

## RESEARCH ARTICLE

## Study of physical and electrical properties of CuO-MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> Glasses

Gawande WJ<sup>1\*</sup>, Yawale SS<sup>2</sup> and Yawale SP<sup>1</sup>

<sup>1</sup>P.G. Department of Physics, Government Vidarbha Institute of Science and Humanities, Amravati 444604 Maharashtra

<sup>2</sup>Director, Government Vidarbha Institute of Science and Humanities, Amravati 444604 Maharashtra

\*Corresponding author : Mbl : 9421818498 | E-mail: [wasudeo.gawande@gmail.com](mailto:wasudeo.gawande@gmail.com)

### Manuscript Details

Received : 15.04.2015  
 Revised : 01.05.2015  
 Revised Received : 05.05.2015  
 Accepted: 08.05.2015  
 Published: 28.06.2015

ISSN: 2322-0015

Editor: Dr. Arvind Chavhan

### Cite this article as:

Gawande WJ, Yawale SS and Yawale SP. Study of physical and electrical properties of CuO-MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> Glasses *Int. Res. J. of Science & Engineering*, 2015; Vol. 3 (3):77-83.

### Acknowledgement:

The authors express their sincere thanks to Head, Department of Physics and Director, Govt. Vidarbha Institute of Science and Humanities, Amravati for providing laboratory facilities.

**Copyright:** © Author(s), This is an open access article under the terms of the Creative Commons Attribution Non-Commercial No Derivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

### ABSTRACT

Glasses are very much stronger than organic fibre. Besides glass being a totally non combustible material it greatly improves the fibre endurance of composite. Due to many uses of CuO-MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses, dc-conductivity measurement with increasing concentration of MnO<sub>2</sub> (in the range of 5-30 mol%) have been reported in the temperature range of 313-573 K in the present study. In addition, the physical properties like density, molecular weight, molar volume, hopping distance, polaron radius and number of ions per cm<sup>3</sup> have been reported. A plot of  $-\log \sigma$  versus  $1/T$  shows two different regions of conduction. The DC conductivity increases with increase in temperature of the sample and it is composition dependent. Activation energy calculated from both regions (LTR and HTR) is below 1 eV. Thus electrical conduction is electronic. Activation energy in LTR and HTR are independent of temperature but depends on composition. The values of effective dielectric constant, polaron binding energy, polaron hopping energy, polaron band width and pre-exponential factor are reported. The nature of hopping conduction is found to be adiabatic. The data has been analysed in the light of polaronic hopping conduction model. The values of dielectric constant at different temperature (313-573K) at a constant frequency of 1 KHz are reported. It is observed that the dielectric constant does not change with temperature upto certain temperature, but then dielectric constant increases with temperature fastly. The dielectric constant of all the samples studied is found to depend on composition. In the glasses studied dipole relaxation phenomenon is observed.

**Keywords:** CuO- MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses, physical and electrical properties, adiabatic hopping conduction, dielectric constant.

## 1. INTRODUCTION

Now days glasses have a prominent role in the field of electronics and have wide applications in industry, space research, computer memories etc. Since 1954 when the electronically conducting oxide glasses were discovered, glass formation and properties in transition metal oxide systems have been extensively studied due to their important semiconducting behavior (Mott, 1968, Austin and Mott, 1969; Denton *et al.*, 1954; Sayer and Mansing, 1972) Chaudhury, 1995 have discussed in brief the general procedure for making glass ceramic superconductors and some of their physical properties. All the glasses which become superconductors after properly annealing at higher temperatures are in general transition metal oxides (TMO) with copper ions. (Ghosh and Chaudhury, 1984) discussed the results of dc-conductivity of semiconducting vanadium bismuth oxide, containing 80-95 mol% vanadium pentaoxide in the 300-500 K temperature range on the basis of polaronic hopping model similarly they observed adiabatic hopping conduction. The electrical properties of  $V_2O_5$ - $B_2O_3$  glasses are discussed on the basis of small polaron hopping model by (Culea and Nicula, 1986). The charge transfer mechanism plays a dominant role in semiconducting glasses. Dc-conducting and hopping mechanism in  $Bi_2O_3$ - $B_2O_3$  glasses has been studied by (Yawale and Pakade, 1993). The physical and transport properties such as density, hopping distance, polaron radius, dc-conductivity and activation energy are reported by them. The small polaron hopping model is applied to the glass system. Dc-conductivity, density and infrared investigation have been carried out on  $ZnO$ - $PbO$ - $B_2O_3$  glasses by (Doweldar *et al.*, 1994 Mandal *et al.*, 1987) have reported the dielectric behaviour of glass system  $BaO$ - $PbO$ - $TiO_2$ - $B_2O_3$ - $SiO_2$ . The electric relaxation study of  $V_2O_5$ - $B_2O_3$  glasses has been done by (Singh and Tarsikka, 1988) In the present work it is decided to measure the variation of physical parameters and dc-electrical conductivity and dielectric constant with temperature in  $CuO$ - $MnO_2$ - $B_2O_3$  glasses and to study nature of hopping conduction.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of glass samples

The glass samples were prepared in a fireclay crucible. The muffle furnace used was of Heatreat Co. Ltd. (India) operating on 230 volts A.C. reaching upto a maximum temperature of  $1500 \pm 10^\circ C$ . Glasses were prepared from A R grade chemicals. Homogenous mixture of an appropriate amounts of  $CuO$ ,  $MnO_2$  and  $B_2O_3$  (mole%) in powder form was prepared. Then, it was transferred to fire-clay crucible which was subjected to melting temperature ( $1300^\circ C$ ). The duration of melting was generally two hours. The homogenized molten glass was cast in steel disc of diameter 2 cm and thickness 0.7 cm. Samples were quenched at  $200^\circ C$  and obtained in glass state by sudden quenching method. All the samples were annealed at  $350^\circ C$  for two hours.

### 2.2 Density Measurement

The densities of glass samples were measured using the Archimedes principle. Benzene was used as a buoyant liquid. The accuracy in the measurement of density was  $0.001 \text{ g/cm}^3$ . The densities obtained  $d_{\text{expt}}$  were compared with corresponding theoretical valences, calculated  $d_{\text{theo}}$  according to the additive rule given by (Demkina, 1960) a  $d_{\text{theo}} = (\text{Mol\% of } CuO \times \text{density of } CuO + \text{mol\% of } MnO_2 \times \text{density of } MnO_2 + \text{Mol\% of } B_2O_3 \times \text{density of } B_2O_3) / 100$

### 2.3 Electrical Measurement

The dc resistance of the glass sample was measured by using D.C. microvoltmeter, Systronics 412 India; having an accuracy of  $\pm 1 \mu V$  and input impedance  $10 \text{ M}\Omega$ , by voltage drop method given by (Kher and Adgaonkar, 1972). Before electrical measurements all the samples were polished to smooth surfaces using fine quality emery paper. After application of conducting silver paint at either sides, the samples were used for electrical measurements. The silver paint acts like electrodes for all the samples.

### 2.4 Dielectric Constant

The dielectric constant of the glass samples was measured by measuring the capacitance of the samples at constant frequency 1 KHz in the temperature range 313 to 573 K. Digital LCR meter 925, systronics made (India), was used for the measurement of capacitance. The accuracy in the capacitance measurement was ±0.1 pF

### 3 Theory

The d c conductivity of semiconducting oxide glasses for the hopping of polarons in non-adiabatic approximation is given by (Mott, 1968, Austin and Mott, 1969).

$$\sigma = [ v_o N e^2 R^2 C (1 - C) \exp (-2\alpha R) \exp (- W/K_B T) ] / K_B T \dots\dots\dots(1)$$

Where  $v_o$  is the characteristic phonon frequency,  $\alpha$  is the electron wave function decay constant, C is mol fraction of sites occupied by an electron, N is the number of metal ions per unit volume, R is the hopping distance (sites spacing) and W is the activation energy. The term  $\exp (-\alpha R)$  represents electron overlap integral. When this term approaches unity, the hopping conduction is adiabatic in nature and it is to be mainly controlled by activation energy. Therefore equation (1) reduces to

$$\sigma = ( 1 / K T ) [ v_o N e^2 R^2 C (1-C) \exp (- W/K T) ] \dots\dots\dots(2)$$

The polaron hopping energy [10]  $W_H$  is given by

$$W_H = W_P / 2 = e^2 \frac{1}{r_p} - \frac{1}{R} / 4 \epsilon_p$$

Where  $1/\epsilon_p = 1/\epsilon_\infty - 1/\epsilon_s$ ,  $\epsilon_p$  the effective dielectric constant,  $\epsilon_\infty$  and  $\epsilon_s$  are the dielectric constant at infinite frequency and static dielectric constants. The polaron radius ( $r_p$ ) is given by (Murawaski,1979)

$$r_p = (\frac{1}{2}) (\pi/6)^{1/3} \times R$$

In generalized polaron model(Setty,1979) the polaron band width [J] is given by

$$W = W_H - J \dots\dots\dots(3)$$

Where J is related to electron wave function overlap on adjacent sites.

The polaron band width J should satisfy the inequality suggested by (Holstein ,1959)

$$J > (2 K T W_H / \pi)^{1/4} ( h \omega_{ph} / \pi )^{1/2} \dots\dots\dots(4)$$

$$\text{Or } J > J^*$$

> for adiabatic

< for non-adiabatic

Where

$$J^* = ( 2 K T W_H / \pi )^{1/4} ( h \omega_{ph} / \pi )^{1/2} \dots\dots\dots(5)$$

The polaron band width J can be estimated from

$$J \approx e^3 [ N ( E_F ) ]^{1/2} / \epsilon_p^{3/2} \dots\dots\dots(6)$$

Where  $N(E_F)$  is the density of states at fermi levels.

## RESULT AND DISCUSSION

### 4.1 Physical properties

The physical parameters such as density (d), molecular weight (M), molar volume (V), hopping distance (R), polaron radius ( $r_p$ ) and number of ions per unit volume (N) are reported in table 1 for CuO- MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses. The density, molecular weight and number. of ions per cm<sup>3</sup> increases with increasing mol% of MnO<sub>2</sub> but molar volume, hopping distance and polaron radius decreases with increasing mol% of MnO<sub>2</sub>. In glasses the structure depends on the glass network in which the number of ions enter. In what way they entered and what is the nature of the ions, decides the density of the glass. The increase in the density with increasing mol% of MnO<sub>2</sub> suggest the decrease in the number of non-bridging oxygen ions. The hopping distance is reduced with the increase in MnO<sub>2</sub> mol% in the glass system. This indicates that the conduction processes becomes fast, because of the small hopping distance the polaron requires smaller

**Table 1 : Physical parameters of CuO- MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses**

Glass No.	Composition (mol%) CuO- MnO <sub>2</sub> - B <sub>2</sub> O <sub>3</sub>	Density		Molecular weight M(gm)	Molar volume V(cm <sup>3</sup> /mol)	No.of ions per cm <sup>3</sup> N(cm <sup>-3</sup> ) x 10 <sup>22</sup>	Hopping distance R(A <sup>0</sup> )	Polaron radius r <sub>p</sub> (A <sup>0</sup> )
		d <sub>the</sub> gm/cc	d <sub>expt</sub> gm/cc					
G B1	20-5-75	2.58	2.806	66.76	23.79	2.54	3.40	1.37
G B2	20-10-70	2.76	2.949	68.00	23.05	2.66	3.36	1.35
G B3	20-15-65	2.93	3.066	69.25	22.58	2.72	3.34	1.34
G B4	20-20-60	3.11	3.223	70.50	21.87	2.78	3.31	1.33
G B5	20-25-55	3.29	3.372	71.74	21.27	2.84	3.28	1.32
G B6	20-30-50	3.47	3.534	72.99	20.65	2.97	3.24	1.30

**Table 2 : Transport Properties of CuO-MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses**

Glass No.	Activation energy W (eV)		Effective dielectric constant ε <sub>p</sub>	Polaron binding energy W <sub>P</sub> (eV)	Polaron hopping energy W <sub>H</sub> (eV)	Pre-exponential factor σ <sub>0</sub> (Ohm x cm <sup>-1</sup> ) 10 <sup>-9</sup>	Polaron band width LTR		Polaron band width HTR	
	LTR (W <sub>L</sub> )	HTR (W <sub>h</sub> )					J eV	J* eV	J eV	J* eV
	G B1	0.0035					0.250	9.6	0.327	0.164
G B2	0.0052	0.181	10.2	0.313	0.157	6.60	0.152	0.0337	0.024	0.0368
G B3	0.0060	0.258	10.8	0.298	0.149	5.62	0.143	0.0342	0.109	0.0374
G B4	0.0069	0.310	20.0	0.162	0.081	3.16	0.074	0.0297	0.229	0.0324
G B5	0.0086	0.422	22.4	0.155	0.078	14.7	0.069	0.0297	0.344	0.0324
G B6	0.0090	0.474	22.8	0.145	0.073	1700	0.064	0.0297	0.401	0.0324

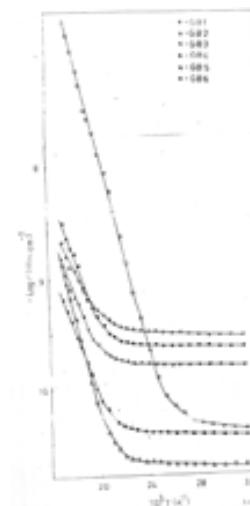
time to hop between nearest neighbour place. The values of physical parameters reported are found to be of the order of glasses reported in literature (Soppe *et al.*, 1988; Damodaran and Rao, 1989; Royle *et al.*, 1994; Ghosh, 1995).

**4.2 Transport Properties**

D.C. electrical conductivity of the glass samples is measured in the temperature range 313 to 573 K. The value of d.c. conductivity is found to be of the order of 10<sup>-10</sup> to 10<sup>-11</sup> ohm<sup>-1</sup> cm<sup>-1</sup> at 313 K.

Fig 1 shows the plot of - log σ versus 1/T. It is observed that, the conductivity of all the glass samples studied increases with increasing temperature.

This plot is found to consists of two distinct straight linear regions called as low temperature regions (LTR) (313 to 413 K) and high temperature region (HTR) (493 to 573 K).



**Fig. 1-Temperature Dependence of dc-electrical conductivity for the glasses of different compositions**

In LTR conductivity increases linearly with increasing temperature at very slow rate where as in HTR conductivity increases linearly with increasing temperature at a faster rate. Obviously two activation energies and two conduction mechanisms are associated with electronic conduction in all the glasses studied. The same type of dc conductivity behaviour is reported in literature. The activation energies are obtained from slope of the plot of  $-\log \sigma$  versus  $1/T$  in both the regions and reported in table 2. It is observed that the activation energy is temperature independent but depends on composition. The activation energies obtained are found to be of order of borate vanadate and other semiconducting glasses reported in literature (Sayer and Mansing, 1972; Nassa, 1982; Kulkarni *et al.*, 1984; Ghosh and Chaudhuri, 1986; Sing and Tarsikka, 1988). Activation energy calculated for both regions (LTR and HTR) is found to be less than 1 eV, thus the electrical conduction is electronic.

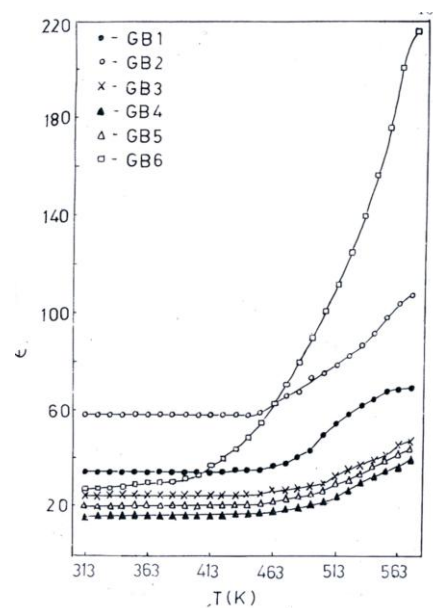
Table 2 reports the values of activation energy, effective dielectric constant calculated from optical study, polaron binding energy, polaron hopping energy, polaron band width and pre-exponential factor of  $\text{CuO-MnO}_2\text{-B}_2\text{O}_3$  glasses. The values of different parameters reported in the table agreed with the values reported for semiconducting glasses in the literature (Gawande *et al.*, 2014; Sayer and Mansing, 1972; Yawale and Pakade, 1993; Nassa, 1982; Kulkarni *et al.*, 1984; Ghosh and Chaudhuri, 1986; Sing and Tarsikka, 1988; Mori *et al.*, 1993).

To check the nature of hopping conduction, the condition given by Holstein *et al.* (1959) is applied. He has suggested that the polaron band width  $J$  should satisfy the inequality equation (4). Accordingly the values of  $J$  and  $J^*$  are calculated from equation (3) and (5). The value of  $J$  for all the glass samples studied in LTR and HTR both are found to be greater than the value of  $J^*$ , suggesting the nature of hopping conduction is adiabatic for all the glass samples. The same method was applied to examine the nature of hopping conduction in  $\text{V}_2\text{O}_5 - \text{Bi}_2\text{O}_3$  glasses by (Ghosh and Chaudhuri, 1986; Dhote, 2014),  $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$  glasses by (Yawale and Pakade, 1993), phosphate glasses

by (Sayer and Mansing, 1972) and Vanadate glasses by (Mori *et al.*, 1993).

### 4.3 Dielectric Constant :

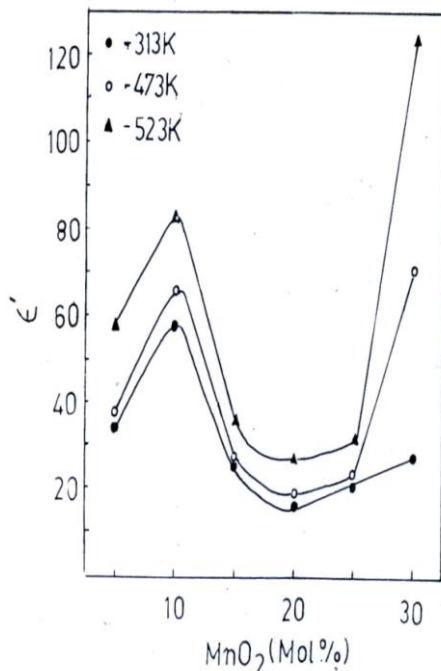
The variation of dielectric constant ( $\epsilon'$ ) at different temperature (313-573K) at a constant frequency of 1 KHz for the glass samples is shown in Fig. 2. It is observed that the dielectric constant ( $\epsilon'$ ) is independent of temperature upto certain temperature range, but after that the dielectric constant increases with temperature rapidly. A similar trend has been reported for different transition metal oxide glasses by (Sayer and Mansing, 1972) [4], (Mansing *et al.* 1983) [28]. This increase in dielectric constant is partly due to a change in electronic structure and partly due to thermal expansion. In glasses rise of temperature may increase the free carrier density to introduce conduction losses. The change in dielectric constant at high temperature is a characteristics of Debye type relaxation process where symmetrical distribution of relaxation time takes place. The rapid rise is likely to arise from the other sources of polarization possibly from enhanced electrode polarization as temperature rises. More sharp rise of ( $\epsilon'$ ) at high temperature was also observed in other oxide glasses by (Sunder and Rao, 1982) [29] and (Sing and Tarsikka, 1988) [23].



**Fig 2: Variation of dielectric constant with temperature at constant frequency of 1KHz for the glass samples**



The dielectric constant of all the sample studied is found to be composition dependent. Variation of dielectric constant with composition at a constant temperature is shown in figure 3. A tip is observed at 10 mol% of MnO<sub>2</sub>. In these glasses dipole relaxation phenomenon is observed.



**Fig 3 : Variation of dielectric constant with composition at a constant temperature for the glass samples**

## 5. CONCLUSIONS

The physical parameters of CuO-MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses studied are found to be composition dependent and their values reported are found to be of the order of semiconducting glasses. D-C conductivity of these glasses studied in the temperature range 313-573 k is found to be temperature and composition dependent. The activation energy is temperature independent but composition dependent. The activation energy and other transport properties are found to be in the range of semiconducting glasses. The electrical conduction is electronic. The nature of hopping conduction is found to be adiabatic. The dielectric constant of the glass samples is found to be temperature and composition dependent. In the glasses dipole relaxation phenomenon is observed

## REFERENCES

1. Austin LG, Mott NF. Polarons in crystalline and non-crystalline materials, *Advances in Physics*, 1969, 18(71): 41-102. Doi. 10.1080/00018736900101267.
2. Chaudhury BK. Some aspect of glass-ceramicsuperconductors, *Bulletin of Material Science*, 1995, 18(1): 27-46.
3. Clay R H and Murthy MK, *J. Am. Cerm. Soc (USA)*, (1970) 53
4. Culea E and Nicula AI. Electrical properties of V<sub>2</sub>O<sub>5</sub> 璦 B<sub>2</sub>O<sub>3</sub> glasses, *A Solid state Commun (USA)*, 1986, 58 : 545. DOI: 10.1016/0038-1098(86)90793-3.
5. Damodaran KV and Rao KJ. Elastic properties of alkali phosphomolybdate glasses, *J. Am. Ceram. Soc.* 1989; 72, 533 - 539.
6. Denton EP, Rawson H, Stanworth JE. Seed Production, Testing and Distribution in European Countries, *Nature (GB)*, 1954, 173, 4413 1030. doi:10.1038/1731030a0.
7. Dhote DS. Transport properties of Vanadium Borate Glasses, *Int. Res. J. of Sci. & Engg.*, 2014; 2 (5):161-166.
8. Doweldar M, El-Damrawi G M and Moustafa Y M. Transport properties of semiconducting Fe<sub>2</sub>O<sub>3</sub>-PbO-B<sub>2</sub>O<sub>3</sub> glasses, *Journal of Physics*, 1994, 6 (42): 8829.
9. Gawande WJ, Yawale SS and Yawale SP. Electrical conduction in CuO-MnO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glasses, *Int. Res. J. of Sci. & Engg.*, 2014; 2 (4): 145-149.
10. Ghosh A, *Bull Mater Sci*, (1995) 18 1 53.
11. Ghosh A, Chaudhury BK. Adiabatic hopping in V<sub>2</sub>O<sub>5</sub> - Bi<sub>2</sub>O<sub>3</sub> glasses,, *Indian Journal of Physics*, 1984, 58A:62.
12. Ghosh A, Chaudhury BK. Dc conductivity of V<sub>2</sub>O<sub>5</sub> - Bi<sub>2</sub>O<sub>3</sub> glasses, *Journal of Non-Cryst Solids*, 1986, 83:151.
13. Giridhar A and Mahadevan Sudha. DC electrical conductivity of some Cd-Ge-As glasses, *Bulletin of Material Science*, 1989, 12(2): 107-115.

14. Holstein T. Studies of polaron motion : Part II. The "small" polaron, *Ann Phys* (1959) 8 (3) 343-389.
15. Karimi N A and Gupta D, *Current Trends in Physics of materials*, 1987, 201.
16. Kher V G and Adgaonkar C S, *Indian Journal of Pure Applied Physics*, 1972, 10 :902.
17. Kulkarni A R, Maiti H S and Paul A. Fast ion conducting lithium glasses—Review, *Bulletin of Material Science*, 1984, 6 (2) 201-221.
18. Mandal R K, Durgaparshad C Omprakash and Kumar D. Dielectric behaviour of glasses and glass ceramics in the system BaO-PbO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, *Bulletin of Material Science*, 1987, 9 (4): 255-262.
19. Mansingh A, Dhawan V K and Sayer M, Dielectric relaxation and modulus of V<sub>2</sub>O<sub>5</sub>—TeO<sub>2</sub> glasses, *Philosophical Magazine*, Part B, 1983; 48(3):215-236.
20. Marshall JM and Owen AE, The mobility of photo-induced carriers in disordered As<sub>2</sub>Te<sub>3</sub> and As<sub>30</sub>Te<sub>48</sub>Si<sub>12</sub>Ge<sub>10</sub>, *Philosophical Magazine*, 1975; 31, (6): 1341-1356.
21. Mori H, Igarashi J and Sakata H, Electrical Properties of V<sub>2</sub>O<sub>5</sub>-ZnO-TeO<sub>2</sub> Glasses, *Journal of Ceram Soc (Japan)*, 1993, 101 1351-1357.
22. Mott NF., *Journal of Non-Cryst. Solids*, 1968, 1: 1
23. Sayer M and Mansingh A, *Physics Review.*, 1972 , B6 4629.
24. Setty MS, Ind J. *Pure & Appl Phys*, (1979) 17 283.
25. Singh B and Tarsikka P S, *Indian Journal of Pure Applied Physics*, 1988, 26 660.
26. Murawaski L, Chung C H and Mackenzie J D, *J. Non-cryst solids*, (1979) 32 91.
27. Nassar A N , *Indian Journal of Pure and Applied Physics*, 1982, 20 337.
28. Royle M, Meckenzie J, Taylor MS and Feile, J *Non-Cryst solids*, (1994) 17 242.
29. Soppe W, MareCV, GunsterenWF and Hartog HW, *J Non-cryst, solids*, (1988) 1032
30. Sunder, H G K and Rao K J, *Pramana. AC conductivity and dielectric properties of sulphate glasses*, *PRAMAN*, 1982, 19(2): 125-131
31. Yawale SP and Pakade SV. D.C. conductivity and hopping mechanism in Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses, *Journal of Material Science*, 1993, 28(20):5451-5455