Solid State Science and Technology, Vol. 13, No 1 & 2 (2005) 251-256
ISSN 0128-7389

OPTICAL ABSORPTION EDGE AND TRANSITION STUDIES OF BISMUTH PHOSPHATE $(Bi_2O_3)_X(P_2O_5)_{1-X}$ GLASSES

Sheik Azrif Bux Sheik Azmi Bux, Sidek Hj. Abdul Aziz,
Zainal Abidin Talib, & W. Mohd. Daud W. Yusoff

Ultrasonic and Glass Research Laboratory, Physics Department
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
43400 UPM Serdang, Malaysia.

Email:bux_79@hotmail.com

ABSTRACT

Glasses with composition xBi$_2$O$_3$.(1-x)P$_2$O$_5$ were prepared over the range $0.05 \leq x \leq 0.23$ by a single step process of Bi_2O_3 and P_2O_5. The amorphous nature of the glass compositions was confirmed by x-ray powder diffraction (XRD) studies. The optical absorption was recorded at room temperature in a wavelength range of 200-800 nm using UV-Visible Spectrophotometer. The values of optical band gap (E_{opt}) have been evaluated and were found to depend on the glass composition. It gives a very good fit for indicating indirect transitions. Different Thermal Analysis (DTA) data were used to determine the glass transition temperatures of the glass and has been interpreted in terms on the role of alkaline oxide in the matrix.

INTRODUCTION

Bismuth glasses have been extensively investigated because of their interesting technological applications due to their optical properties. The study of optical absorption and particularly the absorption edge is a useful method for providing useful information about the band structure and energy gap of non-crystalline materials. Absorption in the visible region results from the superposition of the tails of the electronic and vibration transition to which must be added contributions from impurities such as transition element ions and colour centers (Scholze, 1990). For many desirable applications in optical systems, optical transparency in the UV region below 400nm will be an advantage. This requirement is not met in the conventional silicate glasses [2].

MATERIALS AND METHOD

Series of bismuth phosphate glasses were prepared from laboratory reagent of bismuth oxide (Bi_2O_3, molecular weight 465.9608), and phosphorus pentoxide (P_2O_5, molecular weight 141.945) using the melt quenching technique. This procedure was employed to prepare glasses with a glass formation range of 5-23% Bi_2O_3 for phosphate glasses. The reagents were mixed and heated (in a covered alumina crucibles of 100 cm^3 capacity) at 673K for about 30 minutes. This allows the boron oxide and phosphorus pentoxide to decompose and react with the rare earth oxide. The mixture was then taken out and placed into a second, preheated furnace at a temperature of 1273K in order to achieve good homogeneity of the melts. To produce the glass, each melt was cased into a stainless-steel mold to form glass cylinders 2 cm long by 1cm diameter. After casting, each glass was immediately transferred to an annealing furnace held at 673K for 1 hour. The furnace was the switched off and the glasses then were allowed to cool down.

X-ray diffraction measurements were made using a Philips x-ray diffractometer and showed no peak in the diffraction pattern, which is characteristic of amorphous materials. The densities were measured by the Archimedes method using acetone as the immersion liquid. The optical absorption of the polished samples was recorded at room temperature in wavelength range of 200-800nm, respectively using Camspec M350 Double Beam UV-Visible Spectrophotometer.

The thermal properties of bismuth phosphate glasses were analyzed using a differential thermal analysis (DTA) equipment. Glass samples were crushed to fine grains. All measurements were done in flowing nitrogen atmosphere, using alumina sample holders. For the first series the samples were rapidly heated to 300 ^oC and a heating rate of 5 K/min was applied within the temperature range 300 ^oC – 420 ^oC. The peaks were determined from the measured data.

RESULTS AND DISCUSSION

Table 1: Glass composition, density, optical band gap, and transition temperature of bismuth phosphate glass system.

Bi_2O_3 (mol %)	Density (g/cm^3)	Optical band gap, E_{opt} (eV)	Transition temperature, T_g (^oC)
5	3.671	3.9170	332.27
10	4.048	3.6119	367.82
13	4.139	3.9284	397.01
15	4.418	3.6902	398.33
18	4.478	3.8648	404.67
20	4.576	3.7779	406.89
23	4.650	3.7512	407.66

The density of the glass samples listed in Table 1 shows an increase with Bi_2O_3 content. This is probably due to a change in cross-link density and coordination numbers of Bi^{3+} ions (El-Adawy and Moustafa, 1999).

Solid State Science and Technology, Vol. 13, No 1 & 2 (2005) 251-256
ISSN 0128-7389

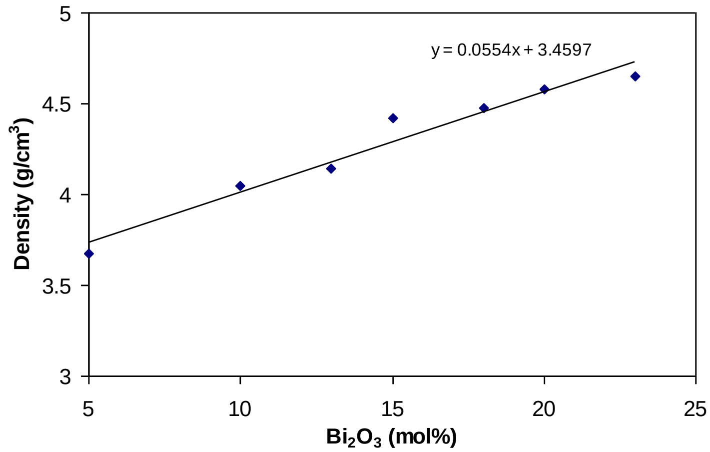

Figure 1: Variation of density with mol% Bi_2O_3-P_2O_5 glass systems.

The optical absorption spectra shown in Figure 2 clearly indicated that there are no sharp absorption edges, a characteristic of the glassy state (Al-Ani et al., 1991). The position of fundamental absorption edge varies with increase in content of Bi_2O_3 in the glass system and shift towards longer wavelengths with an increase in the alkali content [2]. The absorption coefficients, α were calculated from the following formula:

$$\alpha(\omega) = (1/t) \ln (I/I_o) \qquad (1)$$

where t is the thickness of each sample and ln (I/I_o) corresponds to absorbance. Davis et al. (1970) suggested the general relation proposed for amorphous materials

$$\alpha(\omega) = \text{const.}(\hbar\omega - E_{opt})^r / \hbar\omega \qquad (2)$$

where r takes different values depending on the mechanism of interband transitions and $\hbar\omega$ is the photon energy of the incident radiation. The equation above with r = 2, was found to fit well for most oxide glasses and hence is associated with indirect allowed transitions (Al-Ani, 1985).

The values of optical band gap, E_{opt} noted in Table 1 is obtained by extrapolating to meet the $\hbar\omega$ axis at $(\alpha\hbar\omega)^{1/2} = 0$. The figure shows that the value of E_{opt} decrease to lower energies with increasing Bi_2O_3 content in $(Bi_2O_3)(P_2O_5)$ glass. The structure of phosphate glass is dependent upon its composition. The ratio of oxygen to phosphorus ions (O/P) determines how the tetrahedra link together. Continuing to add more modifiers into the glass network will decrease the length of the chains as the O/P ratio increases. Therefore, more and more tetrahedra become linked at only two corners (polyphosphates) rather than three (metaphosphates).

Solid State Science and Technology, Vol. 13, No 1 & 2 (2005) 251-256
ISSN 0128-7389

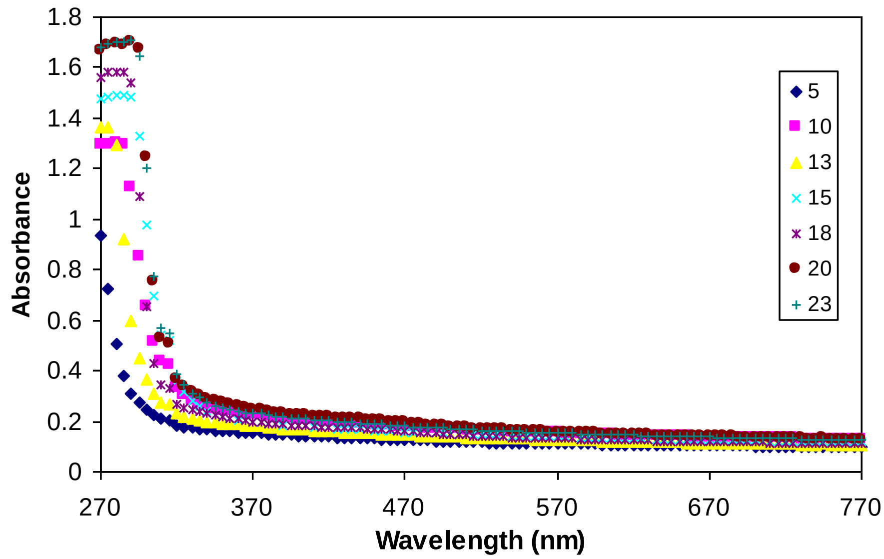

Figure 2: Optical absorption spectra for Bi_2O_3-P_2O_5 glass system.

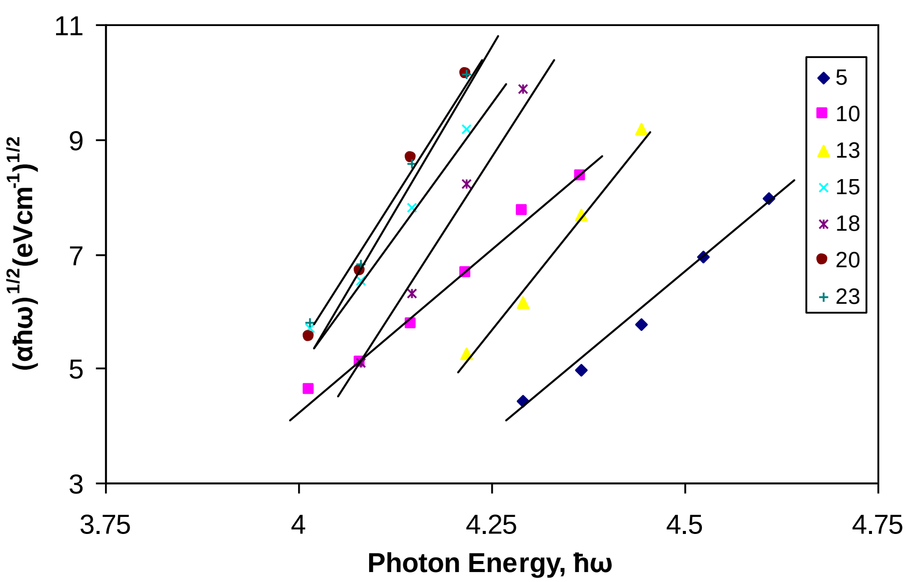

Figure 3: Tauc's plot for Bi_2O_3-P_2O_5 glass systems.

Solid State Science and Technology, Vol. 13, No 1 & 2 (2005) 251-256
ISSN 0128-7389

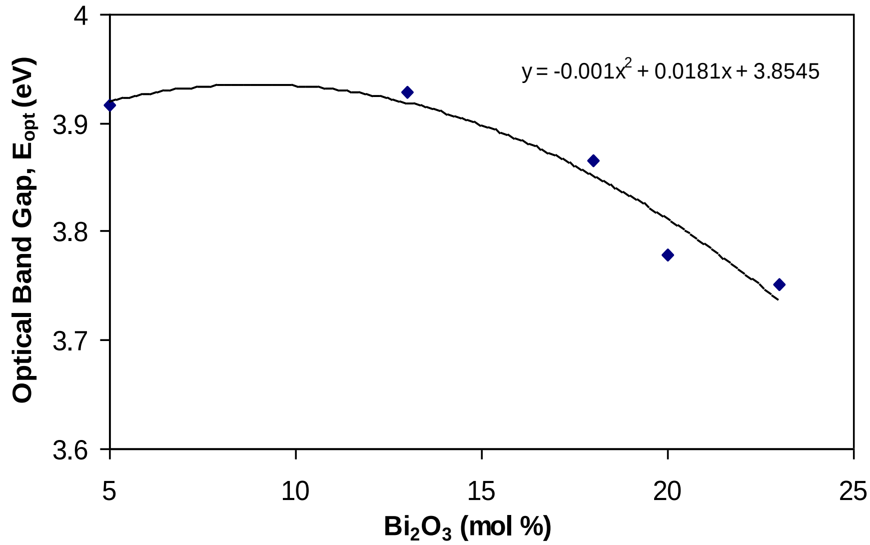

Figure 4: Optical band gap for Bi_2O_3-P_2O_5 glass systems.

The determination of the glass transition temperatures of bismuth phosphate glasses as given in Figure 5 shows a significant trend as the temperature increase with decreasing P_2O_5 content in phosphate glasses. From x = 5% to x = 15%, the glass transition shows a linear increase. The trend also shows what seems to be a slight increase in the transition temperatures at the limit of the glass making region. It seems that the pentavalence of phosphorus ions, P introduces nonbridging oxygens in the absence of alkali (network modifiers). Thus the weakest, low melting, pure P_2O_5 glass is structurally strengthened rather than weakened by the addition of Bi_2O_3. Therefore, alkali phosphates have higher melting points than pure P_2O_5.

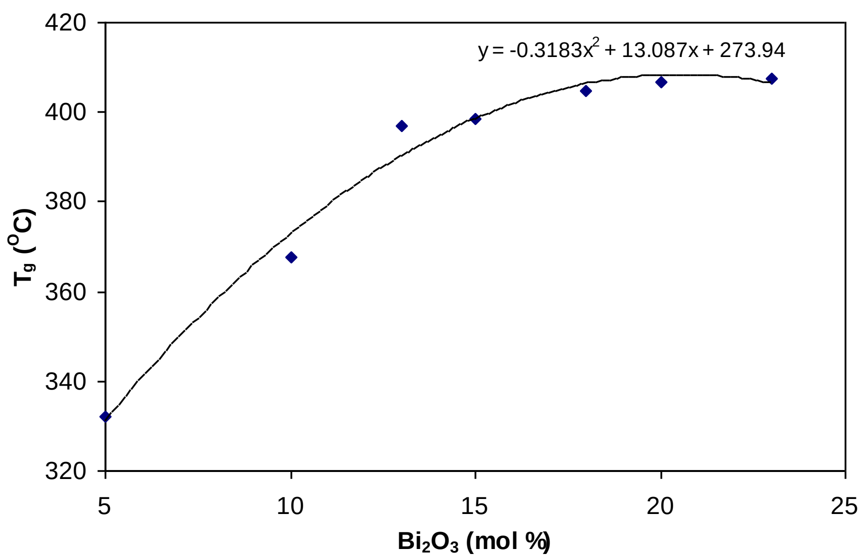

Figure 5: Transition temperature for Bi_2O_3-P_2O_5 glass systems.

CONCLUSION

The optical and thermal properties of $(Bi_2O_3)_X(P_2O_5)_{1-X}$ have been studied. A greater mole weight of the bismuth atom and the coordination numbers of Bi^{3+} ion influenced the increases in density. It could be shown that the glass modifier has no significant effect on the optical property of bismuth phosphate glass at low alkali content. The increasing amount of Bi_2O_3 in the range of 15-23% hardly effects the transition temperature.

ACKNOWLEDGEMENT

The authors would like to thank the Ministry of Science, Technology and Innovation (MOSTI) and Universiti Putra Malaysia for the IRPA grant Vote: 54275.

REFERENCES

[1] H. Scholze. (1990). Glass Nature, Structure and Properties, Springer, Berlin.
[2] C. Dayanand, R.V.G.K. Sarma, G. Bhikshamaiah and M. Salagram, Optical properties of lead phosphate glasses, *J. Non-Cryst. Solids*. **167** (1994) 122-126.
[3] A El-Adawy and Y Moustafa, Elastic properties of bismuth borate glasses, J. Phys. D: Appl. Phys. **32** (1999) 2791-2796.
[4] S.K.J. Al-Ani and A.A. Higazy, Study of optical absorption edges in MgO-P2O5 glasses, J. Mater. Sc. **26** (1991) 3670-3674.
[5] S.K.J. Al-Ani, C.A. Hogarth and R.A. El-Malawany. (1985). *J. Mater. Sci.* **20**: 661.
[6] E.A. Davies and N.F. Mott. 1970. *Philos. Mag.* 22: 903.
[7] C.A. Hogarth and A.A. Hosseini, Optical absorption near the fundermental absorption edge in some vanadate glasses, J. Mater. Sc. **18** (1983) 2697-2705.