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39. Stress Build-up in Binary Borate Glasses by Ultra-violet Irradiation

Stress in Glass Caused by Ultra-violet Irradiation (Part 6)

By

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Abstract

As the first step to determine the kinds or the compositions of glasses that show the stress build up caused by ultra-violet irradiation, binary borate glasses containing respectively oxides of Li, Na, K, Ca, Sr, Ba, Cd, La, Bi, Pb, Tl, Si, and Zn, were prepared and subjected to ultra-violet irradiation. The irradiated surface layers of the glasses were examined photoelastically. Stress build-up was observed only in the glasses containing Li_2O, Na_2O and K_2O. Possible mechanisms of the stress build-up and the behaviour of alkali ions or change of coordination number of B^{3+} ions were discussed.

With alkali germanate glasses, although change of coordination number of Ge^{4+} ions seems possible with change of glass composition, stress build-up was not found by ultra-violet irradiation.

I. Introduction

Stress build-up by ultra-violet irradiation was observed in commercial and prepared borosilicate glasses[1]. On the other hand, the addition of some metal oxides to glass composition seemed to prevent the stress from being build-up[1-c)]. It was presumed to be necessary to find the kinds or composition ranges of glasses that show the stress build-up caused by ultra-violet irradiation. In the present paper, the results of examination on stresses in binary borate glasses after ultra-violet irradiation are reported. Also the results of preliminary examination on binary alkali germanate glasses are reported.

II. Glass samples and experimental methods

Bianary borate glasses were melted from reagent grade chemicals (HBO_3, alkali and alkaline earth carbonate and other metal oxides) in a platinum crucible in an electric furnace with silicon carbide heating elements. The composition of the glasses were selected by refering to the report by Imaoka[2]. There were, however, some exceptions, namely, cases of SiO_2-B_2O_3 glass (melted in a gas fired furnace from purified sand), Bi_2O_3-B_2O_3 and Sb_2O_3-B_2O_3 glasses (melted in alumina crucibles). Germanate glasses were melted from GeO_2 and alkali carbonates in alumina crucibles. Batch composition of the glasses are shown in Table 1.

Table 1. Batch composition of binary borate and germanate glasses (Only oxides added to B_2O_3 or to GeO_2 are shown in mol%).

glass No. (borate glasses)			Glass No. (borate glasses)			Glass No. (germanate glasses)		
1	Na_2O	12	10	La_2O_3	25	19	Na_2O	15
2	Na_2O	30	11	PbO	30	20	Na_2O	30
3	K_2O	12	12	PbO	50	21	K_2O	15
4	K_2O	30	13	PbO	70	22	K_2O	30
5	Li_2O	12	14	Bi_2O_3	25			
6	CaO	35	15	Sb_2O_3	25			
7	SrO	35	16	Tl_2O_3	30			
8	BaO	30	17	SiO_2	65			
9	CdO	50	18	ZnO	45			

Each glass was stirred several times with silica glass rod during melting. After fining, it was poured on a stainless steel plate to form tetragonal column and then it was annealed. By cutting and polishing surfaces, a prism ($10\times10\times5$ mm) of the glass was obtained, and it was subjected to irradiation by 400 W mercury discharge lamp made of silica glass tube. Conditions of irradiation were as follows; time of irradiation : 1000 hr, outer diameter of the lamp : 17 mm, length of the lamp : 150 mm, distance between an irradiated surface and axis of the lamp : 18 mm.

After irradiation, the prism of the glass was examined by a photoelastic method and the stress, if existed, at the surface and the depth of thestrained layer were measured. Relaxation of thestress by heating was measured on one of the samples.

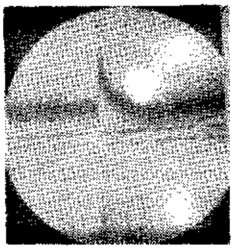
As the complementary experiments, thermal glow of the glasses irradiated by γ-ray (Co^{60}, 1.4×10^5 r/hr, 4 hr) was measured. Apparatus for thermal glow measurements was the same as that already reported.

III. Results

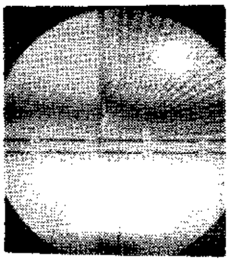
Stress build-up by irradiation was observed only in binary alkali borate glasses (glass No. 1–5 in Table 1). The stress and the thickness of the strained layers in these glasses are given in Table 2. In other glasses stress was not recognized. Some examples of photoelastic patterns of irradiated surface layers of the glasses are shown

Table 2. Stress at irradiated surfaces and thickness of strained layers of test glasses.

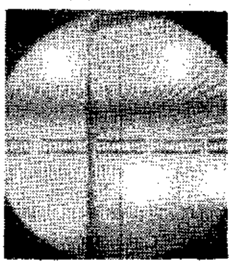
Glass No.	Stress at surface (kg/cm^2)	Thickness of strained layer (mm)
1	20 (tension)	0.5
2	10 (〃)	0.5
3	15 (〃)	0.4
4	5 (〃)	0.4
5	5 (〃)	0.4



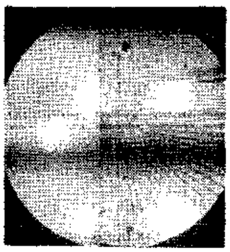
(2) Na_2O 30



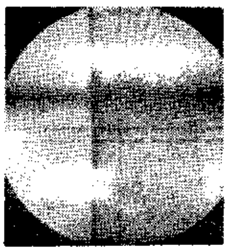
(4) K_2O 30



(8) BaO 30



(10) La_2O_3 25



(12) PbO 50

Fig. 1. Some examples of photoelastic observations with quartz wedge on the irradiated surface layers of the glasses (Composition: in mol%).

* The values in Table 2 are probably affected by haze produced at the irradiated surfaces of glasses during irradiation. Glasses containing no alkali oxides were chemically durable enough and haze was not observed. This, however, does not alter the conclusions of this paper.

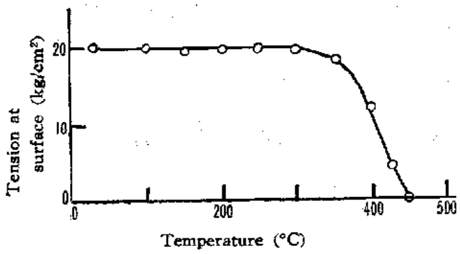
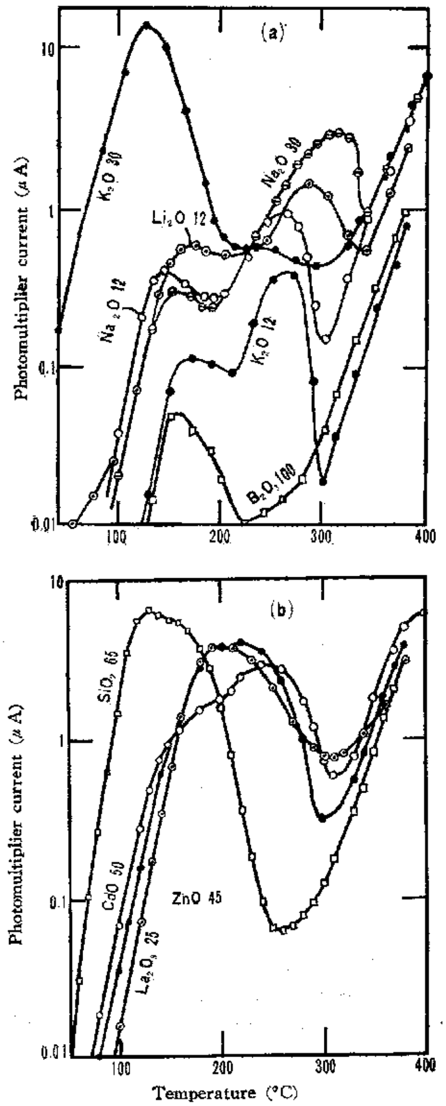


Fig. 2. Thermal release of the stress at the irradiated surface of No. 1 glass.

in Fig. 1. *

Thermal release of the stress in glass No. 1 is shown in Fig. 2. The stress faded away at 450°C and did not reappear on cooling.

Thermal glow curves of the glasses irradiated by γ-ray are shown in Fig. 3. Background currents caused by thermal radiation of the furnace were about $0.01\,\mu A$ at 250°C and $10\,\mu A$ at 400



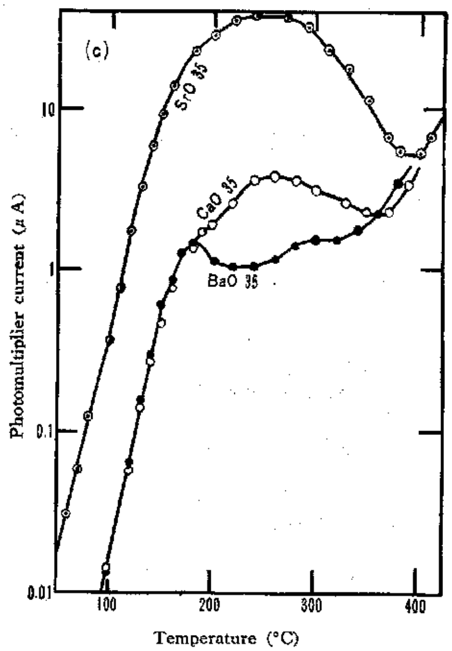


Fig. 3. Thermal glow curves of the binary borate glasses irradiated by γ-ray. (Composition : in mol%)

°C. Borate glasses of Pb, Bi, Sb and Tl did not show thermal glow.

IV. Discussion

IV. 1. As was already described, stress build-up by ultra-violet irradiation was found only with alkali borate glasses. Some of the possible interpretation of this phenomenon would be as follows :

1) The compaction of the glass and the stress build-up are initiated by the action of ultra-violet ray on alkali ions or non-bridging oxygen ions. Work functions or excitation energies of these ions are expected to be low compared to those of other kinds of cations. Even when they are far greater than quantum energies of photons of ultra-violet ray, excitation of these ions takes place by two-or multi-photon processes. The excited ions give their energy to the network structure of glass and give rise to compaction of the network and arouse stress in the irradiated surface layers.

2) Change of the coordination number ($3 \rightleftarrows 4$) of B^{3+} ions by ultra-violet irradiation is possible by rearrangement of ions including non-bridging oxygen ions loosely bonded with alkali ions. The density of the glass increases with the change of structure of glass, and the stress at the irradiated thin surface layer breakes out accordingly.

3) Owing to the low valency and relatively large ionic radii of alkali ions, the structure of alkali borate glass have something characteristic such as high free volume, low short range order or freedum of structural change.

The electronegativety[6)] of alkali atoms or bond energy of cation-oxygen chemical bonds[7)] of alkali ions are generally lower than those of other metal atoms or cations. These values are shown in Table 3. As are seen in the table, alkali atoms or ions do not always belong to the groups of those which have the lowest electronegativity or with the lowest cation-oxygen bond energies. The low electronegativity or low cation-oxygen bond energies do not seem to be decisive factors which contribute to the stress build-up.

Table 3

a) Sequence of cations in electronegativity scale

K	Na	Ba	Li	Sr	Ca	Zn	Cd
0.8	0.9	0.9	1.0	1.0	1.0	1.6	1.7
Si	Ge	Pb	Tl	Bi	Sb	B	
1.8	1.8	1.8	1.8	1.9	1.9	2.0	

b) Sequence of cations in cation-oxygen bond energies (kcal/mol)*

K^+	Cd^{2+} VI	Na^+	Cd^{2+} IV	Sr^{2+}	Ca^{2+}	Ba^{2+}	Zn^{2+} IV
13	20	20	30	32	32	32	36
Pb^{2+} IV	Li^+	Pb^{2+} VI	La^{3+}	Cd^{2+} II	Pb^{2+} II	Zn^{2+} II	
36	36	39	58	60	73	72	
Sb^{5+} IV	B^{3+} IV	Ge^{4+} IV	Si^{4+} IV	B^{3+} III			
85~68	89	108	106	119			

c) Sequence of cations in ionization potential (×10 kcal/mol)

Tl^+	K^+	Pb^{2+}	Ba^{2+}	Cd^{2+}	Zn^{2+}	Sr^{2+}	Na^+
46	74	74	83	87	92	99	108
Ca^{2+}	O^{2-}	Bi^{4+}	Tl^{3+}	Li^+	Ge^{4+}	Al^{3+}	Si^{4+}
117	127	129	165	173	214	274	382
B^{3+}							
593							

* Roman numerals show coordination numbers

It should be noted that the effect of alkali ions on stress build-up is essencial. For example, B_2O_3 35–SiO_2 65 mol% binary glass (glass No. 17) did not show stress build-up, although with 96% silica glass (containing about B_2O_3 4, Na_2O 0.3 in mol%) stress was observed in a sample irradiated by ultra-violet ray[1,a)]. Trace amount of alkali ions in glass seems sufficient for stress build-up.

IV. 2. The coordination number of Ge^{4+} ions in glasses changes ($4 \rightleftarrows 6$) with change of the composition of the glasses[9),16)]. Stress build-up, however, was not found in germanate glasses. Thorough study on germanate glasses seems necessary.

IV. 3. The thermal glow measurements were carried out with the following expectations : The longer the life time of photochemically excited states for structural change in glass is, the greater the rate of the process is. On the other hand, if the life time of excited states for luminescence is short, the number of excited centers decreases rapidly after the cease of γ-irradiation, and the thermal glow cannot be observed any more. Contrary, when the life time of excited centers is sufficiently long, de-excitation of the centers by heating arouses thermal glow. Correlation between life times of two kinds of excited states, that is, correlation beween stress built-up and thermal glow was suspected. Experimental results were contrary to this expectation.

V. Conclusion

Many kinds of binary borate glasses were melted, and after forming and polishing, they were irradiated by ultra-violet ray. Stress build-up was found only in alkali (Li, Na and K; Rb and Cs were not examined.) borate glasses. As the possible interpretations for this phenomenon, the behaviour of alkali ions or change of coordination number of B^{3+} ions were discussed.

Although coordination numbers of Ge^{4+} ions change (with the composition of glass), stress to be build-up in alkali germanate glasses was not found.

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紫外線照射による2成分系硼酸塩ガラスの応力発生

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紫外線照射によって応力を発生するようなガラスの種類と組成を決定するための一段階として，Li, Na, K, Ca, Sr, Ba, Zn, Cd, La, Pb, Bi, Sb, Tl, Si の酸化物をそれぞれ含む2成分系硼酸塩ガラスを熔融し，紫外線照射をした後，照射面の応力発生の有無を光弾性で調べた．Li, Na, K の硼酸塩ガラスだけが応力を発生した．応力発生の考えうる機構およびアルカリイオンの挙動，B^{3+} イオンの配位数変化などについて推測をした．

アルカリゲルマン酸塩の場合には Ge^{4+} の配位数が組成により変りうると考えられているのにかかわらず，紫外線照射による応力発生は見られなかった．

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