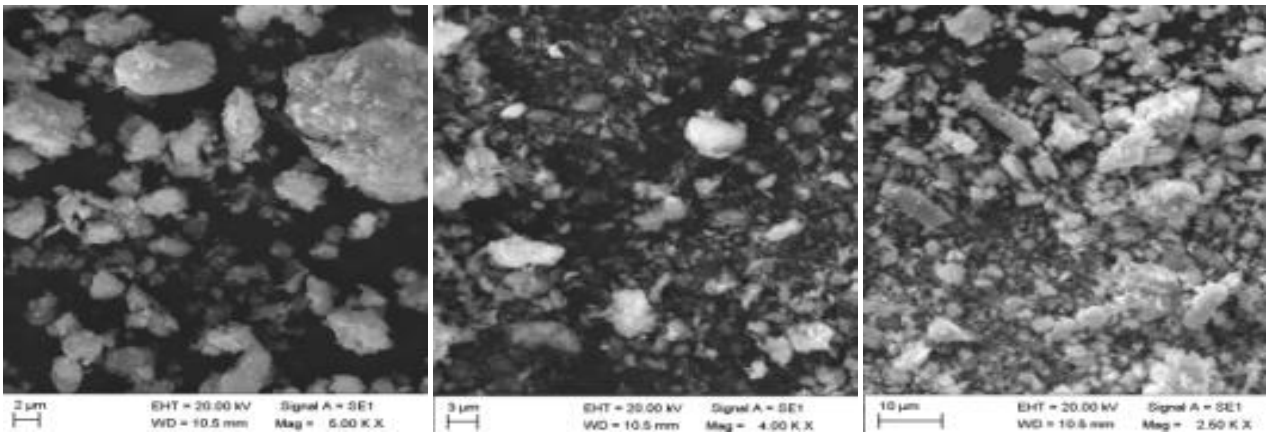

Fig 4: SEM image of irradiated sample (CuO- B)

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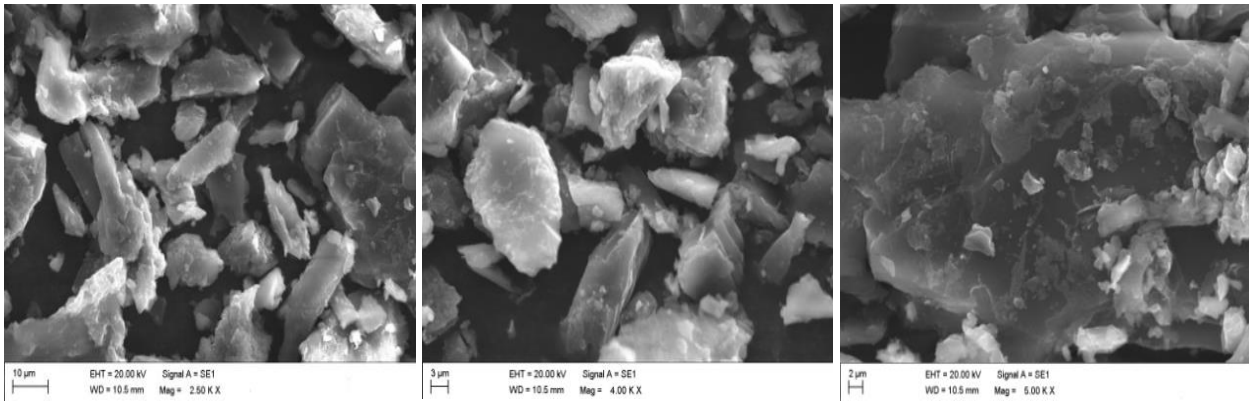

Fig 5: SEM image of as prepared sample- PANI-CuO (PC - A)

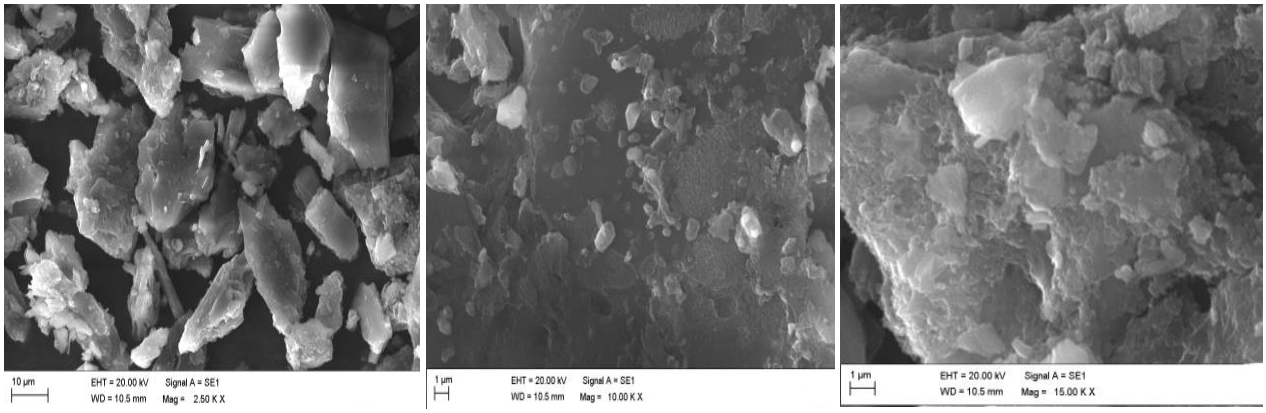

Fig 6: SEM image of as irradiated sample- PANI-CuO (PC- B)

The SEM images of CuO particles prepared and irradiated are as shown in Figures 3 and 4 respectively. The micrographs show a higher tendency of conglomerations. We collected the SEM images in different scales. The particle sizes are found to be increased after gamma irradiation and nano clusters are formed. When applying radiation to the sample the surface of the particles does not vary so the morphology of the sample will remain same from the SEM image. We conclude that irradiation does not affect the surface of the sample but increases the particle size [7].

The SEM images of PANI -CuO particles prepared and irradiated are as shown in Figures 5 and 6 respectively. From the image and cluster morphology shows the copper oxide particles are well dispersed in the PANI matrix. The presences of solid blocks are confirmed by the oxide particles. PANI-CuO composites exhibits well distribution of CuO on PANI sheets and displays highly aggregated.

3.3 Optical Studies:

The UV-Visible absorption spectrum analysis was done for the prepared and irradiated samples at Thiagarajar College Madurai. The optical properties of the prepared and irradiated samples were studied using optical absorption spectrum. Energy band gap studies of these materials have been reported using absorption spectra. Fig. 7, 9 and Fig 8, 10 shows a plot of $(\alpha h\upsilon)^2$ vs. photon energy (E) before and after irradiation of the pure and composite CuO respectively. From this the value of the band gap was determined The graph shows $(\alpha h\nu)^2$ plotted against Energy ($h\nu$). Tauc et al [8] and Pan cove [9] had analyzed the optical properties of the semiconducting materials and given the following relation between photon energy and band gap E_g for a given transition:

$$\alpha h\nu = A\,(h\nu - E_g)^{m/2}$$

where, m=1 for direct transition, m=4 for indirect transition, α – absorption coefficient, ν – Photon frequency, A – constant. The band gap E_g, was determined by extrapolating the straight portion to the energy axis at $(\alpha h\upsilon)^2=0$, and it is given in Table 1[10].

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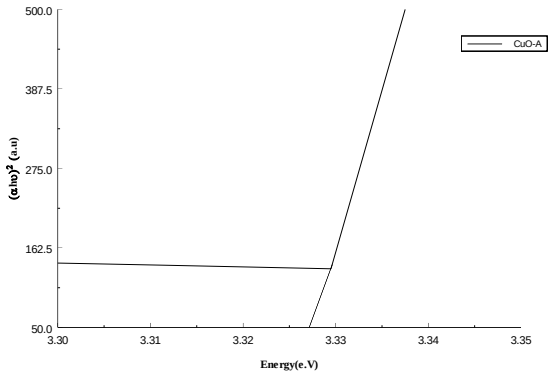

Fig 7: UV graph befor irradiation

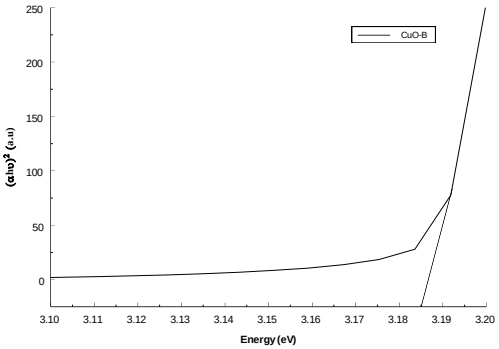

Fig 8: The UV graph after irradiation

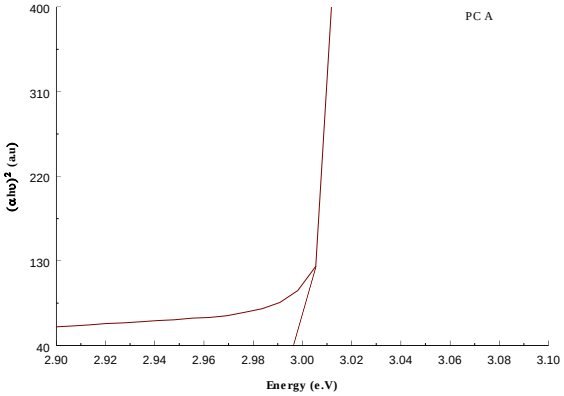

Fig 9.:UV graph befor irradiation

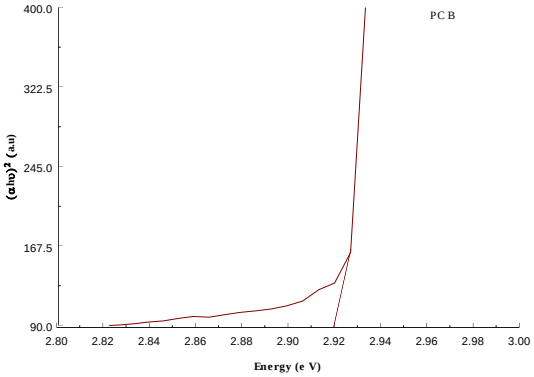

Fig 10: The UV graph after irradiation

TABLE 1: The band gap value of CuO and Pani-CuO for before and after irradiation

S.No	Sample	Band gap value (eV)
1	CuO – A	3.327
2	CuO – B	3.185
3	PANI-CuO PC-A	2.990
4	PANI-CuO PC-B	2.910

The localized energy widths of the band tails are increased and the corresponding band gaps are decreased. The standard band gap energy for CuO nano particle is 4.68 eV. As a result of increasing the radiation, which increases the particle size and decrease the band gap.

3.4 Vibrational studies:

FTIR spectrum of before and after irradiation of the nano particle of CuO and PANI –CuO are shown in the Fig. 11 and 12 respectively. The blue shift observed in nano particles corresponding to the copper bands at 418.55 cm^{-1} and 607.58 cm^{-1} are assigned to the stretching vibrations of Cu-O. Due to the quantum confinement a blue shift is observed in the stretching frequency of bulk CuO is 491 cm^{-1}. The broad absorption peak centered at 3458.37 cm^{-1} corresponds to O-H stretching and bending frequencies of H_2O, indicating the existence of water in the surface of nano particles [11]. The water molecules is not present in PANI-copper oxide composite materials. Variations of the peak positions of CuO and Pani-CuO relative to irradiate CuO are presented in the Table 2 and Table 3 respectively. From the data's presented in the table revealed that the irradiated CuO induces a shift in the absorption bands as compared to the prepared CuO and there is no change in observation of PANI -CuO composites.

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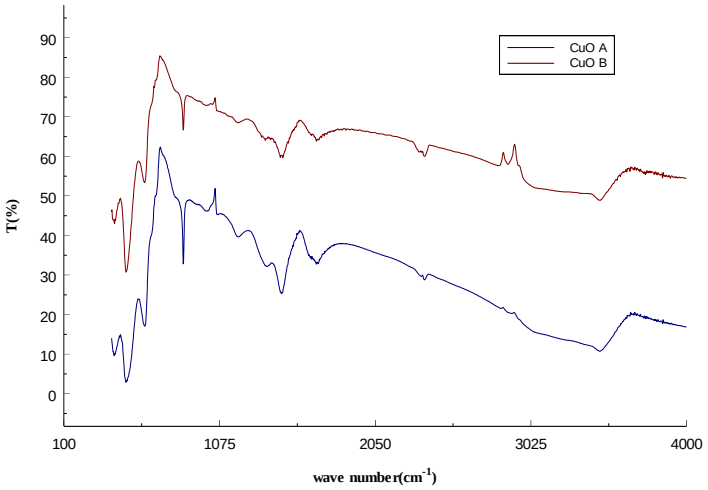

Fig 11: FTIR spectrum of before and after irradiation of CuO Nano particle

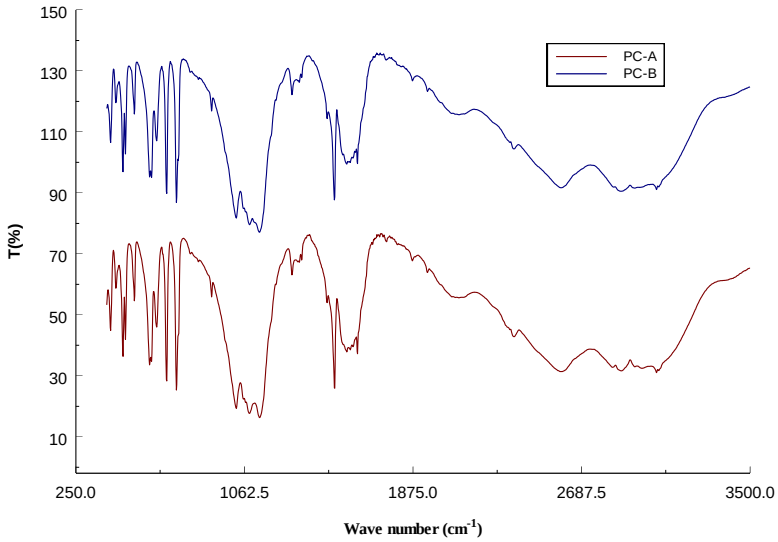

Fig 12: FTIR spectrum of before and after irradiation of Pani-CuO Nano particle

TABLE 2: Vibrational mode of before and after irradiation of CuO Nano particle

Assignment of bond	CuO – A (cm^{-1})	CuO – B (cm^{-1})
OH	3458.37	3458.37
Metal- Oxygen (M-O rocking out of plane)	1684	1685
Metal- Oxygen (M-O rocking in plane)	1371.39	1361.74
CuO-wagging	607.58	605.65
CuO stretching	418.55	459.05

TABLE 3: Vibrational mode of before and after irradiation of Pani-CuO Nano particle

Assignment of bond	PC-A (cm^{-1})	PC-B(cm^{-1})
Stretching of ZnO	435	437
C=C quinoid rings	1606.70	1606.70
C=C benzenoid	1496.76	1496.76
C–N stretching mode	1292.31	1292.31
N=Q=N quinoid ring	1136.07	1136.07
CuO-wagging	611.43	609.51
Metal- Oxygen (M-O rocking out of plane)	1747.1	1747.1
Metal- Oxygen (M-O rocking in plane)	1292.31	1292.31

4. CONCLUSION

XRD pattern revealed copper oxide and their composites have monoclinic structure. SEM photograph shows good agglomeration of CuO nano particles and slightly change in pani composite material. UV shows the band gap decreases due to increase of radiation dose. FTIR revealed the vibrational modes are changing after absorbing the gamma radiation of the prepared sample. It is concluded that it is possible to explore the PANI -CuO composites as radiation dosimetry in which can detect lower range of radiation.

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