

## **Study of Electrical and Optical properties of PVC Composites filled with Zinc-Oxide (ZnO) Nanoparticles, Synthesized by Sol-gel and Dropwise Mixing Process**

**Aman Kumar<sup>1,\*</sup>, Waheed Hassan Raja<sup>1</sup>, M.K.Bhatt<sup>1</sup>, Anwarul Hoda<sup>2</sup>,  
N.A.Karimi<sup>1</sup>**

<sup>1</sup> *Department of Physics, B.N.College, Patna University, Patna – 800004, Bihar, India.*

<sup>2</sup> *Department of Physics, Magadh University, Bodhgaya, Gaya- 824234, Bihar, India.*

### **Abstract**

In this paper nanoparticles of ZnO was filled into Polyvinyle Chloride (PVC) matrix to form ZnO/PVC nanocomposites. Different films of the composites were prepared by solution cast method having varying concentration of ZnO nanoparticles. The Characterizations were done by XRD and SEM. The XRD result confirms the hexagonal structure and grain size was found to be 34.5 nm. The surface morphology shows the sponge like appearance at different magnifications at  $5\mu m$  and  $10\mu m$  bar scale. It is evident that dielectric constant increases with the increase of concentration ZnO nanoparticles. The ac conductivity also increases with temperature and frequency. The optical energy gap of virgin and doped composites were calculated, which comes to be 0.375 eV and 0.39eV respectively. The intensity peaks of ZnO/PVC Composite show that it is higher when the doping concentration is high. After doping, the film shows the higher degree of structural order. The value of dielectric constant shows greater than 5 at temperature 373 K and 0.12 gm/cc concentration of ZnO nanoparticles.

**Keywords:** Scanning Electron Microscope (SEM), PVC, XRD, ZnO nanoparticle, LCR Bridge.

### **1. INTRODUCTION:**

Due to the diverse technological applications, ZnO has been an active area of research for more than half a century. It has many interesting optoelectronics properties such as wide band gap  $\approx 3.37\text{eV}$ , a large excitation binding energy of 60meV at room temperature and high dielectric constant, therefore, possesses important applications

---

\* Corresponding Author's Email: [dr.aman03@rediffmail.com](mailto:dr.aman03@rediffmail.com), [na\\_karimi2000@yahoo.com](mailto:na_karimi2000@yahoo.com)

in the fabrication of electronic and optical devices such as UV/ blue laser and LEDs<sup>1</sup>.

Zinc oxide is mostly an n-type II-IV, wide direct band gap 3.7eV semiconducting material. Hence its applications are increasing in current decade<sup>2</sup>. It is transparent to most of the solar spectrum, therefore widely used as window material in solar cells, optical waveguides, light modulators and optical sensors<sup>3</sup>. Therefore controlled synthesis of good quality of ZnO nano-structures, nano crystals, nano wires and other nano architecture are very important. Several routes have been employed for the synthesis of ZnO nano materials such as Salvo-thermal, thermal evaporation, Spraypyrolysis sol-gel synthesis and chemical vapour deposition etc, despite the crystalline quality being inferior to other vacuum deposition techniques, the sol-gel processing still offers possibility of preparing a small as well as a large area coating of ZnO thin films at low cost for technological applications<sup>4</sup>. So we have adopted the sol-gel method for the preparation of ZnO nano materials.

It is well known that PVC is only the cheap and most important polymer used as commercial polymer and have wide range of application<sup>5</sup>. Now a day's there have been a great importance in the preparation of PVC films and its behaviour doped with metal oxide which may enhance electrical conductivities, dielectric constant may play an important role in photovoltaic Cell, Sensors, Fuel Cells etc<sup>6</sup>. In the past three decades Polymers such as PVC had been studied as a gel forming Polymer matrix. Such as microwave absorber, Light emitting diode, biomaging, antibacterial activity, and in dye sensitized solar cell, Gas Sensors<sup>7</sup>.

The PVC is very important and suitable materials to be used as matrix in different type of nanocomposite materials<sup>8</sup>. PVC is one of the largely commercially used polymers. It is a polar polymer having density 1.332 and melts at and above 310°C. Its glass transition temperature is 81°C. A large number of filler materials have been used and reported to have enhance the thermal and electrical properties of PVC<sup>9</sup>.

In this paper we have reported the synthesis of ZnO – Nanoparticle by Sol-gel method and PVC films were prepared by solution–cast method. The ZnO nanoparticles in different proportions are being reinforced into polymer matrix. The characterization has been done by XRD, SEM and IR respectively<sup>10</sup>. Next the electrical properties such as electrical conductivity ( $\sigma_{ac}$ ) and dielectric constant ( $\epsilon$ ) was measured of the said nanocomposite films<sup>11</sup>.

## 2. EXPERIMENTAL

### 2.1 Preparation of ZnO nanoparticle by Sol-Gel Method:

ZnO is prepared by conventional precipitation method using sodium hydroxide and zinc sulphate solutions, the sodium hydroxide is mixed dropwise in Zinc Sulphide solution<sup>12</sup>.

## **2.2 Preparation of PVC film by Solution – Cast Method:**

We have acquired PVC (polyvinyl chloride) from Reliance Industries Gujarat, India in granular form. We have measured 4 gm PVC by analytical Balance OHAUSE, U.S.A. and 20 cc cyclohexanone (acquired from SDFCL Fine –Chem. Limited, Mumbai) was taken in burette. We put 4 gm PVC into 20 cc cyclohexanone. It was left for 72 hrs to dissolve completely then it was stirred for 30 minutes. Thus the solution was prepared.

**Preparation of Nanoparticle doped Composite film:** The nanoparticle of ZnO (Concentration = 0.003265 gm/cc) as prepared was spread on the solution of (PVC + cyclohexanone) uniformly. Then it was stirred for 4.30 hrs and that it was spread on the glass plate floating on mercury for leveling and left for approx 1 week for drying in vacuum oven at temperature 50<sup>0</sup>c. It was then removed from glass plate. Thus the film of PVC doped with nanoparticle was prepared. In the same way different types of films were prepared with different concentration of nanoparticles.

## **3. RESULT AND DISCUSSION:**

### **4. Study of Dielectric constant and Electrical Conductivity of PVC Composite filled with ZnO nanoparticles**

The dielectric constant and a.c. conductivities of composites were carried out using the LCR Meter Bridge. A special type of sample holder was used in which a capacitor was formed by considering the PVC and PVC/ZnO Composite films separately in between Copper electrodes of same diameter. The capacitance and conductance were measured by LCR Bridge at different frequencies and temperatures. The Sample holder along with sample was then kept in a thermostat, where the temperature was controlled by contact thermometer. The values of dielectric constant were calculated using the relation.

$$\epsilon_r = cd / \epsilon_0 A$$

Where

c = Capacitance of apacitor

d = Thickness of the film

A = Area of cross section of the film

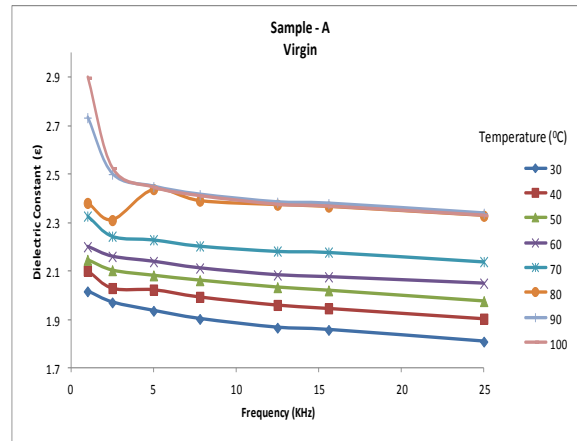
$\epsilon_0$  = Permittivity of free space

Whereas the values of ac conductivities of the film was determined from the relation,

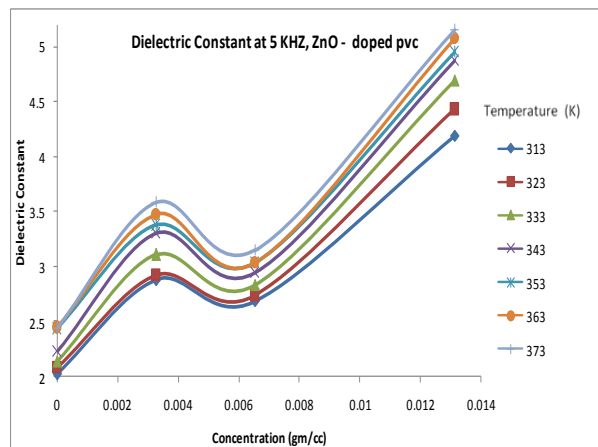
$$\sigma_{ac} = Gd / A$$

Where 'G' is the conductance, 'd' is the thickness of the film and 'A' the area of cross section.

Fig: 1 shows the variation of dielectric constant with frequency of virgin film of PVC at a particular temperature. The dielectric constant decreases rapidly at low frequency and slowly at high frequency. The suddenly decrease in dielectric constant with frequency is due to scattering of charge and the chaotic (disordered) thermal oscillation of the molecules. It is also observed that dielectric constant increases initially with temperature. The increase in dielectric constant with rise in temperature is due to the space charge polarization. At low temperature the dipoles are not aligned properly.



**Figure 1.** Variation of dielectric constant with frequency



**Figure 2.** Variation of dielectric constant with concentration of ZnO nanoparticle

As the temperature raises, the orientation of dipoles is also facilitated and hence polarization increases, this also causes the increases in dielectric constant.

Fig: 2, shows the variation of dielectric constant with concentration of ZnO nanoparticle doped in PVC film at particular temperature which shows that the dielectric constant increases when the concentration of doped nanoparticle increases.

This is due to surface charge polarization. The impurities ion in the crystal captures the surface electron, causing the surface charge polarization. The electron capture process increases initially with the rise in temperature causes to increase the dielectric constant. When the temperature is further increased and reaches at high value the ionic and electronic polarization occurs due to resonance process. However the two polarization dipolar or orientation polarization and space charge polarization process are strongly dependent on temperature, and concentration of ZnO particles which causes to increase in dielectric constant. The dielectric constant touches the value greater than 5 at higher concentration and high temperature.

Figure 3: shows the variation of Electrical conductivity (A.C.) with temperature at a particular frequency for virgin films which shows that conductivity remain constant for a low range of temperature and slightly increases at higher temperature. In low frequency region, the increase in conductivity is due to the mobility of charge carrier, which is dependent on the impurity concentration. But when the temperature increases, the ac electrical conductivity increases due to the increase in drift velocity of thermally activated electrons.

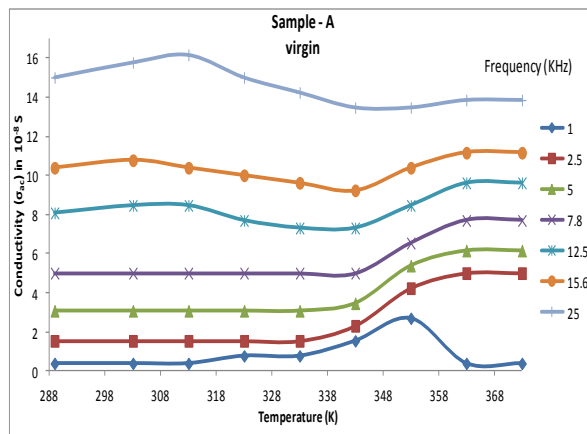


Figure-3. (Variation of conductivity with temperature)

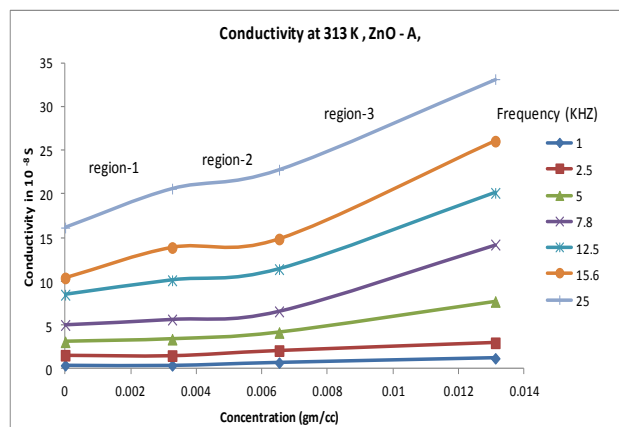


Figure- 4. (Variation of conductivity with concentration)

Therefore the conductivity increases with the increases of frequency and temperature. The real conductivity increases with frequency as it is directly proportional to the frequency. Conductivity at higher frequency and temperature becomes high confirming that a polaron hopping present in the sample. Total conductivity of the sample is given  $\sigma_{\text{total}} = \sigma_o + \sigma_{\text{ac}}$ ;  $\sigma_o$  is frequency – independent and temperature dependent which arises due to drift mobility of charge carriers.  $\sigma_o$  is actually dc electrical conductivity, and  $\sigma_{\text{ac}}$  is frequency and temperature dependent.

Figure 4: shows the variation of Conductivity with Concentration, which increases with the increasing of the concentration of the nanoparticle. At low concentration (region1), with the increase of nanoparticle, the conductor sites increases in matrix for electron hopping mechanism. In region 2, conductivity is impeded by increase of nanoparticle. In this region Vander Waals interaction causes agglomeration of nanoparticle and PVC matrix. In fact, this plateau region is a compromise between electron hopping effects and agglomeration of nanoparticle that is a consequence of increasing of nanoparticle. The sharp increase in conductivity in region 3 is probably due to contact thin polymer coated nanoparticle or uncoated nanoparticle which leads to increasing the path numbers between opposite sites and formation of nanoparticle network.

The increase in conductivity with temperature is also supported as being due to a hopping mechanism between co-ordination sites, local structural relaxations and the segmental motion of the polymers. As the amorphous region progressively increases, however, the polymer chain requires faster internal modes in bond rotation produces segmental motion. This in turn favours the hopping of inter-chain and intra- chain ion movements and the conductivity of the polymer becomes high.

## 5. OPTICAL MEASUREMENT:

The optical band gap of materials is associated with the photon energy and absorbance ( $\alpha$ ) by the given relation<sup>13</sup>.

$$\alpha h\nu = A (h\nu - E_g)^n$$

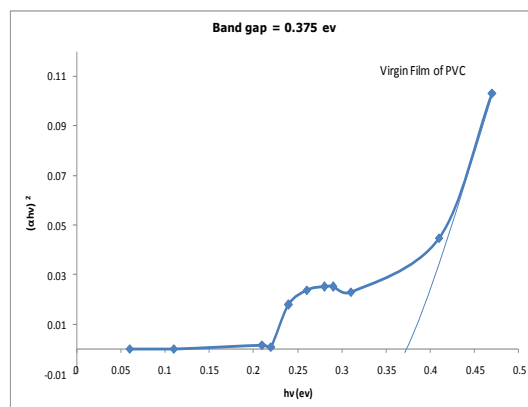
Putting  $n = 1/2$

$$\text{Hence } \alpha h\nu = A (h\nu - E_g)^{1/2}$$

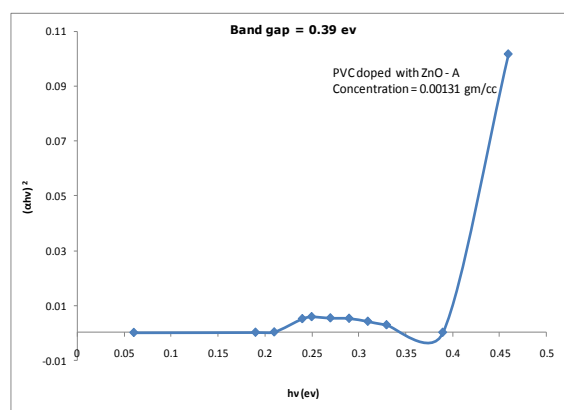
$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where  $\alpha$  = absorbance,  $\mu$  = frequency of light

$h$  = Planck's constant,  $n$  = different type of electronic transitions (such as  $n = 1/2, 2, 3/2, 3$  for direct allowed, indirect allowed, direct forbidden and indirect forbidden transition respectively). In our case, the FTIR absorbance spectra was obtained by putting  $n=1/2$  in above equation.



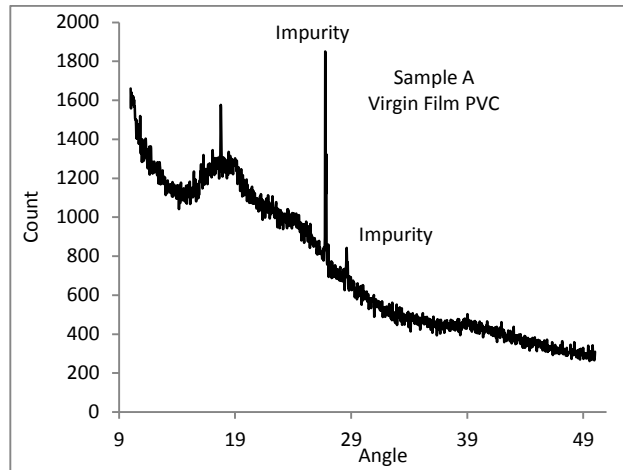
**Figure 5.** Absorption spectrum to determine Band gap of PVC film doped nanoparticle.



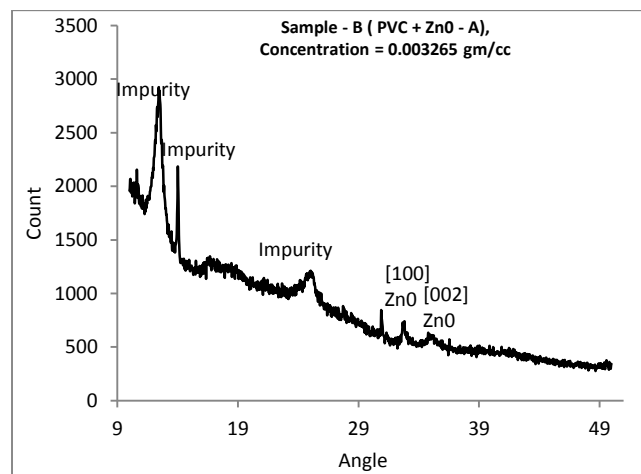
**Figure 6.** Absorption spectrum to determine the band gap of to determine the band gap of virgin film of PVC.

The fig-(5) and fig-(6) shows the FTIR absorbance spectrum of virgin and doped ZnO nanoparticle into PVC matrix. From the plots of  $(\alpha h\nu)^2$  verses  $h\nu$  of virgin and doped film, the value of energy gap of the film as determined by extrapolation of linear plots was calculated to be 0.375 eV for virgin film, while that of the doped film of ZnO nanoparticle was calculated to be 0.39 eV. It shows that the interaction between the nanoparticle and the polymer matrix, where shifting and new peaks also formed due to doping nanoparticle. The value of energy gap of ZnO doped film is higher than that of virgin PVC film.

The fig-7 shows the diffractogram of virgin film of pure PVC film, where some impurity peaks are observed at angles  $2\theta = 18.5^\circ$  and  $27.0^\circ$ . The pattern shows the amorphous nature of pure PVC which is very much comparable to the nature<sup>14</sup>.

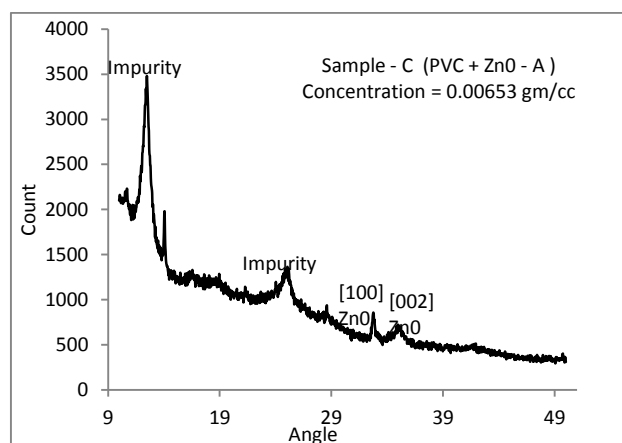


**Figure 7.** (Intensity Count verses angle of virgin film)



**Figure 8.** (Intensity Count verses angle of doped film)

Fig-8 and fig-9 shows the XRD pattern of doped ZnO nanoparticle having concentration 0.003265 g/cc and 0.00653 g/cc respectively. The intensity of Peaks shows higher when the doping concentration becomes high. Hence after doping the film shows the higher degree of structural order.



**Figure9.** (Intensity Count verses angle of doped film)

## 6. CONCLUSION

1. The size of the ZnO nanoparticle was found 34.5nm having hexagonal structure, their lattice parameter are very close to PDF#36-1451.
2. The dielectric constant of virgin PVC film decreases very fast at initial rise of frequency upto 7 KHz, then decreases slowly at higher frequency range upto 25 KHZ.
3. The dielectric constant increases both at low and high concentration of ZnO nanoparticles where as it show low value between 0.004 to 0.007 gm/cc concentration range of doped nanoparticle.
4. The dielectric constant increases both with concentration of ZnO nanoparticles and temperature and its value becomes greater than 5 at concentration 0.13 gm/cc and temperature 373<sup>o</sup>k
5. The a.c. conductivity increases with the increase of the concentration of ZnO nanoparticle reinforced into PVC matrix. But it is impeded between 0.003 to 0.006 gm/cc region of concentration due to vanderwaal interaction of agglomeration.
6. The value of energy gap of nanocomposite film calculated from tauc relation is recorded as 0.375 ev and 0.39 ev for virgin and doped film respectively which confirms the interaction takes place between nanoparticles and polymer matrix.
7. The XRD plot of virgin PVC film shows the amorphous nature where as it turns to crystalline when filled with ZnO nanoparticles. Thus the crystallinity increases with the increase of concentration of ZnO nanoparticles.
8. The amorphous nature of virgin PVC film turns to crystalline with the increase of concentration of ZnO nanoparticles.

**ACKNOWLEDGEMENT:**

We are very much obliged to U.G.C. for providing financial assistance for running the Major Research Project No. 34–33/2008 (SR) dt. 29/12/2008 and for encouraging and initiating the research oriented education in B. N. College, Patna University, Patna-4. We are very much thankful to Dr. O. N. Shrivastav, H.O.D Physics B.H.U., Varanasi for providing facility of SEM and Dr. Amrendra Narayan, P. G. Deptt. of Physics, Patna University, Patna for providing the facility of XRD. We are also thankful to UGC- DAE Consortium for Scientific Research Indor, for providing their FT-IR Spectroscopic Facilities to characterize nanocomposite films.

**Reference:**

- [1] Jhonson, J.C, Yan. H, Schaller R D, Haver L H, Saykally R J and Yang P 2001, *J. Phys. Chem.* B105:113875.
- [2] Wang Z, Zhang H, Zhang L, Yuan J, Yan S and Wang C, 2003, *Nanotechnol.* 11 :14.
- [3] R Murugesan and E Subramanian T.D.M.S. College, Tirunelveli 627113, *India App.*. 2003.
- [4] Agashe C, Kulth O, Hupkes J, Zastrow U, Ruched and Wuttig M, 2004, *J. Appl. Phys.*, 95 1911.
- [5] Karimi N.A.,et, al. *Bulletin of Pure Applied Science*, Vol.25-D,2006.
- [6] Bahadur Harish, Srivastava A K, Haranath Divi, Chandra Harish, Basu A, Samanta S B, Sood K N, Ramkishore, Sharma R K, Rashmi, Bhatt Vivekanand, Pal Prem, and Chandra Sudhir. *Ind. J. P. Appl. Phys.* Vol 45, April 2007, pp 395-399.
- [7] Xiang B, Wang P, Zhang X, Dayeh S A, Aplin D P R, Soci C Yu D and Wang D, 2007 *Nano Lett.* 7 : 323.
- [8] Yadav B C, Srivastava Richa, Alok Kumar, 2007.*Inter. J.of Nanotechnology and application*, vol- 1, No-2,2007, pp 1-11.
- [9] Yadav B C, Srivastava Richa, Dwivedi C. D., Pramanik P., 2008. *Sensors and Actuators*, B 131 (2008) 216-222.
- [10] R.Damble, P N Kulkarni and S V Bhat, Indian Institute of Science, Bangalore, *India*, 29 *App.* 2008.
- [11] *Nanotechnology* by Er. Rakesh Rathi First ed. 2009, S. Chand ISBN: 81-219-3082-0Code: 10378.
- [12] Karimi, N.A., Kumar A., *J. surface sci. Technol.* Vol31(3-4) pp.179-183 December 2015.
- [13] G. Louis Hornyak, Joydeep Dutta, John J. Moore and Harry F. Tibbals, 2009, *Fundamentals of NanoTechnology*, CRC Press of Taylor and Francis Group

LLC (ISBN 14-2004-8031).

- [14] G. Louis Hornyak, Joydeep Dutta, John J. Moore and Harry F. Tibbals.(2009). *Fundamentals of NanoTechnology*, CRC Press of Taylor and Francis Group LLC (ISBN 14-2004-8031).
- [15] A.Sarfraz.Bull mattSc vol-35 No-4 page -542

