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The formation of BO_4^- tetrahedra and nonbridging oxygen ions in borosilicate glasses with low silica content

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Alkali-, mixed alkali- and mixed alkali-alkaline earth aluminoborosilicate glasses with low silica content have been prepared and annealed. Molar volume measurements and structural analysis using X-ray diffraction, IR spectra, and UV-transmission were carried out. It is shown that the formation of nonbridging oxygen ions bonded with the silicon ions takes place during the formation of BO_4^- tetrahedra for $0.4 \leqslant R \leqslant 0.8$ where R is the alkali oxide to the boron oxide ratio. From X-ray diffraction patterns, it is found that no crystalline phases can be detected. The UV-transmission spectra elucidated that the probability of formation of nonbridging oxygen ions in the glass with a single alkali ion (Li^+) is higher than that in the glass with mixed alkali ions ($Li^+ + K^+$) under the same conditions. It is assumed that the shift of the UV-edge to lower or longer wavelengths may be due to the phase separation process in these glasses.

1. Introduction

Many investigations were carried out on the alkali borosilicate glasses to determine the relative proportions of three- and four-coordinated boron ions as a function of composition. Sheerer *et al.* [1] showed that there is preferred association of the alkali oxide with the boron units forming BO_4^- tetrahedra up to a certain saturation concentration. The maximum fraction of four-coordinated borons in alkali borosilicate glasses is greater than that in alkali-borate glasses and increases with increasing silica content. Milberg *et al.* [2] concluded that sodium borosilicate glasses with sodium oxide to boron oxide ratio (R) of 0.5 or less behave with regard to boron coordination as if they were sodium borate glasses diluted with silica. Glasses with sodium to boron ratios of less than 0.5 contain essentially no nonbridging oxygen ions. In glasses with higher sodium oxide contents, the fraction of nonbridging oxygen ions increases with increasing the concentration of sodium oxide, at fixed silica content. On the other hand, for glasses with fixed alkali content, the fraction of nonbridging oxygen ions increases with the increase of SiO_2 content. The same results were obtained by Zvyagin *et al.* [3] for potassium borosilicate glasses. The above mentioned results were confirmed by Araujo [4]. He assumed that nonbridging oxygen ions are not bonded to silicon ions in alkali borosilicate glasses of $R \leqslant 0.5$. Konijendijk [5] found that in a Na_2O–B_2O_3–SiO_2 glass of molar composition $x Na_2O \cdot (0.85 - x) B_2O_3 \cdot 0.15 SiO_2$ the alkali oxide can be consumed in the silicate network to form nonbridging oxygen ions prior to the formation of borate groups containing BO_4^- tetrahedra.

Recently, it is indicated by Doweidar *et al.* [6] that the alkali oxide in sodium borosilicate glasses with low silica content preferred to associate itself with SiO_2 rather than with B_2O_3. This process is controlled by the relative value of R and K, where K is the molar fraction of SiO_2/B_2O_3.

In this paper, the investigations on alkali- and alkaline earth borosilicate glasses are extended to obtain more information about their structure.

2. Experimental details

2.1. Sample preparation

The glasses listed in Table I were prepared from pure reagent grade chemicals. Alkali oxides and alkaline-earth oxides were introduced as carbonates. Silica was introduced in the form of highly purified pulverized quartz. Boron was introduced in the form of boric acid. The glasses were melted in well-fired clay crucibles in a gas furnace at about 1400° C. The melt was poured into preheated steel moulds and given coarse anneal. The specimens were allowed to cool overnight from 450° C to room temperature. Glass discs were ground and polished to obtain two parallel surfaces.

TABLE I Compositions of the studied glasses (in mol %)

	Glass no.					
	G1	G2	G3	G4	G5	G6
Li_2O	18	24	30	36	12	12
K_2O	–	–	–	–	–	12
BaO	–	–	–	–	12	–
Al_2O_3	3	3	3	3	3	3
SiO_2	20	20	20	20	20	20
B_2O_3	59	53	47	41	53	53

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2.2. Density and molar volume measurements

The density of glasses was measured at room temperature using the suspended weight method based on Archimedes principle. Xylene was used as the immersion liquid. All measurements were made not less than three times with a maximum error ± 0.005. The molar volume was calculated from the relation

$$V_m = \frac{\Sigma n_i M_i}{D}$$

where M_i is the molecular weight for the component i, n_i its molar ratio and D is the glass density.

2.3. X-ray analysis

The X-ray diffractions were carried out for all glasses using an X-ray diffractometer system type: Geiger flex D/Max-IA (1.5 kW), with a scanning rate $2° \mathrm{min}^{-1}$. The obtained X-ray spectra are not presented in this work. It was indicated that if there would be any degree of crystallinity it might be less than 5% (the permissible accuracy of the used diffractometer).

2.4. Infrared spectroscopy

The infrared spectra for some chosen glasses were recorded at room temperature using KBr technique by a spectrophotometer (Berkin Elmer 1430) in the wave number range $200–4000\,\mathrm{cm}^{-1}$.

2.5. UV-transmission spectra

The UV-transmission measurements for some glasses were carried out using a spectrophotometer (Perkin Elmer Lambda 3B).

3. Results and discussion

3.1. Density and molar volume

Figure 1 represents the molar volume as a function of R for glasses 1–4. It is shown that the molar volume decreases steeply with a higher rate until $R \simeq 0.4$ then remains approximately constant although R still increases. This drastic change in the molar volume curve at $R \simeq 0.4$ may refer to a structural change at that R-value. These results can be explained on the basis of the formation of BO_4^- units and the nonbridging oxygen ions in the different glasses. In Table II the values of R and K for glasses 1–4 are given. R is calculated considering the quantity of Li_2O, consumed by Al_2O_3 to introduce the latter as AlO_4^- tetrahedra in the glass network.

TABLE II The values of R and K for glasses 1–4

Glass No.	Li_2O–Al_2O_3	K	R	Li_2O	SiO_2	Al_2O_3	B_2O_3
1	15	0.34	0.25	18	20	3	59
2	21	0.38	0.4	24	20	3	53
3	27	0.43	0.57	30	20	3	47
4	33	0.49	0.8	36	20	3	41

It is indicated that for glass 1, $K < R$ while $K > R$ for the glasses 2–4. For all glasses $K \leqslant 0.5$, NMR studies by Doweidar *et al.* [6] indicated that in borosilicate glasses with $R \geqslant K$ and $K \leqslant 0.5$ in the range of $R < R_{max}$ (R_{max} is the value of R corresponding to maximum fraction of BO_4^- groups) no nonbridging oxygen ions (NBOs) are formed in the borate network whereas these are formed in the silicate network. It can be deduced that NBOs cannot be formed in glass 1 in both of the borate and silicate networks, but such ions begin to form in the silica network from $R \simeq 0.4$. According to Takahashi and Osaka [7] who investigated Na_2O and K_2O–B_2O_3–SiO_2 glasses the molar volume in the present work must remain constant until $R \simeq 0.6$, since Li^+ ions are also small and can be accommodated in voids as Na^+ ions. This is in contradiction with the presented results.

In Fig. 2 the dependence of N_4 on R for alkali borosilicate glasses, in the composition range of the glasses studied, are represented. Curve A is drawn after a model given by Araujo [4] in which alkali oxide (for $R < 0.5$) is assumed to be incorporated in the borate network. Curve B represents NMR data

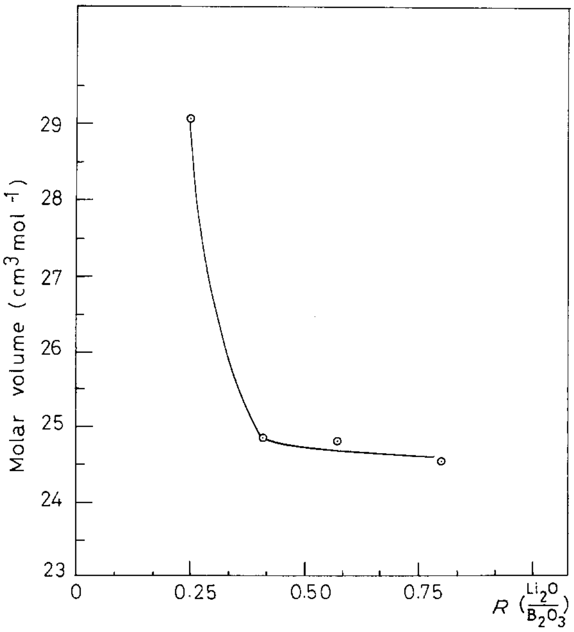

Figure 1 Dependence of molar volume for glasses 1–4 on R (Li_2O/B_2O_3).

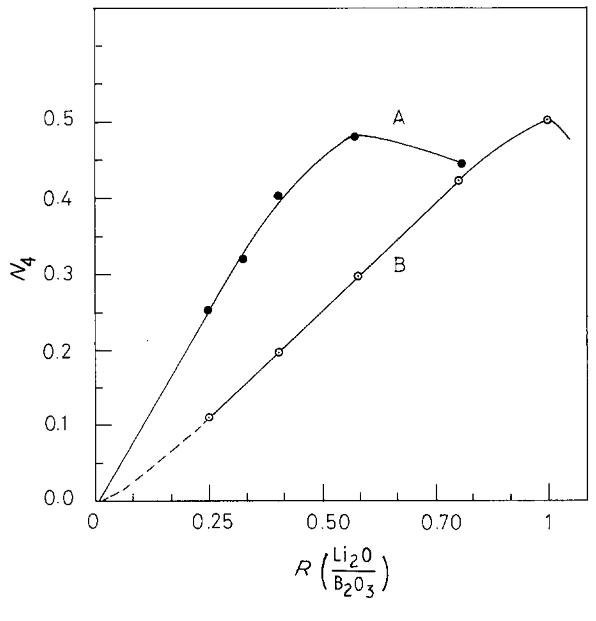

Figure 2 N_4 against R for alkali borosilicate glasses in the composition range of the glasses 1–4. (A) drawn after a model given by Araujo [4], (B) represents NMR data given by Doweidar *et al.* [6].

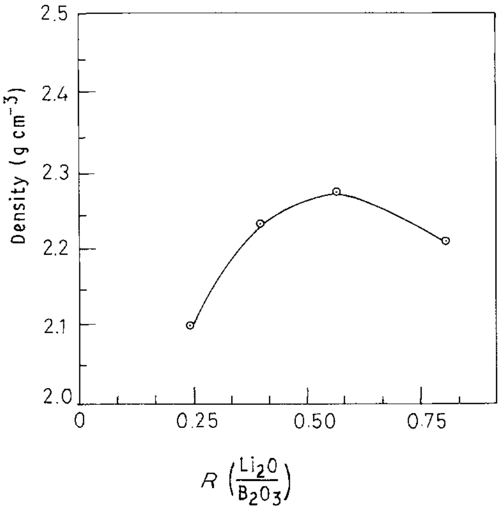

Figure 3 Dependence of density for glasses 1–4 on R.

given by Doweidar *et al.* [6], who suggested that alkali oxide associates itself with both the silicate- and the borate networks in glasses of $R > K$ and $K \leqslant 0.5$. The N_4-value difference for a specific R value results from the quantity of alkali oxide taken by the silica network. This means that the two curves A and B must lie on each other if no NBOs are formed, in the range of $R \leqslant 0.5$, in the silica network.

As $K > R$ for glass 1 it is deduced that there are no NBOs formed in this glass, whereas NBOs can exist in glasses 2–4 with $R > K$ and $K \leqslant 0.5$ [6]. The decrease of V_m between $R = 0.25$ to $R = 0.4$ can be, therefore, attributed to the strengthening and compaction [8–10] of the borate network due to the formation of BO_4^- tetrahedra, as in the case of binary Na_2O–B_2O_3 glasses. The compaction is attributed to the efficient use of the space by the tetrahedron structure of the four-coordinated borons as compared to the planar structure of three-coordinated borons (Shibata *et al.* [11]). This causes the decrease in the molar volume and at the same time an increase in the density, Fig. 3, of glasses on increasing R.

The formation of NBOs in the region $0.4 \leqslant R \leqslant 0.8$ for the studied glasses may compensate and control the decrease in the molar volume to become approximately constant, as shown in Fig. 1. However this is accompanied by a decrease of density for glasses with $R > 0.5$, Fig. 3.

On the basis of the previous discussion, it is assumed that the formation of BO_4^- units, in the studied glasses, takes place at the same time with the formation of NBOs in the silicate network for $R \geqslant 0.4$.

One can derive the composition range into two regions I ($R < 0.4$) and II ($0.4 \leqslant R \leqslant 0.8$). A third region III is expected, which starts elsewhere with $R > 0.8$, in which NBOs can form in the borate network causing a change in the V_m dependence. This leads one to assume that the mechanism

$$\equiv\text{Si–O–Si}\equiv \; + \; R_2O \rightarrow 2(\equiv\text{SI–OR}),$$

suggested by Takahashi and Osaka [7] for the formation of NBOs in the silicate network, is not effective only in regions II and III but can also be applied in region I ($R \leqslant 0.6$) for alkali borosilicate glasses with low silica content. Figure 4, represents the variation of both the molar volume and density as a function of tempering temperature. The observed change in the molar volume for the heat-treated samples is $\sim 0.74\,\text{cm}^3$. The decrease of the molar volume with increasing tempering temperature can be considered as a result of compaction produced by phase separation processes in such glasses, as can be deduced from Fig. 5. Phase separation in these glasses will be treated in a separate article. Figure 6 shows no observable changes in the molar volume with the tempering time for glasses 1–4. This is to be expected since the relative volumes of the separated phases remain the same with prolonged times of heat treatment [10, 12].

3.2. IR spectra

Figure 7 shows IR spectra of glasses 2 and 6. Absorption bands appear at 460, 700, 1000, 1400 and

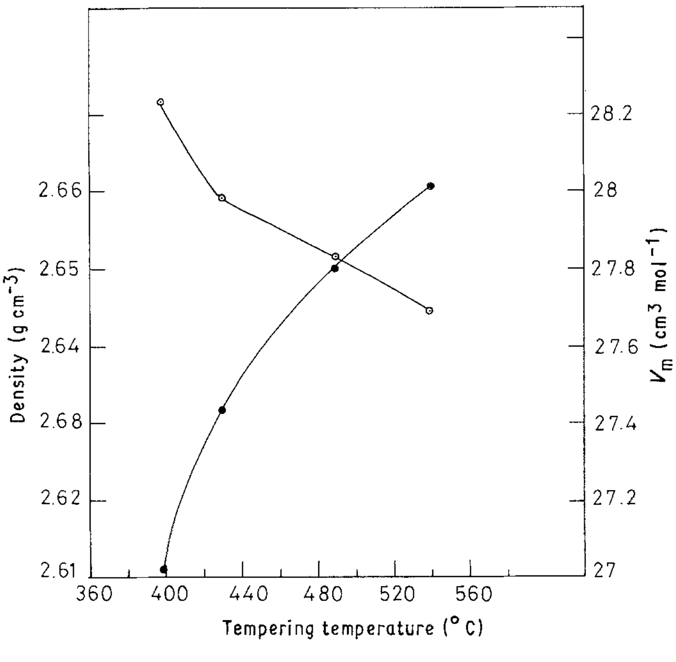

Figure 4 Molar volume and density as a function of tempering temperatures for glass 6. (The samples are heated for 5 h.)

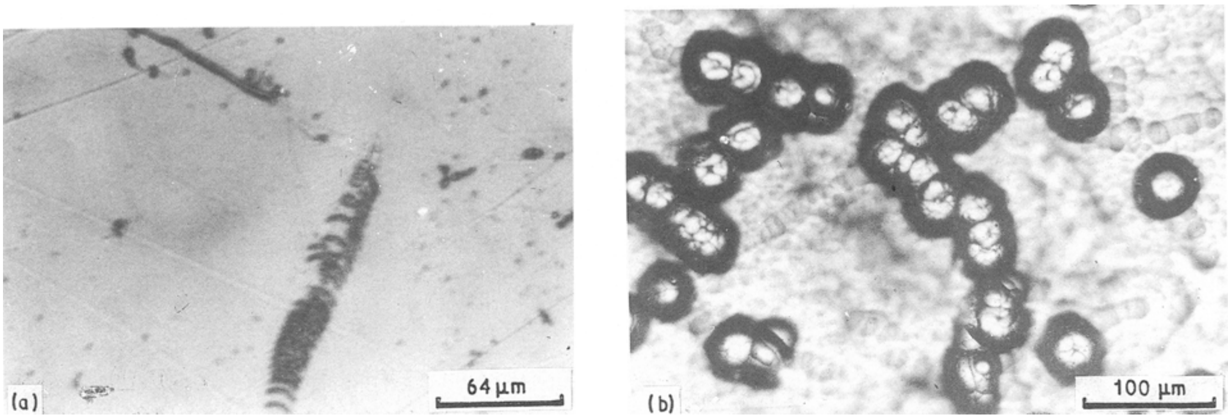

Figure 5 Etch surfaces of glass 2 after using 1 N HNO_3 acid as etching solution at room temperature for 4 min. (a) Etch surface of the non-heat treated sample, (b) etch surface of the heated sample at 490° C for 2 h.

$3500\,cm^{-1}$. A weak shoulder at $1265\,cm^{-1}$ is observed in the IR spectra of heat treated glasses (G2; 10 h, 490° C and G6; 2 h, 490° C). The IR absorption band at about $1380-1400\,cm^{-1}$ is attributed to the ring-stretching vibration of the boroxol ring [13].

The band at about $1000\,cm^{-1}$ does not appear in the IR spectra of crystalline $Li_2O \cdot 2B_2O_3$ or crystalline $Li_2O \cdot B_2O_3$ [5], but it is observed in the spectra of the glasses of the series $xLi_2O \cdot (0.85 - x)B_2O_3 \cdot 0.15SiO_2$ and $xNa_2O \cdot (0.85 - x)B_2O_3 \cdot 0.15SiO_2$. Tenny and Wong [14] attributed this band to stretching vibration of the B–O–Si linkage.

So, the band at $1000\,cm^{-1}$ is due to the formation of SiO_4 tetrahedra with nonbridging oxygen ions. The band of the IR spectra at about $460\,cm^{-1}$ could be due to a vibrational mode involving BO_4^- groups, while the band at about $700\,cm^{-1}$ is assumed to arise from a bondbending motion of the B–O–B groups within the network [14].

The weak shoulder which appears at about $1265\,cm^{-1}$ for heat treated samples of glasses 2 and 6 is attributed to the bond-stretching vibration of the B–O bond associated with B–O–B linkage in which boron atoms triangularly coordinated [5]. The band at $3500\,cm^{-1}$ is due to the O–H stretching [15, 16].

The formation of SiO_4 tetrahedra with nonbridging oxygen ions, which is related to the absorption band at $1000\,cm^{-1}$ should be reflected on the change of the molar volume as deduced before.

3.3. UV transmission

Results of UV transmission spectra of the examined glasses are summarized in Table III. Figure 8 represents spectral transmission curves of samples a, b and c for glass 1 and of samples a and b for glass 4 as example. It is observed that, the position of the UV-edge was unaltered (327 nm) for the untempered and tempered samples of glass 1. Only a little shift in UV-edge of about 3 nm is observed by heating glass 1 (sample e) at 490° C for 10 h. Similar results are obtained for the glasses 2, 4 and 5 which shown no shift in UV-edge positions (glass 2 ~ 330 nm, glass 4 ~ 330 nm and glass 5 ~ 314 nm) after heating them.

For glass 1 (low concentration of R_2O (Li_2O) = 18 mol %–3 mol % which is exhausted in the conversion of Al_2O_3 to AlO_4 to be incorporate into the glass network, i.e. with 15 mol % Li_2O), the migration of Li^+ converts BO_3 in this phase to BO_4^- tetrahedra which causes an increase in the coherence of the network [10]. The Madelung potential of the bridging oxygen ions is higher than that of NBO ions. The binding forces for the electrons in the bridging oxygen ions are therefore stronger than those in the NBOs. So, an electron belonging to a NBO needs lower energy (longer wavelength) to be excited. Verwey [17], Scholze [18] and McSwain *et al.* [19] studied the mechanism of UV absorption in glass. They found that the transmission of glass in the UV-region and the

TABLE III UV-edge for spectral samples

Glass No.	Sample	Tempering temperature (° C)	Tempering time (h)	UV-edge position (nm)
1	a	untempered	–	327
	b	400	5	327
	c	430	5	327
	d	490	2	327
	e	490	5	327
	f	490	10	327
2	a	490	10	330
4	a	490	10	330
	b	490	17	330
5	a	untempered	–	313
	b	490	10	314

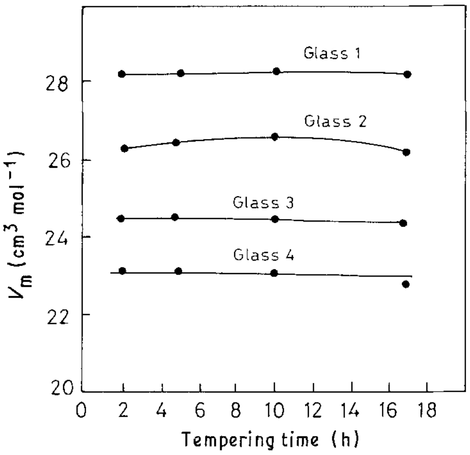

Figure 6 Molar volume against the time of heat treatment for glasses 1-4.

position of the UV-edge to be dependent on the concentration of the nonbridging oxygen ions.

Also, they deduced that the lower concentration of nonbridging oxygen ions in the network causes a higher UV transmission. Therefore, one can assume that the reason for shifting UV-edge to the lower wavelength (~ 323 nm) in sample e for glass 1 is the formation of BO_4^- units. For the untempered glasses 1 and 5, the UV-edge appears at ~ 327 and ~ 313 nm respectively nevertheless $R < 0.5$ for both glasses. Also, by heating glasses 2 (sample a) and 5 (sample b) at the same temperature and the same time the UV-edge appeared at 330 and 314 nm, respectively.

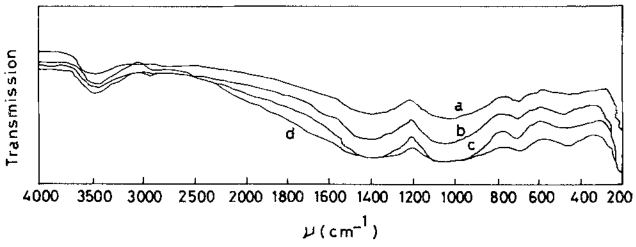

Figure 7 IR spectra of the glasses 2 and 6. (a) Untempered sample of glass 2. (b) Heated sample at 490° C for 2 h of glass 2. (c) Heated sample at 490° C for 10 h of glass 2. (d) Heated sample at 490° C for 2 h of glass 6.

This trend can be explained on the basis of what is called "mixed alkali effect". On this basis various interactions occur between dissimilar alkali ions [20].

Lim and Day [21] assumed another concept called the independent path model. They found that the mobility of alkali ion decreased whenever it was partially substituted by other cation. As a result of tempering the mobility of Li^+ ion in glass 2 is higher than in glass 5 (Li^+ + K^+).

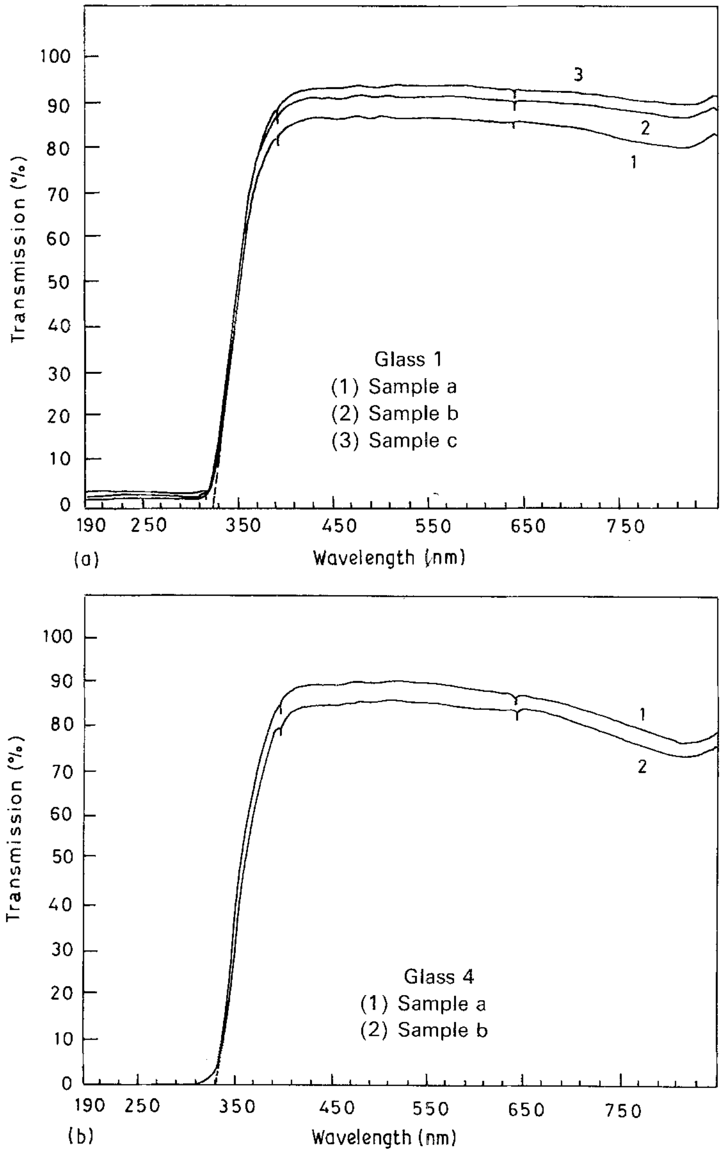

Figure 8 Spectral transmission curves of samples (a, b and c) of glass 1 and samples a and b of glass 4.

Accordingly, it seems that the strengthening and coherence of the glass network containing a single alkali ion is less than that containing a mixed alkali ions.

It is noticed from the previous discussion, the following points:

1. In borosilicate glasses with low silica content, nonbridging oxygen ions can be formed and bonded with the silicon ions during the formation of BO_4^- tetrahedra.

2. IR spectra showed a characteristic band for OH-stretching besides the coexisting of BO_3 triangles and BO_4^- tetrahedra.

3. Both of the phase separation process and the existence of single or mixed alkali affect the formation of BO_4^- tetrahedra and NBOs consequently on the coherence of the network in these glasses.

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