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Density and Mechanical Properties of Sodium Borotellurite Glasses

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Abstract

Sodium borotellurite glasses in the system $xNaF_2$-(20-x) Na_2O-40B_2O_3-40TeO_2 ($0 < x < 20$ mol%) were prepared by melt quenching method. The density related parameters such as molar volume elastic constants and thermal properties were studied for present glasses with increasing NaF_2 concentration. The results show that the calculated parameters strongly depend on increasing NaF_2 concentration. The density reduction is due fluorine ions will enters interstitial spaces of the network and breaking B-O-Te bonds which results decreasing density of the present glasses. The elastic constants of the present glasses were found to decrease with NaF_2 content. This results in an increase of the discontinuity of the glass network. The thermodynamically parameters such as glass transition temperature and onset of crystallization temperature of the present glasses and were found to decrease as a function of NaF_2 concentration.

Keywords: Borotellurite Glasses, crystallization

1. Introduction

The study of tellurite glasses have been increased due to variety of applications in the field of optical communication due to their remarkable properties like high refractive index, high optical non-linearity and excellent infrared transmittance [1-3]. Compare to silica glasses tellurite glasses having higher Raman gain coefficients and also find application in Raman amplifiers and waveguides [4]. It has been reported that tellurite glasses are suitable to make photonic devices due low melting temperature, thermal stability, low phonon energy and nonlinear refractive index, [5,6].

In the current world of technology glass material performance an important role. Among oxide glasses, borate glass is exclusive and can be used as thermal insulators and textile fiber glass. B_2O_3 is the best glass former and borate glasses have good nonlinear optical properties [7]. Its existence in tellurite glasses result in complex glass network consisting of TeO_4, TeO_{3+1}, TeO_3, BO_4 and BO_3 structural units. The adding of B_2O_3 into TeO_2 glass, tellurite transforms TeO_4 into TeO_{3+1} and TeO_3 units and enhances the glass forming ability of TeO_2. The addition of B_2O_3 also effects in decreasing B-O co-ordination with increase in B_2O_3 concentration in borotellurite glasses [8]. Whereas, boron oxide (B_2O_3) is excellent material for combination with TeO_2 as it improves the glass quality in terms of transparency, RE ions solubility, hardness and glass stability [9,10].

Presently Sodium based glasses are very attractive many scientists because of low melting and easy fabrication. The glasses have also extensive applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows, IR domes, and laser windows [11-14]. Sodium borosilicate glasses have a widespread interest in a number of fields such as bioactive glasses or the storage of nuclear waste [15]. They are chemically inert, mechanically strong, and resistant to thermal shocks; these properties explain their widespread usage in the glass industry.

The introduction of sodium with different glass former haven been reported in literature. The glassy system $Na_2O–B_2O_3– SiO_2$ found wide application in various composite materials used in laser engineering and optoelectronics [16]. Antropova et al. studied thermophysical characteristics of glasses based on the $Na_2O–B_2O_3– SiO_2$ system [17]. Pacaud et al. [18] also studied $Na2O–B_2O_3– SiO_2$ glasses from moliecular simulation and conclude that the impact of sodium ions on the boron coordination at room temperature is in good agreement with experimental observations. Wakasugi et al. [19] studied Crystallization Tendency of $Na_2O–B_2O_3– Al_2O_3$ glassy system. They have found that the glass stability increasing with increasing Al_2O_3 concentration. Mansour [20] studied FTIR spectra binary sodium borate glasses containing TeO_2. It has been observed that introducing TeO_2 into Na_2O-B_2O_3 glasses may delay the expected loss of non-bridging oxygens (NBOs) in the complete glass network with the decreasing sodium oxide content.

Fluoride glasses are the most important materials for the optical fiber technology [24, 25] due to their improved infrared transmission characteristics. Fluoroborate glasses composition a vital role in the development of new optoelectronic devices due to their high ionic conductivity. Kamitsos and Karakassids [24] reported spectroscopic properties of fluoride containing sodium borate glasses and discussed the role of fluorine ions in the conducting properties. Shelby and Ortolano [26] prepared of $NaF–Na_2O–B_2O_3$ glasses and studied the refractive index, density and glass transition temperatures of all glasses. Karunakaran et al. [27, 28] studied Structural, optical and thermal investigations of fluoroborate glasses doped with Dy3+ ions. The variation of optical properties discussed with Dy3+ ions. Karthikeyan et al. [29] also investigated Spectroscopic and glass transition of Nd3+ doped fluoroborate glasses.

Fluorine ion has almost the same radius as an oxygen ion, the possibility of substitution of the oxygen ions with fluorine ions is high, but the fluorine ions could also occupy interstitial positions. Moreover, fluorine has a greater electronegativity than oxygen which would reason the breakdown of the glass network structure, the glass transition and deformation temperatures would be likely to decrease with the substitution of fluoride ions in place of oxide ions. Several studies on the introduction of fluorine ions into oxide ions were reported for ternary sodium borate glasses [24,25,28]. Nearly all the studies are focused on the ternary borate system. There are no reports on introduction of fluorine ions into oxide ions in quaternary sodium borotellurite glasses. In the present work, an effort has been made for the preparation, physical and mechanical properties of$xNaF_2$ - (20-x) Na_2O-$40B_2O_3$-$40TeO_2$ glasses.

2. Experimental

In the current study, the glass samples of composition $xNaF_2$ -(20-x)Na_2O-$40B_2O_3$-$40TeO_2$ ($0 < x < 20$ mol%) were ready by melt quench technique. High purity (99.99%) sodium fluoride (NaF_2), sodium oxide (Na_2O), tellurium oxide (TeO_2) and Boron trioxide (B_2O_3) (all Sigma Aldrich) were used as initial materials. A batch of 15 g of the above high purity chemicals in powder form was considered, well mixed and melted in a silica crucible in the temperature range 1200-1250^{0}C subject on the glass composition in an electrical furnace for about 30 min. The melt was swirled frequently until a bubble free clear liquid was formed. The resulting melt was then transferred into a stainless steel mould warmed to 200^{0}C and pressed with another steel disc conserved at the same temperature. All the glass samples were annealed at 200^{0}C for a duration of about 12h. For samples taken from different regions of the bulk specimen, the absence of any Bragg peaks in the X-ray diffraction pattern complete that the ready glasses are amorphous.

The room temperature density (q) of the glass was determined by the standard principle of Archimedes by means of xylene as the buoyant liquid. The density was calculated by the formula. The thermal performance of the glass samples was examined using a differential scanning calorimeter (Mettler-Toledo: TGA/DSC1/1600HT). Samples in the form of powder balancing about 15 mg were sealed in aluminum pans and scanned with a heating rate of 10^0C/min from 30 to 600^0C in dry nitrogen atmosphere. The glass transition temperature (T_g) and the crystallization beginning temperature (T_x) were determined based on the DSC curves using the onset method. The uncertainty in T_g and T_x are ± 0.1^0C.

3. Results and discussion

3.1 XRD

X-ray diffraction picture of the current glass samples are shown in Fig. 1. The Figure 1 shows no continuous or discrete sharp peaks but show wide halo, which reveals the features of amorphous glass structure.

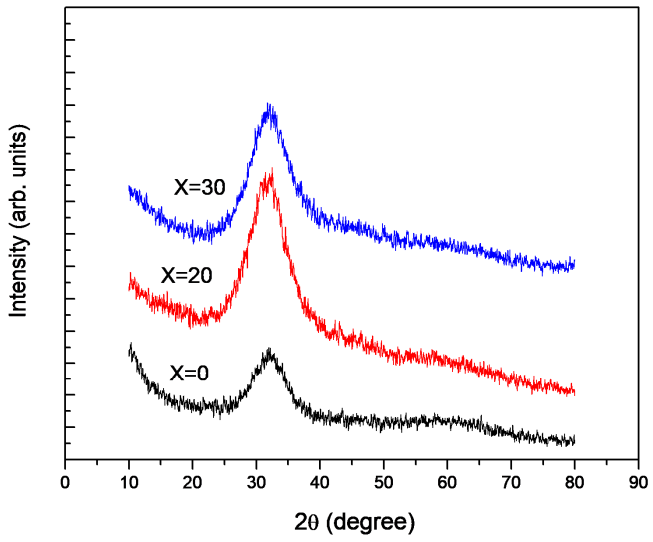

Figure 1: XRD spectra of present glasses

3.2 Density

The density and molar volume was calculated by the formula

$$\rho = a * 0.86 / (a-b) \quad (1)$$

where a and b are the weights of the glass sample measured in air and xylene, respectively. The density of xylene at room temperature is 0.865 g/cc.

$$V_m = M / \rho \quad (2)$$

Where M is the average molecular weight of the glass and ρ is its density.

The density of the existing glass system varies from 3.944 to 3.824 g/cc and shown in table 1. Figure 2 shows the variation of density with NaF_2 concentration. The density reduction of the present glasses with NaF_2 concentration may be due to the low density of NaF_2 compared with that of NaO. The density decrease in the contemporary glasses can be described through the bond formation in present glasses. An significant chemical feature of Te atoms is their increasing valence from 3 to 4. But Boron has poor electron valence, when B_2O_3 joint with TeO_2 when a modifier Na_2O is added, the modifier ion may also be attracted towards BO_3 units leading to the construction of tetrahedral borate units or

it may be taken up by the TeO_2 for construction to network structure [30]. Monsour [20] studied Na_2O-B_2O_3-TeO_2 glass system through FTIR spectroscopy and conform that that these glasses has high rich of B-O-Te bonds. In the present glasses when NaF_2 replaced with NaO, fluorine ions will enters interstitial spaces of the network and breaking B-O-Te bonds which results decreasing density of the present glasses. In the present glass system, the variation of molar volume as a function of NaF_2 content is also illustrated in figure 1. Since the behavior of molar volume mainly depends on the density of the glass and hence the variation of molar volume in these glasses is as expected.

Table 1:

Parameters	**X=0**	**X=4**	**X=8**	**X=12**	**X=16**	**X=20**
Density	3.944	3.914	3.886	3.859	3.835	3.824
Molar Volume	26.393	26.582	26.762	26.938	27.097	27.168
Ionic pacing density	0.546	0.539	0.533	0.525	0.518	0.514
Dissociation energy (K cal/cc)	14.380	14.234	14.088	13.942	13.796	13.650
Young's modulus (GPa)	157.115	153.399	149.868	146.391	143.064	140.267
Bulk modulus (GPa)	101.618	99.212	95.652	92.225	89.014	86.478
Shear modulus (GPa)	63.233	61.735	60.482	59.246	58.056	57.032
Poisson's ratio	0.245	0.242	0.238	0.235	0.232	0.229
Thermal Properties						
T_g	426.2	412.6	376.9	373.9	362.2	344.3
T_x	496.3	502.1	491.7	487.8	469.3	459.7
S	70.06	89.48	114.77	113.86	107.02	115.39

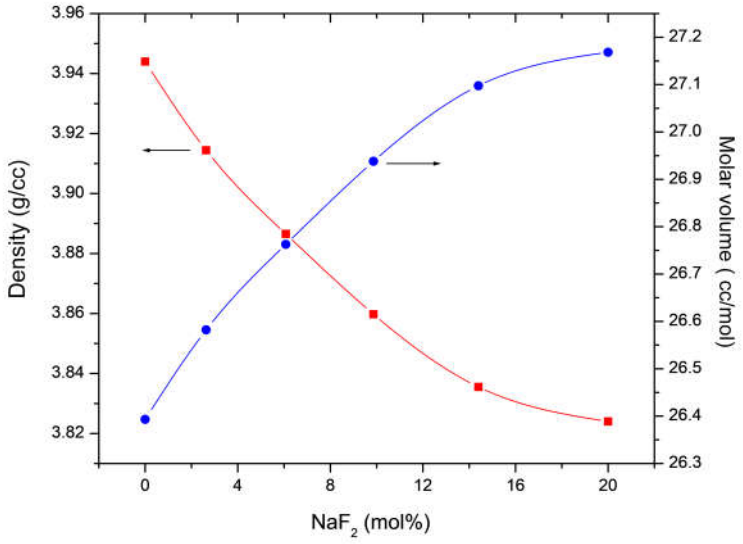

Figure 2: Density and Molar volume of $xNaF_2$ -(20-x)Na_2O-40B_2O_3-40TeO_2 glasses.

3.3 Elastic constants

Recently, Inaba and Fujino [31] described an experimental equation for ionic packing ratio, which is used to develop the density model. The ionic packing density V_t is expressed by

$$V_t = (\rho / M) \times \sum (V_i \times x_i) \quad (3)$$

Where M is molar weight (kg/mol), x_i is molar fraction (mol%), ρ is density (kg/m^3) and V_i is packing density parameter (m^3/mol).

For a typical glass composition 4NaF_2-16NaO-40B_2O_3-40TeO_2, the value of V_t is given by (1/26.8522) [(0.04)V_i (NaF_2) + (0.16)V_i (NaO) + (0.40)V_i (B_2O_3) + (0.40)V_i (TeO_2)]. The values of $V_i(NaF_2)=10\times10^{-6}$ m^3/mol, $V_i(Na_2O)=12.3\times10^{-6}$ m^3/mol, $V_i(TeO_2)=14.7\times10^{-6}$ m^3/mol and $V_i(B_2O_3) = 15.2\times10^{-6}$ m^3/mol are used [31-33]. The calculated ionic pacing density V_t of all the present glasses are summarized in table 1.

The elastic modulli of glasses may be calculated according to a model built upon the dissociation energy of the bonds and ionic radii of elements. This model was adopted by Makishima-Mackenzie [34, 35]. According to this model elastic constants is given by

$$G_t = \Sigma (x_i \times G_i) \quad (4)$$

$$E = 2\, V_t\, G_t \quad (5)$$

$$K = 1.2\, V_t\, E \quad (6)$$

$$S = 3\, E\, K / (9\, K - E) \quad (7)$$

$$\mu_{cal} = 0.5 - 1/ (7.2 V_t) \quad (8)$$

where G_i is the dissociation energy per unit volume of i^{th} oxide and x_i is the mol % of the i^{th} oxide.

The values of dissociation energy per unit volume G_i of various oxides used in the present study are $G(Na_2O)$=8.90 kcal/cc, $G(NaF_2)$=5.25 kcal/cc, $G(TeO_2)$=12.85 kcal/cc and $G(B_2O_3)$ =18.6 kcal/cc [36]. Using the above values, the dissociation energy G_t, the Young's modulus E, bulk modulus K, shear modulus S and Poisson's ratio μ_{cal} of the present glass system were calculated and are presented in table 1.

Figure 3 explains the variation of Young's modulus and Figure 4 explains the variation of shear modulus and bulk modulus and as a function of NaF_2 content in current glass system. From the Figures 3,4 it is clear that the elastic constants decreases with compositional parameter NaF_2.

In the existing study, the elastic moduli decrease with the increase in NaF_2 content can be interpreted through the decrease in the dissociation energy per unit volume (G_t) calculated according to Makishim-Mackenzie model [34, 35], indicating the decrease in bond strength and the rigidity.

Decreasing in elastic constants can also be explained by taking into account the relationship between the bulk and Young's modulli and the molar volume. The bulk modulus (K) and the molar volume (V_m) are related by the relation; $KV_m^n = C$ [37] (where C is a constant). As stated earlier, the value of n for oxide glasses is 4 [38], and the variation of n in the bulk modulus–volume relationship is determined by the nature of the bonding, and the coordination polyhedra. When the volume change occurs without change in the nature of the bonding or change in the coordination polyhedra, log(K) verses log(V_m) plot in generally is linear. Thus the log(K) verses log(V_m) plot for the present glass system as shown in Figure 5, shows an increase in the molar volume associated with an expected decrease in bulk modulli. Thus the continuous substitution of NaF_2 for NaO in the present glasses results in an increase of the discontinuity of the glass network. Such a decrease in both bulk and Young's modulii- volume relationship was observed in some other types of glasses [39,40].

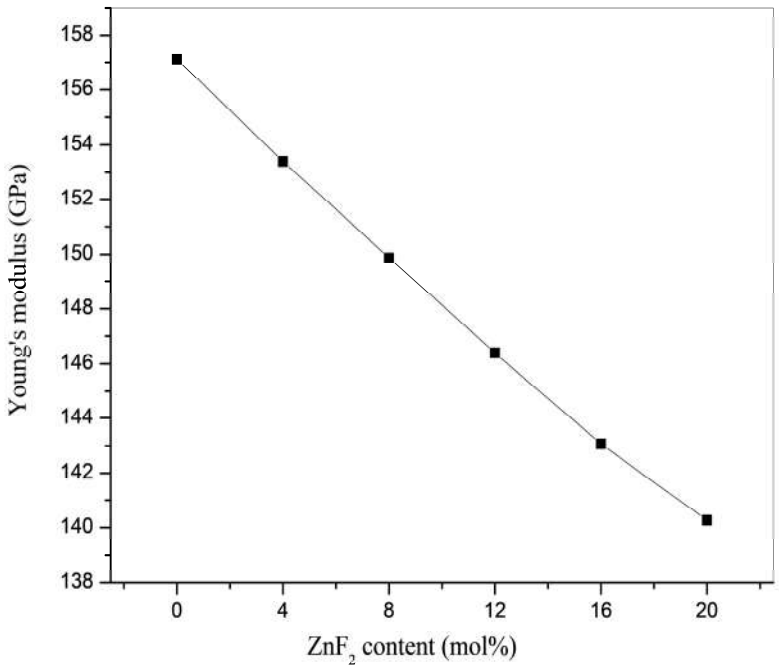

Figure 3: Young's modulus of the current glasses

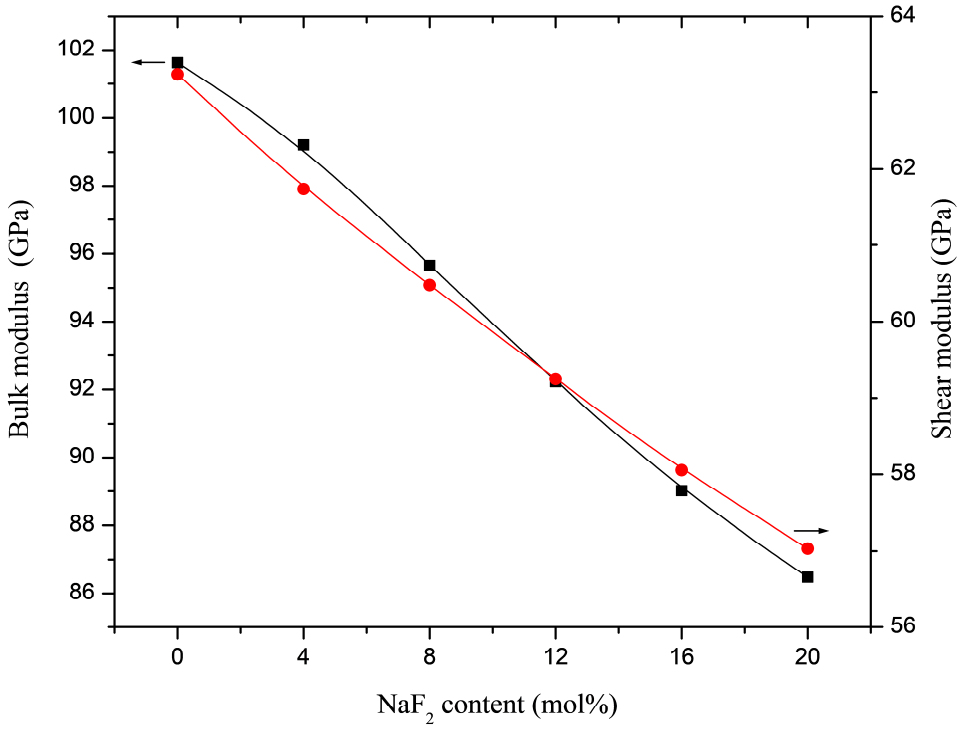

Figure 4: Bulk and Shear modulus of the present glasses.

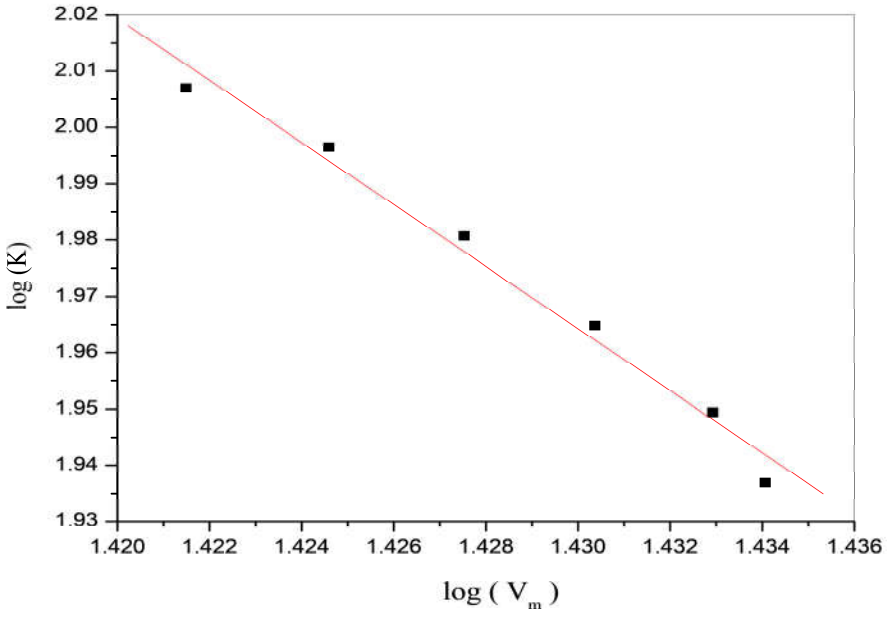

Figure 5: log(K) verses log(V_m) plot for the present glass system.

Figure 6 illustrates the variation of Poisson's ratio with NaF_2 content in the present glass system. From the above figure it is observed that the Poisson's ratio μ_{cal} decreases with glass composition. In present glass system the Poisson's ratio varies between 0.245 to 0.229.

It is known that Poisson's ratio is small if atoms are loosely packed in the oxide glass whereas tightly packed glass has a higher Poisson's ratio. In solid materials, the axial strain produced in the network is unaffected by the cross-links while the lateral strain is greatly decreased with increasing covalence of bonds [41]. Bridge and Higazy [42] have suggested a close correlation between Poisson's ratio and cross-link density which is defined as the number of bridging bonds per cation. According to Rao [43] Poisson's ratio depends on the dimensionality of the structure and cross-link density. A three dimensional network structure has lower Poisson's ratio than that of a two dimensional structure, since the number of bonds resisting a tranverse deformation decreases in that order.

It is known that Poisson's ratio is affected by the changes in the cross-link density of the glass network. This means that as reported by Rajendran *et al* [38, 44], a high cross-link density has Poisson's ratio in the order of 0.1-0.2, while a low cross-link density has Poisson's ratio between 0.3 and 0.5. In the present glass systems, Poisson's ratio as shown in table 3.3 decreases and varies between 0.245 to 0.229. The values of the Poisson's ratio suggests that the present glasses have a low cross-link density. Some structural readjustments are presumed to take place when NaO is substituted by NaF_2

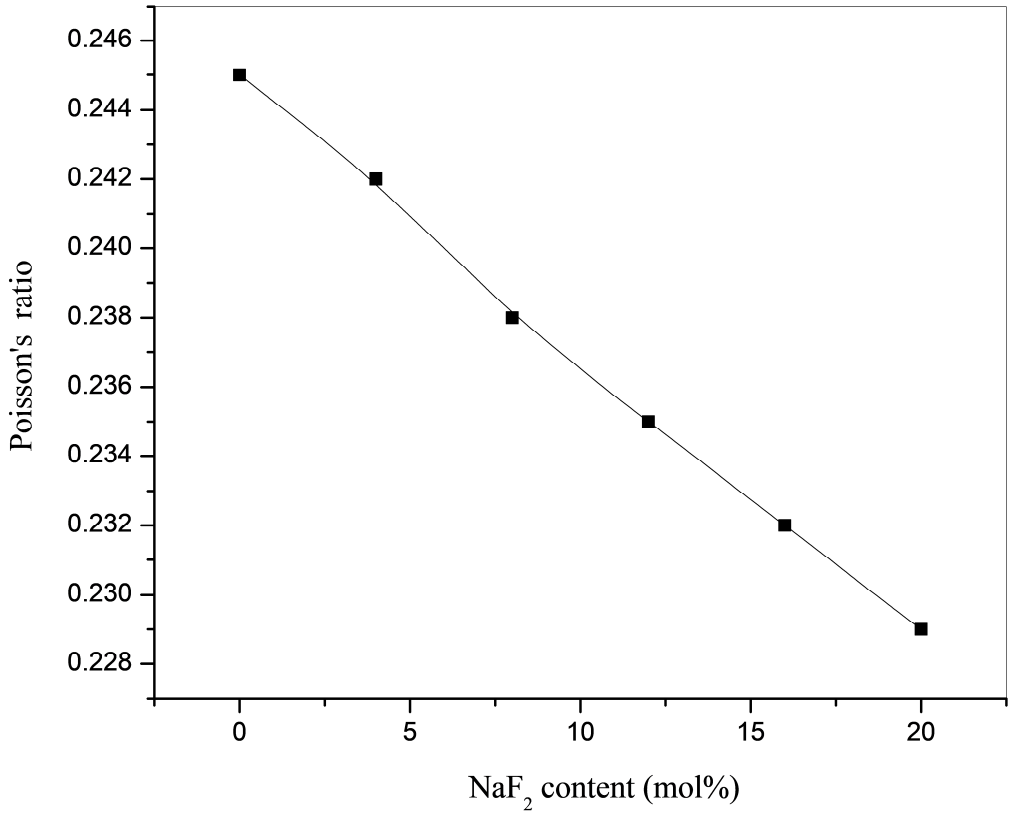

Figure 6: Variation of Poisson's ratio with NaF_2 content in the present glass

3.4. Differential scanning calorimetry

The differential scanning calorimetry (DSC) is used to characterize the glass and to determine the thermodynamical parameters. The DSC thermograms of all the glass samples are shown in Figure 7. The glass transition temperatures (T_g) and onset of crystallization temperate (T_c) were determined based on the DSC curves using the onset method. The glass transition temperature T_g was taken as the temperature corresponding to the intersection of the two linear portions adjoining the transition elbow in the DSC traces. The uncertainty in T_g and T_c is ± 0.1˚C. The glass stability S was determined by using the formula $S = T_c - T_g$. The determined values of T_g, T_c and S were presented table 2. The glass transition temperature decreases from 426.2 to 344.3 ˚C. The crystallization onset temperature is also shifted to lower temperature range from 496.3 to 459.7˚C. The glass stability (S) varies in the range 70 to 115 ˚C and is large enough to obtain stable glass. Figure 8 plots the variation of T_g, T_c and S as a function of NaF_2 content. The reduction in glass transition temperature and onset of crystallization can be summarized as follows:

The reduction in glass transition temperature in present glass may be due to the fact that the fluorine has a higher electronegative than oxygen, it would be expected that the substitution of fluoride ions for oxide ions decrease glass transition temperature and deformation temperature. Since two fluoride ions are substituted for an oxide ion, which causes the breakdown of the glass network structure and the fluorine atoms are introduced in oxide network can be considered not to act as bridge between two tellurium atoms because of single valence of fluorine. Breaking the oxide network, the cross linking degree of the glass former could be reduced which results in decrease of both T_g and T_c.

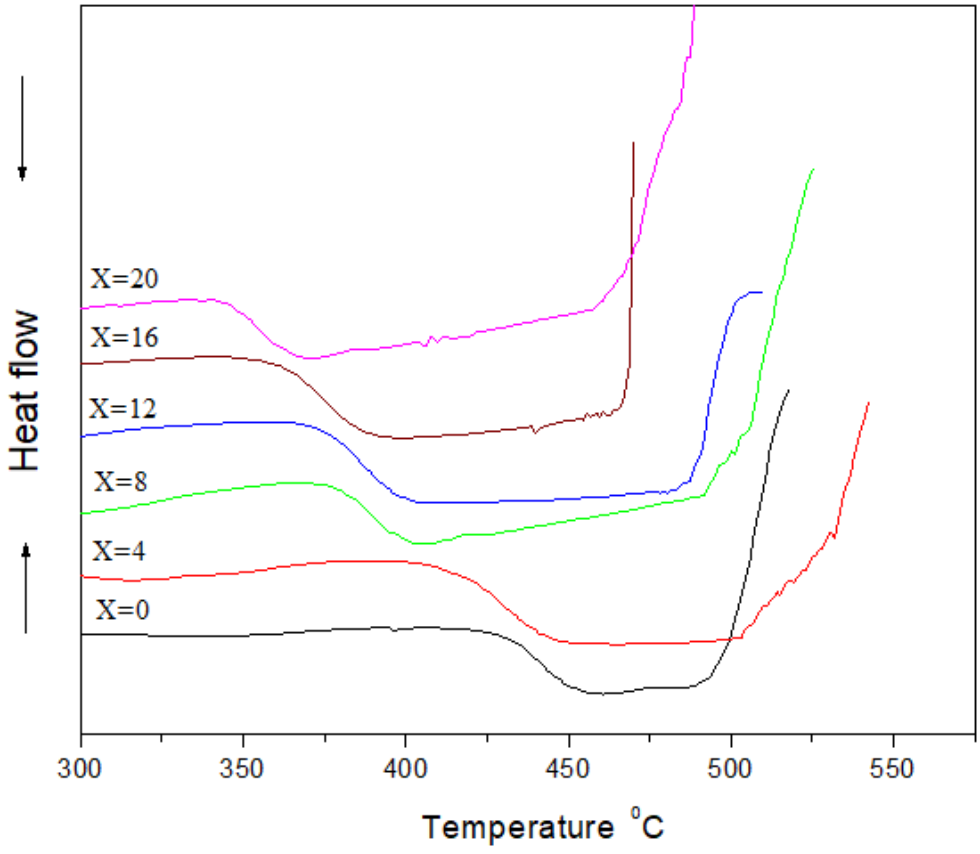

Figure 7: DSC thermograms of $xNaF_2$ -(20-x)Na_2O-40B_2O_3-40TeO_2 glasses.

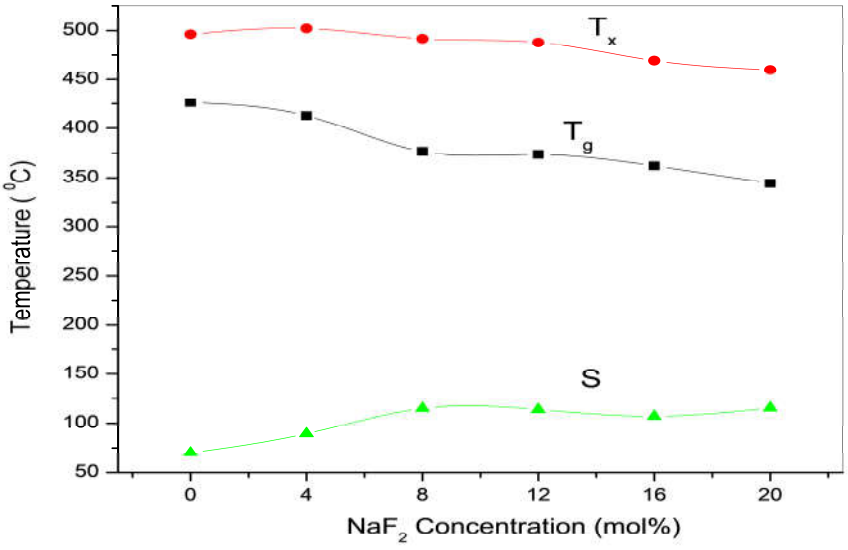

Figure 8: Variation of T_g, T_c and S as a function of NaF_2 content

4. Conclusions

The following conclusions are drawn from the study of various physical properties on $xNaF_2$-(20-x) Na_2O-40B_2O_3-40TeO_2 glasses.

- The room temperature density of $xNaF_2$ -(20-x)Na_2O-40B_2O_3-40TeO_2 glasses decreased non linearly as a function of NaF_2 content and the density reduction is due fluorine ions will enters interstitial spaces of the network and breaking B-O-Te bonds which results decreasing density of the present glasses
- Young's modulus, bulk modulus, shear modulus and Poisson's ratio of the present glasses were determined using the density data and the dissociation energy per unit volume. The elastic constants of the present glasses were found to decrease with NaF_2 content. This results in an increase of the discontinuity of the glass network.
- The Poison's ratio of the present glass system decreases from 0.245 to 0.229 proposing that the current glasses have a low cross link density.
- The thermodynamically parameters such as glass transition temperature and onset of crystallization temperature of the present glasses and were found to decrease as a function of NaF_2 concentration.

References

1. H. Nasu, O. Matsushita, K. Kamiya, H. Kobayashi and K.i. Kubodera, Journal of Non-Crystalline Solids 124, 275-277 (1990).
2. M.H. Bhat, M. Kandavel, M. Ganguli and K.J. Rao, Bulletin of Materials Science 27, 189-198 (2004).
3. Shaik kareem Ahmmad, M.A. Samee, A. Edukondalu, Syed Rahman, Results in physics 2 (2012) 175–181
4. P. Gayathri Pavani, K. Sadhana and V. Chandra Mouli, Physica B: Condensed Matter 406, 1242-1247 (2011).
5. M. N. Azlan, M. K. Halimah, S. Z. Shafinas, and W. M. Daud, Materials Express, 5 (2015) 211–218.
6. I. Jlassi, H. Elhouichet, and M. Ferid, 46 2011 (3) 806–812.
7. P. Becker, Adv. Mater. 10 (1999) 979–992.
8. N. Kaur, A. Khanna, J. Non-Cryst. Solids 404 (2014) 116–123.

9. A.V. Deepa, M. Priya, S. Suresh, 11 (5) (2016) 57–63.
10. YANG Yanmin, LIU Yanzhou, CAI Peiqing, Ramzi , Hyo Jin Seo, 33 (2015) 939.
11. K. Gerth, C. Russesl, J. Non-Cryst. Solids 221 (1997) 10.
12. R.A.F. El-Mallaway, Tellurite Glasses Handbook: Properties and Data, CRC, BocaRaton, FL, 2002.
13. J.S. Wang, E.M. Vogel, E. Snitzer, Opt. Mater. 3 (1994) 187.
14. S.H. Kim, T. Yoko, S. Sakka, J. Am. Ceram. Soc. 76 (1993) 865.
15. M. J. Plodinec, Glass Technol. 41, 186–192 (2000).
16. K. Meshkovski., *Composite Optical Materials Based on Porous Matrices* St. Petersburg,1998.
17. T. V. Antropova, S. V. Stolyar, and V. L. Stolyarova
18. Fabien Pacaud, Jean-Marc Delaye, , Thibault Charpentier, Laurent Cormier, Mathieu Salanne The Journal of Chemical Physics 147, (2017) 161711.
19. Takashi Wakasugi, Rikuo Om, and Jiro Fukunaga, J. American ceramic society 75[11]3129
20. E. Mansour, Journal of Molecular Structure 1014 (2012) 1–6
21. A. Lecoq, M. Poulain, J. Non-Cryst. Solids 41 (1980) 209.
22. M.C. Brierely, C.A. Millar, Electron. Lett. 24 (1988) 438.
23. Y. Ohishi, M. Yamada, T. Kanamori, S. Suda, Opt. Lett. 22 (1997) 1235.
24. Kamitsos and Karakassids, solid state ionics, 28-30 (1988) 783-787.
25. Shantala D patil, V. M jail, R.V Anavekar, Bull. Mater. Sci, 31 (2008) 631–634.
26. J.E. Shelby, R.L. Ortolano, Phys. Chem. Glasses 31 (1990) 25.
27. R.T.Karunakaran, K.Marimuthu, S.Surendra Babu, S. Arumugam, Physica B 404 (2009) 3995–4000.
28. R.T.Karunakaran, K.Marimuthu, S.Surendra Babu, S.Arumugam, Journal of Luminescence 130 (2010) 1067-1072
29. B. Karthikeyana, S. Mohan, Materials Research Bulletin 39 (2004) 1507–1515.
30. V.C. Veeranna Gowda, C. Narayana Reddy, K.C. Radha, R.V. Anavekar, J Etourneau, K.J. Rao, J. Non-Cryst. Solids 353 (2007) 1150–1163.
31. S. Inaba, S. Fujino, J. Am. Ceram. Soc. 93 (2010) 217.
32. R.D. Shannon, C.T. Prewitt, Acta Crystallogr B 25 (1969) 925
33. R.D. Shannon, C.T. Prewitt, Acta Crystallogr B 26 (1970) 1046
34. A. Makishima, J.D. Mackenzie, J. Non-Cryst. Solids 12 (1973) 35
35. A. Makishima, J.D. Mackenzie, J. Non-Cryst. Solids 17 (1975) 147
36. S. Inaba, S. Oda, K. Morinaga, J. Non-Cryst. Solids 325 (2003) 258
37. E. Gopal, T. Mukuntan, J. Philip, S. Sathish, Pramana, J. Phys. 28 (5) (1987) 471
38. V. Rajendran, N. Palanivelu, B.K. Chaudhuri, K. Goswami, J. Non-Cryst. Solids 320 (2003) 195
39. Y.B. Saddeek, J. Alloys and Compounds 467 (2009) 14.
40. M.S. Gaafar, H.A. Afifi, M.M. Mekawy, Physica B 404 (2009) 1668.
41. N. D. Patel, D. N. Waters, Phys. Stat. Sol. (a) 77 (1983) 655
42. B. Bridge, A. A. Higazy, Phys. Chem. Glasses 27 (1986) 1
43. K. Rao, Structural Chemistry of Glasses, Elsevier, North Holland, 2002.
44. V. Rajendran, N. Palanivelu, D.K.Modak, B.K. Chaudhuri, Phys. Stat. Sol. A 180 (2000) 467
45. Shaik Kareem Ahmmad, M. A. Samee, S. M. Taqiullah, and Syed Rahman, AIP Conference Proceedings 1591, 730 (2014);