Effect of TeO$_2$ on Mechanical and Structural Properties of Zinc Lithium Borate glasses

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Abstract: *To investigate Mechanical and structural properties of glass samples of the Quaternary system (60-x) B$_2$O$_3$−xTeO$_2$-10ZnO-30Li$_2$O with x=0, 5, 10, 15, and 20 mole% were prepared by conventional melt quenching technique. Amorphous nature of glass samples was confirmed by X-ray diffraction. Density (ρ) of glass samples was measured with the increase of TeO$_2$ mole concentration. Mechanical properties like Young's modulus (E), Shear modulus(S), Bulk modulus (K) etc., were calculated with the help of Makishima-Mackenzie model interms of Packing ratio(V$_p$), Dissociation energy (G$_t$). Raman and FTIR spectroscopy studies reveal that glass network consists of TeO$_3$ and TeO$_4$ structural units along with BO$_3$ and BO$_4$ units with various modes.*

Keywords: *Dissociation energy, Oxygen Packing density, FTIR and Raman spectra, Elastic moduli.*

1. INTRODUCTION:

B$_2$O$_3$ is one of the best and well known glass formers. Addition of small amounts of TeO$_2$ into borate glass network enhances refractive index and transparency. Glass network produces low rates of crystallization and enhances glass forming ability. Synthesis, physical, optical and structural properties of heavy metal oxide glasses are very interesting   due to their high density, high refractive index and high IR transparency [1, 2].Tellurium oxide (TeO$_2$) based glasses are of scientific and technical interest on account of their various unique properties and have been considered as promising materials for use in optical amplifiers because of their large third order non-linear susceptibility [3, 4]. Optically transparent TeO$_2$ based glasses showing second harmonic generation have been discovered [5, 6].

Elastic properties play an important role in studying the nature of bonding between the atoms of crystals or localized structured amorphous materials. Elastic properties too explain the mechanical behavior to understand the rigidity of materials [7, 8]. Elastic properties also explain the forces between the atoms or ions comprising the glass structure. Several Researchers reported the results on binary and ternary glass systems. Yasser B. Sadeek et al [9] studied the mechanical and structural properties of Li$_2$O -TeO$_2$- B$_2$O$_3$ glasses and concluded that the experimental results of mechanical properties   same as the theoretical results. A.Edukondalu et al studied Thermal, Mechanical and Raman studies on mixed alkali Boro tungstate glasses in particular they were calculated the mechanical properties theoretically [10] . The main objective of present work is to evaluate the elastic moduli using familiar and convenient Makishima and Mackenzie model and also aimed to study the structural changes with the addition of network modifier TeO$_2$ with the help of Raman spectra and FTIR spectra of the glass system.

2. PREPARATION OF GLASSES:

Quaternary glass system with composition (60-x) B$_2$O$_3$-10ZnO-xTeO$_2$-30Li$_2$O where x= 0, 5, 10, 15, 20 were prepared by conventional melt quenching technique. For this purpose Analar grade chemicals with high purity (Sigma Aldrich-99.9%) purity like H$_3$BO$_3$, ZnO, TeO$_2$, LiCO$_3$ were used as starting materials taken in the appropriate mole ratios and they were mixed in the porcelain crucible of J-brand. Mixture was kept in the electric cylindrical muffle furnace which is approximately at 950^{0}C for 30 minutes. The mixture was melt and stirred to get the homogeneity. It was poured on the pre heated metal plate of stainless steel at 150^{0}C then pressed with a metal rod. Transparent glasses was formed and then annealed at 300^{0}C in the furnace to remove thermal strains for 12 hours. The prepared glass samples were kept inside the paraffin oil to avoid hydroscopic behavior of the glasses. Further the glass samples were characterized by various experimental techniques. Glass samples with codes and compositions are given in table 1.

Table.1.Detailed composition:

Sample code	Composition in mole percentage			
	B$_2$O$_3$ %	ZnO %	TeO$_2$ %	Li$_2$O %
BZL 1	60	10	0	30
BTZL 2	55	10	5	30
BTZL 3	50	10	10	30

BTZL 4	45	10	15	30
BTZL 5	40	10	20	30

2.1. CHARACTERIZATION TECHNIQUES:
2.1.1. X-ray diffraction:

 To determine the nature of the prepared glass samples X-ray diffraction technique have been carried out using X-ray diffractometer with k_α radiation ($1.54A^0$) at room temperature .The patterns (Philips PW 1140) were recorded Bragg angle in the range of 10^0-80^0 with counting rate 0.2/sec.

2.1.2. Density measurements:

The density (ρ) of the glass samples were measured at room temperature by Archimedes principle with xylene (ρ = 0.86 g/cc) as the immersion liquid .Density of the glass measured by using the following relation.

$$Density\ (\rho) = \left[\frac{a}{a-b}\right] * 0.86 \qquad (1)$$

where   a - Weight in air,   b - Weight in xylene

2.1.3. FTIR and Raman Spectra:

The FTIR spectra of the obtained glass samples was recorded at room temperature using KBr pellet technique in the range of 400-4000 cm^{-1} on FTIR spectrophotometer .The Raman spectra of prepared Quaternary glass system were recorded at room temperature in the spectral range of 200-2000 cm^{-1} with micro Raman system from a Jobin Yvon Horiba (LABRAM HR-800) spectrometer. The system is equipped with high stability confocal microscope to focus the laser beam using Diode LASER of wavelength 473nm was used for excitation at Consortium for Scientific Research, Indore, India.

3. RESULTS AND DISCUSSION:
3.1 XRD:
The XRD patterns of all the glass samples are found that there is no sharp peak in the patterns therefore it is confirmed the glasses are amorphous in nature as shown in figure.1.
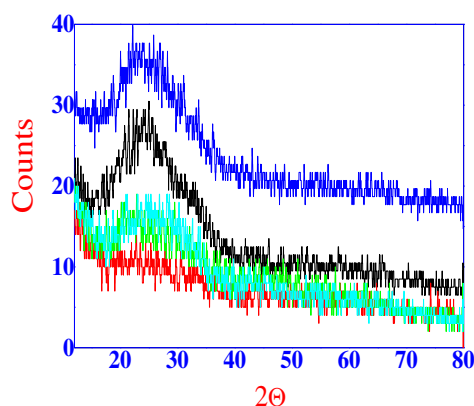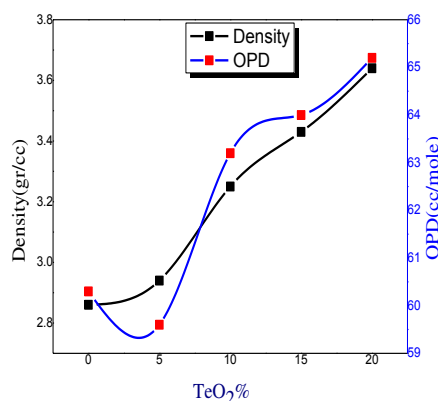

Fig.1.XRD patterns of glasses   **Fig.2**.Variation of density and OPD

3.2 Density (ρ)
        Density is the physical property of a material which is an important tool capable of exploring the tightness in the structural changes of material. It is also closely relative by the structural softening, change in the co-ordination number geometrical configuration, and dimension of of the glass. Density was increased from 2.86 gr/cc to 3.64 gr/cc with the addition of network modifier TeO_2 from zero mole fraction to 20 mole fraction as shown in Fig.2. The change may be due to the breaking of continuous boron group networks and TeO_2 enters into glass network [11].

3.3. Oxygen Packing Density :
        Oxygen packing density (OPD) of the samples was calculated in terms of Density and molar volume. It was increased with TeO_2 mole percentage from 60.3-65.2 (g atm/1) due to more number of oxide ions entering to the glass network as shown in figure.2. OPD also plays an important role in studying elastic moduli. Oxygen packing density (OPD) of the glass samples were calculated from the equation relation as follows [12]

$$OPD = 1000 * \frac{Cp}{Mi} \qquad (2)$$

where ρ, M_i and C are density, molar and number of oxygen ions present in the formula unit respectively.

3.4. Direct Calculation of Elastic moduli:

Young's modulus (E) of crystalline oxides according to Gilman [13] is given by

$$E = \frac{2\alpha U}{r_0 3} \qquad (3)$$

Where, U is electrostatic energy of attraction between a pair of ions of opposite sign with the spacing r_0, α is the Modeling constant. It is quite difficult to adopt satisfactory Modeling constant for the amorphous solids due to disorder of structure where crystalline oxides holds good Modeling constant.

Makishima-Mackenzie model is the most successful model to evaluate the elastic properties of the glasses directly by using a semiempherical formula in terms of ionic packing ratio(V_p) and Dissociation energy (G_t)of the chemical composition of the system. Dissociation energy measures the strength of a chemical bond. G_i is the dissociation energy per unit volume of ith oxide and Dissociation energy per unit volume (G_t) of various oxides in the present study are G_{Li2O}=77.9GPa, G_{TeO2}=54GPa ,G_{ZnO}=41.4 GPa and G_{B2O3}=82.8 GPa [13]. The standard values of Packing factors(V_i)of various components in the glass system given as B_2O_3 = 20.8x10^{-6} m^3/cal, TeO_2 = 14.7x10^{-6} m^3/cal , ZnO = 7.9x10^{-6} m^3/cal and Li_2O=8x10^{-6} m^3/cal [14]. Density dependent Ionic packing density (V_p),Young s modulus(E), bulk modulus(K), shear modulus(S) and Poisson's ratioμ_{cal} of the glass samples were theoretically calculated by the following relations.

$$V_p = \frac{\rho}{M} \sum x_i V_i \qquad (4)$$
$$G_t = \sum x_i \ G_i \qquad (5)$$
$$E = 2V_p G_t \qquad (6)$$
$$K = 2.4 G_t V_p^2 \qquad (7)$$
$$S = \frac{3EK}{9K-E} \qquad (8)$$
$$\mu_{cal} = 0.5 - \frac{1}{7.2Vp} \qquad (9)$$

Where Packing factors of the various components is given as V_p . With the help of above formulae, dissociation energy per unit volume G_t, Young's modulus E, bulk modulus K, shear modulus S and Poisson s ratio μ_{cal} of the present glass systems were calculated and presented in the table.1.

Elastic moduli of the prepared glasses was increased from 66.22-68.35GPa non-linearly due to the change in the structural unit of the glass network from TeO_3 to TeO_4 with the formation of bridging oxygen atoms whereas Bulk modulus was increased from 32.99 to 38.46 GPa which indicates the increase of elastic moduli of the glass samples with addition of TeO_2 [15,16]. The value of Poisson's ratio increases from 0.202 to 0.246 as the concentration of TeO_2 increases from zero mole percentage to 20 mole %. Poisson's ratio is increased means that the structure of the prepared glasses has high cross-link density [17, 18] and also be attributed to the change in the type of bonding from covalent bonds to ionic bonds [19]. The earlier reported results of mechanical properties were approximately same as the experimental results. Young's modulus was measured from 62 GPa to 74 GPa for $Li_{0.6}Te_xB_{1.4-2x}O_{2.4-x}$ glass system by   Sadeek et al [20].

Table.2.Mechanical properties of glass samples

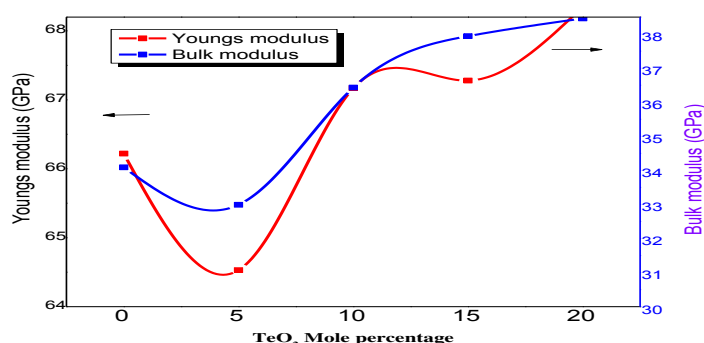| Code	BZL 1	BTZL2	BTZL3	BTZL4	BTZL5
G_t * (10^{9}J/m^3)	77.19	75.75	74.31	72.87	71.43
V_p	0.429	0.426	0.452	0.469	0.471
E(Gpa)	66.24	64.53	67.17	67.28	68.35
K(Gpa)	34.09	32.99	36.43	37.94	38.46
S(Gpa)	24.90	27.06	28.15	27.93	28.39
μ	0.202	0.216	0.224	0.230	0.246

Fig.3. Variation of Young's, Bulk modulus with TeO_2%
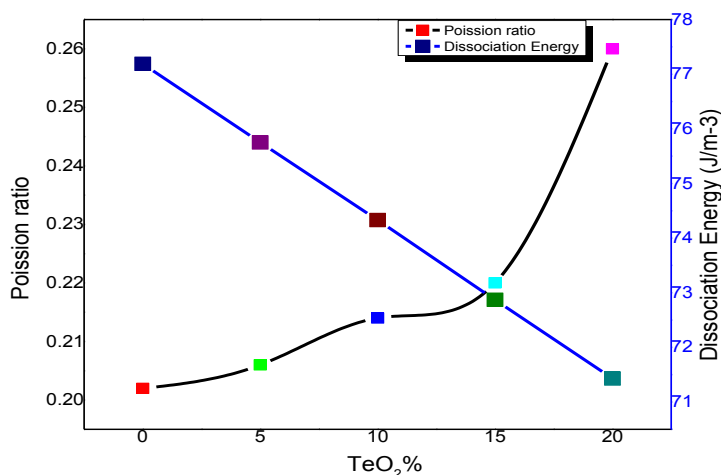
Fig.4. **Variation of Poisson ratio, Dissociation energy with TeO$_2$%.**

3.5 .FTIR and Raman Spectra :

Raman spectra is the complementary to FTIR spectra which is useful to study various changes of structural units with the addition of network modifier ions like Lithium, Zinc ions .FTIR and Raman spectra of the prepared glass samples with variation of TeO$_2$ content as shown in Fig.5,Fig.9 respectively. Raman spectra have been estimated by deconvolutation of the spectra as shown in figures 6,7,8 for different samples.

Raman peak was observed in the range 288-292cm^{-1} is attributed to Bending vibrations of Zn-O bonds in ZnO$_4$ tetrahedron [21]. In the same wave number region there is no peaks found in the FTIR spectra. Tellurite glasses shows a peak in the range of 460cm^{-1} which assigned to Te-O-Te linkages in many systems [22].A Raman peak was observed in between 457 cm^{-1}-485 cm^{-1} which is due to Bending vibrations–[Te–O–Te] or [O–Te–O] linkages whereas a peak found at 413-421 cm^{-1} in FTIR spectra due to stretching vibrations of ZnO$_4$ units[12].Exclusively there is a Raman peak is observed at wavenumber 607 cm^{-1} which is the characteristic peak of stretching vibrations of Te-O-B linkages for BTZL5 sample having highest mole fraction(20%) of TeO$_2$.

In the present study prominent and high intensified Raman peak observed in the range of 776-782cm^{-1} was attributed to stretching vibration modes TeO$_3$ and TeO$_{3+1}$ structural unit[23,24] where a sharp peak found in the wavenumber region 698-707 cm^{-1} which was attributed to trigonal pyramids of TeO$_3$ units in FTIR spectra. Raman band at 918-1100 cm^{-1} was assigned to stretching vibrations of BO$_4$ units where FTIR peak observed at the region of 987-1001 cm^{-1} due to bending vibrations of BO$_4$ units. Raman band in the range of 1200–1400 cm^{-1} are assigned to Stretching vibrations of BO$_3$ units [25]. The Raman bands in the high frequency range 1429–1547 cm^{-1} has been assigned to stretching of B–O bonds attached to large number of borate groups [26,27] where FTIR peak was observed at 1363-1387 cm^{-1} due to stretching vibrations of B-O-B in (BO$_3$) triangles. Finally there was no common peaks found in Raman and FTIR spectra.
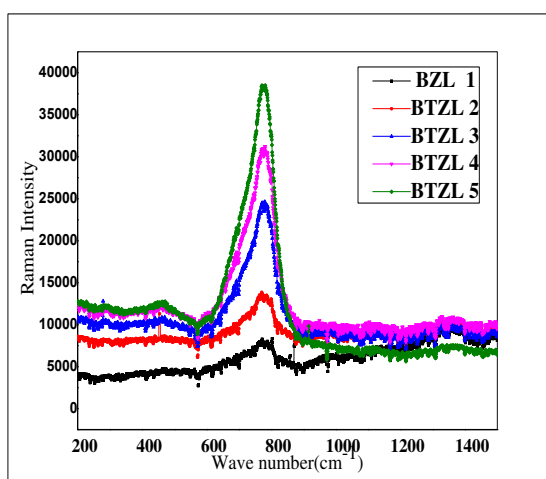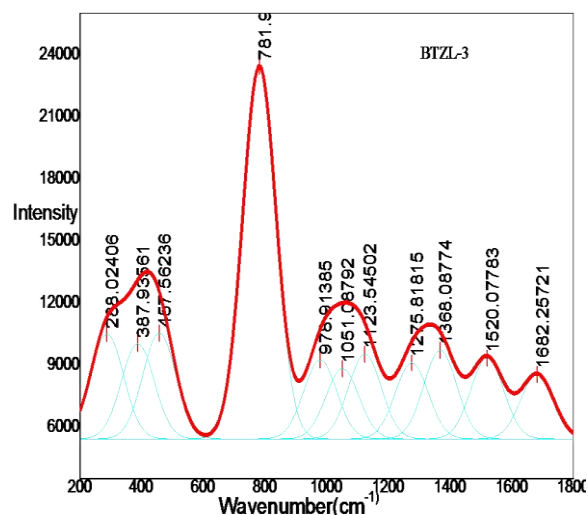

Fig.5.Raman spectra of glass samples .
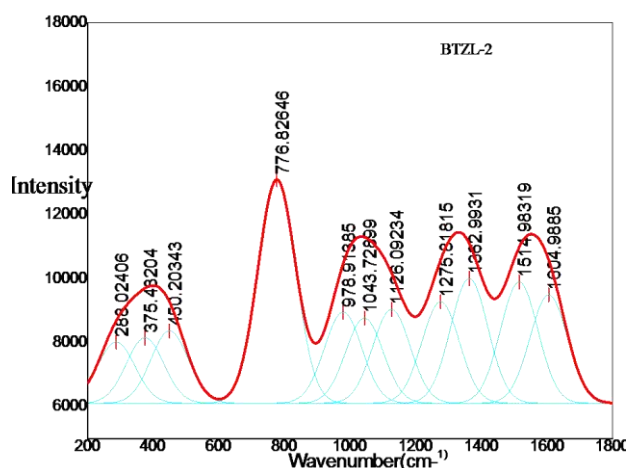

Fig.6.Deconvoluted Raman spectra of BTZL3.
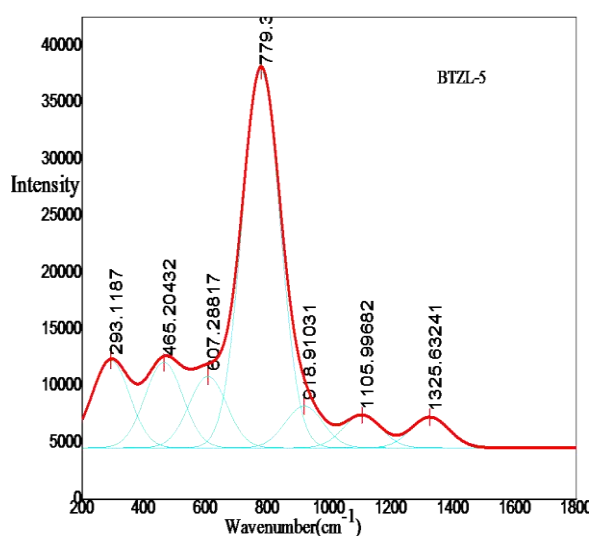
Fig.7. De-convoluted Raman spectra of BTZL 2.

Fig.8. De-convoluted Raman spectra of BTZL5.

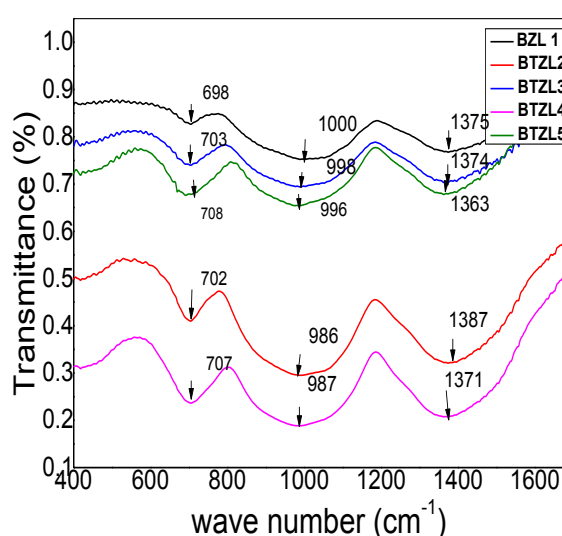Fig.9. FTIR Spectra of glasses

Table.3.Band assignments of Raman and FTIR spectra

Wave Number (cm^{-1})	FTIR band assignments	Wave Number (cm^{-1})	Raman band assignments
-	-	~288-292	Bending vibrations of Zn-O bonds in ZnO_4 units.
~413-421	Stretching vibrations of ZnO_4	457-485	Bending vibrations–[Te–O–Te] or [O–Te–O] linkages
~698-707	Trigonal pyramids of TeO_3 units.	~776–782	Stretching vibrations of Te-O-B linkages
~987-1001	Bending vibrations of BO_4 units	~918–1100	Stretching vibrations of BO_4 units.
~1363-1387	Stretching vibrations of B-O-B in (BO3) triangles	~1200–1400	Stretching vibrations of BO_3Units.

4. CONCLUSIONS:

The amorphous nature of glass samples were confirmed by X-ray diffraction technique. Density of glasses increases with addition of TeO_2. Mechanical properties were calculated using Makishima and Mackenzie model. Raman spectra and FTIR Spectra of the glasses were studied and it is observed that structural changes takes place with addition of TeO_2 . No common peak was observed in FTIR and Raman spectra.

REFERENCES:

1. C.E. Stone, A.C. Wright, R.N. Sinclair, S.A. Feller, M. Affatigato, D.L. Hogan, N.D. Nelson, Y.B. Dimitrov, E.M. Gattet, D. Ehrt, Phys. Chem. Glasses 41 (2000) 409.
2. A. Pan, A. Ghosh, J. Non-Cryst. Solids 271 (2000) 157.
3. J.S. Wang, E.M. Vogal, E. Sintzer, Opt. Mater. 3 (1994) 187.
4. S.H. Kim, T. Yoko, J. Am. Ceram. Soc. Jpn. 78 (1995) 1061.
5. M. Imoka, T. Yamazaki, J. Ceram. Soc. Jpn. 76 (1968) 160.
6. S.K. Lee, M. Tatsumisago, T. Minami, Phys. Chem. Glasses 35 (1994).
7. L. Hwa, K. Hsieh, L. Liu, Mater. Chem. Phys. 78 (2002) 105.
8. R. El Mallawany, N. El Khoshkhany, H. Afifi, Mater. Chem. Phys.95 (2006) 321
9. Y. Saddeek, H. Mohamed, M. Azzoz, Phys. Status Solidi A 201 (9)(2004) 2053.
10. A. Edukondalu et al. / Physica B 438 (2014) 120–126
11. P. Gayathri Pavani, R. Vijay Kumar & V. Chandra Mouli Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B, April 2016, 57 (2), 104–110
12. P. Gayathri Pavani et al. / Physica B 406 (2011) 1242–1247
13. J.J.Gilman,Micromechanics of flow in solids,MC Graw-Hill,Newyork(1969)29.
14. E.Kamitsos.J.Phys.Chem 91(1987)1073.
15. M. K. Halimah, W. M. Daud, H. A.A. Sidek, Ionics, 16(9), 807. (2010).
16. E. S. Yousef et al ,SolidStateCommunications,139(3),108(2006).
17. Y. B. Saddeek, L. A. El. Latif, Physica B: Condensed Matter, 348, 475 (2004).
18. E. S. Yousef, N. El-Khesh Khany, Solid State Communications,108 (2006).
19. M. S. Gaafar, N. S. A. El-Aal, O. W. Gerges, G. El-Amir, Journal of Alloys and Compounds, 475(1-2), 535 (2009).
20. Y.B. Saddeek et al. / Physica B 398 (2007) 1–7
21. Bale, S.Rahman,S.,Awasthi, A.M. and Sathe, V.(2008). Journal of Alloys and   Compounds, 460, 699-703
22. V. Kamalaker, G.Upender, C.H. Ramesh, V.ChandraMouli, Spectrochimica 89 (2012)
23. Swapna et al. / Journal of Taibah University for Science 11 (2017) 583–592
24. T.W. Bril, Philips Res. Rep. Suppl. No. 2 (1976) 111.
25. B. Kartthikeyan and S. Mohan, *Phys. B* 334, 298-302(2003).
26. Kamitsos, E.I., Karakassides, M.A. and Cryssikos, G.D. (1987) Far-Infrared Spectra of   Binary Alkali Borate Glasses .*Solid State Ionics*, 28-30, 687-692
27. Li1 Feng He1*, Zijun He2, Junlin Xie1, Yuhui,2 American Journal of Analytical Chemistry, 2014, 5, 1142