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Effects of Small Additives on Stress Build-Up in Glass by Ultra-Violet Irradiation: Transition Metal Oxides

By

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1. Introduction

It was found that stress is built up by ultra-violet irradiation in alkali borate, alkali borosilicate and alkali aluminogermanate glasses[1)~8)]. Effects of minor additives in an alkali borate glass were examined and were found complicated[8)]; i.e. alkali and alkaline earth oxides up to 3 mol% added in the glass did not suppress the stress build-up. Alkali halogenides and chalcogenides effectively prevented the stress build-up. Although preliminary results were shown also on the effects of transition metal oxide additives, the effects of transition metal oxides when added in a small amount are not yet fully understood. Further investigations were carried out with the results described below.

2. Experimental methods

Compounds of transition metals were added into batches of an alkali borosilicate glass. Composition of the glass was Na_2O 15, B_2O_3 65, SiO_2 20 in mol% or Na_2O 14, B_2O_3 68, SiO_2 18 in weight percent. The additives are listed in Table 1.

Compounds of Pb, Ge, Ce and U were also added, respectively, for comparison. The glasses were melted in a platinum crucible in an electric furnace with silicon carbide heating elements. Prisms 20×10×5 mm in size with polished surfaces were made of the glasses and they were exposed to ultra-violet light. The methods of ultra-violet irradiation, stress measurement and the examination of threshold photon energy of stress build-up were described in the previous paper.

3. Results

Stresses built up after 1000 hr's of ultra-violet irradiation are plotted against the amounts of the additives (Fig. 1). Time-stress curves for some of the glasses are shown in Fig. 2. In Fig. 3, stresses are plotted against transmission at 220 mμ of the glass filters which were inserted between the samples and the light source during ultra-violet irradiation. Transmission curves of the doped glasses 5 mm thick are shown in Fig. 4.

Table 1. Oxides doped in Glass.

Element	Oxide*	Raw Material
Ti	TiO_2	TiO_2
V	V_2O_5	V_2O_5
Cr	Cr_2O_3	Cr_2O_3
Mn	MnO	$MnCO_3$
Fe	Fe_2O_3	Fe_2O_3
Co	CoO	CoO
Ni	NiO	NiO
Cu	CuO	Cu_2O
Y	Y_2O_3	Y_2O_3
Zr	ZrO_2	ZrO_2
Nb	Nb_2O_5	Nb_2O_5
Mo	MoO_3	MoO_3
Hf	HfO_2	HfO_2
Ta	Ta_2O_5	Ta_2O_5
W	WO_3	HWO_4
Ge	GeO_2	GeO_2
Ce	CeO_2	CeO_2
Pb	PbO	Pb_3O_4
U	UO_2	$Na_2U_2O_7$

* Nominal formula used for calculation of the amounts doped.

4. Discussion

4.1 Effects of the amounts of the additives on stress value

Effects of the amount of the additives can be classified as follows:

Group A. The stress increases at first with

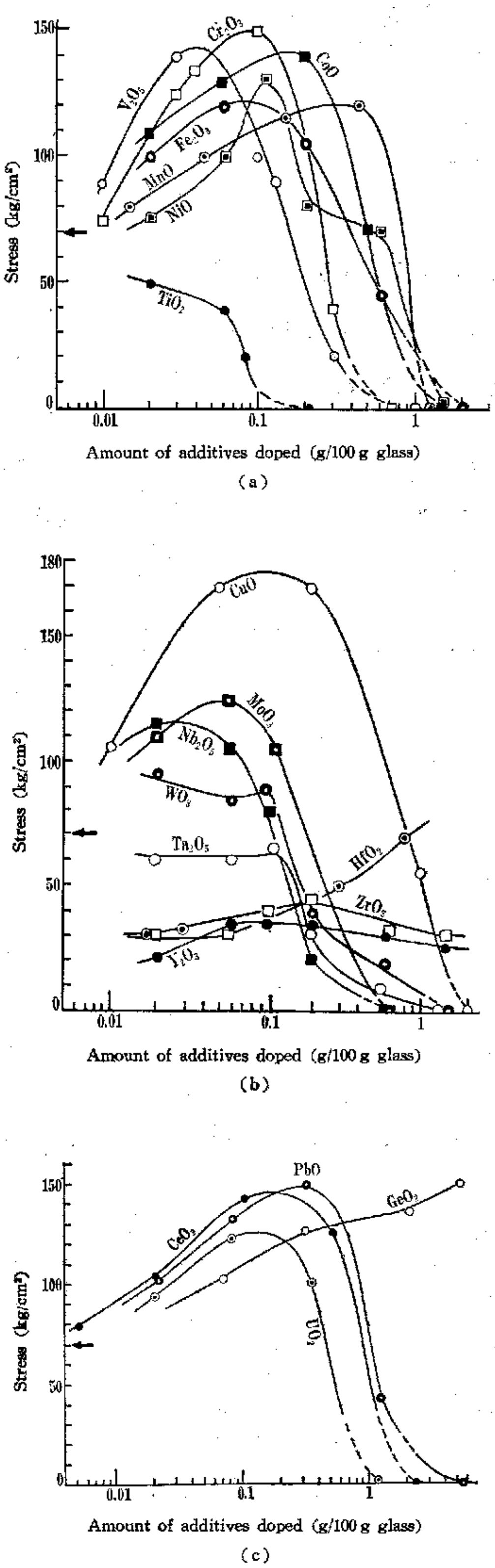


Fig. 1. Concentration vs stress at surface. Arrows indicate the stress value of undoped reference glass.

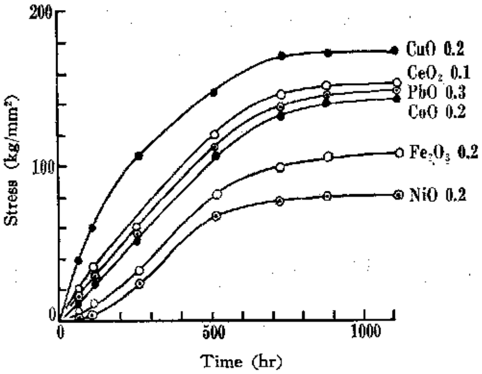


Fig. 2. Time vs stress during ulta-violet irradiadiation.

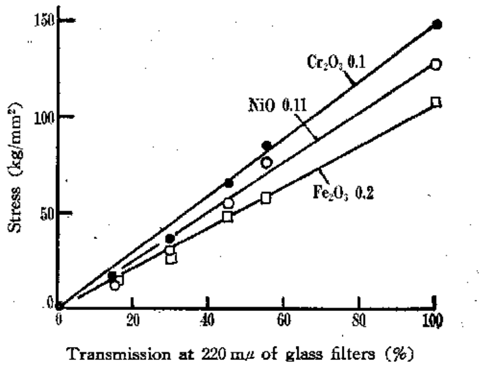
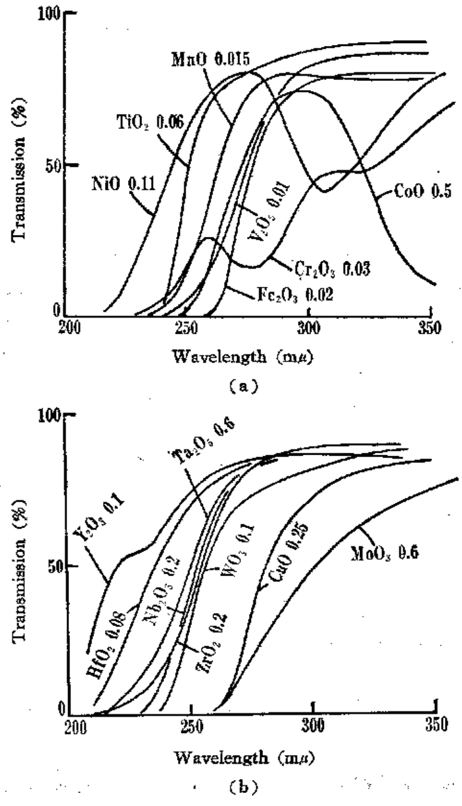
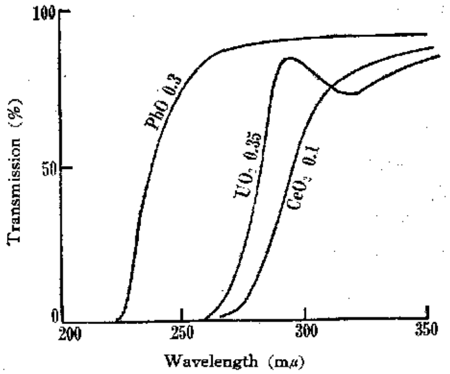


Fig. 3. Results of the examination on the threshold energy for stress build-up.





(c)

Fig. 4. Tpansmission curves for doped glasses 5 mm in thickness.

increase of the amount of the additive. After reaching a maximum at about 0.1~1 (g/100 g glass) addition, the stress decreases down to zero at 1~3 (g/100 g glass). Many kinds of metal oxides, namely V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Ce, Pb and U oxides belong to this group.

Group B. The stress decreases with a small amount of the additive and keeps the low level of stress value in some concentration range. This group contains Y, Zr and Hf oxides.

Group C. The stress increases (GeO_2) or decreases (TiO_2 and Ta_2O_5) monotonously with increase of the concentration.

4.2 Threshold photon energy for the stress build-up

The linear relations in Fig. 3 show that photon energy corresponding to 220 mμ wavelength or higher is the threshold energy for the stress build-up. This is similar to the cases of commerical borosilicate glasses containing very small amounts of Fe_2O_3. The threshold photon energies are not influenced by the addition of Cr_2O_3, NiO and Fe_2O_3. This indicates that fundamental processes of the stress build-up are not modified by the additives and that two photon processes (processes caused by simultaneous absorption of the energies of two photons) are unlikely.

4.3 Time-stress relation during ultra-violet irradiation

In the cases of commercial borosilicate glasses, time-stress curves were similar to those of, for example, the glasses doped with Fe_2O_3 or NiO; namely, they showed both induction period at the initial stage of ultra-violet irradiation and saturation after long periods, about 800 hours, of irradiation. The glasses doped with CoO, CuO, CeO_2 or PbO lack induction period.

The induction period was assumed to be the period in which the backward or compensating reactions against the stress build-up take place rather easily. If this is true, some transition or other kinds of metal ions enhance the foreward reaction of the stress build-up and suppress the backward reaction. As the reaction process of the stress build-up is explained on the basis of the behaviours of the electrons in the network, the effects of the dopants seem to be caused by release or trapping of the electrons or positive holes by the dopants or by charge tranfer between the dopants and the surrounding oxygen ions (cf. 4.4).

4.4 Roles of dopants in glass

Roles of dopants in a glass network can be classified as follows:

1. Modifications of the glass structure, for example, filling vacant spaces in the network
2. High efficiency photon energy absorber
3. Participants in photochemical reactions which lead to stress build-up

4.4.1 The dopants belonging to Group A

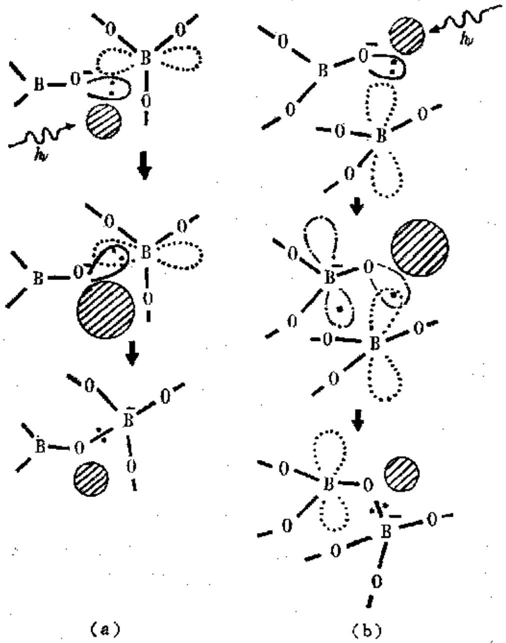
The dopants in group A increase the amount of photon energy absorbed per unit volume in the irradiated surface layers of the glasses.

The mechanisms of light absorption by these ions in the wavelength region near the threshold are not yet fully understood. However, processes assumed are; "charge transfer" in the case of V, Fe, Ni and Cr ions, "charge transfer" or $3d$–$4p$ electron transition in the case of Co ion, and s^2–sp electron transition in the cases of Ge and Pb ions, respectively[10]. Detailed processes of "charge transfer" are not yet fully clear. These transitions are, however, similar to each other in the point that electrons are expelled from the inner to outer orbitals of the dopants by excitation. In order to neutralize or compensate for the transient and unstable electric field caused by the excitation of the orbital electrons of the dopants, rearrangement of the chemical bonds in the glass network occurs around the doped ions. These processes can be represented schematically in Fig. 5. In this way, it can be understood why many kinds of dopants belonging to group A behave similarly to each other.

Furthermore, if the dopants trap tranfered or ionized electrons, for example, of the surrounding oxygen ions, the backward reactions are suppressed, thus causing enhancement of the stress build-up.

Filling the glass network with dopants, along with the internal filter effect by them,can be the cause of decrease of the stress at high concentration ranges.

4.4.2 Y, Zr, Ti, Hf and Ta Ions No simple explanation can be given for the behaviours of these ions, at present. These elements, however, belong to IIIa (Y), IVa (Zr, Ti, and Hf) and Va (Ta) groups in the periodic table, respectively, and have larger atomic or ionic radii and smaller



• electron
.... vacant *p*-orbital of boron
—·—·— orbital containing unpaired electron
——— orbital containing lone pair of electrons
—:— bond formed by electron pair
hatched area : electron cloud of doped ion

Fig. 5. Schematic illustration of the processes of chemical bond rearrangement around the the doped ions.
(a) Process caused by repulsion of a lone pair of non-bridging oxygen ions by excited dopant.
(b) Process caused by charge transfer in a B-O unit which is initiated by excited dopant.

electronegativities than those of the other transition elements. They are also classified as "intermediate", which means they can join into the glass network[11].

4.4.3 Ge Ions Germanium dioxide differs from other oxides in that it is a network former. Similarly to boron ions, Ge ions can change coordination number with glass composition. In some germanate glasses, for example, in alkali aluminogermanate glass, stress is built up by ultra-violet irradiation. Thus, it is natural that doping a borosilicate glass with GeO_2 enhances the stress build-up.

5. Conclusion

The effects of addition of many kinds of transition metal oxides on stress build-up in an alkali borosilicate glass caused by ultra-violet irradiation were examined. Ge, Ce, Pb and U oxides were also investigated for comparison. The effects were classified as follows : In group A; The stress increases at first with increase of the amount of the additive and then decreases to zero at their higher concentration (V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W, Ce, Pb and U).

In group B; The stress decreases with a small amount of the additive and keeps the low level of stress value in some concentration range (Y, Zr and Hf). In group C; The stress increases (Ge) or decreases (Ti and Ta) monotonously with increase of the concentration.

Possible mechanisms of the enhancement stress by the addition of elements of Group A are discussed. Although an explanation on the behaviors of elements Y, Zr, Hf, Ti and Ta was not possible, attention is given to their "intermediate" character in the glass network.

In some cases, time-stress relations during ultraviolet irradiation for the doped glasses differed from those for the undopd glasses. Threshold energies for the stress build-up in the doped glasses, however, were the same as those of the undoped glasses. There was no indication of occurence of the two-photon process.

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紫外線によるガラスの応力発生への添加物の効果：遷移金属酸化物

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Na_2O 15, B_2O_3 65, SiO_2 20 モル% の組成のガラスに遷移族金属酸化物を添加し，紫外線を照射して発生する応力を測定した．添加物を効果によって分類すると，A：少量添加では応力を増加し，ついで極大を経て 1～3 g/100 g ガラスで応力が零になる（V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, W の酸化物：なお Ce, Uの酸化物も同様），B：少量添加で応力を減らすが，かなり大量加えても零にはならない（Y, Zr, Hf の酸化物），C：添加量とともに応力は単調に零まで減少する（Ti, Ta の酸化物）．二，三の試料について，応力発生のための光量子エネルギーのしきい値を測ると，5.5 eV（波長 220 mμ）で無添加のものと同じであった．A群の場合には添加イオンの励起によって網目構造内の電子分布が変って化学結合が変化すると考えて，添加イオンの影響を説明できる．他種のものについては未解決である．

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