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STRESS BUILD-UP IN GLASS BY ULTRA-VIOLET IRRADIATION

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Severe ultra-violet irradiation can generate stresses on the surfaces of borate or borosilicate glasses. Experiments revealed that the stress is the result of contraction of the irradiated surface of the glass by the action of ultra-violet light, and that the threshold photon energy for the stress build-up is 5.5 eV (220 nm) or more. The stress can be released by heating at comparatively low temperatures far below the annealing point of the glass, and the experimental activation energy for the stress build-up is estimated to be 20–30 kcal/mol. This process of stress build-up in glass probably involves: 1) Translation of alkali-ions caused by elongation of $\rangle$B–O$^-$ bonds; 2) Rotation of BO_3 or BO_4 groups caused by twisting or change of bond angle; and 3) formation of a new B–O–B bond between two BO_3 triangles by elongation, charge transfer or photoionization of $\rangle$B–O$^-$ unit.

1. Introduction

In the course of the development of high power mercury discharge lamps in the authors' factory, stress build-up had been observed in lamp protection bulbs after long periods of lighting. In some cases, even spontaneous fracture of the bulbs took place. The authors' investigation on the phenomenon made clear that severe ultra-violet irradiation generates stress in irradiated surface layers of certain glasses[1, 2]).

Ionizing radiations, for example, X- or γ-ray, fluxes of neutrons, protons, deuterons etc. cause stress in glasses and often lead to cracking or fracture[3–7]). On the other hand, photon energy of ultra-violet light is far less than those of ionizing radiations and has been thought to be insufficient to cause substantial structural changes in inorganic glasses. Therefore, a new theory seems necessary to explain the process of the stress build-up in glass caused by ultra-violet light.

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This paper reviews the results of the authors' investigation and describes the mechanisms of stress build-up assumed and suggested by the authors.

2. Mercury lamp

Structure of a high power mercury discharge lamp[8]) is shown schematically in fig. 1. A discharge tube made of transparent fused silica glass is sealed hermetically in a protection bulb made of Pyrex-type borosilicate glass. The lamps were used in photochemical reaction vessels and were cooled by flowing water when lit. After long periods of lighting, some of the protection bulbs fractured spontaneously (fig. 2). Photoelastic observation of a cross section of the bulb showed concentrated tension at the inner surface layer (fig. 3). The density of the inner layer was 6×10^{-4} g/cm^3, larger than that of the outer layer. This indicated that ultra-violet light caused compaction (density increase) of the glass structure.

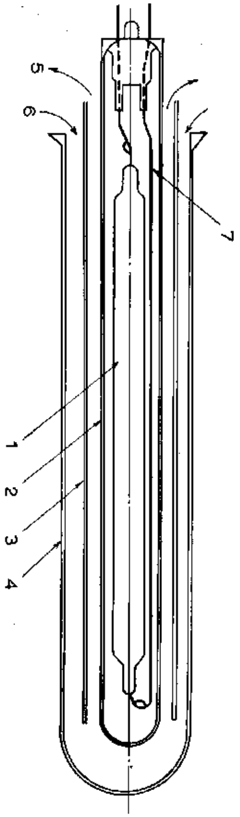


Fig. 1. Structure of high power mercury discharge lamp. (1) Discharge lamp made of transparent fused silica glass. (2) Protection bulb made of Pyrex type borosilicate glass. (3) Middle tube for water cooling (borosilicate glass). (4) Outer bulb for water cooling (borosilicate glass). (5) Water in. (6) Water out. (7) Lead wire.

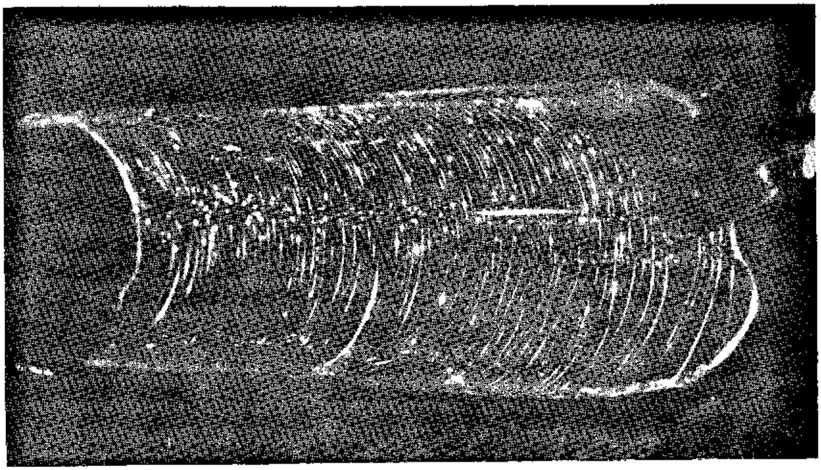


Fig. 2. A fragment of a fractured protection bulb of a high power mercury discharge lamp.

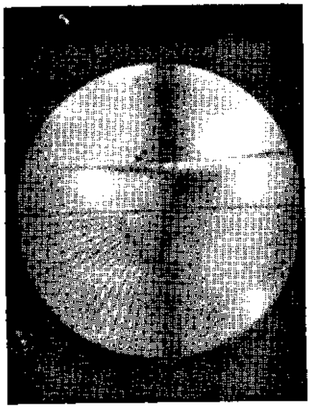


Fig. 3. Photoelastic observation of a cross section of the damaged Pyrex type borosilicate glass.

3. Thermal release experiments

On heating[9]) at a rate of 5 °C/min, the stress at the inner surface began to release at about 250 °C and completely disappeared at 470 °C, as shown in fig. 4. On soaking at various constant temperatures, distinct stress release was observed even at 250 °C. At 400 °C, the stress disappeared in a short time (fig. 5). These temperatures were far below the annealing point of the glass, i.e. 545 °C, at which permanent stress in the glass is released by viscous flow. Successive soaking runs (fig. 6) classified stresses which were released at low and high temperatures, respectively.

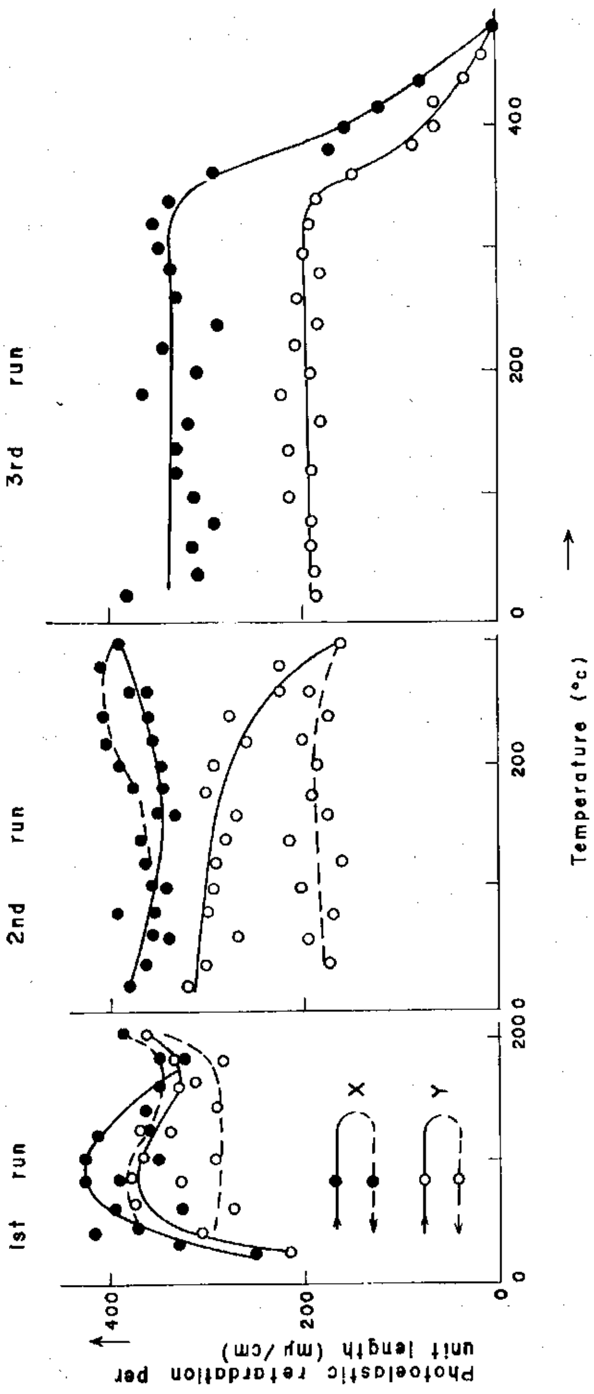


Fig. 4. Stress release at the inner surface of the protection bulb on heating. (X) Stress at irradiated inner surface of the bulb. (Y) Stress at outer surface which was caused by the inner stress.

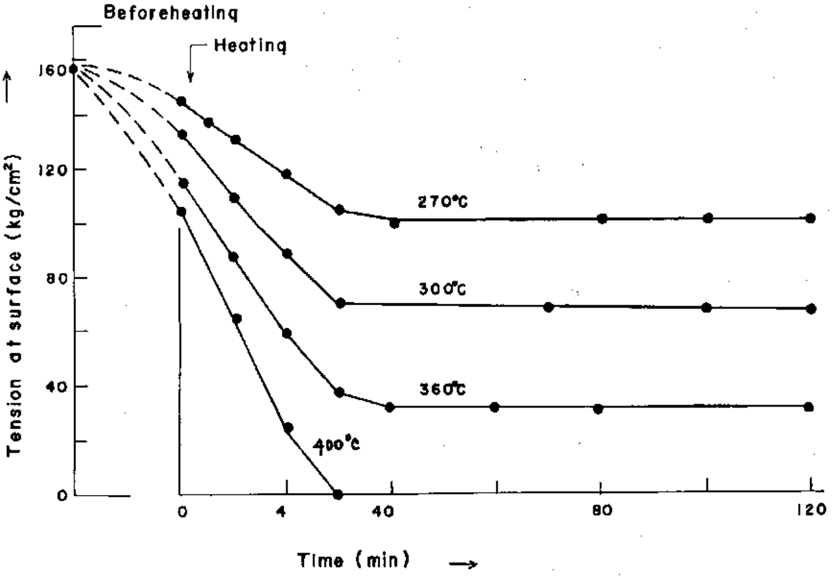


Fig. 5. Stress release at the irradiated inner surface on soaking at various constant temperatures.

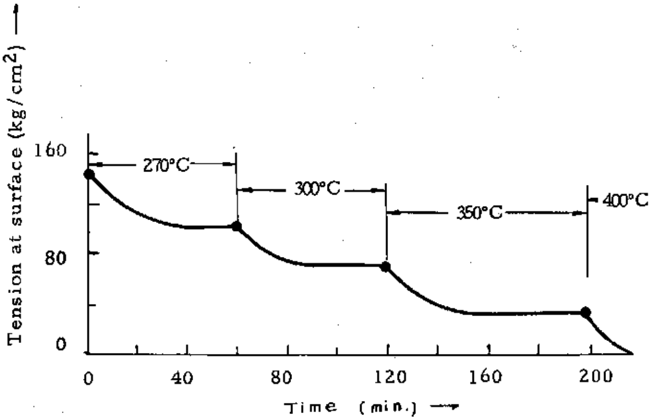


Fig. 6. Stress release by successive soaking runs at various temperatures.

The results indicated that there must be several kinds of mechanisms of stress release and that the experimental activation energy of stress release is less than 30 kcal/mol (1.3 eV), which is far less than that of viscous flow (about 100 kcal/mol, 4.3 eV). The value of 1.3 eV is also less than the energy of ultra-violet light (3 eV or more).

The behaviour of some electronic centers at the time of heating, i.e. thermal glow, thermally released current, and thermal bleaching of optical ab-

TABLE 1

Chemical compositions of commercial glasses

Glass No.		SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	Li_2O	PbO	BaO	CaO	MgO	ZnO	As_2O_3	
1	Silica glass (transparent)	100												
2	Borosilicate glass	80.6	12.3	2.5	4.5								0.1	
3	Borosilicate glass with Li_2O	80.6	12.5	2.4	3.9		0.5						0.1	
4	Borosilicate glass	78.3	14.8	1.5	5.3								0.15	
5	Lead borosilicate glass	71.2	16.8	2.0	4.5			6.0					0.2	
6	Barium borosilicate glass	65.4	18.0	7.5	1.9	3.0	1.0		3.0				0.15	
7	Barium borosilicate glass	63.0	19.4	7.0	1.5	4.0	0.8		1.0					
8	Borosilicate glass with ZnO	72.4	15.5	2.2	7.6							2.3		
9	Borosilicate glass with Ce_2O_3	68.5	15.5	2.3	3.4		0.2	10.0						Ce_2O_3 0.5
10	30 % lead glass	56.5		1.4	4.5	7.6		29.5					0.2	
11	Barium glass	67.6		4.5	7.0	6.8	0.5		13.0				0.2	Sb_2O_3 0.5
12	Soda lime glass	67.6		2.0	18.4					7.3	4.2		0.3	
13	Commercial plate glass	72.0		2.0	13.5					8.0	4.0		0.2	

sorption, was investigated for fractured protection bulbs. Direct relationships, however, were not found between this thermal behaviour and the thermal release of the stress. The existence of electronic centers did not seem to correspond to the existence of the stress, although the generation of the stress might accompany electronic processes such as photo-excitation and photo-ionization caused by ultra-violet light.

4. Stress build-up in various kinds of glasses

To determine[10–12]) the kinds of glasses in which stress is built up by ultra-violet light, commercial glasses shown in table 1 were irradiated by a 400 W mercury lamp for 1000 hr. The lamp was made of transparent fused silica. Stresses at the irradiated surfaces and thickness of the stressed layers are given in table 2. Stresses were built up only in some borosilicate glasses. In borosilicate glasses containing zinc or lead oxides, the stresses were weak or not detected. In fused silica glass, soda-lime, lead and barium glasses, no stress was detected.

Next, the effects of ultra-violet light on binary borate glasses (cf. table 3) were examined. After 1000 hr irradiation, stresses were found only in alkali borate glasses.

In addition, ternary alkali borosilicate glasses were examined. The ratios b_4/b [(number of four coordinated boron ions)/(number of total boron ions)]

TABLE 2

Stress at surfaces and thickness of stressed layers measured after 500 and 1000 hr irradiation

Glass No.	Tension at surface (kg/cm^2)		Thickness (mm)
	500 hr	1000 hr	
1	*	*	
2	36	69	0.15
3	25	42	0.15
4	25	53	0.20
5	*	*	–
6	47	74	0.15
7	47	72	0.15
8	*	10**	–
9	*	*	
10	*	*	–
11	*	*	–
12	*	*	–
13	*	*	–

* Not recognized

** 20 kg/cm^2 after 2000 hr irradiation.

TABLE 3

Composition of binary borate glasses

Glass No.	Oxides	mole %	Glass No.	Oxides	mole %
1	Na_2O	12	11	PbO	30
2	Na_2O	30	12	PbO	50
3	K_2O	12	13	PbO	70
4	K_2O	30	14	Bi_2O_3	25
5	Li_2O	12	16	Sb_2O_3	25
6	CaO	35	17	Ti_2O	30
7	SrO	35	18	ZnO	34
8	BaO	30			
9	CaO	50			
10	La_2O_3	25			

TABLE 4

Chemical compositions of test glasses and rations b_4/b [(numbers of four coordinated boron ions)/(numbers of total boron ions in the glasses)]

Glass No.	SiO_2 (mole %)	B_2O_3 (mole %)	Na_2O (mole %)	b_4/b
21	65.0	22.5	12.5	0.30
22	70.0	17.5	12.5	0.36
23	60.0	30.0	10.0	0.42
24	70.0	20.0	10.0	0.47
25	60.0	32.5	7.5	0.30
26	70.0	25.0	5.0	0.25
27	80.0	15.0	5.0	0.34
28	70.0	27.5	2.5	0.08
29	75.0	22.5	2.5	0.16

determined by nuclear magnetic resonance and the compositions of the glasses are given in table 4. Stress measurement after 1000 hr irradiation showed that the stress decreases with increase of b_4/b until the decrement slows down near the value of 0.4 of b_4/b, as shown in fig. 7.

These results indicate that the stress is built up in glasses containing both alkali and boron oxides, and that the composition of the glasses strongly affects the value of the stress.

Effects of ultra-violet light on many kinds of glasses, including silicate, phosphate, germanate and tellurite glasses, were examined. At the present stage of the authors' investigation, stress build-up was found only in alkali-aluminogermanate glasses. These findings strongly suggest that the stress build-up would be closely related to coordination change of boron and germanium ions in glasses.

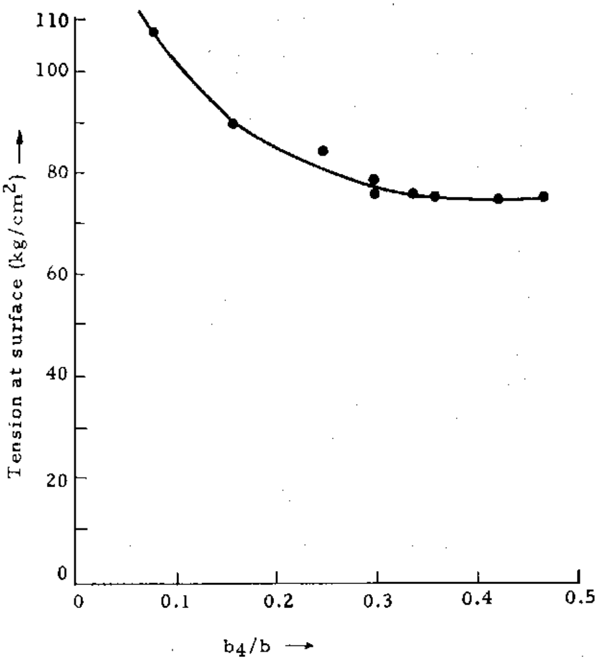


Fig. 7. Relation between the stress and b_4/b [(number of four coordinated boron ions)/(number of total boron ions)] of test glasses.

5. Effects of small additives in glasses

Effects of small additives in an alkali borate glass, Na_2O 20 mole% and B_2O_3 80 mole%, on the stress value generated by ultra-violet light were investigated[13,14]. Kinds and concentrations of the additives and the stress values determined after 1000 hr of ultra-violet irradiation are given in table 5. The results are shown graphically in the form of the periodic chart in fig. 8. Small amounts of alkali and alkaline earth oxides do not suppress the stress. Ions in b-groups having high negativity or high atomic number suppress the stress. Some of the transition, rare earth and actinide ions enhance the stress when the concentrations are considerably small, while they suppress the stress when the concentrations are larger.

Small amounts of the additives in glasses seem to play various roles, that is, as sensitizers which convert the photon energy of ultra-violet light into activation energy for stress build-up, as internal filters which dissipate photon energy, or as fillers by which the glass networks are compacted.

No.	Additives	Materials for additives	Concentration (mole %)	Stress (kg/cm²)	No.	Additives	Materials for additives	Concentration (mole %)	Stress (kg/cm²)
3	Li_2O	Li_2CO_3	3	35	40	ZrO_2	ZrO_2	3	*
4	BeO	BeO	3	49	41	Nb_2O_5	Nb_2O_5	3	*
5	B_2O_3	HBO_3	3	50	42	MoO_3	MoO_3	0.1	*
9	NaF	NaF	3	*	47	Ag_2O	Ag_2O	0.1	+
11	Na_2O	Na_2CO_3	3	64	48	CdO	CdO	3	46
12	MgO	$MgCO_3$	3	52	49	In_2O_3	In_2O_3	3	*
13	Al_2O_3	$Al(OH)$	3	45	50	SnO_2	SnO_2	3	*
14	SiO_2		3	50	51	Sb_2O_5	Sb_2O_5	3	*
15	P_2O_5	P_2O_5	3	*	52	TeO_2	TeO_2	3	*
16	Na_2S	Na_2S	3	*	53	NaI	NaI	3	*
17	$NaCl$	$NaCl$	3	*	55	Cs_2O	Cs_2CO_3	3	100
19	K_2O	K_2CO_3	3	59	56	BaO	$BaCO_3$	3	49
20	CaO	$CaCO_3$	3	30	57	La_2O_3	La_2O_3	3	*
22	TiO_2	TiO_2	3	*	58-1	CeO_2	CeO_2	0.1	230
23	V_2O_5	V_2O_5	0.1	*	58-2	CeO_2	CeO_2	3	*
24	Cr_2O_3	Cr_2O_3	0.1	§	60	Nd_2O_3	Nd_2O_3	0.1	*
25	MnO_2	MnO_2	0.1	§	63	Eu_2O_3	Eu_2O_3	0.1	80
26	Fe_2O_3	Fe_2O_3	0.1	70	73	Ta_2O_5	Ta_2O_5	3	*
27	CoO	CoO	0.1	150	74	WO_3	WO_3	0.1	36§
28	NiO	NiO	0.1	§	81	Tl_2O	Tl_2O	3	*
29	CuO	CuO	0.1	210	82-1	PbO	PbO	0.1	210
30	ZnO	ZnO	3	72	82-2	PbO	PbO	0.5	40
31	Ga_2O_3	Ga_2O_3	3	52	82-3	PbO	PbO	3	*
32	GeO_2	GeO_2	3	177	83	Bi_2O_3	Bi_2O_3	3	*
33	As_2O_5	As_2O_5	3	*	90	ThO_2	ThO_2	0.1	*
34	SeO_2	Na_2SeO_3	1	*	92-1	UO_2	Na_2UO_7	0.1	160
35	$NaBr$	$NaBr$	3	*	92-2	UO_2	Na_2UO_7	3	*
37	Rb_2O	Rb_2CO_3	3	79	I	Na_2SO_4	Na_2SO_4	3	*
38	SrO	$SrCO_3$	3	65	II	$NaNO_3$	$NaNO_3$	3	*
39-1	Y_2O_3	Y_2O_3	0.1	40	III	CH_3COONa	CH_3COONa	3	*
39-2	Y_2O_3	Y_2O_3	1	*					

* Stress was slight or not defected + Devitrified during irradiation § Stress was not clearly detected

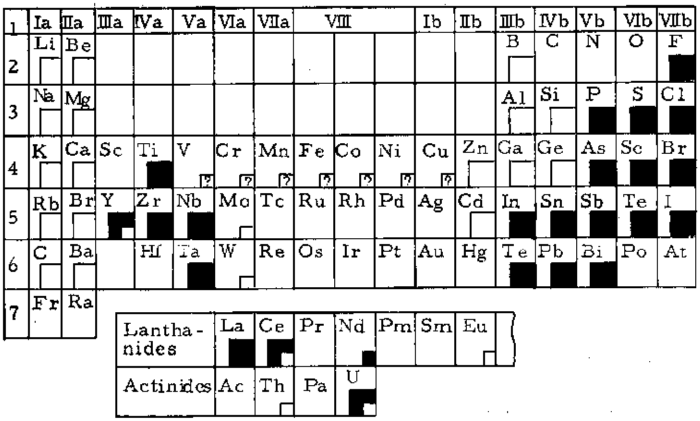


Fig. 8. Classification of the effects of small additives in borate glass on the stress build-up by ultra-violet irradiation. Big white square: Stress was observed in 3 mol % addition. Small white square: Stress was observed in 0.1 mol % addition. Big black square: Stress was not detected in 3 mol % addition. Small black square: Stress was not detected in 0.1 mol % addition.

6. Effects of atmosphere during glass melting

Alkali borate and alkali borosilicate glasses were melted using boric oxide, sodium carbonate and powder of rock crystal as raw materials. Atmosphere during melting was adjusted by bubbling O_2, N_2 or H_2 gases or by adding $NaNO_3$ or NH_4BO_7 to the batches. The glasses were subjected to 1000 hr of ultra-violet irradiation. The results are given in tables 6a and 6b. The stress values are larger in the glasses melted under oxidizing condition (O_2 gas

TABLE 6a

Effects of melting atmosphere on the stress caused by ultra-violet irradiation

Glass compositions (mole %)	Melting conditions (gas bubbling)	Stress at surface (kg/cm²)
$10\,Na_2O \cdot 90\,B_2O_3$	O_2	70
	N_2	60
	H_2	*
$20\,Na_2O \cdot 80\,B_2O_3$	O2	35
	N_2	30
	H_2	*
$27\,Na_2O \cdot 73\,B_2O_3$	O_2	20
	N_2	20
	H_2	*
$35\,Na_2O \cdot 65\,B_2O_3$	O_2	*
	N_2	*
	H_2	*

* The stress was not detected.

TABLE 6b

Effects of melting atmosphere on the stress by ultra-violet irradiation in borosilicate glass

Glass composition (mole %)	Melting condition	Stress (kg/cm²)
10 $Na_2O \cdot 15\ SiO_2 \cdot 75\ B_2O_3$	Ordinary atmospheric condition	80
	O_2 bubbling	126
	$NaNO_3$ addition	70
	N_2 bubbling	78
	Ar bubbling	77
	NH_4BO_7 addition	69
	H_2 bubbling	30

bubbling or $NaNO_3$ addition) and are smaller or nonexistent in the glasses melted under reducing condition (H_2 gas bubbling or NH_4BO_7 addition).

7. Kinetics of stress build-up including wavelength and light flux intensity dependence

Time–stress curves of a commercial borosilicate glass during ultra-violet irradiation[15,16]) are shown in fig. 9. In this figure, l represents the distance

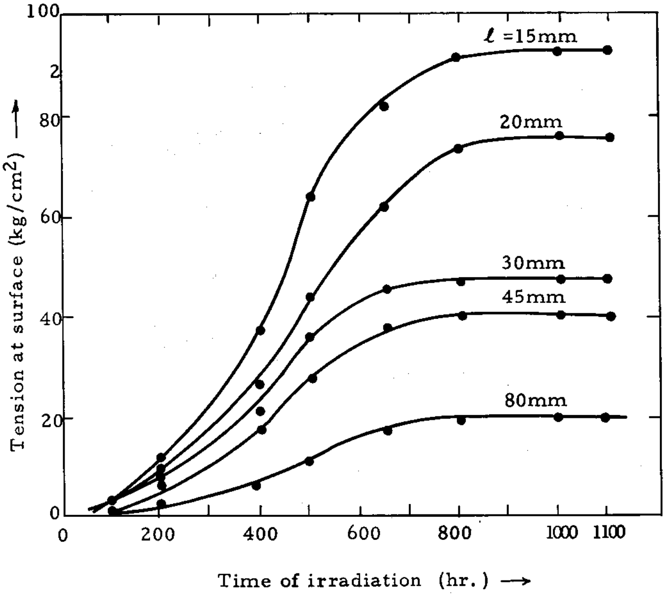


Fig. 9. Relation between the stress and time of ultra-violet irradiation, i.e. the time–stress curves of Pyrex type borosilicate glass. l=distance between the axis of the tubular mercury lamp and the sample surface.

between the axis of a tubular mercury lamp and the irradiated surfaces of the glass samples. On the curves, the induction periods are found at the initial stage of irradiation, and then the stresses increase approximately linearly with time until the stresses reach saturation points after about 800 hr. The stress value is inversely proportional to l. Assuming that the light source is linear in shape, and that the propagation of light flux from the source is reduced to a two-dimensional problem in a cross section perpendicular to the axis of the source, the light flux which passes outward per unit time through a unit area of the irradiated surfaces of the glasses is inversely proportional to l. So, the stress value is proportional to the intensity of ultraviolet light.

The kinetics were simulated using a reaction model shown in fig. 10. In this figure, N represents the sites at which atomic rearrangement takes place

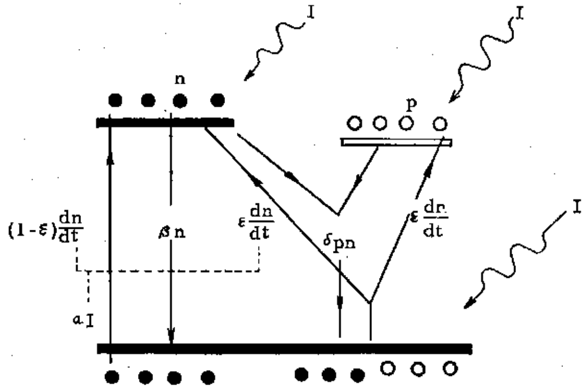


Fig. 10. A reaction model of the stress build-up in glass by ultraviolet irradiation. (●) N; (○) P.

by the action of ultra-violet light. The rearrangement at the N sites is partly prestored by atomic rearrangement at the neighboring sites P. N and P increase in number under the action of ultra-violet light and decrease by backward reaction and recombination. The following equations represent the rates of change in number of the N and P sites

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \alpha I - \beta_{\mathrm{n}} - \delta_{\mathrm{pn}}, \qquad \frac{\mathrm{d}p}{\mathrm{d}t} = \varepsilon\frac{\mathrm{d}n}{\mathrm{d}t} - \delta_{\mathrm{pn}}.$$

Here, t is the time, n and p are the numbers of N and P sites, respectively, I is the light intensity and α, β, δ and ε are constants.

The stress is assumed to be in linear relation with $(n-\nu p)$, where ν is constant. The constants were determined by a trial and error method using an electronic computer, and the curves in fig. 11 were obtained. These are good reproductions of the experimental curves shown in fig. 9.

Wavelength dependence of the stress was studied by inserting short cut glass filters between the light source and glass samples. Fig. 12 shows the transmission curves of the filters. The stresses observed after 1000 hr irradiation were plotted tentatively against the transmission of the filters at 220 nm (fig. 13). The results that the stress build-up is suppressed by inserting the No. 6 filter which absorbs light of 220 nm or less wavelength and that the stress values are approximately proportional to the transmissions of the filters at 220 nm indicate that threshold photon energy for structural change of glass is 5.5 eV (which corresponds to 220 nm) or more. Owing to experimental difficulties, however, examinations using monochromic ultra-violet light has not been carried out.

8. Effects of prior irradiation by ionizing ray

A commercial borosilicate glass was irradiated by Co^{60} γ-ray or in a nuclear reactor. The kinetics of stress build-up ultra-violet light are shown in figs. 14 and 15, respectively. The kinetics of γ-irradiated glasses resemble those of unirradiated glasses, except for the longer induction period of about 200 hr. This might correspond to the period in which optical bleaching of color centers takes place. On the other hand, the kinetics of neutron irradiated glasses differ from those of unirradiated glasses. The stress is built up in two steps, and there is no induction period. Experiments on the thermal release of the stress suggest the existence of two kinds of stresses (fig. 16). One is built up in the early stage of ultra-violet irradiation and is released at relatively low temperatures. The other is built up and thermally released in a manner similar to that of unirradiated glasses. The effect of neutron irradiation is distinct even at a very low dose. Usually radiation damage of solid substances occurs only at very high doses, for example, 10^{16} neutrons/cm^2.

9. Effects of prior heat treatment

Two kinds of experimental soda borosilicate glasses were heat-treated according to the conditions shown in table 7. The density of the samples was determined by the sink-float method, using well annealed samples as references. They were then subjected to ultra-violet irradiation for 1000 hr. The results of stress measurements are plotted in fig. 17.

The relations shown in fig. 17 are not simple. Heat-treatment at high

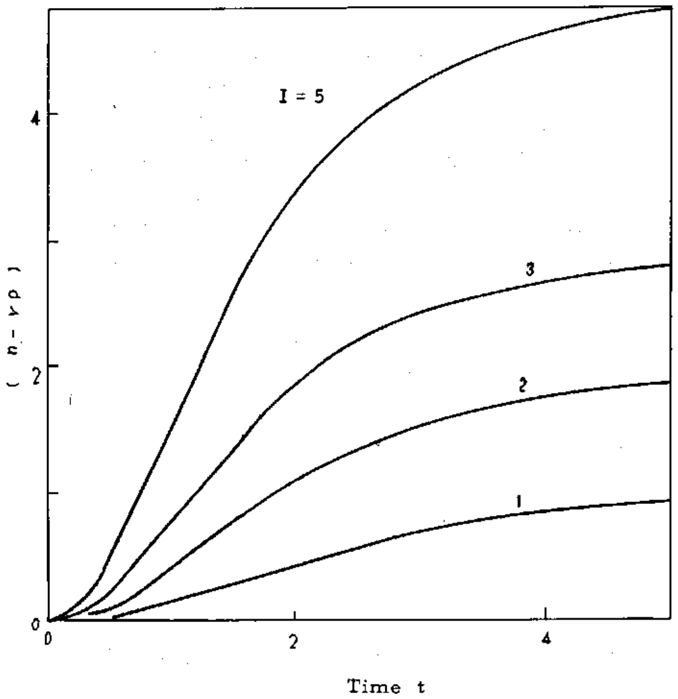


Fig. 11. Time–stress relations computed from the formula, assuming the reaction model shown in fig. 10.

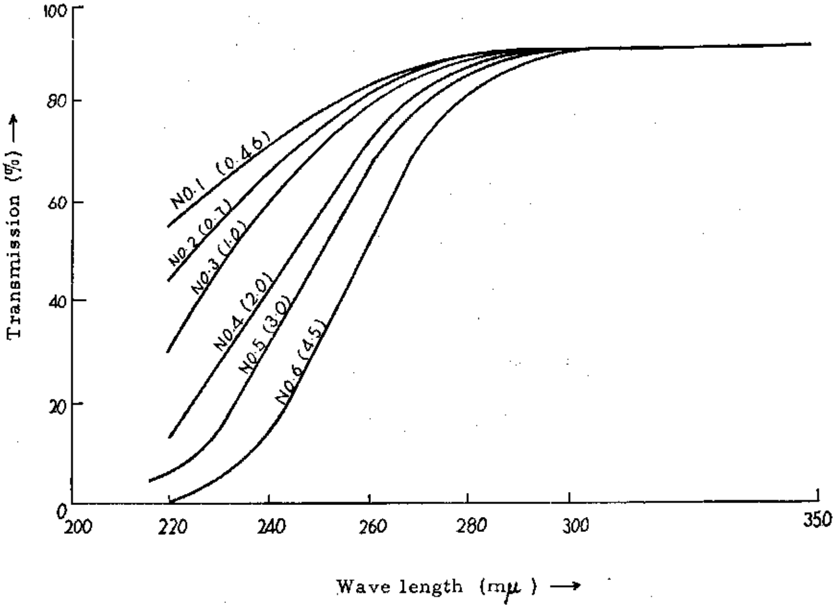


Fig. 12. Spectral light transmission of the filters used for the study of wave-length dependence of the stress. Numerals in parentheses show the thickness in mm of the filters.

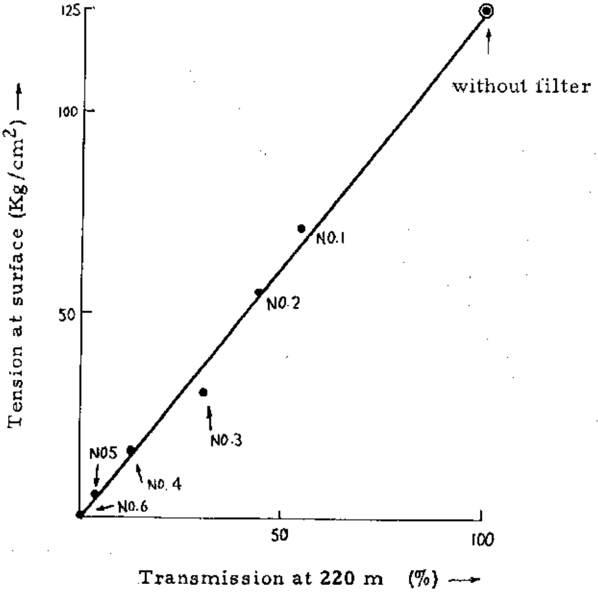


Fig. 13. Relation between the stress and the transmissions at 220 nm of the filters.

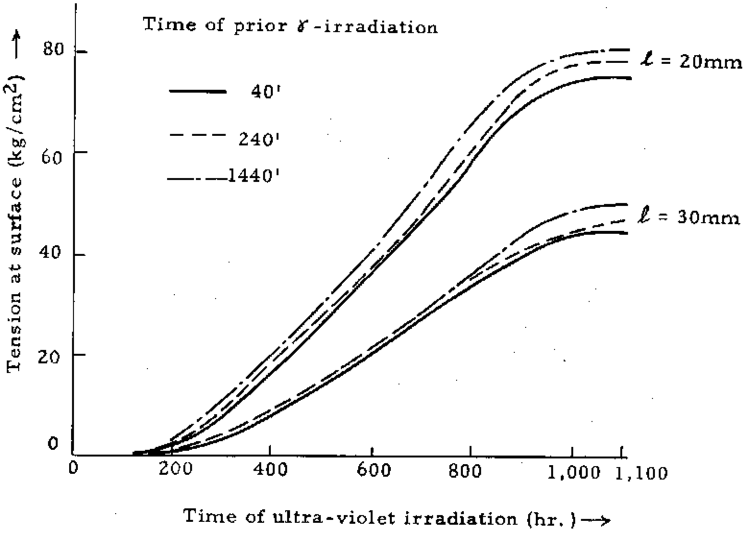


Fig. 14. Time–stress curves of γ-irradiated glasses. l represents the distance between the axis of the tubular mercury lamp and the sample surface.

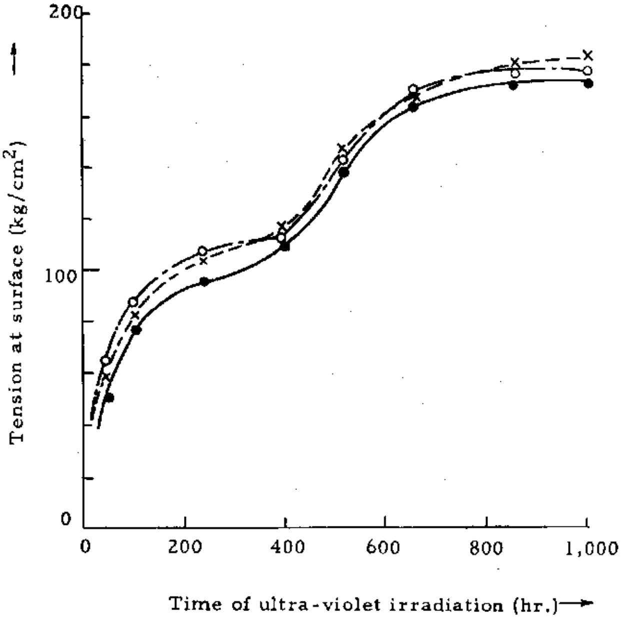


Fig. 15. Time–stress curves of neutron irradiated glasses. (–●–●–) time of neutron irradiation 10 sec; (--×--×-) 90 sec; (–·–○–·–○-) 10800 sec.

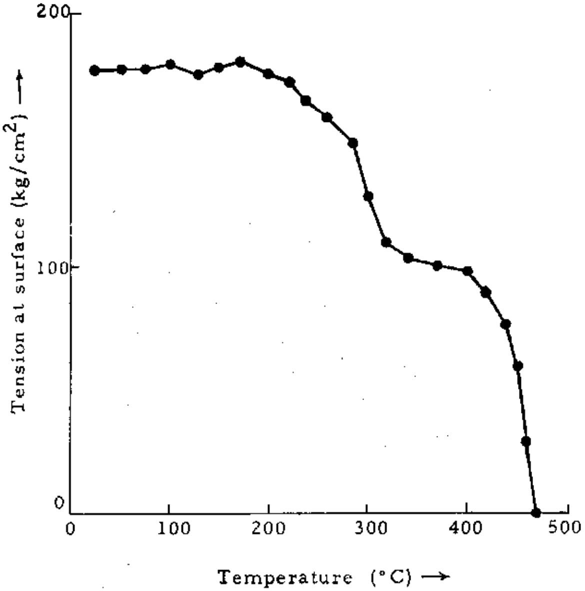


Fig. 16. Thermal release of the stress in glass, priorly neutron irradiated for 1800 sec and then ultra-violet irradiated for 1000 hr.

TABLE 7

Results of measurements of density change and stress caused by ultra-violet irradiation after respective thermal treatment in No.1

(65 $SiO_2 \cdot 22.5 B_2O_3 \cdot 12.5 Na_2O$) and No. 5 (60 $SiO_2 \cdot 32.5 B_2O_3 \cdot 7.5 Na_2O$) glasses

No.	Temperature of heat treatment (°C)	Soaking time (min) (quenching or annealling)	No. 1 Glass		No. 5. Glass	
			Density change to the reference sample (10^{-3}g/cm^3)	Stress by UV irradiation (kg/cm^2)	Density change to the reference sample (10^{-3}g/cm^3)	Stress by UV irradiation (kg/cm^2)
Reference	–	–	0	76	0	79
Sample						
1	450	30 (Q)	+0.6	59	+4.2	40
2	450	60 (Q)	+1.0	56	+4.2	51
3	450	240 (Q)	+1.5	39	+4.0	42
4	450	500 (Q)	+3.0	58	+1.0	31
5	450	30 (A)	+0.6	32	+4.5	13
6	450	60 (A)	+1.0	46	+6.0	17
7	450	120 (A)	+1.0	31	+5.5	15
8	450	500 (A)	+3.5	29	+5.5	18
9	500	30 (Q)	+0.5	31	−4.0	115
10	500	60 (Q)	+2.2	42	−2.2	112
11	500	120 (Q)	+4.5	41	−3.1	120
12	500	500 (Q)	+6.2	52	−2.9	123
13	500	30 (A)	+1.1	52	+2.0	98
14	500	60 (A)	+3.2	48	+2.8	118
15	500	120 (A)	+4.0	57	0	116
16	500	500 (A)	+6.2	60	−0.7	107
17	550	30 (Q)	+0.7	44	+0.5	39
18	550	60 (Q)	+3.5	59	+0.5	38
19	550	180 (Q)	+4.5	61	+0.5	38
20	550	500 (Q)	+3.5	70	−1.2	58
21	550	30 (A)	+4.0	57	+1.8	33
22	550	60 (A)	+5.0	60	+1.2	37
23	550	180 (A)	+4.8	58	+1.2	45
24	550	500 (A)	+4.8	62	+0.9	47
25	600	15 (Q)	−6.0	128	+1.0	170
26	600	30 (Q)	−6.0	154	+0.8	150
27	600	60 (Q)	−6.1	110	0	180
28	600	450 (Q)	−4.8	107	−2.1	160
29	600	15 (A)	+1.5	38	+2.2	99
30	600	30 (A)	+0.2	49	+1.0	118
31	600	60 (A)	+1.2	49	0	91
32	600	450 (A)	+0.7	49	−1.4	111

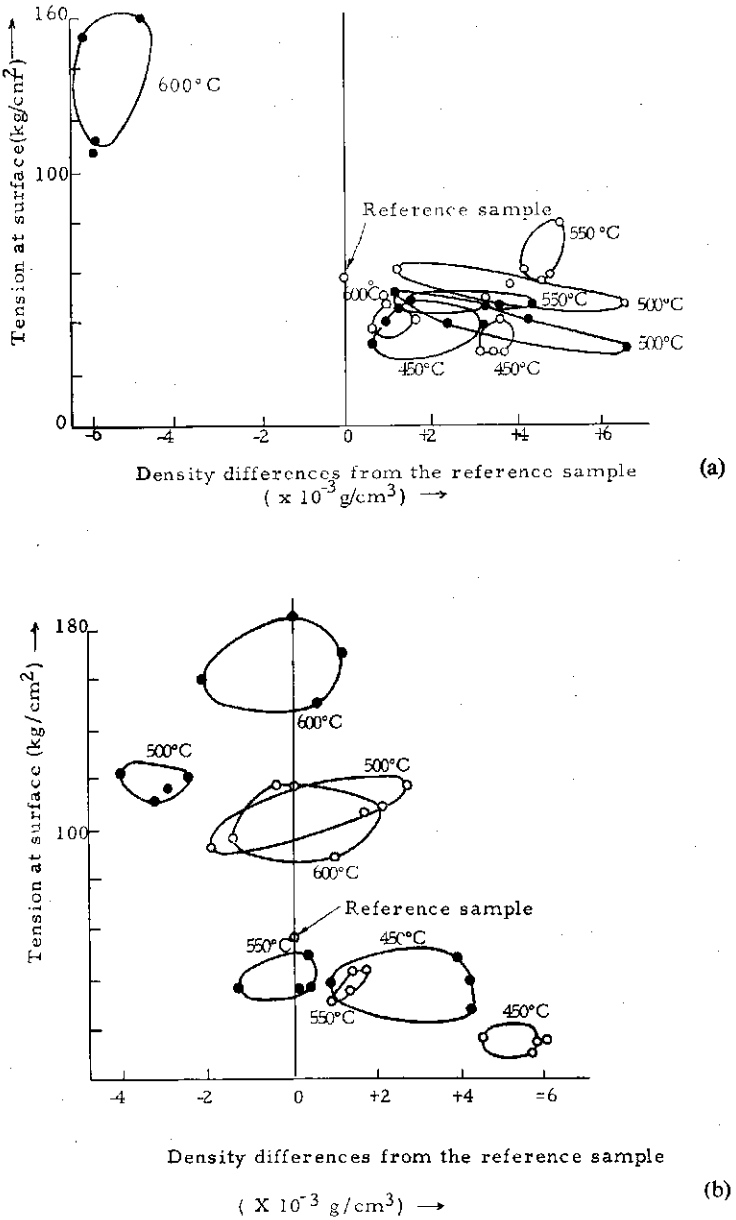


Fig. 17. (a) Relations between stresses and densities of No. 1 glass samples heat treated as shown in table 8. (b) Relations between stresses and densities of No. 5 glass samples heat treated as shown in table 8. (●) Samples cooled rapidly after soaking at constant temperatures shown in figure. (○) Samples cooled slowly after soaking at constant temperatures.

temperatures and rapid cooling from high temperatures, however, seem to enhance the stress build-up. This might be due to loose and unstable structure of rapidly cooled glasses, and structural change caused by ultra-violet light might accompany stabilization (compaction) of the glass network.

10. Mechanisms of stress build-up in glass caused by ultra-violet light

The mechanisms of stress build-up in glass were suggested by the authors[18]), referring to the experimental results described above and the peculiarities of chemical bonds in the network of borate glasses.

Primary processes of the stress build-up are thought to be photo-excitation and photo-ionization in the network, as in the case of ordinary photochemical reactions. The photon energy of ultra-violet light used in this study is comparable to the bond energy of the B–O$^-$ bond and is sufficient to ionize non-bridging oxygen ions. Non-bridging oxygen ions in borate glass are responsible for the absorption of ultra-violet light and are ionized by ultra-violet light.

The network of alkali borate glass consists of BO_3 triangles and BO_4 tetrahedrons. Chemical bonds in the network have the following peculiarities. Three coordinated boron ions have sp^2 hybrid σ-orbitals and a vacant p-orbital. The latter forms additional bonds with neighbouring oxygen ions (fig. 18), which are π-bonds in character. The double bond character is especially distinct in the bonds between boron and non-bridging oxygen ions and B–O$^-$ units have resonance structure between $\rangle$B–O$^-$ and $-\!\!\rangle$B$^-$–O–. The structure allows the bonds to twist, elongate or form new bonds under the effect of photo-excitation and photo-ionization by ultra-violet light, causing changes in the coordination numbers of the ions and the network structure of the glass.

Possible mechanisms of structural change of glass brought about by ultra-violet light are as follows:

1) Change of bond angle and bond length in excited B–O–B or B–O$^-$ groups. Electrons belonging to π-orbitals in the network are excited to anti-bonding π^*-bonds by ultra-violet light. Changes of bond angle and bond distance and twisting of the bonds take place, causing structural change of the network. Alkali ions near the bonds are expelled into nearby vacant spaces and, by closing the vacant spaces left behind expelled alkali ions, the network contracts. The compacted and rather unstable structure of the network is stabilized by the migration and trapping of the expelled alkali ions.

2) Formation of new bonds caused by excitation of non-bridging oxygen ions. By excitation of a B–O$^-$ unit (in other words, by the transition of an

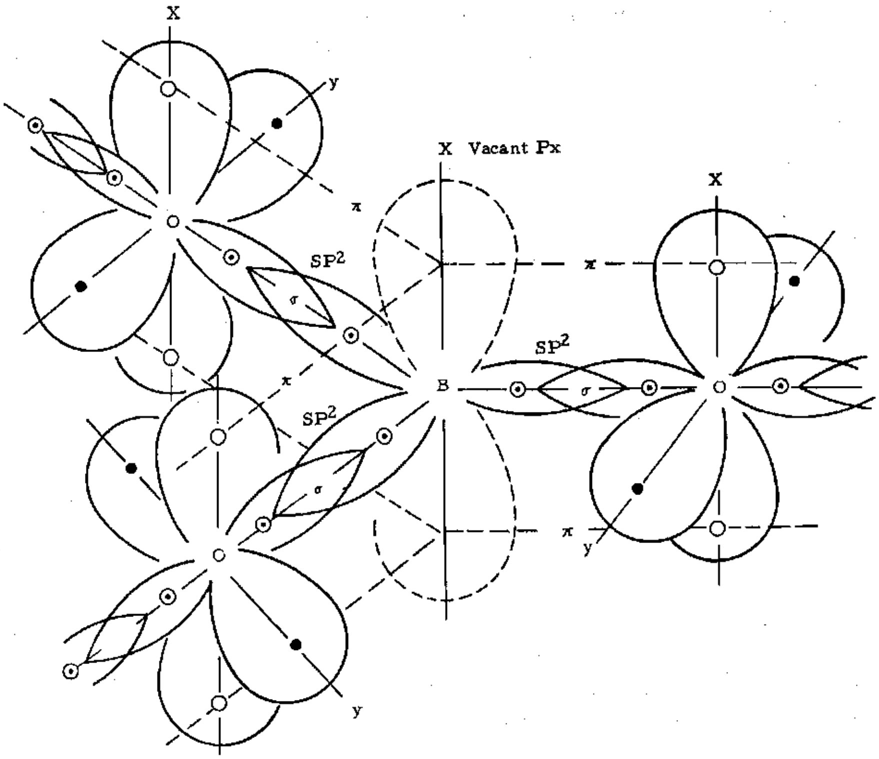


Fig. 18. Electronic configuration of BO_3 structural unit in borate glass. ⊙, ○ and ● represent σ, π and non-bonding electrons, respectively.

electron in the unit from bonding π- to antibonding π^*-orbital), the interatomic distance between the boron and oxygen ions becomes longer. A lone pair of the oxygen ion superposes on a vacant p-orbital of a neighbouring boron ion, forming a new O–B bond and a BO_4 group. This results in compaction of the network (fig. 19).

3) Formation of a new bond caused by charge transfer in a $B–O^-$ unit. By excitation or by internal photoelectric effect in a $B–O^-$ unit caused by ultraviolet light, an electron of the non-bridging oxygen ion is transfered to the boron ion (fig. 20). New additional valences are formed in both the boron and oxygen ions, and a new bond is formed between the oxygen and neighbouring boron ion, converting a neighbouring BO_3 group into a BO_4 group. The glass network is thus compacted.

4) Formation of new bond caused by photo-ionization of non-bridging oxygen ion. An electron of a non-bridging oxygen ion in a $B–O^-$ unit is ejected by ultra-violet light and is captured in a vacant p-orbital of a boron

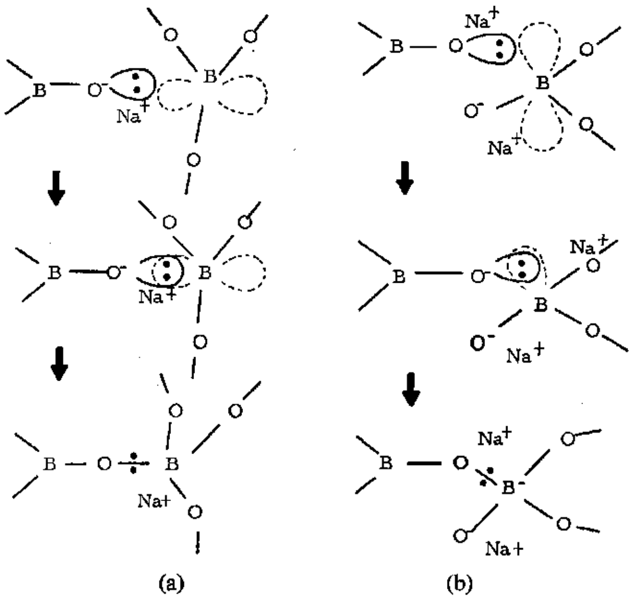


Fig. 19. Structural change of glass network caused by formation of new bond by photo-excitation and elongation of $>$B–O$^-$ bond. (----) vacant p orbital of B. (———) non-bonding lone pair of B. (●) electron. (-·-·-) orbital containing unpaired electron.

ion in a neighbouring BO_3 group. New valences are formed, both in the oxygen and boron ions, and they are bonded together. The BO_3 group is converted into a BO_4 group, causing compaction of the network (fig. 21).

All these processes are based on excitation and ionization of ions or bonds in glass and are compatible with the structure sensitive character of the stress build-up. Also, the bond energy of B–O$^-$ bond and the excitation and ionization energies of non-bridging oxygen ions are comparable with the experimentally determined threshold energy. Transfer of electrons in the processes causes migration of neighbouring alkali ions, and the migration and trapping of the alkali ions stabilizes the compacted, rather unstable structure of the network. Thermal or optical activation of the trapped alkali ions cause backward reaction, resulting in thermal release or saturation of the stress.

In organic photochemistry, double bonds are often twisted by excitation and groups adjacent to the bonds are rotated around the bonds (for example, cis-trans isomerization)[19]). This process is similar to that described in ref. 1. The double bond character in the network of borate glass has an important role in the stress build-up.

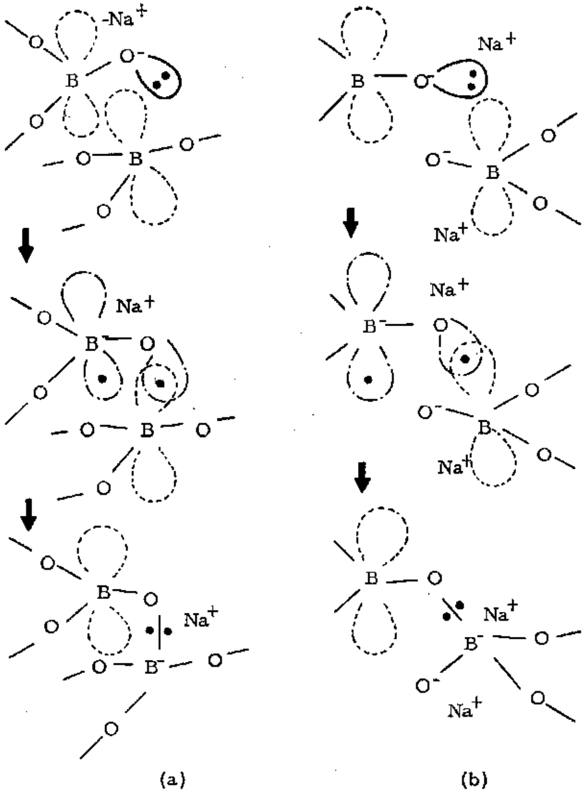


Fig. 20. Structural change of glass network caused by formation of new bond by charge transfer in a $\rangle$B–O$^-$ unit. Notations: cf. fig. 19.

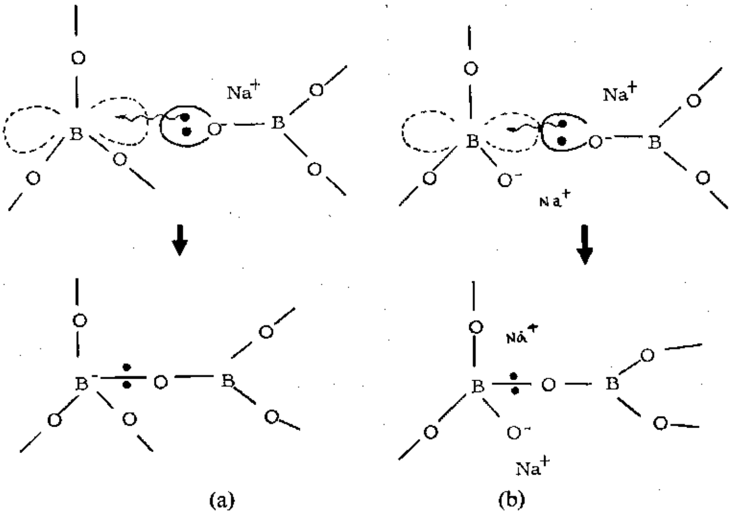
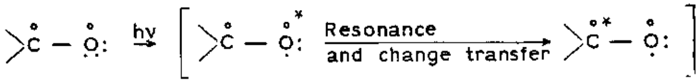
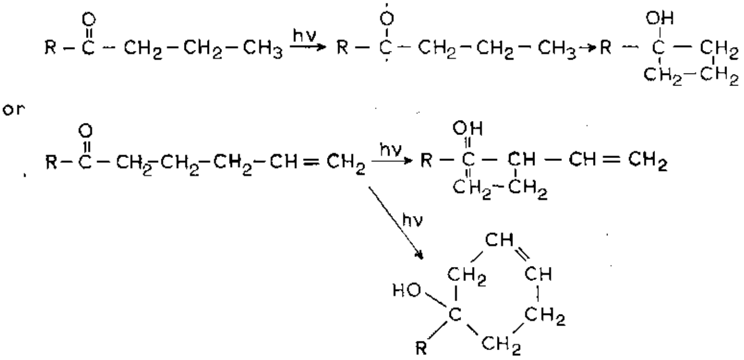


Fig. 21. Structural change of glass network caused by formation of new bond by photo-ionization of a non-bridging oxygen ion. Notations: cf. fig. 19.

Intramolecular charge transfer and generation of new valences described in refs. 2–4 are well known in organic photochemistry. The case of the carbonyl group is one of the examples 20) π- or non-bonding electrons of the oxygen ion in the group are excited by ultra-violet light and the electrons are rearranged between the oxygen and carbon ions. This is schematically represented as follows.



Here, °, • and * represent π-, non-bonding and anti-bonding electrons, respectively. By excitation, the C–O distance increases and the bond is twisted. Unpaired electrons in the group give the group radical-like character, and rearrangements of chemical bonds in or between molecules occur (for example, intra- or intermolecular hydrogen abstraction). Examples of such reactions are



11. Concluding remarks

Based on their own experimental results, the authors suggested detailed mechanisms or sequences of the stress build-up in glass caused by ultra-violet light. Although they should be confirmed or modified by investigations in the future, they are useful as a working hypothesis for the investigations. Processes of charge and energy transfer in glasses, structure sensitive character of the phenomenon, or release of the stress by ionizing radiations have to be studied in detail.

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