[研究速報]

Stress Build-up in Some Germanate Glasses by Ultra-violet Irradiation

(Stress build-up in glass by ultra-violet irradiation Part 9)

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Successive investigation by the authors following the discovery of the stress build-up in glass by ultra-violet irradiation elucidated that the phenomena were found only for glasses containing both boric oxide and alkali oxides, and that the phenomena were influenced by the addition of small amount of some kinds of metal oxides in the glass[1].

Further study was made for wider range of composition of glass as shown in Table 1. Reagent grade boric acid, carbonates of alkali and alkaline earth metals, aluminum hydroxide, oxides of lead, cadmium, zinc, antimony, bismuth, tellurium, and germanium, and metaphosphate of aluminum, sodium, potassium, and also semi-conductor grade germanium oxide containing 0.08 weight percent chlorine were used as the raw materials.

After melting in an electric furnace with silicon carbide heating elements, the glasses were casted, annealed and then polished to form tetragonal columns ($10\times10\times20$ mm). Glasses in Group 1 and 2 were melted in platinum crucibles and the others wers melted in alumina crucibles. The columns were exposed to ultra-violet radiation for 1000 hours. The light source was 400 W mercury discharge lamp made of fused silica glass (length 150 mm, outer diameter 15 mm). Distance between the outer surface of the lamp and irradiated surfaces of the columns was 20 mm. During irradia-

Table 1. Batch composition of glasses tested (mol%)

Group 1 $70B_2O_3\cdot(30-x)BaO\cdot xM_2O$ glasses

M	x	M	x
Li	0.5, 3	Rb	0.5, 3, 7
Na	0.2, 10, 20	Cs	0.2, 0.5, 3
K	0.5, 3, 10		

Group 2 $X\,B_2O_3\cdot xNa_2O\cdot(100-x-X)\cdot M_pO_q$ glasses

M_pO_q	X	x
GeO_2	80	0.5, 3, 10
CaO, SrO	65	0.5, 3, 10
CdO	55	3, 10
CdO	50	0.3
ZnO	50	10
	52	3
	54.5	0.5
Sb_2O_3, La_2O_3, Bi_2O_3	75	0.5, 3, 10
PbO	70	0.5, 3, 10

Group 3 Phosphate and tellurite glasses

$50\,Al(PO_3)_3\cdot 50\,NaPO_3$

$65\,TeO_2\cdot 35\,NaPO_3$

$65\,TeO_2\cdot 35\,KPO_3$

Group 4 Germanate glasses

No.	
4- 1	$70\,GeO_2\cdot 30\,PbO$*
4- 2	50 〃 $\cdot 50\,PbO$*
4- 3	80 〃 $\cdot 20\,Bi_2O_3$*
4- 4	90 〃 $\cdot 10\,Bi_2O_3$*
4- 5	80 〃 $\cdot 10\,Al_2O_3\cdot 10\,Na_2O$*
4- 6	80 〃 $\cdot 10\,Al_2O_3\cdot 10\,K_2O$*
4-11	$70\,GeO_2\cdot 10\,Al_2O_3\cdot 20\,Na_2O$ §
4-12	60 〃 $\cdot 20$ 〃 $\cdot 20$ 〃 §
4-13	60 〃 $\cdot 10$ 〃 $\cdot 30$ 〃 §
4-14	80 〃 $\cdot 5$ 〃 $\cdot 15$ 〃 §
4-15	70 〃 $\cdot 10$ 〃 $\cdot 20\,K_2O$ §
4-16	60 〃 $\cdot 10$ 〃 $\cdot 30$ 〃 §
4-17	80 〃 $\cdot 10$ 〃 $\cdot 10$ 〃 §
4-18	80 〃 $\cdot 10$ 〃 $\cdot 10\,Li_2O$ §

*: from reagent grade GeO_2

§: from semiconductor grade GeO_2

tion, the columns were cooled by dry air flow.

After irradiation, irradiated surface layers were examined photoelastcally. Stress build-up was observed in alkali aluminogermanate glasses (Table 2).

After the measurements, some of the glasses were annealed to release the steress and then irradiated again for 1000 hours. Stresses observed after the second irradiation are also given in Table 2.

Table 2. Tension at irradiated surface layers (kg/cm^2)

Glass No.	After the first irradiation	After the second irradiation
4- 5	50	45
4- 6	55	50
4-11	20	
4-12	10	
4-17	20	

It is seen that the stress is not detected in alkali aluminogermanate glasses containing lithium oxide or comparatively large amount of sodium oxide and potaasium oxide, and that the stress is lower in glasses made from semiconductor grade germanium dioxide. Suppression of stress by lithium oxide, or by comparatively large amount of sodium oxide, potassium oxide, and also by chlorine ion in glass has already been noted in borate or borosilicate glasses[1),2)].

Theory on the mechanisms of stress build-up in borate and borosilicate glasses is not yet fully established. Change of coordination number of B^{3+} ions ($3\rightleftarrows 4$) and of valency state of B^{3+} and O^{2+} ions are, however, supposed to have an important role on the structural change of the glasses. The change of valency state and coordination numbers of Al^{3+} and Ge^{4+} ions in alkali aluminogermanate glasses with change of glass composition has bes been reported[3)]. The mechanism of the stress build-up in alkali aluminogermanate glasses is considered to be the same as in alkali borate glasses, and the change of coordination number or valency state of Al^{3+} and Ge^{4+} might be a cause of the compaction of the glass structure and the induced stress.

References

1) T. Kishii, K. Ōoka, T. Ōomori, *J. Ceram. Assoc. Japan*, **72** [11-1] 193 (1964); **73** [4] 82 (1965); **73** [7] 147 (1965); **73** [8] 163 (1965); **74** [7] 226 (1966); **74** [12] 363 (1966); **75** [4] 96 (1967); Preprint of Annual Meeting of Intern. Commission on Glass (1966) p. 259.

2) T. Kishii, K. Ōoka, The Autumn Meeting of Societies and Associations related to Chemistry; (1966) Nov.

3) M.K. Murthy, B. Scroggie, *Phys Chem. Glass*, **6** [5] 162 (1965). [Received March 17, 1967]