Thermal properties and optical band gap of a novel high UV-transmitting glass

ZHIWEI LUO, ANXIAN LU*
School of Materials Science and Engineering, Central South University, Changsha 410083, People's Republic of China

High UV-transmitting Glasses with composition 10SrO-10ZnO-33.3P_2O_5-xB_2O_3-(46.7-x)SiO_2 have been prepared using the normal melt-quench technique. Glass transition temperatures (T_g) and thermal expansion coefficients (*CTE*) were determined using thermo mechanical analysis. The optical studies in the UV-visible region for these glasses show different cut-off and transmitting window depending on composition. Increasing the B_2O_3 content to 16.67 mole% in the glasses can enhance the UV transmittance to greater than 60% at 200 nm. The values of both of the optical band gap (E_{opt}) and Urbach energy (ΔE) were calculated from optical absorption data. Generally, a novel high UV-transmitting glass was obtained successfully, and it is possible to produce glasses of high UV-transmittance using common commercial reagents at a relatively lower cost.

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1. Introduction

Recent demand for high-performance glass as UV-transmitting materials has increased for applications in microlithography equipment, laser systems and special ultraviolet optics [1-5]. Glasses capable of transmitting well in the ultraviolet (UV) are rare, and those that do so are difficult to fabricate. Fluoride crystal, fuse silica and fluoride glasses, exhibit excellent UV transmission, but also present very difficult manufacturing challenges, particularly, the difficulty in scaling up the process to produce large parts. Phosphate glasses, produced based on ultra-high pure materials can enhance the UV transmittance of these glasses, but the purification of raw materials and the complexity of glass melting may increase the production costs, which actually makes it harder to mass-produce. Shih PY [4-5] investigated the properties and structural investigations of UV-transmitting vitreous strontium zinc metaphosphate, who found that UV-transmitting phosphate glasses with transmittance greater than 70% at 250 nm were obtained using reagent-grade raw materials. But there are some obvious shortcomings in the glass series (high thermal expansion coefficient, poor relative chemical durability, for example).

In this article, B_2O_3 and SiO_2 were introduced into the phosphate glasses, adjusting the composition of glass to improve the performance of the phosphate glasses. Moreover, these UV-transmitting glasses can be produced at low price. The main objective of this investigation is to develop a novel UV-transmitting glass using the reagent-grade raw materials. This study is of great significance because the high UV-transmitting of borophosilicate glasses have not been reported by other authors so far as we know.

2. Experimental

The glasses with compositions of 10SrO-10ZnO-33.3P_2O_5-xB_2O_3-(46.7-x)SiO_2 (x=6.67~26.67 mole%) were melted, the chemical composition of all materials used was presented in Table 1. Laboratory reagent-grade ZnO, $SrCO_3$, $(NH4)_2HPO_4$ and H_3BO_3, SiO_2 powders were chosen as the raw materials. These were placed in a quartz crucible which was introduced into a preheated furnace at 450 °C to allow for removal of H_2O, CO_2 and NH_3 (especially for removal of NH_3) then followed by melting at 1400~1500 °C for 3 h, depending on composition. Upon removal of the crucible from the furnace, the melted glass was then poured into a pre-heated graphite mould at 480 °C for 3~8 h to relieve internal stress. The mould was then allowed to cool to room temperature in the furnace overnight. The obtained samples were cut and polished into suitable shape for optical analyses.

Glass transition temperatures (T_g) and thermal expansion coefficients (*CTE*) were determined using thermomechanical analysis (TMA, Elmer TMA7 Analyzer) at a heating rate of 10 °C/min. The UV-vis transmittance spectra of the glasses were recorded with a UV-vis spectrometer (Cary 5000) in the spectral range 200-780 nm at room temperature. The glass samples were polished down to a thickness of 1.00 mm.

Table 1. Characteristics of the 10SrO-10ZnO-33.3P_2O_5-xB_2O_3-(46.7-x)SiO_2 glasses.

Samples No.	x (mole%)	CTE(25, 600°C) (10^{-6}/°C)	T_g (°C)	E_{opt} (eV)	ΔE (eV)
BS-3	x=6.67	8.15	532	5.4	0.39
BS-4	x=10.00	6.28	602	5.3	0.41
BS-5	x=13.33	5.82	620	5.1	0.55
BS-6	x=16.67	5.91	613	4.7	0.82
BS-7	x=20.00	5.73	608	4.6	0.86
BS-8	x=26.67	6.66	584	4.1	1.18

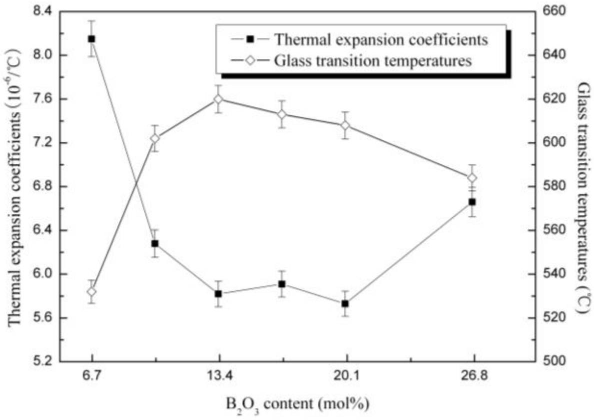

Fig. 1 Variation in thermal expansion coefficients and glass transition temperature of the glass series with different B_2O_3 content.

3. Results and discussion

Clear, homogeneous glasses could be cast to thicknesses of 1.0 cm from 6.67 to 26.67 mol% B_2O_3 content. The characterization data are listed in Table 1. The variation of glass transition temperatures (T_g) and thermal expansion coefficients (*CTE*) of these glasses is shown in Fig. 1. The *CTE* is found to be ranged from 4.82 to 8.15×10^{-6}/°C. The T_g obtained from the thermal expansion curve. In the series of glasses, T_g increases from 532 °C (sample BS-3) to 620 °C (sample BS-5) but then decreases to 584 °C (sample BS-8) with increasing B_2O_3 content. The high-performance glass as UV-transmitting materials should to be lower thermal expansion coefficients and higher glass transition temperatures in order to achieve mechanically stable stacks.

Substitution of B_2O_3 for SiO_2 results in the increase in T_g and decrease in *CTE* of these glasses. The *CTE* of the glasses firstly decreases but then increases with increasing B_2O_3 content. From the analysis of glass structure, the addition of boron oxide makes the glass structure more tighter and enforces the network structure, So the *CTE* is supposed to decrease. This can be explained for that *CTE* of glasses are determined by both the intensity of the glass network structure and bond force between the cations and the oxygen ions [6]. When the B_2O_3 content was relatively low, the boron atoms partly form [BO_4] tetrahedral, the microscopic structural of glasses becomes tighter, so the glass transition temperatures of glasses increase with the addition of boron oxide firstly. As the B_2O_3 content is more than 16.7 mol%, the proportion of [BO_3] triangles unit increases. [BO_3] triangles units create more non-bridging oxygens (NBOs), which forms loosened glass network, so the T_g of glasses decrease, the *CTE* is supposed to increase.

UV-vis spectra of these glasses are shown in Fig. 2, which reveals that the UV cut-off of these glasses firstly tends to shift to short wavelength but then shift to length wavelength with increasing B_2O_3 content. The UV transmittance of 6.67 mole% B_2O_3 glass exhibits only 1.5% at 200 nm and 61.9% at 250 nm, while the UV transmittance of 16.67 mole% B_2O_3 glass exhibits 61.5% at 200 nm and 81.1% at 250 nm. This value of UV transmittance is slightly lower than that of the glass with the same composition but made with high purity raw materials. The studied glasses were prepared using common commercial reagents, and glasses with some trace impurity ions may result in UV absorption. Generally, increasing the B_2O_3 content in borophosilicate glasses can enhance the UV transmittance to greater than 60% at 200 nm. It is possible to produce glasses of high UV transmittance using common commercial reagents at a relatively lower cost.

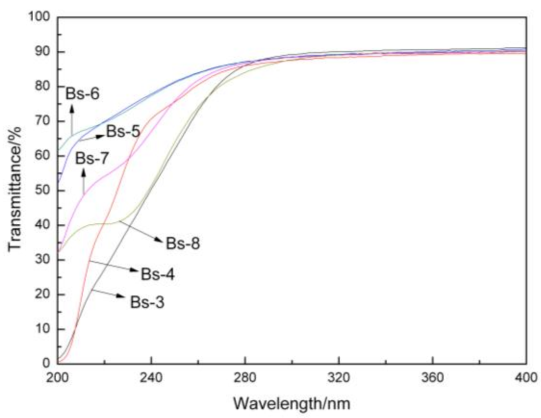

Fig. 2. UV-vis spectra of glass series with different B_2O_3 content.

The study of optical absorption edge is useful information for understanding the optically induced transitions and optical band gaps of materials. The principle of the technique is that a photon with energy greater than the band gap energy will be absorbed [7]. The optical absorption coefficient, $\alpha(\omega)$, of a material can be evaluated from the transmittance, reflectance and the thickness of the sample (d), using the following formula (1):

$$\alpha(\omega) = \frac{1}{d}\ln\left(\frac{I}{I_0}\right) \quad (1)$$

In the formula (1), $\ln(I/I_0)$ corresponds to absorbance. The optical absorption coefficient, $\alpha(\omega)$, may be displayed in a number of ways as a function of photon energy, $\hbar\omega$, and the most satisfactory results were obtained by the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$. The optical absorption coefficient $\alpha(\omega)$ for many amorphous and glassy materials is found to obey the formula (2):

$$\alpha(\omega)\hbar\omega = B(\hbar\omega - E_{opt})^{p} \quad (2)$$

E_{opt} is the optical gap; B is a constant and $\hbar\omega$ is the photon energy. For amorphous materials indirect transitions are valid according to Tauc [8], i.e. power part $p = 2$; so, the values of indirect optical band-gap energy (E_{opt}) can be obtained from formula (2) by extrapolating the absorption coefficient to zero absorption in the $(\alpha\hbar\omega)^{1/2}$-ħω plot. The respective values of E_{opt} are obtained by extrapolating to $(\alpha\hbar\omega)^{1/2} = 0$ for the indirect transitions [7, 9, 10, 11, 12, 13].

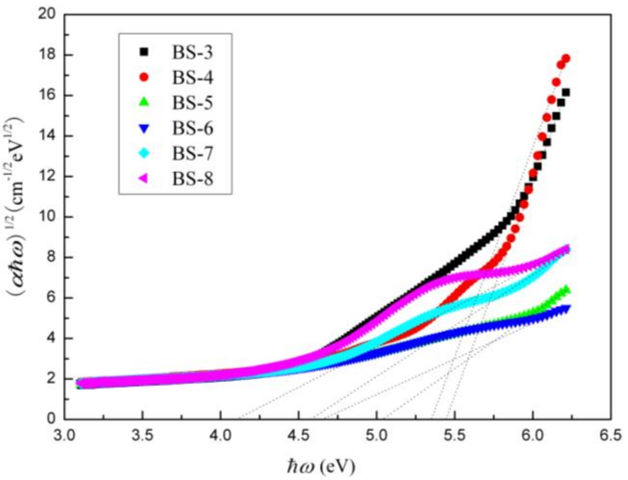

Fig. 3. Plots of the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for various glasses.

The compositional dependence of E_{opt} almost shows a decrease trend with increasing B_2O_3 content as shown in Table 1 and Fig. 3. The decreasing values of E_{opt} can be understood in terms of the structural changes that are taking place in the studied glass system. The addition of B_2O_3 content to the glass network may lead to the formation of new non-bridging oxygen (NBOs). Hence increase in B_2O_3 content results in progressive creation of NBOs at the expense of bridging oxygen (BO). The NBOs which bound an excited electron less tightly than the BOs and NBOs are more polarizable than the BOs. Thus, creation of NBOs seems to be reason for shift of cut-off wavelength towards higher wavelengths and in turn decreases the E_{opt} values.

The extent of band tailing is a measure of the disorder in the material and can be estimated using Urbach law [14, 15].

$$\alpha(\omega) = \alpha_0 \exp\left[\frac{\hbar\omega}{\Delta E}\right] \quad (3)$$

$$\ln\alpha = \frac{1}{\Delta E}(h\omega - E_0) \quad (4)$$

α_0 is constant and ΔE is the width of the band tails of electron states in the forbidden band gap and which is also known as the Urbach energy [9]. Fig. 4 shows the variation of $\ln\alpha$ with photon energy ($\hbar\omega$) for present glass system (Urbach plot). The values of Urbach energy (ΔE) were calculated from the reciprocal of the slope of the linear region of the curves. The value of ΔE was obtained from the inverse of the slope of $\ln\alpha$ vs. $\hbar\omega$ and is given in Table 1 and Fig. 5 with estimated probable error of ±0.01eV. The width of the edge ΔE, is also related to another parameter which is slope of Urbach edge, $\sigma = kT/\Delta E$, k is the Boltzmann's constant and T is the temperature.

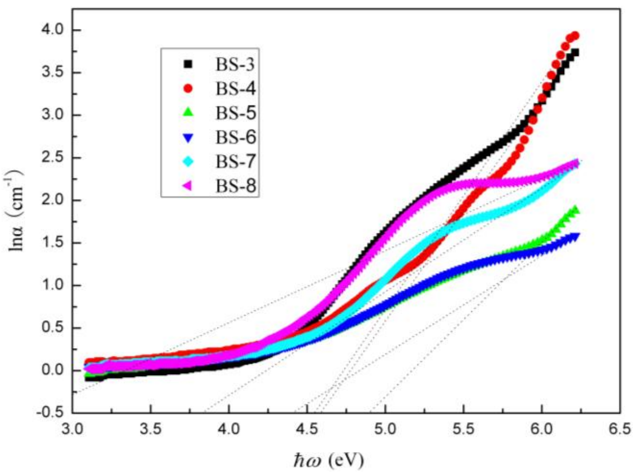

Fig. 4. The ln α as a function of photon energy (ħω) of various glasses.

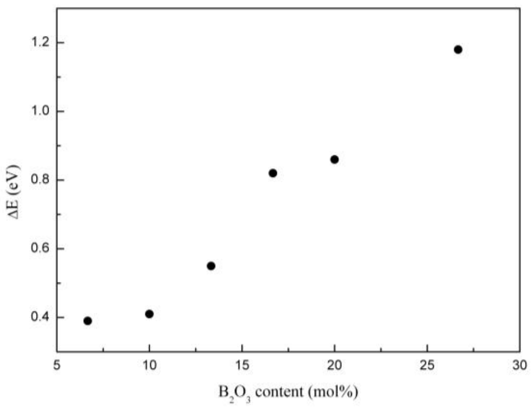

Fig. 5. Variation of ΔE (eV) with different contents of B_2O_3 content.

4. Conclusion

A novel high UV-transmitting glass was obtained successfully using common commercial reagents at a relatively lower cost In the glass series, T_g increases from 6.67 to 16.7 mol% B_2O_3 but then decreases for higher boron contents, while *CTE* shows an opposite trend. Generally, increasing the B_2O_3 content in borophosilicate glasses can enhance the UV transmittance to greater than 60% at 200 nm. The values of Urbach energy (*ΔE*) increase progressively as increase of the B_2O_3 content. The values of (*ΔE*) with its composition dependence show an in inverse trend to the values of E_{opt}. Moreover, the new composition revealed a non-linear optical relation, which promises to be useful for future high-performance glass as UV-transmitting materials has increased for applications in microlithography equipment, laser systems and special ultraviolet optics.

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* Corresponding author: axlu@csu.edu.cn