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Non-linear Optical Properties of Bi_2O_3-TeO_2-B_2O_3-GeO_2 Glasses

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Abstract: New bismuth tellurite boro-germanate glasses according to composition xBi_2O_3-$(80-x)TeO_2$-$10B_2O_3$-$10GeO_2$ where (x=40, 45, 50, 55, 60 and 65 mol%) have been prepared by melt quench technique at 1150 °C. The room temperature optical absorption spectra have been recorded. The indirect band gap energy E_g was determined and found to decrease with Bi_2O_3 content. The increase in Urbach energy with glass composition indicates the decrease in structural stability. The ionic and covalent bonding parameters were determined. The present glasses are found to be 99 % ionic in nature. The two-photon absorption coefficient was found to increase from 11.89 to 14 cm/GW. The non-linear optical properties such as non-linear refractive index, linear optical susceptibility and third order non-linear optical susceptibility were evaluated using optical data. The authors determined theoretically the optical band gap (E_g) and refractive index (n) of the present glasses using optical electronegativity data. The relationship between E_g and n followed the relation $E_g n^4 = 99$. The present glasses were found suitable for drawing optical fibers.

INTRODUCTION

It is known that B_2O_3 and GeO_2 are mostly used glass formers that comprises of boroxol rings, BO_3 units and GeO_4 and GeO_6 units to form two dimensional random network [1,2] Tellurium oxide based glasses attracted the scientific community due to their various applications like optical amplifiers and nonlinear optical devices. These glasses have large third-order nonlinear susceptibility, dielectric constants and refractive indices [3, 4].

Bi_2O_3 glasses also exhibit high second and third order non-linear optical susceptibility due to which they are used in up-conversion lasers and non-linear optical materials. Addition of Bi_2O_3 and TeO_2 to B_2O_3 and GeO_2 glasses shows remarkable changes in both physical and optical properties. The influence of Bi_2O_3, TeO_2 have been observed in various glasses like B_2O_3-TeO_2-Li_2O-CoO, TeO_2-ZnO-B_2O_3-Bi_2O_3, TeO_2-Li_2O-B_2O_3, TeO_2-MoO_3-Bi_2O_3, TeO_2-ZnO-Nb_2O_5-Gd_2O_3 [5-10].

Hasegawa [11] and Saddeek *et al*. [12] developed Bi_2O_3-TeO_2-B_2O_3 ternary glass system and investigated their physical, linear and non-linear optical properties. Munoz-Martin *et al*. [13] prepared ternary tellurite-tungstate glass system with alkaline oxide, ZnO, Bi_2O_3 or Li_2O as third component and demonstrated that these ternary glasses are promising materials for developing broad band integrated optical amplifiers. Zhou *et al*. [10] prepared and characterized new tellurium quaternary TeO_2-PbO-Bi_2O_3-B_2O_3 glass system and explained the variations in thermal stability with the glass composition using FTIR measurements. The present glasses can be used for photonic devices and low melting point sealing glasses.

There are many reports on ternary and quaternary glasses with $Bi_2O_3/TeO_2/B_2O_3/GeO_2$. To the best of our knowledge, there are no proper reports on Bi_2O_3-TeO_2-B_2O_3 glasses containing GeO_2. We have studied the effect of Bi_2O_3 content on non-linear optical properties of Bi_2O_3-TeO_2-B_2O_3-GeO_2 glass system. Further, the present study

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optimizes the content of Bi_2O_3 in Bi_2O_3-TeO_2-B_2O_3-GeO_2 glass system to use it as non-linear optical material in different types of technological applications.

EXPERIMENTAL

A series of six glasses with molar formula xBi_2O_3-(80-x)TeO_2-10B_2O_3-10GeO_2(x = 40,45, 50, 55, 60 and 65 mole %) were prepared using conventional quenching method. High purity bismuth oxide (Bi_2O_3), tellurium oxide (TeO_2), germanium oxide (GeO_2) and boron trioxide (B_2O_3) (Sigma Aldrich 99.999% pure) were used as starting materials. A batch of 10 g raw materials (powdered form) in appropriate molecular ratios were weighed and mixed thoroughly. The mixture then melted in a porcelain crucible in an electrically pre-heated furnace at about 1150 °C for 1 hour and for the good homogeneity and bubble free melt, crucibles were swirled frequently. The transparent melt was then poured on to a stainless steel mold preheated at 200 °C which was then pressed instantaneously with another steel plate to get flat disc and square shaped glass samples. Each glass was then annealed at 250 °C for 24 hours to reduce mechanical stress. The prepared glasses are faint yellow in color.

X-ray diffraction experiment was performed to confirm the amorphous state pertaining to the prepared glass samples. The diffractograms were recorded on a Phillips PW 1830 model Cu Kα radiation of wavelength 1.54Å, 30kV and 40mA, at a scanning rate of 2° per minute from 10° - 80°. The room temperature densities (ρ) of quaternary bismuth tellurium boro-germanate glasses were measured by Archimedes principle using Xylene as the buoyant liquid. The thermal behavior of the glass samples was investigated using (DSC METTLER TOLEDO DSC1) within the temperature range 100-600°C with a 10 °C/min heating rate. **U**sing double beam UV- Visible spectrometer (LAB INDIA MODEL UV 3092) in the wavelength range of 200 to 800 nm the optical absorption spectra at room temperature in the visible and near ultra violet region was recorded on highly polished glass samples. The thickness of the glass sample is around 1mm.

RESULTS AND DISCUSSION

FIGURE 1 presents the density of the glasses with composition xBi_2O_3-(80-x)TeO_2-10B_2O_3-10GeO_2 as a function of Bi_2O_3 content. As observed from the above figure the density varied nonlinearly, the maximum value obtained for x = 50 mole% of glass. The density related to existing glass system fluctuates from 5.343 to 5.220 gm/cc. Therefore, the changes in the density are the most likely cause of the mixed glass former effect (MGFE). The initial increase in density indicates a restructuring of the network and the decrease can be attributed to the increase in the fraction of non-bridging oxygens which destroy the network structure. The results are in agreement with the values found in the literature [14, 15]

The density, molar volume and the average molecular weight values of the presented glasses was summarized in TABLE 1.

FIGURE 2 presents the DSC thermogram of all the present glasses under study. A typical DSC thermogram for 40Bi_2O_3-40TeO_2-10B_2O_3-10GeO_2 glass is shown in the inset of FIGURE 2. The thermo-dynamical parameters such as T_g and T_x were determined and represented in TABLE 1. The T_g values increase from 455 °C to 540 °C with increase of Bi_2O_3 content. The thermal stability for the prepared glasses was calculated and tabulated in TABLE 1.
The optical absorption coefficient given by the equation

$$\alpha(\nu) = \frac{B\,(h\nu - E_g)^n}{h\nu} \quad (1)$$

Here hν is the energy of incident photon, B is a constant related to the amount of band tailing, E_g is the optical energy gap and n is a digit which symbolizes the transition progression (for n=1/2, 2, 3/2, and 3 the transitions are direct allowed, indirect allowed, direct forbidden, and indirect forbidden respectively). FIGURE 3 represents the Tauc plots {(αhν)1/2*vs* hν} for different glass samples. The determined optical band gap energy (E_g) values for all the glasses are given in TABLE 1. The recorded decrease in E_g from 3.07 to 2.81 eV is due to the structural changes occurred in the prepared glasses.

Using the optical band gap energy, the refractive index of the glass can be evaluated by the following equation [16]

$$\frac{n_0^2-1}{n_0^2+2} = \left(1 - \sqrt{\frac{E_g}{20}}\right) \quad (2)$$

TABLE 1 presents the obtained values of refractive index n_o of the prepared glasses. It was found that refractive index increased with Bi_2O_3 content. This is because of the cation polarizability of Bi^{3+} ion (1.508 $Å^3$) is weaker as compared to that of Te^{2+} ion (1.595 $Å^3$).

Non-linear optical properties

TABLE 1. Average molecular weight M, density ρ, molar volume Vm, glass transition temperature Tg, onset of crystallization temperature Tx, glass stability S, indirect optical band gap energy Eg, refractive index *n*o, two photon absorption coefficient (β), non-linear refractive index n2 (×10-11 esu), linear optical susceptibility χ(1), third order non-linear susceptibility χ(3) (×10-12 esu), theoretical refractive index n, ionic bonding factor Ic and covalent bonding factor Cc of xBi2O3-(80-x)TeO2-10B2O3-10GeO2 glass system.

Parameters	**x=40**	**x=45**	**x=50**	**x=55**	**x=60**	**x=65**
M (g/mol)	267.645	282.963	298.281	313.599	328.917	344.235
ρ (g/cc) (±0.005)	5.343	5.580	5.598	5.562	5.238	5.220
V_m (cc/mol) (±0.005)	50.09	50.71	53.28	56.38	62.79	65.94
T_g (°C) (±1)	455	470	474	477	534	540
T_x (°C) (±1)	546	570	560	567	561	562
S (°C) (±1)	91	100	86	90	27	22
E_g (eV) (±0.01)	3.07	3.01	2.91	2.88	2.86	2.81
n_o	2.378	2.394	2.421	2.430	2.436	2.450
β (cm/GW)	11.893	12.379	13.189	13.432	13.594	14.00
n_2	5.062	5.368	5.915	6.108	6.239	6.559
$\chi^{(1)}$	0.370	0.376	0.386	0.390	0.392	0.398
$\chi^{(3)}$	3.192	3.408	3.797	3.936	4.030	4.261
n	1.866	1.859	1.853	1.846	1.839	1.833
Ic (%)	99.838	99.854	99.871	99.887	99.903	99.919
Cc (%)	0.161	0.145	0.129	0.112	0.096	0.080

Oxide glasses have related applications in photonic devices because of their non-linear optical properties which arise due to the presence of heavy metal oxides such as Bi_2O_3. The two-photon absorption (β) can be described using the expression given by [17]

$$\beta\ (\text{cm/GW}) = 36.76 - 8.1E_g \quad (3)$$

where E_g is the optical band gap. The obtained values of two-photon absorption coefficient given in TABLE 1 found to increase from 11.89 to 14 cm/GW as Bi_2O_3 content increases. Non-linear optical properties strongly depends on the linear refractive index and electronic polarization of the materials [18,19] The non-linear optical properties such as non-linear refractive index n_2 can be obtained from the refractive index n_o data and the third order non-linear optical susceptibility $\chi^{(3)}$ from the following equations [20]

$$n_2 = \frac{12\pi}{n_o} \text{Re } \chi^{(3)} \quad (4)$$

$$\chi^{(3)} \simeq \text{Re } \chi^{(3)} = [\chi^{(1)}]^{1/4} \times 1.7 \times 10^{-10} \text{ (esu)}. \quad (5)$$

Where $[\chi^{(1)}]$ is the linear optical susceptibility given as

$$[\chi^{(1)}] = [\frac{n_o^2}{4\pi} - 1] \quad (6)$$

The calculated non-linear optical parameters of the present glasses are given in TABLE 1. It is clear from the above table that the values of n_2, $\chi^{(1)}$ and $\chi^{(3)}$ were found to increase with composition of the glass.

Theoretically, the energy gap of the glass samples can be calculated from the values of the energy gap of its constituents by using the formula [21, 22].

$$E_g = 3.27 \, \Delta\chi^* \quad (7)$$

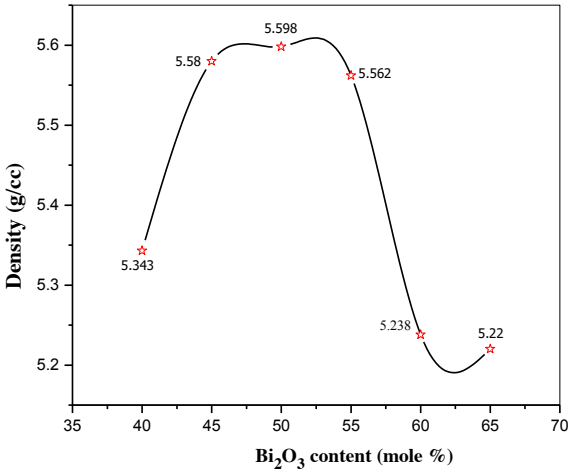

FIGURE 1. Variation of density as function of Bi_2O_3 content in present glasses.

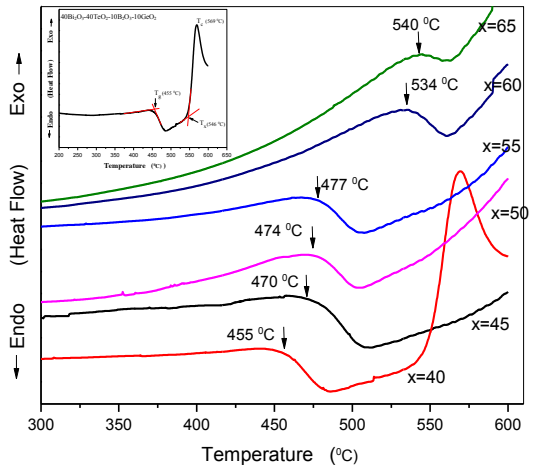

FIGURE 2. DSC thermograms of present glasses.

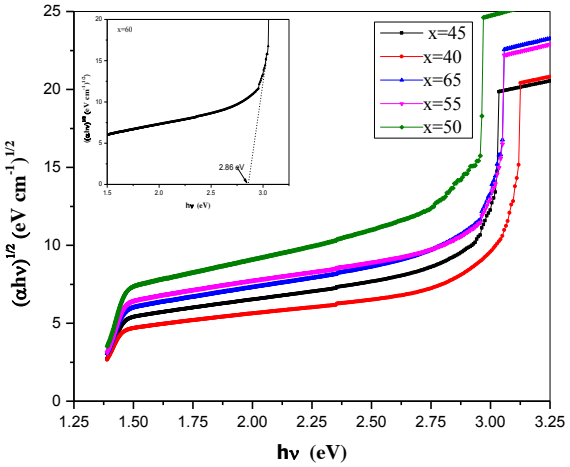

FIGURE 3. Taucs plots ($(\alpha h\nu)^{1/2}$ vs $h\upsilon$) of xBi_2O_3-(80-x)TeO_2-10B_2O_3-10GeO_2 glass system.

where $\Delta\chi^*$ is the difference of the optical electro negativity between anion and cation. The E_g values of Bi_2O_3, TeO_2, B_2O_3 and GeO_2 are calculated and are equal to 5.95, 5.20, 5.58 and 6.32 eV, respectively. Using the above values, the energy gap of the present glasses can be obtained from the proposed formula

$$E_g = \sum x_i \left(E_g\right)_i \quad (8)$$

where x_i is the mole fraction of the i^{th} component and $\left(E_g\right)_i$ its energy gap. To adjust the calculated values of E_g with that obtained experimentally the above proposed equation should be multiplied by a constant equal to 0.5. Therefore,

$$E_g = 0.5 \sum x_i \left(E_g\right)_i \quad (9)$$

The calculated values of E_g are given in TABLE 1. Theoretically the refractive index n of the glass constituents can be estimated using the formula [22]

$$n = -\ln(0.102\ \Delta\chi^*) \quad (10)$$

The values of the refractive index, n of Bi_2O_3, TeO_2, B_2O_3 and GeO_2 are calculated and are equal to 1.8127, 1.9463, 1.8773 and 1.7521, respectively. The refractive index n of the studied glasses was calculated using the formula

$$n = \sum x_i\, n_i \quad (11)$$

Where n_i is the refractive index of the i^{th} component. The calculated values of n are given in TABLE 1. The change in the refractive index is because of the cation polarizability of Bi^{3+} ion (1.508 $Å^3$) is weaker as compared to that of Te^{2+} ion (1.595 $Å^3$). The refractive index is related to energy gap by well-known Moss relation [23] given as

$$E_g\, n^4 = 173 \quad (12)$$

Kumar et al [24] proposed the modified Moss formula as

$$E_g\, n^4 = 52 \quad (13)$$

In this study, the relationship between refractive index and energy gap E_g will follow the relation

$$E_g\, n^4 = 99 \quad (14)$$

Covalency and ionicity

The degree of covalent parameters such as ionic bonding character factor (I_c) and covalent bonding character factor (C_c) for all prepared glasses are given by the following expressions [25]

$$I_c\ (\%) = [1 - \exp\{-0.25(\Delta\chi^2)\}] \times 100 \quad (15)$$

$$C_c\ (\%) = [\exp\{-0.25(\Delta\chi^2)\}] \times 100 \quad (16)$$

where, $\Delta\chi$ is the Pauli electronegativity difference of glass constituting oxides calculated by the relation $\Delta\chi = \chi_C - \chi_A$ (χ_C and χ_A are Pauling electronegativity of cation and anion respectively. The calculated electronegativity values, ionic character parameter and covalency character parameter are presented in TABLE 1. It was observed from the table that all the prepared glasses have $I_c > 99\%$ which implies that they are highly ionic in character.

CONCLUSIONS

From the present study of composition xBi_2O_3-$(80-x)TeO_2$-$10B_2O_3$-$10GeO_2$ quaternary glasses the following conclusions can be drawn: The density varied nonlinearly with Bi_2O_3 content. The T_g values found to increase from 455 °C to 540 °C with increase of Bi_2O_3 content. The indirect optical band gap E_g decreases from 3.07 to 2.81 eV and is due to the structural changes occurred in the prepared glasses. The proposed equations are given to calculate the refractive index of the present glasses. The values of refractive index, the non-linear optical properties such as non-linear refractive index n_2, the third order non-linear optical susceptibility $\chi^{(3)}$ were correlated with the composition of the present glasses. The change in the refractive index is because of the cation polarizability of Bi^{3+} ion (1.508 $Å^3$) is weaker as compared to that of Te^{2+} ion (1.595 $Å^3$). The present glasses have covalency parameter greater than 99% which implies that they are highly ionic in character.

REFERENCES

1. M. Kodama, T. Matsushita, S. Kojima, Jpn. J. Appl. Phys. **34**, 2570 (1995).
2. K. Blaszczak, A. Adamczyk, J. Molecular structure **596**, 61 (2001).
3. J.N. Ayuni, M.K. Halimah, Z.A. Talib, H.A. Sidek, W.M. Daud, A.W. Zaidan, A.M. Khamirul, Mater. Sci. Eng. **17,** 1 (2011).

4. A. Edukondalu, T. Sripathi, Shaik Kareem Ahmmad, Syed Rahman, K. Sivakumar, J. Elect. Mater. **46 (2)** 808 (2017).
5. J.S. Ashwajeeth, T. Shankarappa, T. Sujatha, R. Ramanna, J. Non-Cryst. Solids **486**, 52 (2018).
6. D. Sunil, R.S. Kundu, R. Parmar, S. Muragavel, R. Punia, Solid State Sci. **48**, 230 (2015).
7. Yasser B. Saddeek, H.A. Afifi, N.S. Abd El-Aal. Physica B. **398**, 1 (2007).
8. O.A. Zamyatin, A.D. Plekhovich, E.V. Zamyatina, A.A. Sibirkin. . J. Non-Cryst. Solids **452**, 130 (2016).
9. N. Elkhoshkhany, Rafik Abbas, R. El-Mallawany, K.S.H. Humoud Sharba. Ceramics International **40**, 11985 (2014).
10. Y. Zhou, Y. Yang, F. Huang, J. Ren, G. Chen, J. Non-Cryst. Solids **386**, 90 (2014)
11. T. Hasegawa, J. Non-Cryst. Solids **357**, 2857 (2011).
12. Y.B. Saddeek, K.A. Aly, K.S. Shaaban, Atif Mossad Ali, E.A. Abdel Wahab, J. Non-Cryst. Solids **489**, 82 (2018).
13. D. Munoz-Martin, M.A.Villegas, J. Ganzalo, J.M. Fernadez-Navarro, J. European Ceramic Society **29**, 2903 (2009).
14. J.F. Ducel, J.J. Videau, Mater. Lett., **13**, 271 (1992).
15. R. Christensen, J. Byer, G. Olson, S.W. Martin, J. Non-Cryst. Solids **358,** 583 (2012).
16. Y.S. Rammah, A.S. Abouhaswa, M.I. Sayyed, H.O. Tekin, R. El-Mallawany, J. Non-Cryst. Solids **509**, 99 (2019).
17. F. El-Diasty, M. Abdel-Baki. J. Appl. Phys.**106**, 05321 (2009).
18. V. Dimitrov, S. Sakka, J. Appl. Phys. **79**, 1736 (1996).
19. V. Dimitrov, T. Komatsu, J. Non-Cryst. Solids. **249**, 160 (1999).
20. A.M. Ibrahim, A.H. Hammad, A.M. Abdelghani, G.O. Rabie, J. Non-Cryst. Solids **495**, 67 (2018).
J. Duffy, Physics C **13**, 2979 (1980).
21. R.R. Reddy, Y.N. Ahmmad, K.R. Gopal, D.V. Raghuram, Opt. Mater. **10,** 95 (1998).
22. T.S. Moss, *Photo conductivity in the elements*, (Butterworths, London, 1952).
23. A. Kumar, N.M. Ravindra, R. Rath, J. Phy. Chem. Solids **40**, 1141 (1979).
24. M. Mariyappan, K. Marimuthu, M.I. Sayyed, M.G. Dong, U. Kara. J. Non-Cryst. Solids **499**, 75 (218).