Effect of F ions on physical and optical properties of fluorine substituted zinc arsenic tellurite glasses

Shaik Kareem Ahmmad 1, Edu kondaul 2Syed Rahman 2

1 Physics department, Muffakham jah college of Engineering and Technology, Hyderabad, India
2 Department of Physics Osmaia universities, Hyderabad, India
Email: kareem.physics@gmail.com

Abstract. The effect of substitution of fluoride ions for oxide ions on the physical and optical properties of glass system (20-x) ZnO-xZnF2-40As2O3-40TeO2 where x = 0, 4, 8,12,16,20 mole % were investigated. The samples prepared by melt quenching method under controlled condition. The amorphous nature of these glasses was checked by X-ray diffraction technique. The density was measured according to Archimedes principle. The room temperature absorption spectra of all glass samples were determined using UV-Vis-NIR spectrometer. The thermal behaviour, glass transition temperature and stability of glass samples were studied by a differential scanning calorimetric (DSC). The density reduction of present glasses with ZnF2 concentrations may be due to the low density of ZnF2 compared with that of ZnO. Breaking the oxide network, the cross linking degree of the glass former could be reduced which results in decrease of both Tg and Tx. In the present glass system when F ions replaced by oxygen ions UV-Vis absorption cut-off wavelength decreases. This resulted form the conversion of structural unit in the glass from TeO4 to Te(O,F)4 and then to Te(O,F)3.

Key words: zinc arsenic tellurite glass, XRD, density, DSC, and UV-Vis-NIR.

1. Introduction

In recent years the study on tellurium oxide based glasses has been the subject of high interest due to their potential applications as IR domes, optical fibers, modulators, memories and laser windows. These glasses are well known for their high density, high refractive index, high dielectric constants, a wide band infrared transmittance and large third order non-linear optical susceptibility and numerous devices including optical amplifiers, planar waveguides and nano wires have been fabricated using tellurite glasses [1-6]. A variety of studies on mechanical, electrical and optical properties of tellurium based glasses with different modifiers are present in literature [7-10]. Since tellurium oxide is a conditional glass former, the addition of arsenic oxide (As2O3) to tellurium oxide glasses improves the glass forming ability and the optical transparency in the blue region [11] and this addition affect the infrared transmission of TeO2 glasses to a less extent, since the frequencies of some of the fundamentals modes of vibrations of As2O3 structural groups lay in the region of vibrations of TeO4 structural groups [12].

The TeO2-ZnO system shows good and stable glass forming stability with a broad region. However this glass formation strongly depends on the cooling rate and the size of the melt, especially in the TeO2-rich region [13]. Several studies [14-18] on infrared and optical absorption were reported on zinc tellurite glasses. It has been reported that absorption properties in TeO2-ZnO glasses were observed to be very much dependent on the ZnO content. The ZnO-TeO2 glass was used as a basis for multi-component optical glass system. Since fluorine has a higher electronegativity than oxygen, the
addition of the modifiers like ZnF\(_2\) to ZnO-TeO\(_2\) glass matrix or the substitution of fluorine ions for oxide ions is expected to increase the glass forming range and glass stability, lower the viscosity and improves the transparency to a substantial extent and makes the glass more moisture resistant [19, 20]. Moreover, it would be expected that the glass transition temperature and liquidus temperature decreases with substitution of fluoride ions for oxide ions, since two fluoride ions are substituted for an oxide ion, which causes the breakdown of the glass network structure. Several studies [19, 21-23] on introduced fluorine ions into oxide ions were reported with zinc tellurite glasses. To the best our knowledge there are no reports on fluoride substituted quaternary zinc tellurite glasses. Recently, Kitamura et al. [24] reported the effects of substitution of fluoride ions for oxide ions on the thermal and optical properties of ZnO-Bi\(_2\)O\(_3\)-P\(_2\)O\(_5\) glasses. In the present study, we prepared xZnF\(_2\)-(20-x)ZnO-40As\(_2\)O\(_3\)-40TeO\(_2\) glasses and evaluated the effect of fluorine substitution on physical and optical properties.

2. Experimental

2.1 Glass preparation

In the present study, the glass samples of composition xZnF\(_2\)-(20-x)ZnO-40As\(_2\)O\(_3\)-40TeO\(_2\) (x = 0, 4, 8, 12, 16 & 20 mole%) were prepared by melt quench technique. High purity (99.99%) zinc fluoride (ZnF\(_2\)), zinc oxide (ZnO), tellurium oxide (TeO\(_2\)) (all Sigma Aldrich) and arsenic oxide (As\(_2\)O\(_3\)) (May and Baker) were used as starting materials. A batch of 15 g of the above high purity chemicals in powder form was weighted, well mixed and melted in a porcelain crucible in the temperature range 650-700°C depending on the glass composition in an electrical furnace for about 30 minutes. For samples taken from different regions of the bulk specimen, the absence any Bragg peaks in the x-ray diffraction pattern confirmed that the prepared glasses are amorphous. The room temperature density (\(\rho\)) of the glass samples was determined by the Archimedes principle. The thermal behavior of the glass samples was investigated using a differential scanning calorimeter Mettler-Toledo: TGA/DSC1/1600HT. The glass transition temperature (\(T_g\)) and the crystallization beginning temperature (\(T_c\)) were determined based on the DSC curves using the onset method. The optical absorption spectra for all glass samples were recorded on a jasco model V-570 UV-Vis-NIR spectrometer in wavelength region of 200 to 1000 nm.

Results and discussion

X-ray diffraction patterns of all the present glass samples are shown in Fig.1. The above figure shows no continuous or discrete sharp peaks, which reflects the characteristics of amorphous glass structure.

The room temperature density (\(\rho\)) of the glass was determined to an accuracy of ±0.001 by standard principle of Archimedes’ using xylene as the buoyant liquid. The density was calculated by the formula

\[ \rho = \frac{a \times 0.86}{a-b} \]

Fig. 2 presents the room temperature density of present glasses measured by Archimedes method as a function of ZnF\(_2\) content. From the above figure, it is clear that the density decreases non-linearly. The density of the present glasses varies from 5.374 to 5.516 g/cc.

The density reduction of oxy-fluoride zinc arsenic tellurite glasses with ZnF\(_2\) concentrations may be due to the low density of ZnF\(_2\) compared with that of ZnO. An increase in the ZnF\(_2\) concentrations in the present glass system increases the F/O ratio, and the density reduction is due to the replacement of the Zn=O double bonds by two Zn-F single bonds, the structure of glasses becomes loose. At high ZnF\(_2\) concentrations some ZnF\(_2\) molecules transform into ZnO molecules during the melting process in an atmosphere of air. Similar results were absorbed in TeO\(_2\)-ZnO-ZnF\(_2\)-Na\(_2\)O-La\(_2\)O\(_3\) glasses [21]. The molar volume of the glass samples were calculated.
The DSC thermograms of all the glass samples are shown in fig. 3 and values decreasing form 338.6 to 297 °C. The glass transition temperatures ($T_g$) and onset of crystallization temperature ($T_x$) were determined based on the DSC curves using the onset method. The uncertainty in $T_g$ and $T_x$ is ± 0.1 °C. Fig. 4 plots the variation of $T_g$, $T_x$ and $S$ as a function of ZnF$_2$ content. The reduction in glass transition temperature and onset of crystallization temperature may be due to the addition of fluorine in higher proportion and consequently, 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 $T_x$. Similar results were obtained in TeO-ZnO-ZnF$_2$-Na$_2$O-La$_2$O$_3$ and TeO$_2$-ZnO-ZnF$_2$ glasses [19, 21].

The study of optical absorption is a useful method for the investigation of optical transitions, electronic band structure in crystalline and non-crystalline materials. The optical absorption spectra of present glass system is shown in Fig 3. The variation of cutoff wavelength as a function of ZnF$_2$ content is illustrated in Fig 4. Cutoff of values decreasing from 465nm to 443nm. The UV absorption edge of all glasses fabricated in the present study is blue shifted with increasing ZnF$_2$ content from approximately 465 nm to 443.5 nm. This trend agrees with other results [19, 29-31] on oxyhalide tellurite and silicate glasses but differs from that observed for some lead germanium and lead silicate glass samples [32, 33], where a typical red shift of the absorption edge with the addition of glass.

### 3 Conclusions

Glasses based on present system were fabricated and characterized. The addition of ZnF$_2$ in the tellurite glass changed significantly glass properties such as density, $T_g$, $T_x$ as well as the glass optical properties as UV-Vis absorption etc. The density, glass transition temperature $T_g$ decreased with increasing ZnF$_2$ content. It is noted that the glass thermal stability ($S$) was significantly increased, particularly when the ZnF$_2$ concentration was X=12%, which indicates could be a promising candidate for optical fiber fabrication against divitrification. Due to optical loss would allow them to good candidate materials for this application.
4. Acknowledgment

One of the authors (Shaik Kareem Ahmad) wishes to thank Dr. M.G. Krishna, UOH for providing UV-Vis-NIR spectrometer, Principle Scientific Officer, CIL for providing DSC and EDAX and Principle MJCET for suggestions and helps with this work.

References

[1] A. Mori  2008 *J.Ceram.Soc.Japan.* **116** 1040-1051
[2] A. Mori, Y. Ohishi, S. Sudo, 1997 *Electron.Lett.* **33** 863-864
[3] H. Masuda, A. Mori, K. Shikano, M. Shimzu, 2006 *J.Lightwave Technol.* **24** 504-515
[4] G. Qin, H. Sotobayashi, M. Tsuchiya, A. Mori, T. Suzuki, Y. Ohishi 2008 *J.Lightwave Technol* **26** 492-498
[5] P. Nanid, G. Jose, C. Jayakrishnan, S. Debbarma, K. Chalapathi, A.K. Dharmadhikari, J.A. Dharmadhikari, D. Mathur, 2006 *Opt. Express.* **14** 12145-12150.
[6] L. Tong, L. Hu, J. Zhang, J. Qiu, Q. Yang, J. Lou, Y. Shen, J. He, Z. Ye, 2006 *Opt. Express* **14** 82-87
[7] M. Pal, Y. Tsujigami, A. Yoshikado, H. Sakata, 2000 *Phys. Stat. Sol.* A **182** 727
[8] G. El-Damrawi, 2000 *Phys. Stat. Sol.* A **177** 385
[9] G. El-Damrawi, S. Abd-El-Maksoud, 2000 *Phys.Chem. Glasses.* **41** 64
[10] R. A. Montani, S. E. Giusia, 2001 *Phys. Chem. Glasses.* **42** 12
[11] B. V. Raghavaiah, N. Veeraiah, 2004 *J. Phys. Chem. Solids.* **65** 1153
[12] A. Bishay, C. Magarabi, 1969 *Phys. Chem. Glasses.* **10** 1
[13] V. Kozhuakharov, S. Neov, I. Gerasimova, P. Mikula, 1986 *J. Mater. Sci.* **21** 1707.
[14] A. Narazki, K. Tanaka, K. Hirao, T. Hashimoto, H. Nasu, K. Kamiya, 2001 *J. Am. Ceram. Soc.* **841** 214.
[15] S. Rosmawati, H. A. A. Sidek, A. T. Zainal and H. Mohd Zobir, 2007 *J. Appl. Sci.* **20** 3051.
[16] A. Nukui, T. Taniguchi, M. Miyata, 2001 *J. Non-Cryst. Solids* **260** 293.
[17] J. C. Boyer, F. Vetrone, J. A. Capobianco, A. Speghini, M. Bettineli, 2003 *J. Appl. Phys.* **93** (12) 9460.
[18] H. A. A. Sidek, S. Rosmawati, Z. A. Talib, M. K. Halimah, W. M. Daud, Am. 2009 *J. Appl. Sci.* **6** (8) 1489.
[19] V. Nazabal, S. Todoroki, A. Nukui, T. Matsumoto, S. Suehara, T. Hondo, T. Araki, S. Inoue, C. Rivero, T. Cardinal, 2003 *J. Non-Cryst. Solids* **325** 85
[20] M. M. El-Desoky, M. M. Abo-Nafs, M., 2004 *J. Mater. Sci. Mater. Electron.* **15** 425
[21] G. Wang, S. Dai, J. Zhang, S. Xu, L. Hu, Z. Jiang, 2005 *J. Luminiscence* **113** 27
[22] G. Wang, S. Dai, J. Zhang, S. Xu, L. Hu, Z. Jiang, 2005 *J. Non-Cryst. Solids* **351** 2147.
[23] M. D. O'Donnell, C. A. Miller, D. Furniss, T. K. Tikhomirov, A. B. Seddon, 2003 *J. Non-Cryst. Solids* **331** 48
[24] N. Kitamura, K. Fukumi, J. Nakamura, T. Hidaka, T. Ikeda, H. Hashima, J. Nishii, 2011 *J. Non-Cryst. Solids* **357** 1188
[25] S. Inaba, S. Fujino, 2010 *J. Am. Ceram. Soc.* **93** 217
[26] S. Toyoda, S. Fujino, K. Morinaga, 2003 *J. Non-Cryst. Solids* **355** 821
[27] R. D. Shannon, C. T. Prewitt, 1969 *Acta Crystallogr.* B **25** 925
[28] R. D. Shannon, C. T. Prewitt, 1970 *Acta Crystallogr.* B **26** 1046
[29] G. Liao, Q. Chen, J. Xing, H. Gebavi, D. Milanese, M. Fokine, M. Ferraris, 2009 *J. Non-Cryst. Solids* **355** 447
[30] M. D. O'Donnell, K. Richardson, R. Stolen, 2007 *J. Am. Ceram. Soc.* **90** 1448
[31] K. Saito, A. J. Ikushima, 2002 *J. Appl. Phys.* **91** (8) 4886
[32] H. Jia, G. Chen, Z. Hou, 2003 *J. Non-Cryst. Solids* **319** 322
[33] D. Lezal, J. Pedikova, J. Hoaka, 1996 *J. Non-Cryst. Solids* **196** 178.