化への第一の障害が取除かれたものと考えられる。さらに c 軸をそろえられるような加圧方法、キュリー点をもう少し（出来れば 80°C ぐらいまで）上昇させられるような組成の研究など、残された問題はまだまだ多いが、それらについては次の機会に述べることにしたい。

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[研究速報]

Effects of Minor Additions on the Stress Build-up in a Sodium Borate Glass by Ultra-violet Irradiation

(Stress in Glass Caused by Ultra-violet Irradiation Part 11)

By

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Stress is built up in alkali borate and borosilicate glasses by ultra-violet irradiation¹⁾. The values of the stresses are strongly affected by small addition of some kinds of ions in the glasses²⁾. Effects of additions of many kinds of ions in a sodium borate glass were examined with the results described below.

Glasses of the batch composition $x\text{R}_m\text{O}_n \cdot 20\text{Na}_2\text{O} \cdot (80-x)\text{B}_2\text{O}_3$ or $x\text{Na}_p\text{X} \cdot 20\text{Na}_2\text{O} \cdot (80-x)\text{B}_2\text{O}_3$ in mol% were prepared. Here, R and X indicate cations and anions, respectively. The glasses were melted in a platinum crucible in an electric furnace from reagent grade chemicals (Na_2CO_3 , HBO_3 ,). They were formed into tetragonal columns ($15 \times 10 \times 5$ mm) with polished surfaces.

The columns were then exposed to ultra-violet light for 1000 hr. The light source was a 400 W mercury discharge lamp made of silica glass ($15 \phi \times 150$ mm). The distance between the surfaces of the columns and the axis of the lamp was 28 mm. During irradiation, the columns were cooled by dry air flow. After irradiation, the stresses in the irradiated surfaces were examined photoelastically with a Toshiba precision strain meter. The results are given in Table 1. Stresses lower

than about 20 kg/cm^2 were not conclusive owing to residual thermal stresses in the glass columns and they are indicated in the table with asterisks. The effects of additions are classified graphically in Fig. 1.

In the cases of 1~3 mol% addition, the results are summarized as follows: Stress is built up in glasses containing Ia (alkali) and IIa (alkaline earth) ions; Vb (P, As, Sb and Bi), Vlb (S, Se and Te) and VIb (halogen) ions in glasses seem to suppress the stress. Ions of heavier elements in the IIb, IIIb and IVb groups suppress the stress, but the ions of lighter elements do not.

Relations between the stress and the amounts of the additives seem complex: for example, 0.1 mol% addition of the oxides of Ce, Pb and U intensifies the stresses, but 3 mol% addition of those ions reduces or suppresses the stresses.

Some kinds of additives, for example, CuO , GeO_2 and Cs_2O (and also CeO_2 , PbO and UO_2) distinctly intensify the stress. In the glasses containing 0.1 mol% of Cr_2O_3 , MnO and CoO , stresses seemed to exist in the extremely thin surface layers, but at the present stage of the investigation this is not conclusive.

The authors proposed a theory on the stress-

Table 1. Experimental results.

glass No.	$R_m O_n$ or $Na_p X$	x	stress kg/cm ²	raw material	glass No.	$R_m O_n$ or $Na_p X$	x	stress kg/cm ²	raw material	glass No.	$R_m O_n$ or $Na_p X$	x	stress kg/cm ²	raw material
3	Li ₂ O	3	35	c	29	CuO	0.1	210	o	55	Cs ₂ O	3	150	c
4	BeO	3	49	o	30	ZnO	3	72	o	56	BaO	3	49	c
5	B ₂ O ₃	3	50	HBO ₃	31	Ga ₂ O ₃	3	52	o	57	La ₂ O ₃	3	*	o
9	NaF	3	*	n	32	GeO ₂	3	177	o	58-1	CeO ₂	0.1	230	o
11	Na ₂ O	3	64	c	33	As ₂ O ₃	3	*	o	58-2	CeO ₂	3	30	o
12	MgO	3	52	c	34	SeO ₂	1	*	Na ₂ SeO ₃	60	Nd ₂ O ₃	0.1	*	o
13	Al ₂ O ₃	3	*	h	35	NaBr	3	*	n	63	Eu ₂ O ₃	0.1	80	o
14	SiO ₂	3	50	powder of rock crystal	37	Rb ₂ O	3	79	c	73	Ta ₂ O ₅	3	*	o
15	P ₂ O ₅	3	*	o	38	SrO	3	65	c	74	WO ₃	0.1	36	o
16	Na ₂ S	3	*	n	39-1	Y ₂ O ₃	0.1	40	o	81	Tl ₂ O	3	*	o
17	NaCl	3	*	n	39-2	Y ₂ O ₃	1	*	o	82-1	PbO	0.1	210	o
19	K ₂ O	3	59	c	40	ZrO ₂	3	*	o	82-2	PbO	0.5	45	o
20	CaO	3	30	c	41	Nb ₂ O ₅	3	*	o	82-4	PbO	3	*	o
22	TiO ₂	3	*	o	42	MoO ₃	0.1	*	o	83	Bi ₂ O ₃	3	*	o
23	V ₂ O ₅	0.1	§	o	47	Ag ₂ O	0.1	†	o	90	ThO ₂	0.1	*	o
24	Cr ₂ O ₃	0.1	§	o	48	CdO	3	46	o	92-1	UO ₂	0.1	160	} Na ₂ U ₂ O ₇
25	MnO	0.1	§	o	49	In ₂ O ₃	3	*	o	92-1	UO ₂	3	*	
26	Fe ₂ O ₃	0.1	70	o	50	SnO ₂	3	*	o	I	NaNO ₃	3	*	n
27	CoO	0.1	150?§	o	51	Sb ₂ O ₅	3	*	o	II	Na ₂ SO ₄	3	*	n
28	NiO	0.1	§	o	52	TeO ₂	3	*	o	III	CH ₃ COONa	3	*	n
					53	NaI	3	*	n					

*: very low or zero, †: devitrified during irradiation.

§: Stresses seemed to exist in thin surface layers, but not conclusive.

c: carbonate, o: oxide, h: hydroxide, n: Na-compound

1	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb
2	Li	Be										B	C	N	O	F	
3	Na	Mg										Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
7	Fr	Ra															
Lantha- nides			La	Ce	Pr	Nd	Pm	Sm	Eu								
Actinides			Ac	Th	Pa	U											

big white square: Stress is not suppressed by 1 or 3mol% addition
small white square: Stress is not suppressed by 0.1mol% addition
small black square: Stress is suppressed by 0.1mol% addition
big black square: Stress is suppressed by 1 or 3mol% addition

Fig. 1. Classification of the effect of additive ions.

tural change and stress build-up in borate glasses by ultra-violet irradiation³⁾. The theory indicates that the important factors which enable the structural change in the glasses are (1). The comparatively loose packing of the glass network, (2). The peculiar behaviours of non-bridging oxygen ions in the network and (3). The ability of boron ions to change their valencies and coordination numbers.

Additive ions would fill vacant spaces in the network. Additive cations might either introduce non-bridging oxygen ions in the network and

arrange the oxygen ions around themselves and form ionic bonds with the oxygen ions, or in some cases, affect the $BO_3 \leftrightarrow BO_4$ equilibrium and advance or impede the change of coordination numbers of the boron ions. Additive anions might be replaced for non-bridging oxygen ions and affect the activity of oxygen ions in the network. These behaviours of additive ions are expected to have some effects on the stress build-up, respectively.

On the other hand, from the photochemical point of view, the roles of additive ions would

be classified as follows: 1. Internal filter which absorbs photon energy and dissipates it as thermal vibration of the network, 2. Activator or sensitizer which absorbs photon energy efficiently and converts it into the driving force for structural change of the network and 3. Deexcitation center which remove the energy of excited network and prevent the structural change of the network. Concentration of absorbed photon energy caused by the activator might even provoke structural change by two-photon process. It should be noted that the relation similar to the

heavy atom effects in photochemistry on quenching of excited states exists in IIIb and IVb groups in Table 1.

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ERRATUM

42. The Effectiveness of Alkali Halide Media for the Process of MgFe_2O_4 , MgAl_2O_4 and MgCr_2O_4 Formation

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J. Ceram. Assoc. Japan **75** [12] 349-352 (1967)

page	column	line	error	right
350	left	25	media	medium
350	left	38	Fe_2O_4	Fe_2O_3
350	light	5	methods	method
350	light	10	if not	unless
351	left	11	Media	Medium
351	left	21	midia	medium
351	light	24	graina	grains