Preparation and Characterization of Zinc-Copper Oxide Doped PMMA Films

Manu Faujdar[1,2], Minal Bafna[1] Sushila[2]

[1]Department of Physics, Agrawal P.G. College, Jaipur,
[2]Department of Physics, Vivekananda Global University, Jaipur.

ABSTRACT

In this work we present the synthesis of Zinc Copper Oxide (ZnCuO) nano-powder via sol-gel method using respective metal chlorides as precursors; and insertion of these nano-particles as dopant in poly-methyl-methacyrlate (PMMA) solution to prepare ZnCuO-PMMA composite film using the solution cast method . The structural analysis of the prepared ZnCuO nanopowder and ZnCuO doped PMMA film has been carried out by XRD, FESEM, FTIR and photoluminescence Spectroscopy. From XRD studies the crystalline size of ZnCuO nanoparticles has been evaluated using Scherrer formula as approximately 35nm. FTIR studies revealed that the functional group present in the metal nano particles. The effect of insertion of the zinc-copper oxide nanoparticles on PL properties of poly (methylmethacrylate) has been also studied using from photoluminescence spectrometer it is seen that the intensity of emission as-well-as emission peak wavelength changes with solvent.
.
Keywords: PMMA, mixed metal oxides, ZnCuO, photoluminescence spectra
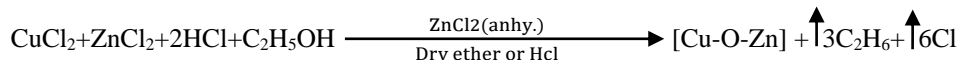
1. INTRODUCTION

Polymer composite materials have steadily gained attention due to their ease of processing, ability to be molded in various shapes and sizes and being economically viable. Poly(methylmethacrylate) (PMMA) has been the most favoured polymer to be experimented for blending, co-polymerizing or insertion of nano-fillers by material scientists as it not only exhibits fascinating properties of being transparent and light weight but also is highly compatible with most organic and inorganic substances. PMMA also possess good tensile strength, insulating properties, ease of handling and processing. A rapid glance at the literature shows that due to presence of any other organic/inorganic material even in small quantities within the PMMA long chain molecule; drastically changes its optical [1-6], electrical [7-12], mechanical [13-14] or thermal properties [17]. Zinc-copper oxide nanoparticles are of interest as they have enormous ability to be used in variety of applications, "such as optical coatings, laser diodes and catalysts, field effect transistors, field emission arrays, ultraviolet lasers, light emitting diode, sensors, biosensors, catalyst, energy storage and solar cells" [15]. Several methods such as hydrothermal, sol-gel, electrochemical deposition, microwave, sonochemical have been adopted for formation of Zn-CuO nano-powders [22]. We have used the simple sol-gel approach. The method includes dissolution of metallic-ion precursors (metal chlorides) in a appropriate solvent and obtaining gel. So to investigate how the mixed metal oxide would affect the structural and fluorescence properties of PMMA we thought of incorporating Zinc copper oxide in PMMA. In the present work, we report the synthesis of Zinc Copper oxide nanopowder using the sol-gel technique and preparation of films by inserting this nano-powder into PMMA and the analysis of the investigated structural and photo-luminescence properties of these prepared sample films. The detailed synthetic process and characterization of sol-gel end products, pure and composite PMMA films are reported here.

2. EXPERIMENTAL WORK

2.1 Chemical involved: Zinc chloride ($ZnCl_2$), copper chloride ($CuCl_2$) and dichloromethane of analytical grade were purchased from Merck Specialties Pvt. Ltd, "Mumbai; PMMA granules were purchased from M/s Gadra Chemicals Bharuch"; hydrochloric acid (HCl) and ethyl alcohol (C_2H_5OH) were purchased from Himedia Laboratories, Mumbai. All these chemicals were used without further purification.

2.2 Synthesis of Zinc-Copper oxide nano-particles by sol-gel technique: Zn–CuO nano-structures were synthesized using the sol-gel method. The precursors, 4 gm of white anhydrous Zinc chloride and 10 gm of blue copper chloride were first powdered into a mortar with pestle for 20 minutes and then were kept in a beaker. Then 20ml of dilute hydrochloric acid was gradually poured into this mixture contained in the beaker kept on a magnetic stirrer for a continuous stirring. After an hour

when the mixture dissolved in the acid, we added ethanol (purity99%) drop-wise into the beaker and the temperature was increased to 60°C to form sol. The reaction produced a solution of yellowish colour with a tinge of blue. We kept it stirring for another four hours at room temperature while the whole mixture got dissolved in ethanol during this process. The precursors react with OH group of ethanol likewise

$$CuCl_2 + ZnCl_2 + 2HCl + C_2H_5OH \xrightarrow[\text{Dry ether or Hcl}]{\text{ZnCl2(anhy.)}} [Cu\text{-}O\text{-}Zn] + {\uparrow}3C_2H_6 + {\uparrow}6Cl$$

The $ZnCl_2$ in the above reaction is anhydrous in nature and is the *Lucas reagent* that acts like a basic reactia.

After this we left the solution to cool down, within several minutes, a reaction occurred showing a rapid formation of a rigid bluish green colored gel. Then the gel was dried at the same temperature. The obtained products were then rinsed multiple times by deionized water so that residual impurities are laid off. The gel now obtained was heated in an oven for about one hour at 80 degree centigrade so that dried Zn-CuO powder is obtained.

Figure1**:** Prepared Zn-CuO sol gel product.

2.3   ***Synthesis of pure and Zn-CuO doped PMMA Films:*** We took two beakers of 100ml and in each a fixed amount of 1gm granule PMMA crystals were made to dissolve in 20ml dichloromethane and 5 ml of ethyl alcohol that acts as solvent. The molten PMMA is stirred uniformly in an ultra-sonicator for 6 hrs at room temperature to assure the homogenous dispersion of polymer particles without concentricity throughout the solvent. After this, solution of one of the beaker was poured into a flat bottom petri dish of radius 3cm. The petri dish is placed floting on a layer of mercury so that the solution spreads homogeneously and film of uniform thickness can be obtained. Then we added 100 mg of zinc-copper oxide nano-particles into the solution of another beaker and allowed this to stir on a magnetic stirrer for 18 hours. When the nano-particles got completely dissolved in to the PMMA solution, we poured this solution into another glass flat bottom petri dish kept floated over mercury and left for 24 hours. Now the solvent is made to evaporate at room temperature and is left to dry as film in the petri dish which are then peeled off later. We obtained transparent PMMA film and fluorescent yellow-green coloured Zn-CuO doped PMMA film of 120μm thickness as shown in figure 2. Now onwards we will refer the sample film of pure PMMA as P1 and that of Zn-CuO doped PMMA as PZCO. These films were then vacuum dried before proceeding for characterization.
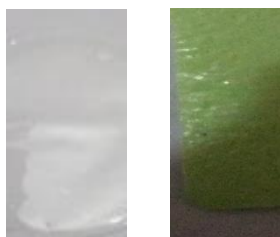

Figure 2**:** Prepared film of pure PMMA and Zn-CuO doped PMMA

2.4   *Characterization:* The synthesized Cu-Zn oxide nano-particles and their doped PMMA films are studied using "X-ray" diffractometer "XRD" (PANalytical unit using software X′Pert°Pro3) equipped "with Cu-K_α radiation" of wavelength λ = "1.5406A°" at accelerating voltage 30 kV. The composition of functional groups of our powdered samples and prepared films were examined by FTIR Perkin Elmer Spectrum Version 10.4.00 FTIR Spectrophotometer in the region 500-4000 cm^{-1}. The surface structure of the composite samples was investigated using S-3700N FESEM field emission scanning electron microscope. The PL spectra was obtained using fluorescence emission spectroscopy

3.   RESULTS AND DISCUSSION

3.1   X-Ray Diffraction Studies : In the available literature, the diffraction peaks of pure hexagonal wurtzite phase of ZnO have been indexed at $2\theta = 31.64°$, $34.48°$, $36.38°$,$47.8°$, $56.5°$, $62.9°$, $68°$ and $69.2°$ corresponding to (*hkl*) values of (100) (103) (112) and (201) planes matched with the file (PDF 13-7585) from software version 2.4, JCODS_ICDD [18-19]. Similarly the prominent peaks of CuO are indexed to a monoclinic phase at $2\theta = 35.5°$, $38.8°$, $48.6°$ corresponding to (*hkl*) value of (100) (201) and (103) planes[19] matched with the JCPDS No 48–1548[15]. In the XRD data of the mixed metal oxide nano powder of Zinc copper oxide, the zinc peaks become dominant as seen in figure 3(a). The smoothened out data has been depicted in the figure. In the obtained diffraction pattern we see the presence of slight broad peaks which can be used to the size of particle in nanometer scale. The average crystallite size evaluated for Zn-CuO powder using the well known Scherrer's equation; $D=0.9\lambda/\beta \cos\theta$, where "$\lambda$ is the wavelength of the incident radiation, D is the grain size, β is the experimentally observed diffraction peak width at full width at half-maximum intensity (FWHM) and θ is the Bragg angle". The average crystalline size of ZnCuO nano particles from the FWHM of the intense peaks is found to be around 34.05 nm.
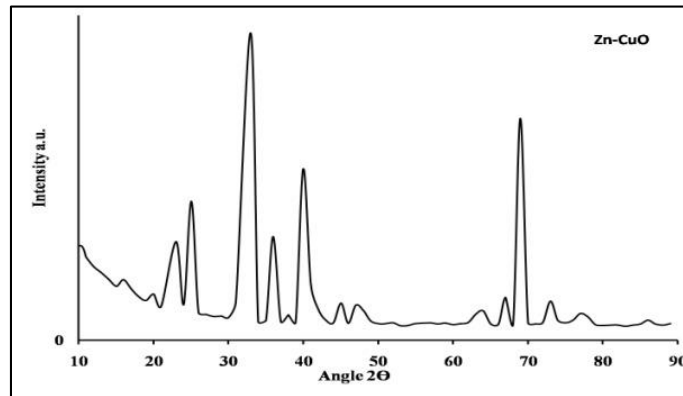

Figure 3(a)**:** XRD pattern obtained for Zn-CuO nano-powder

The XRD data for pure PMMA depicted in figure 3(b). From the figure 3(b) we see the XRD data for pure PMMA depicts a broad high intense peak at $2\theta = 13.89°$ and low intense peaks at $2\theta =30°$ and $2\theta =34°$ to suggest the amorphous type structure of this polymer [23].
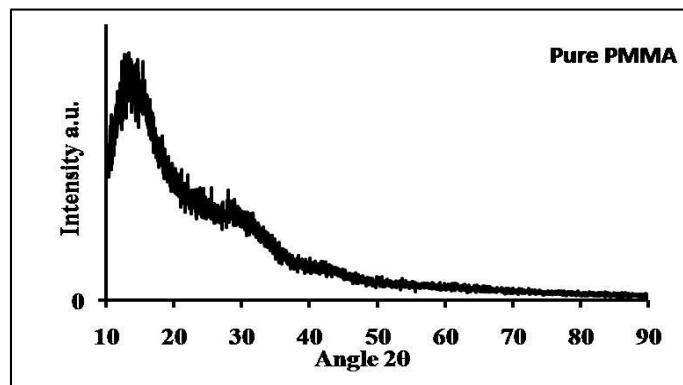

Figure 3(b)**:** XRD pattern obtained for pure PMMA film

The XRD pattern of PCZO film obtained on doping Zn-CuO nanoparticles into PMMA, clearly shows that there is a low broad peak at 13.8° of PMMA and sharp peaks at 31.7°, 34.4°, 36.2°, 63.19°, 63.24°, 64.16° due to zinc and peaks at 2θ =35.5°, 38.8° along with low intensity peaks at due to copper oxide nanoparticles.
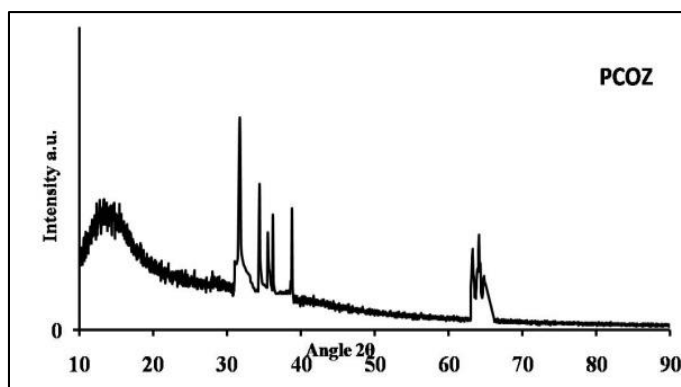
Figure 3(b): XRD pattern obtained for Zn-CuO doped PMMA film

3.2   Analysis of SEM Images: SEM images of sol-gel product Zn-CuO nanoparticles, pure PMMA film and Zn-CuO doped PMMA film are given in figure 4. The Zn-CuO doped PMMA film "possess smooth surface as compared to that for PMMA". The addition of mixed metal oxide has smoothened the rough fractured surface of pure PMMA.
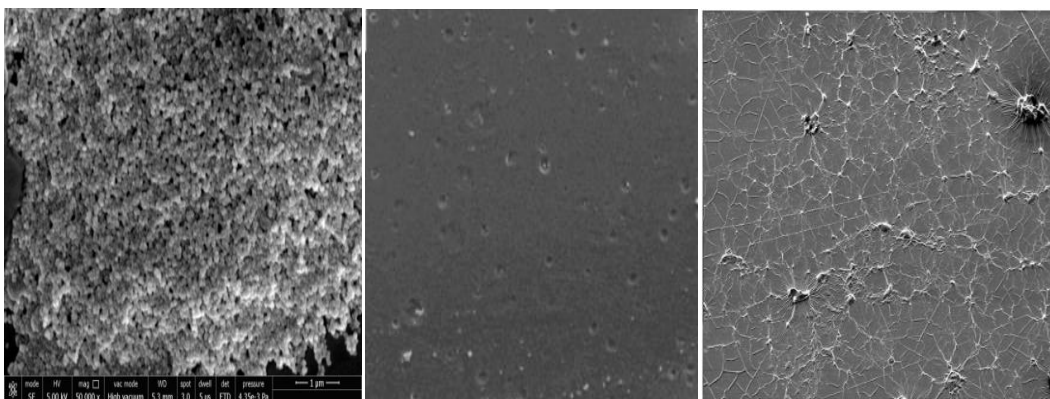

Figure 4: SEM images of ZnCuO nano powder, PMMA and Zn-CuO doped PMMA film .

3.3   Analysis of FTIR Spectra: The FTIR data obtained for sol-gel product Zn-CuO is shown in figure 5(a). The prepared films of pure PMMA and Zn-CuO doped PMMA were cut into very small pieces for FTIR investigations and the obtained spectra are shown in figure5(b) and 5(c) respectively. The characteristic peaks in these figures represent the vibrational modes of the molecules. In figure 5(a), the peak at 450 cm^{-1} is the characteristic absorption of Zn–O bond [20]. The peaks seen in between 610 and 1045 cm^{-1} we observe intense absorption band corresponding to stretching mode of Cu-O in monoclinic phase [20]. The peak seen at 2264 cm^{-1} corresponds to the presence of atmospheric CO_2 [20]. Presence of humid environment resulting in hydrated CuO create peaks in the frequency band 3000 to 3500 cm^{-1} H_2O in the air and hydrated CuO samples are responsible for the creation of peaks[17].
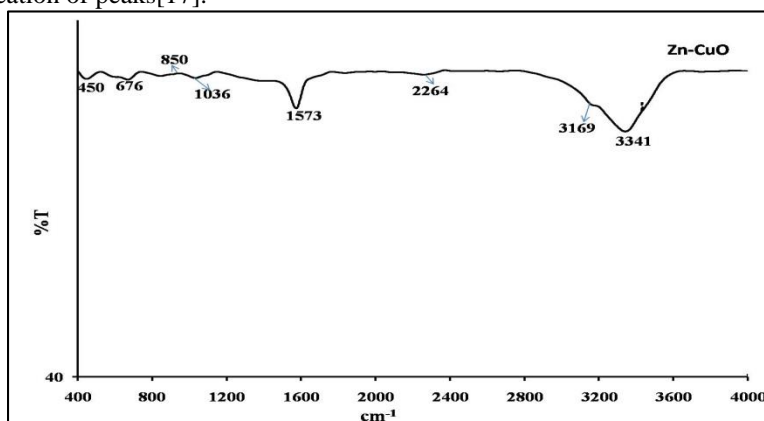

Figure 5(a): XRD pattern obtained for Zn-CuO powder

The modes obtained for the pure PMMA sample are listed in the Table 1 which is in good agreement with the reported ones [24].
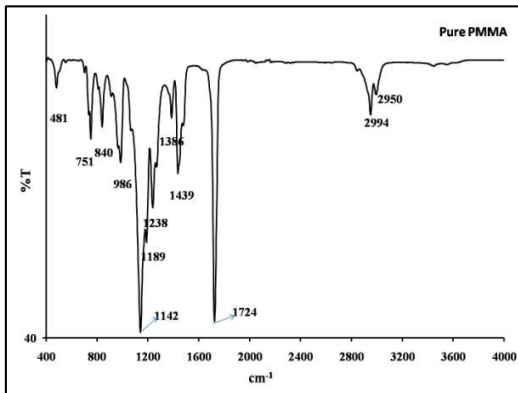

Figure 5(b): FTIR Spectrum obtained for PMMA film

Wave number (cm^{-1})	Mode
751	C– C stretching bands
840	CH$_2$ rocking mode
986	CH$_3$-O rocking
1142	C-O anti symmetric stretching in C-O-C linkage
1189	CH$_2$wagging mode
1238	C-C-O symmetric stretching
1386	CH bending
1439	CH$_3$ bending
1724	C=O stretching mode
2950	C-H symmetrical stretching
2994	C-H asymmetrical stretching

Table 1: Vibration modes of PMMA

However with the incorporation of Zn-CuO in PMMA, we see **appearance of all these peaks** indicating the formation of the composite.
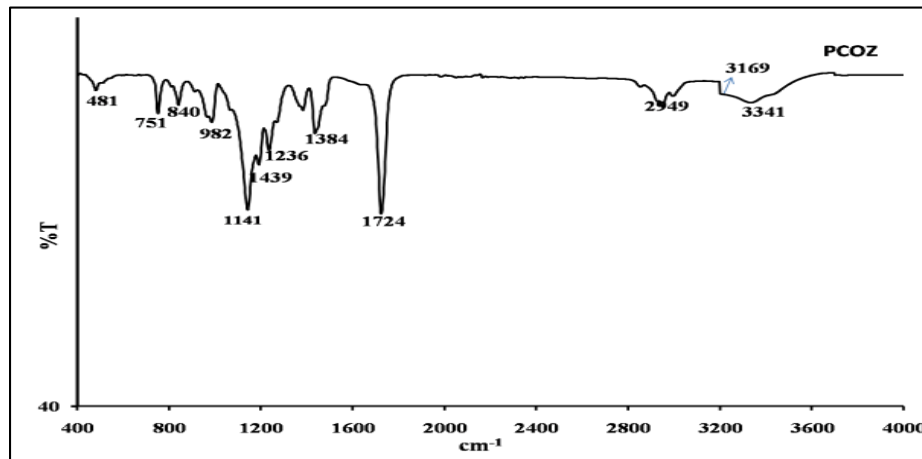

Figure 5(c): FTIR Spectra obtained for Zn-CuO doped PMMA film

3.4 Study of Photo-luminescence properties: "Photoluminescence is a popular spectroscopic technique to perform absorption studies on metal oxide particle systems. The excitation energies for these mixed metal oxides have been chosen on the basis of the most intense PL emission intensities". Figure 6(a) and (b) show the PL spectra at room temperature for the pure PMMA and ZnCuO doped PMMA nano-composite films respectively.
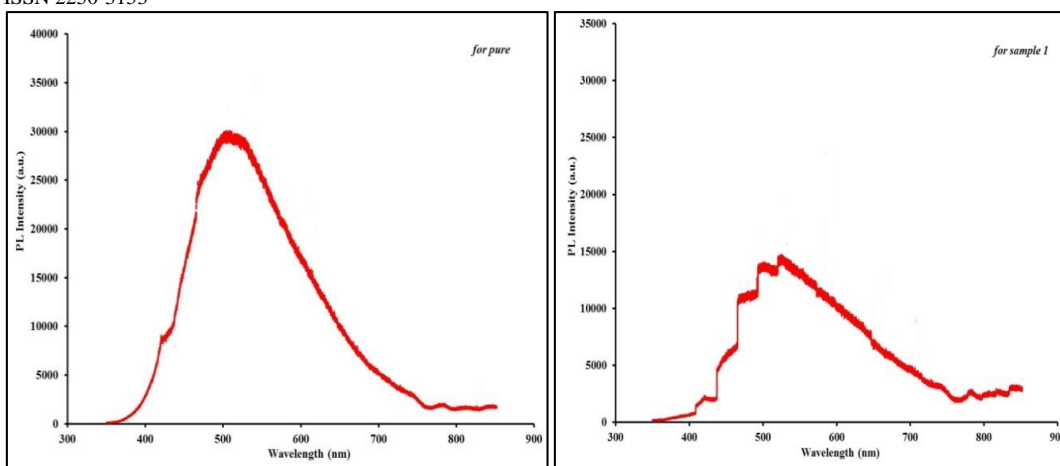
Figure 6: PL spectra of (a)Pure PMMA composite film (b) zinc-copper oxide nanoparticle doped composite film.

We can see that for the pure PMMA film there is only one wide visible emission centered at 510 nm with IR emission at 780 nm, while the PL spectra for Zn-CuO doped PMMA film shows emergence of visible emission peak at 545 nm, 525 nm, 510nm and 410 nm and IR emission peak at 740, 780, 810, 845 nm respectively. From available studies we know that two emission peaks are obtained for ZnO nano particles; one about 371 nm and the other about 525 nm[21]. This 525nm peak due to zinc oxide particles is dominantly seen in our PL spectra too. Further from literature it is known that emission peak at 545nm arises the single ionized electron of CuO recombines with photogenerated hole, green coloured radition at 545nm are emitted. The visible emission peak at 510 and 410 nm are due to the excitonic recombination for PMMA. The visible emission peaks have low intensity compared with that for pure PMMA.

4.   CONCLUSION

Here we have explained the experimental procedure to synthesize zinc-copper oxide nano-powder through sol-gel process and insertion of it in PMMA to cast ZnCuO-PMMA film. The XRD, FTIR, SEM and PL pattern of such film shows that the metal particles get have well blended into the long chains of polymeric material.

REFERENCES

[1]   Kalotra P, Singh N, Dadhich A, Shrivastava S, Soni G and Vijay Y K 2019 *Adv. Sc. Eng. and Med.* 10 1.
[2]   Bafna M, Gupta A K, Khanna R K 2019 *Mater. Today:Proc.* MATPR7592
[3]   Bafna M, Gupta A K, Khanna R K, Vijay Y K 2018 *Bull. of Mat. Sc.* 41 160
[4]   Khodair Z T, Saeed M H and Abdul-Allah M H 2014 *Iraqi J of Phy* 12(24) 47
[5]   Najeeb H N, Dahash G A, Haddawi S F, and Jassim S M 2014 *Chem and Mater Eng* 2(6) 145
[6]   Bafna M and Garg N 2017 *J of Sc. and Tech.* 6(1) 27
[7]   Ramesan T M and Bijudas K 2016 *J. of Chem. & Pharm. Sc.* 1 52
[8]   Roaaramadan, Ramajaj E K, and Hasan A A 2014 *Int. J of Elec. Eng.* 2(3) 6
[9]   Choudhary S 2017 *Ind J of Chem tech*, 24 311
[10]   Bafna M, Gupta A K, Khanna R K 2018 *J. of Emer Tech. and Inno. Res.* 5(2) 433
[11]   Vijay S, Vijayavargiya J K, Sharma A and Vijay Y K 2013 *Amer. Sc Pub* 5 1
[12]   Bafna M, Garg N, Gupta A K 2018 *J. of Emer Tech. and Inno. Res.* 5(1) 494
[13]   Najeeb H N, Balakit A A, Wahab G A and Kodeary A K 2014 *Acad. Res. Inter*. 5(1) 48
[14]   Ali B R and Kadhem F N 2013 *Inter J of App or Innov in Eng & Mgmnt* 2(4) 564
[15]   W. Phoohinkong, T. Foophow and W. Pecharapa, 2017, *J of Adv in Nat Sc: Nanosc and Nanotech,* 8, 2024.
[16]   N. C. Horti, M. D. Kamatagi and S.K.Nataraj, 2010, *AIP conference proceedings,* https://doi.org/10.1063/1.5098602.
[17]   T. Thangeeswari, J. Velmurugan, M.Priya, 2014, *International Conference on Science, Engineering and   Management Research (ICSEMR 2014),* 978-1-4799-7613
[18]   S. Pratap Goutam, A. Kumar Yadav, A. Jyoti Dasn, 2017 *J. of nanosci. and nanotech,* 3, 249-252.
[19]   W. j c da Silva, M.da Silva, K. Takashima, 2015, *J of Chil. Chem. Soc,* 60, 2749-2751.
[20]   V. prakash, R K Diwan, U K Niyogi, 2015, *Indian Journel of pure and applied physics,* 53, 753-758.
[21]   E. Bhawani Harish G S, S. Reddy, 2017, *American Journal of Engineering Research (AJER),* 2320-0847 6, 30-35.
[22]   S. Priscilla Prabhavathi, J. Punitha, P. Shameela Rajam, R. Ranjith, G. Suresh, N. Mala, D. Maruthamuthu, *2014, J of Che. and Pharma. Res, 6, 1472-1478.*
[23]   E. Shobhna , 2012, *International Journal of Modern Engineering Research   (IJMER)*, 2, 1092-1095.
[24]   A. K. Tomara, S. Mahendiaa, S. Kumara, 2011, *Advances in Applied   Science   Research,* 2, 327-333.

AUTHORS

First Author –Manu Faujdar, M.Sc. (Physics), Faculty in Department of Physics, Agrawal P.G. College, Jaipur and Research Scholor in Vivekananda Global University, Jaipur. Email-manu15faujdar@gmail.com

Second Author –Dr. Minal Bafna, M.Sc.(Physics), Net-Ph.D, Head, Department of Physics at Agrawal P.G. College, Jaipur. Email- drminalphysics@rediffmail.com

Third Author –Dr. Sushila, M.Sc. (Physics), Ph.D, Assistant Professor in Vivekananda Global University, Jaipur (Rajasthan).