[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 irradiation[1]. The values of the stresses are strongly affected by small addition of some kinds of ions in the glasses[2]. 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 $xR_mO_n \cdot 20\,Na_2O \cdot (80-x)\,B_2O_3$ or $xNa_pX \cdot 20\,Na_2O \cdot (80-x)B_2O_3$ 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 (15×10×5 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 ϕ×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/cm² 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), Ⅵb (S, Se and Te) and Ⅶb (halogen) ions in glasses seem to supress the stress. Ions of heavier elements in the Ⅱb, Ⅲb and Ⅳb groups supress 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 intensifys the stresses, but 3 mol% addition of those ions reduces or supresses the stresses.

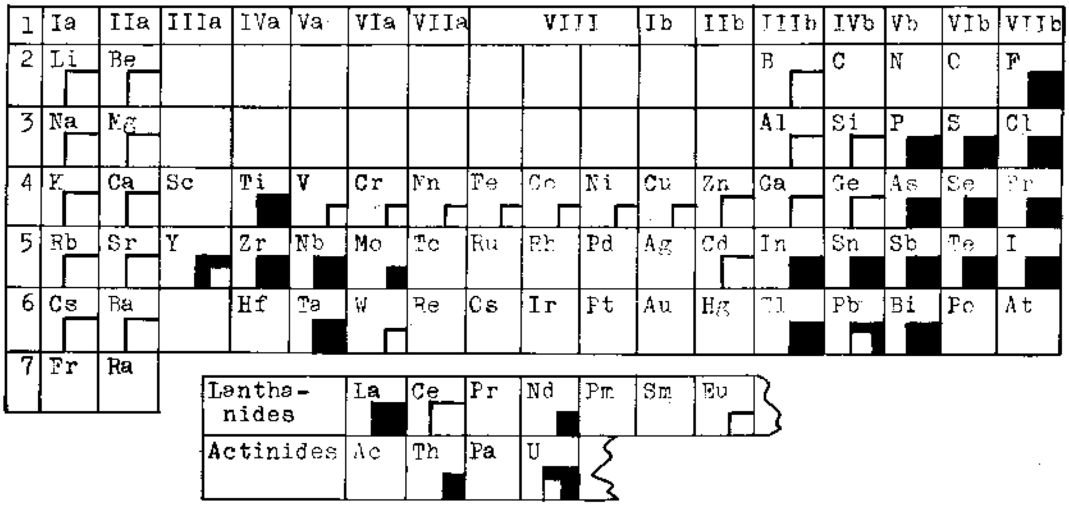
Some kinds of additives, for example, CuO, GeO_2 and Cs_2O (and also CeO_2, PbO and UO_2) distinctly intensify the stress. In the glasses containig 0.1 mol% of Cr_2O_3, MnO and CoO, stresses seemed to exist in the extremely thin surface layers, but at the present stage of the investigation this is not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

The authors proposed a theory on the struc-

Table 1. Experimental results.

glass No.	R_mO_n or Na_pX	x	stress kg/cm²	raw material	glass No.	R_mO_n or Na_pX	x	stress kg/cm²	raw material	glass No.	R_mO_n or Na_pX	x	strass kg/cm²	raw material
3	Li_2O	3	35	c	29	CuO	0.1	210	o	55	Cs_2O	3	160	c
4	BeO	3	49	o	30	ZnO	3	72	o	56	BaO	3	49	c
5	B_2O_3	3	50	HBO_2	31	Ga_2O_3	3	52	o	57	La_2O_3	3	*	o
9	NaF	3	*	n	32	GeO_2	3	177	o	58-1	CeO_2	0.1	230	o
11	Na_2O	3	64	c	33	As_2O_5	3	*	o	58-2	CeO_2	3	30	o
12	MgO	3	52	c	34	SeO_2	1	*	Na_2SeO_3	60	Nd_2O_3	0.1	*	o
13	Al_2O_3	3	*	h	35	NaBr	3	*	n	63	Eu_2O_3	0.1	80	o
14	SiO_2	3	50	powder of rock crystal	37	Rb_2O	3	79	c	73	Ta_2O_5	3	*	o
					38	SrO	3	65	c	74	WO_3	0.1	36	o
15	P_2O_5	3	*	o	39-1	Y_2O_3	0.1	40	o	81	Tl_2O	3	*	o
16	Na_2S	3	*	n	39-2	Y_2O_3	1	*	o	82-1	PbO	0.1	210	o
17	NaCl	3	*	n	40	ZrO_2	3	*	o	82-2	PbO	0.5	45	o
19	K_2O	3	59	c	41	Nb_2O_5	3	*	o	82-4	PbO	3	*	o
20	CaO	3	30	c	42	MoO_3	0.1	*	o	83	Bi_2O_3	3	*	o
22	TiO_2	3	*	o	47	Ag_2O	0.1	†	o	90	ThO_2	0.1	*	o
23	V_2O_5	0.1	§	o	48	CdO	3	46	o	92-1	UO_2	0.1	160	$Na_2U_2O_7$
24	Cr_2O_3	0.1	§	o	49	In_2O_3	3	*	o	92-1	UO_2	3	*	$Na_2U_2O_7$
25	MnO	0.1	§	o	50	SnO_2	3	*	o					
26	Fe_2O_3	0.1	70	o	51	Sb_2O_5	3	*	o	I	$NaNO_3$	3	*	n
27	CoO	0.1	150?§	o	52	TeO_2	3	*	o	II	Na_2SO_4	3	*	n
28	NiO	0.1	§	o	53	NaI	3	*	n	III	CH_3COONa	3	*	n

*: very low or zero, †: devitrified during irraddiation,
§: Stresses seemed to exist in thin surface layers, but not conclusive.
c: carbonate, o: oxide, h: hydroxide, n: Na-compound



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

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

tural change and stress build-up in borate glasses by ultra-violet irradiation[3]. 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 effiiciently 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 ener/gy 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.

References

1) T. Kishii, K. Ōoka, *J. Ceram. Assoc. Japan* **72** [11-1] 193 (1964); Preprint of The Annual Meeting of The Intern. Congress on Glass (1966) p. 259.
2) K. Ōoka, T. Kishii, *J. Ceram. Assoc. Japan* **73** [4] 108 (1965).
3) K. Ōoka, T. Kishii, *J. Ceram. Assoc. Japan* **76** [1] 4 (1968).

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