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Study of Structural and Thermal Properties of Alkaline Borate Glasses Containing Titanium ions

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Abstract: In this study, glass system with composition xCaO-(20-x)BaO-20TiO_2-60B_2O_3 with x=0,10 and 20 were prepared by conventional melt quench method and were named as BTB, BCTB, CTB respectively. The prepared glass samples were characterized using density measurements, molar volume, X-ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA). The amorphous/glassy nature of as prepared glasses was confirmed by XRD. The FTIR spectra of prepared glasses were studied in fingerprint region (i.e. 1600-450cm^{-1}). Presence of BO_3/BO_4 structural units and increase and decrease of non-bridging oxygen (NBO's) were confirms from FTIR spectra of prepared glass samples. The TGA and DTA curve were studied which confirms no weight loss and glassy nature of as prepared glasses. Parameters like glass transition temperature (T_g), crystalline onset temperature (T_x) and crystalline temperature (T_c) were calculated from DTA curve.

Introduction:-

Glassy materials have properties like hardness and transparency at room temperature, which are unique in comparison to other materials [1]. A lot of work has been published on borate glasses and their glass ceramic derivates [2-4]. Some borate glasses and glass ceramics can be used as biomaterials [4], thermo-mechanical sensor's, reflecting windows [5], fiberglass applications [7,3] etc. In such glasses, boron atom makes coordination with three or four oxygen atoms forming BO_3 and BO_4 fundamental structural units. Glasses containing Transition Metal Ions (TMIs) possessing semiconducting behaviour [8]. For semiconducting behaviour of oxide glasses, transition metal ions in glass should be capable for existing in more than one valence state [9], so conduction take place by transfer of electron from lower to higher valence state. Some transition metals which fulfil this condition are Ti, V, W, Fe, Co etc. alkali, alkaline or other oxides (TMIs) react with B_2O_3 to modify or transform the borate network, on addition of modifier some of the triangular borate converges to tetrahedral coordinated borate network with change in number of non-bridging oxygen (NBO's) [10]. This change in NBO's will play important role in properties like density measurements, molar volume [16], glass transition temperature (T_g), optical band gap etc. [11,17]. Glasses like alkaline borate possess important physical properties like second harmonic generation and dielectric properties etc [12]. Crystallization behaviour of barium borate glasses are extensively studied on basis of this property these glasses are used as transparent glass ceramics [2,13]. Marzouk et al. studied the effect of TiO_2 optical, structural and crystallization behaviour of barium borate glasses [13]. They conclude that TiO_2 decreases the glass transition temperature (T_g) and crystallization temperature (T_c) i.e. favours the crystallization behaviour.

In this present work, authors studied the physical and structural properties of alkaline borate glasses containing titanium oxide (20 mol%), and characterized them with density measurements, molar volume, XRD, FTIR, DTA and TGA.

Experimental:-

The alkaline borate glasses containing titanium ions having composition/general formula xCaO-(20-x) BaO-20TiO_2-60B_2O_3 with x=0,10 and 20 were prepared by melt quench technique. Analar grade chemicals (high purity (>99%) of CaO, BaO, TiO_2, B_2O_3 were used as starting materials. For every glass composition, 15g of sample was prepared. The calculated amounts of starting materials were weighed and mixed homogenously. After that the homogenous mixtures was poured into alumina

crucible and shift it to electrical muffle furnace at 1100^{o}C for 1 hour with regular shaking after every 15 minutes in order to keep mixture homogenous and finally melt was quenched.
Transparent glasses pieces with thickness 0.5mm were prepared. A part of prepared glass were powdered and characterized with XRD, FTIR, TGA and DTA, whereas the remaining glass pieces were used for calculating density and molar volume and other characterizations.

Result and Discussion:-

Density and Molar Volume:-

One of the main advantages of borate glasses is its low density (*D*) due to its lower molecular weight. Density measurements for all the prepared glass samples were calculated using 'Archimedes principle and the molar volume (V_m= *M/D*) of the glass samples are found to follow inverse trend to that of density for all the prepared glass samples. A graphical representation of density measurements and molar volume for all prepared samples is shown in Fig.1.

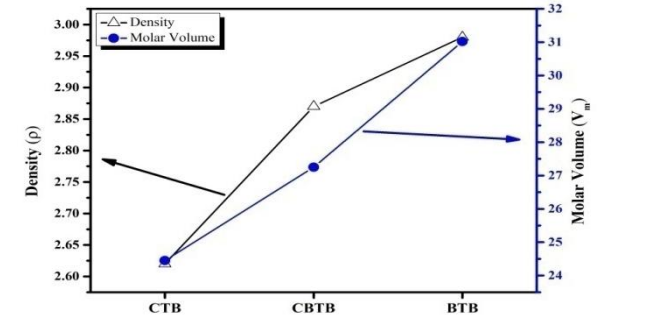

Fig.1:- Density and molar volume variation of as prepared glass samples

From this graph, it is clear that density of glass samples increases with increasing content of barium oxide (BaO). On addition of heavy metal ion like barium, density of the prepared glasses will increase due to large weight of BaO. While CaO has lower molecular weight in comparison of BaO that's why density of glass with composition BTB (2.98g/cc) has highest value and CTB (2.62g/cc) has least density value among all the prepared glasses. The calculated values of density measurements, molar mass and molar volume are shown in Table 1.

Table 1.- Detailed variation of density, molar volume, molar mass and calculated values of N4 using Deconvoluted FTIR spectra for prepared compositions

Composition name	**Density (g/cc)**	**Molar mass (*M*)**	**Molar volume (V_m)**	**N4**
BTB	2.98	92.4	31.02	35.8
CTB	2.62	64.17	24.45	31.6
CBTB	2.87	78.29	27.25	29.4

XRD:-

XRD spectra was recorded for all the prepared samples in range from 2θ=10^{o} to 80^{o}. The XRD spectra confirm the glassy/amorphous nature of prepared samples as there is no sharp peak present in the spectra. Figure 2 Shows XRD spectra for all the prepared glass samples.

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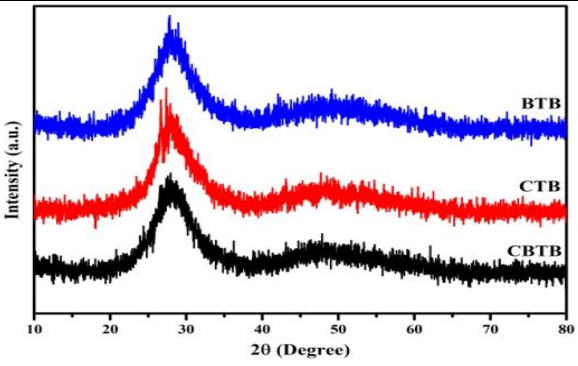

Fig. 2:- XRD spectra of as prepared glass samples

FTIR:-

FTIR spectra will help to study the structure of glass samples. The FTIR spectra of all the prepared glass samples were recorded in fingerprint region (i.e. from 400cm^{-1} to 1600cm^{-1}). Active boron atoms presents in sample give IR sensitivity in 1600cm^{-1} to 600cm^{-1} with three bands in this range [14-16]. The recorded FTIR spectrum for all the prepared glass samples is shown in Fig. 3 (a). It contains three bands ranging from 600-800cm^{-1}, 800-1200cm^{-1} and 1200-1600cm^{-1}. Band ranging from 600-800cm^{-1} (i.e. centred around ~700cm^{-1}) is due to B-O-B bond vibration in BO_3 structural units in borate network, while from 800-1200cm^{-1} may be due to stretching vibrations of tetrahedraly coordinated boron atom, i.e. BO_4 structural units and from 1200-1600cm^{-1} arise due to vibration in asymmetric BO_3 units [16,14]. Band from 400-600cm^{-1} is due to bond vibration of different metal cationic group present inside the glass composition [14] i.e. Ba and Ti in our case. On addition of modifier in borate network, conversion of some structural units i.e. BO_3 units convert into BO_4 structural units or BO_4 to BO_3 takes place. This conversion of structural units cause change in number of non-bridging oxygen's (NBOs), which further affect the structural and physical behaviour of glasses like molar volume (V_m), density (D) [16], glass transition temperature (T_g) [17], optical band gap (Eg) [15,18]etc.

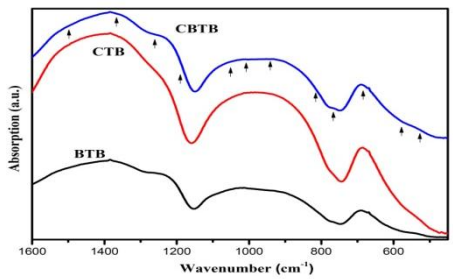

Fig. 3 (a):- FTIR spectra for all samples

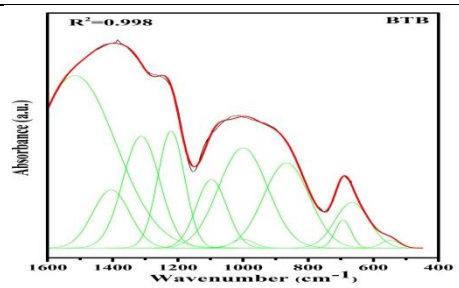

Fig. 3 (b):- Deconvoluted IR spectra for BTB sample

Deconvoluted FTIR spectra were obtained using Gaussian peak fit in origin 9.0 software. The deconvoluted FTIR spectrum for one of the prepared glass sample (BTB) is shown in Fig. 3 (b). It separates all the peaks which are assigned in the recorded spectra. Peak centre, peak area along with band of origin for the obtained peaks are listed in the Table 1.

Table 3:- Detailed observation of deconvoluted FTIR spectra.

Band Origin	**BTB**		**CTB**		**CBTB**	
	C (cm^{-1})	**A**	**C** (cm^{-1})	**A**	**C** (cm^{-1})	**A**
Metal (Barium & Titanium) cationic vibrations	548	0.39	549	0.73	541	0.51
	665	4.24	662	5.77	641	4.23
B-O-B bending vibrations in BO_3 structural units	692	1.22	691	0.99	696	4.4
	---	---	---	---	761	0.15
B-O starching vibrations in tetrahedraly coordinated boron atom	866	10.6	861	13.3	830	4.24
	---	----	932	0.89	928	13.6
	999	0.53	---	----	----	----
	1020	13.3	1014	13.5	1040	7.86
	1096	5.7	1119	5.82	1096	1.61
	----	----	1199	0.85	1192	0.7
Asymmetric B-O stretching vibration occur in BO_3 structural units	1220	8.51	1229	2.425	1219	4.75
	----	----	1275	7.33	---	---
	1312	11.15	----	---	1333	19.2
	1404	5.86	1361	7.51	----	----
	----	----	----	----	1495	6.85
	1516	38.5	1503	40.3	1515	32.6

The fraction of B^{IV} (BO_4) i.e. N4 is calculated by ratio of area of BO_4 units to total area of structural units i.e. sum of BO_4 and BO_3 units [19,16]. The values of N4 were calculated using relation.

$$N4 = \frac{Sum\ of\ relative\ area\ of\ BO4\ uits}{Sum\ of\ relative\ area\ of\ BO4\ and\ BO3\ units}$$

The different peaks assigned for BO_3 and BO_4 units are given in Table 3 whereas the calculated values of N4 for all glass samples are given inside the Table 1. The ratio N4 decreases on addition of BaO which indicates conversion of BO_4 into BO_3 units. In CBTB, N4 value is least, which may be due to mixed alkaline effect. The increase in value of N4 shows increment in NBO's which indicates that glass structure expands and vice-versa.

DTA:-

Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) were performed at heating rate of 10°C/min for 800°C in the aluminium crucible and 20mg of samples is used. The obtained TGA and DTA curve for BTB glass is shown in Fig 4. For study the TGA curve we plot weight percentage against the temperature. This curve is completely straight which shows no lose of molar weight as temperature increases. According to Shelby [20] any amorphous material formed by one of stated process and showing glass transition behaviour can be characterized as glass. The glass transition temperature (T_g), crystallization onset temperature (T_x), crystallization temperature (T_c) were obtained using DTA curve. Differential Thermal Analyses were performed for BTB glass for study different thermal behaviours like T_g, T_x, T_c etc. It is quite possible that all the prepared glass compositions possess almost same thermal behaviour with not any large variation, as in literature

[21]. On DTA curve an endothermic shift occurs which indicates T_g, this endothermic shift was followed for an exothermic peak which corresponds to crystallization temperature (T_c), the onset of this peak indicates crystallization onset temperature (T_x) [16]. The obtained glass transition temperature T_g= 566°C, crystallization onset temperature T_x=631°C and Crystallization temperature T_c=660°C from DTA curve.

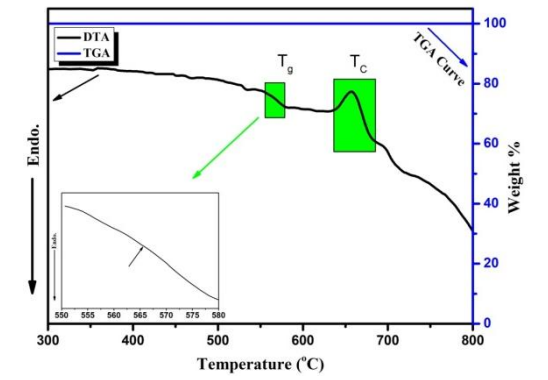

Fig. 4:- A Typical DTA and TGA Curves for BTB sample

Conclusion:-

Glass with composition xCaO-(20-x)BaO-20TiO_2-60B_2O_3 with x=0,10 and 20 were successfully prepared. The amorphous structure of the prepared glass samples is confirmed by XRD analysis. Density of the prepared glasses is low; vary from 2.62 to 2.97g/cc and maximum for BTB. The FTIR spectra depicted the presence of both triangular and tetrahedral borate units (in the form of ortho, penta, meta and pyro-borate units). The absence of peak around ~800cm^{-1} confirms the absence of boroxil ring in glass network. No weight loss on TGA curves shows that glasses are non-volatile. Exothermic peak obtained in DTA curve confirms that prepared glass samples can convert into glass ceramics on annealing and can use for applications like thermo mechanical sensor.

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Reference.

[1] M. Karimi, A. Mehdizadeh, M.H. Hekmatshoar, S. Vafaei, A new method for controlling structural , electrical and optical properties of phosphate glasses , containing transition metal ions (TMIs), J. Non. Cryst. Solids. 525 (2019) 119693. https://doi.org/10.1016/j.jnoncrysol.2019.119693.

[2] A. Bajaj, A. Khanna, B. Chen, J.G. Longstaffe, U. Zwanziger, J.W. Zwanziger, Y. Gómez, F. González, Structural investigation of bismuth borate glasses and crystalline phases, J. Non. Cryst. Solids. 355 (2009) 45–53. https://doi.org/10.1016/j.jnoncrysol.2008.09.033.

[3] M.A. Samee, A.M. Awasthi, T. Shripathi, S. Bale, C. Srinivasu, S. Rahman, Physical and optical studies in mixed alkali borate glasses with three types of alkali ions, J. Alloys Compd. 509 (2011) 3183–3189. https://doi.org/10.1016/j.jallcom.2010.12.039.

[4] W. Höland, G.H. Beall, American Ceramic Society., Glass-ceramic technology, Wiley, 2012.

[5] A. Yadav, S. Khasa, M.S. Dahiya, S. Dalal, A. Hooda, A. Agarwal, Synthesis, thermal and spectroscopic characterization of lithium bismuth borate glasses containing mixed transition

metal ions, Phys. Chem. Glas. Eur. J. Glas. Sci. Technol. Part B. 57 (2016) 146–152. https://doi.org/10.13036/17533562.57.3.018.

[6] J.S. Wang, E.M. Vogel, E. Snitzer, Tellurite glass: a new candidate for fiber devices, 1994.

[7] B.C. Jamalaiah, Erbium doped Bi2O3-B2O3 glass-ceramics containing Bi3B5O12 and CaF2 nanocrystallites for 1.53m fiber lasers, (2020).

[8] L. Srinivasa Rao, AC conductivity and polarization phenomenon of Li2O–MoO3–B2O3:V2O5 glasses, Elsevier B.V., 2019. https://doi.org/10.1016/j.jallcom.2019.02.122.

[9] M. Malik, S. Dagar, A. Hooda, A. Agarwal, S. Khasa, Effect of magnetic ion, Fe3+ on the structural and dielectric properties of Oxychloro Bismuth Borate Glasses, Solid State Sci. 110 (2020) 106491. https://doi.org/10.1016/j.solidstatesciences.2020.106491.

[10] F.A. Abdel-wahab, A.M. Fayad, M. Abdel-baki, H. Abdelmaksoud, Role of non-bridging oxygen defect in the ionic conductivity and associated oxygen trap centers in lead-borate oxide glass : E ff ect of structural substitution of PbO for Ag 2 O and Li 2 O modi fi ers, (2018). https://doi.org/10.1016/j.jnoncrysol.2018.06.033.

[11] S. Thakur, V. Thakur, A. Kaur, L. Singh, Structural, optical and thermal properties of nickel doped bismuth borate glasses, J. Non. Cryst. Solids. 512 (2019) 60–71. https://doi.org/10.1016/j.jnoncrysol.2019.02.012.

[12] Y.-H. Kao, Y. Hu, H. Zheng, J.D. Mackenzie, K. Perry, G. Bourhill, J.W. Perry, Second harmonic generation in transparent barium borate glass-ceramics, OURNAL OF, 1994.

[13] M.A. Marzouk, F.H. ElBatal, H.A. ElBatal, Effect of TiO2 on the optical, structural and crystallization behavior of barium borate glasses, Opt. Mater. (Amst). 57 (2016) 14–22. https://doi.org/10.1016/j.optmat.2016.04.002.

[14] A. Yadav, P. Narwal, M.S. Dahiya, T. Dahiya, A. Agarwal, S. Khasa, XRD and FTIR Analysis Heat Treated Lithium Bismo- Borate Glasses Doped With 1 . 0 mol % Copper Ferrite, 090013 (2018) 3–7. https://doi.org/10.1063/1.5032860.

[15] P. Paşcuţa, M. Boşca, S. Rada, M. Culea, I. Bratu, E. Culea, FTIR spectroscopic study of Gd2O3-Bi 2O3-B2O3 glasses, J. Optoelectron. Adv. Mater. 10 (2008) 2416–2419.

[16] A. Yadav, M.S. Dahiya, A. Hooda, P. Chand, S. Khasa, Structural influence of mixed transition metal ions on lithium bismuth borate glasses, Solid State Sci. 70 (2017) 54–65. https://doi.org/10.1016/j.solidstatesciences.2017.06.011.

[17] M.S. Dahiya, S. Khasa, A. Agarwal, Optical absorption and heating rate dependent glass transition in vanadyl doped calcium oxy-chloride borate glasses, J. Mol. Struct. 1086 (2015) 172–178. https://doi.org/10.1016/j.molstruc.2015.01.023.

[18] V. Kundu, R.L. Dhiman, A.S. Maan, D.R. Goyal, S. Arora, Characterization and electrical conductivity of Vanadium doped strontium bismuth borate glasses, J. Optoelectron. Adv. Mater. 12 (2010) 2373–2379.

[19] M. Farouk, A. Samir, F. Metawe, M. Elokr, Optical absorption and structural studies of bismuth borate glasses containing Er3 + ions, J. Non. Cryst. Solids. 371–372 (2013) 14–21. https://doi.org/10.1016/j.jnoncrysol.2013.04.001.

[20] A.T.S. To, F.O.R. The, D. Of, D.O.F. Philosophy, M. Singh, U. The, S. Of, F.O.F. Science, T. Interface, TO MY, (2015).

[21] G. Ramadevudu, S. Laxmi Srinivasa Rao, M.D. Abdul Hameed Shareefuddin, M. Narasimha Chary, FTIR and some physical properties of alkaline earth borate glasses containing heavy metal oxides, Int. J. Eng. Sci. Technol. 3 (2011) 6998–7005.