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Volume changes in glass induced by an electron beam

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ABSTRACT

Three glasses (float, borosilicate float and Schott D263 glasses) were irradiated by 50 keV electron beams with doses within the range of 0.21–318.5 kC/m^2. Volume changes induced by electron bombarding were monitored by means of Atomic Force Microscopy. Incubation doses, related to mobility of alkali ions, were measured. Low doses showed compaction of all glasses while higher doses revealed volume inflation, except for borosilicate float glass. Both surfaces of float glass were irradiated and significant differences between them were found.

1. Introduction

Silicate glass irradiated with a high-energy electron beam undergoes changes in its structure because of ballistic interactions, atomic ionization, excitation of plasmons and momentum transfer via Rutherford scattering [1–3]. Depending on the dose and energy of the particles, many effects may occur during irradiation, e.g. phase transition, amorphization, changes of volume and refractory index, and/or formation and growth of oxygen-filled gas bubbles [3–6]. The main, and vastly documented modification induced with electron irradiation on silicate structure is the creation of the stable point defects (electron and hole centres) [7] and the changes of the valence states of the lattice atoms. Some of the modified electronic configurations or defects may also cause changes in light absorption. These defects are then called "colour centres" [8]. Electron irradiation also causes changes in mechanical properties such as fracture toughness and hardness [9].

The industry uses silicate glasses in various applications, where an interaction of the particle beam with silicate glass occurs. As an examples can serve glass used in the cosmic space and exposed to the unscreened cosmic radiation, glass used in detectors, lenses, and prisms, glass used for nuclear waste deposition, and glass used as insulator in nuclear power plants [1]. The development of radiation-induced optical absorption in glasses has promoted the use of glass in the laser and dosimeters technologies [10,11].

In general, electron irradiation causes significant defects in the glass structure [12]. The character of most structural defects is difficult to define because of amorphousness of the glass state. Creation of point defects under irradiation has been studied by many authors [13–17]. The most important defects (colour centres) are NBOHC (non-bridging oxygen hole centres), the E′ centres, the peroxy radicals, and the trapped electrons [18].

Electron irradiation is accompanied by the decay of alkali X-ray intensities [19] in alkali-silicate glass. Macroscopic migration of alkali ions may be conveniently observed by EPMA by recording the decay curve (X-ray intensity versus time) [20]. The shape of the curve depends on primary electrons energy and on the current density of the beam. The curve may be divided into two parts [12]; instantly after the start of irradiation the curve shows a slow linear change. During this period the rate of migration is rather slow. After some time, called the incubation period, the curve exhibits an exponential-like decrease. It is supposed the incubation period is correlated with the transport of alkali ions to the bulk [19]. After out-migration the surface-layer structure consists of many dangling non-bridging oxygen atoms (NBO) originally coming from bonds to alkali ions. Three different processes can provide relaxation of these dangling NBOs. The first one preserves the formed dangling oxygens, the second one is the formation of molecular oxygen, and the final process supports the creation of peroxide bonds [10]. Molecular dynamics simulations showed that the last mechanism is favoured [21] although in case of high temperatures of the irradiated glass some flow of oxygen into vacuum was observed [22].

One of the pronounced effects of electron irradiation on silicate glass is its volume change. Structure compaction was observed for small doses and expansion for higher doses [2]. Compaction may be explained by the effect of an additional relaxation of Si–O–Si bonds enabled by the local input of energy gained from the incoming electrons [23]. Nevertheless, incoming electrons also introduce

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disorder into glass structure that may be seen by XPS as a widening of the spectral peaks [24]. Hence, for larger doses the latter effect prevails as the former one is being exhausted and volume expansion is then observed. The fundamental role of relaxation around alkali sites is documented by the observation that vitreous silica reveals just densification.

The aim of this work is to enhance the previous studies of volume effects to commercial float glass, and two borosilicate glasses. The latter ones were chosen so that the first one to have the ratio B/R < 1 (R = alkali ions, B = boron ions) and the second one B/R > 1 to study the influence of structure on radiation resistivity.

2. Experimental

Three glasses were used in this experiment: Float glass, borosilicate float glass and optical borosilicate glass Schott D263, further denoted F, B, and S. Before experiment the glasses were cleaned up by acetone to avoid possible surface contamination. Then, glasses were coated by the 10 nm layer of Au/Pd alloy by means of vacuum sputtering to ensure surface conductivity and to avoid charging of samples during electron irradiation. Chemical compositions of glasses were determined by EPMA (Jeol Superprobe 733, accelerating voltage 15 keV, current 9 nA, WDS, standard analysis, ZAF correction, estimated accuracy – 1 rel.%). The amount of B was not possible to determine by WDS, so it was taken from literature [25]: 8.4% in S glass and 14.4% in B glass. The main difference between S and B glasses is the ratio between alkali and boron atoms. In S glass, the number of alkali atoms exceeds the number of boron atoms so that all boron atoms should be four-bonded [26] and the redundant alkalis form NBOs. On the other hand in B glass boron atoms prevail over alkali ones so that all alkalis have to be located in the vicinity of B to form 4-bonded B. It means some portion of B atoms remain 3-bonded in B glass (See Table 1).

The incubation period is a manifest of alkali transport towards bulk of glass and migration of alkali ions should be therefore related to the volume expansion [19]. Incubation periods were determined from time dependences of X-ray intensities. Immediately after the start of the exposure, the decay curve is constant with time or displays a slow, linear decrease. After the incubation period, the decay curve turns into an exponential-like decay. The shape of the decay curve depends on the current density so it was necessary to choose different values of the current for different glasses to visualize changes of the curve slopes. In particular current of 50 nA caused nearly the immediate migration of sodium ions in the F glass, what resulted in too steep shape of the curve and the point of the slope change was not clearly visible. Because different current densities were used, to unify these measurements, the "incubation dose" is advantageously used (absorbed dose at the point of the slope change). X-ray intensities of sodium were observed for F and B glasses, and that of potassium for S glass. Results can be seen on Figs. 1–3.

While the incubation periods/doses for S and F glasses can be clearly detected, the decay curve of B glass seems to have no incubation dose. Incubation dose for S glass is approximately 9 kC/m^2 and that for F glass is around 3 kC/m^2.

Incubation dose for B glass can't be detected; the curve is clearly linear, without any observable change in the slope.

Table 1
Chemical composition of glasses in wt.%.

	B_2O_3	SiO_2	Na_2O	K_2O	Al_2O_3	MgO	CaO	TiO_2	ZnO
F	–	72.3	13.1	0.7	1.0	4.2	8.7	–	–
B	14.4	78.8	3.4	0.7	2.7	–	–	–	–
S	8.4	64.2	6.4	6.9	4.2	–	–	4.0	5.9

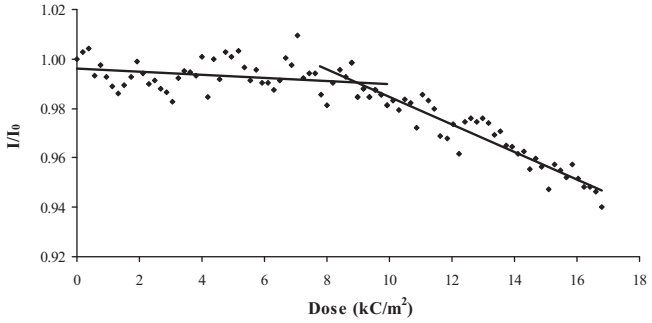

Fig. 1. Decay curve for the S glass (50 nA, K ions).

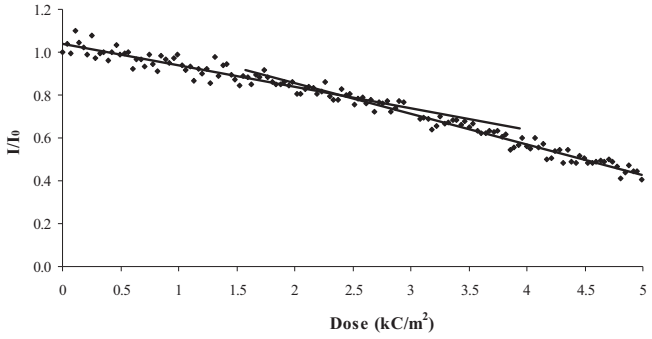

Fig. 2. Decay curve for the F glass (20 nA, Na ions).

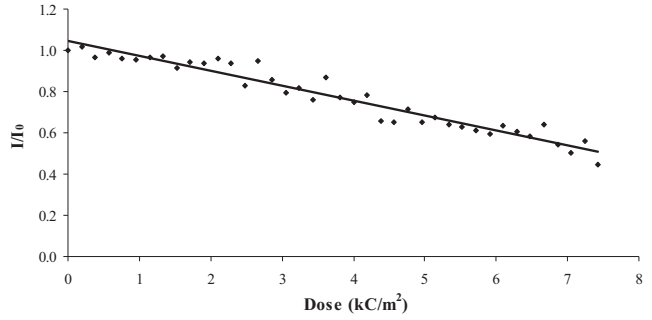

Fig. 3. Decay curve for the B glass (20 nA, Na ions).

Glasses were subsequently irradiated by the series of electron doses from 0.2 to 318.5 kC/m^2, each dose was continual and independent (irradiated places were well separated on the surface not to influence each other). Glass surface was also observed by an optical microscope to avoid locations with evidently worse quality of its surface. Accelerating voltage was set to 50 keV (penetrating range of electrons is about 20 μm). The diameter of the beam was set by the optical microscope to 60 μm, so that a widening of the defocused beam caused by electron scattering may be neglected in comparison to the beam diameter. Under these conditions the temperature increase during irradiation can be neglected. Immediately after irradiation, the morphology of the irradiated spot was examined by AFM (Topometrix TMX 2000).

Low dose irradiation caused a depression within the glass; after some exposure a bump in the middle of the formed pit was created and the bump continuously increased with the dose. Volume change of the irradiated place was described as a difference between the lowest/highest point of the irradiated spot and the line of the pristine unirradiated surface. Negative value indicates volume depression, positive value means expansion. AFM pictures of