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Structural and volume changes and their correlation in electron irradiated alkali silicate glasses

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ABSTRACT

Two binary alkali silicate glasses ($15K_2O{\cdot}85SiO_2$ – denoted as K15 and $15Li_2O{\cdot}85SiO_2$ – denoted as Li15) were irradiated by 50 keV electron beams with doses within the range of 2.1–15.9 kC/m^2. Volume changes induced by electron irradiation were monitored by means of Atomic Force Microscopy (AFM). Raman spectra were taken from the irradiated spots to observe structural changes. Volume compaction observed at lower doses was correlated with the increase of the D2 peak. Volume expansion at higher doses was related to migration of alkali ions. Irradiated glasses were annealed at 400 °C and 500 °C for 60 min. After annealing irradiated spots were again examined by AFM and Raman spectroscopy in order to determine volume and structural relaxation of radiation induced changes. Annealing at higher temperatures resulted in the levelling of the pits created by irradiation, but only for doses below incubation dose. The pits created by doses above incubation dose were not levelled. Annealing caused decrease of D2 peak and shift of the Si-O-Si vibrations band in direction to original structure. Low-frequency region of annealed Li15 glass was undistinguishable from that of pristine glass, while annealing of K15 glass did not result in the full reversion to the original shape. The differences between glasses were attributed to higher T_g of K15 glass. Q-motives bands of both glasses were not completely restored after annealing due to the absence of alkali ions.

1. Introduction

Silicate glass is commonly used material not only for commercial purposes (windows, glass containers, decorations), but it is also utilized for specialized purposes where radiation occurs in any form. The study of radiation effects on glass is important in the fields of cosmic research, nuclear industry, vitrification of nuclear waste or for detectors. Among various types of radiation the electron radiation is one of the most general, because even other types of radiation (neutrons, ions, etc.) generate secondary electrons. In general, fast particles (photons, electrons, etc.) may cause a number of changes in a solid material, depending on the dose, energy, and type of the particles. Structural changes are happening due to the ballistic interactions, atomic ionizations, excitation of plasmons and momentum transfer [1,2]. Many papers documented various changes induced by electron radiation, particularly phase transition, amorphization, changes of volume and refractive index, and growth of oxygen-filled gas bubbles [1–7]. The important phenomenon caused by electron irradiation is the creation of stable point defects and the changes of valence states of the lattice atoms. The origin and formation of point defects (electron and hole centres) has been studied by many authors, mainly because these defects may change the physical properties of silicate glass and therefore limit its technological applications [8–11]. Some of the point defects may also cause changes in light absorption and are denoted as "colour centres" [12]. Other authors observed changes of mechanical properties of electron irradiated glasses, such as fracture toughness or hardness [13,14].

Electron irradiation causes pronounced changes of glass composition within the interaction volume. Previous studies documented the macroscopic migration of alkali ions under electron irradiation, which can be observed by EPMA (Electron Probe Microanalysis) as the decrease of the decay curve (alkali X-ray intensity versus time) [15–17].

Volume changes of irradiated glasses were observed by a number of authors for different glass systems under various doses [2,6,18–20]. Electrons deposit the energy and momentum into the silicate structure, leading to structural rearrangement [6]. Vitreous silica responds to irradiation by volume compaction (volume expansion was documented only for silica glass with high OH content) [20–23]. Volume compaction was explained by the

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Table 1
Chemical composition of glasses in molar %.

	SiO_2	Li_2O	Na_2O	K_2O	Al_2O_3	MgO
Li15	84.3	14.8	0.1	0.1	0.5	
K15	83.2		0.2	15.8	0.5	0.2

local increase of energy and momentum, leading to relaxation of Si-O-Si bonds and optimization of their angles [21]. The response of alkali silicate glass to electron irradiation is more complex. While volume compaction was observed for lower doses, expansion prevailed at higher doses [6,18]. Volume expansion seems to be correlated with the migration of alkali ions out of the irradiated volume [15,18].

Some authors also presented studies about structural changes, observed by Raman spectroscopy in the short/middle range order, induced by electron irradiation in oxide [24–26] and non-oxide [27] glasses. Boizot at all [24] observed the increase of D2 defect peak at 602 cm^{-1} as a function of the dose suggesting the increase is coursed by the increase of the three-membered rings consisted of $(SiO_4)^{4-}$ tetrahedra. This effect was confirmed in our previous study of electron irradiated vitreous silica where the shift of Si-O-Si vibrations band at 450 cm^{-1} and the increase of D2 defect peak at 602 cm^{-1} were correlated with volume changes [21].

The aim of this paper is to extend the previous study of silica glass to more complex systems – alkali silicate glasses and to find correlations between volume changes, measured by AFM, with structural changes determined from Raman spectra.

2. Experimental

Binary alkali silicate glasses $15Li_2O{\cdot}85SiO_2$ (further denoted as Li15) and $15K_2O{\cdot}85SiO_2$ (K15) were used in our experiments. Chemical compositions of glasses, determined by XRF (X-ray fluorescence), are summarized in Table 1. All samples were prism-shaped to a size of $5 \times 3 \times 3$ mm^3. Glasses were annealed for a few hours after casting in order to remove strains in glass. Before irradiation the glasses were cleaned up by acetone to remove 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. The samples were coated using BAL-TEC High Vacuum Sputter Coater SCD 500.

Firstly, the incubation dose (further denoted as ID) of K15 glass was measured by EPMA (impossible for Li15, due to the limitation of the detector). ID was determined from the dependence of the potassium X-ray intensity on the dose, also denoted as decay curve, at the point where the slope changes (see Fig. 1). The precise identification of ID depends on the current density [15] as it influences the sharpness of the curve bending. Current of 50 nA was found to give a sharp enough change of the intensity course and is therefore suitable for the determination of ID. Moreover, this current is also convenient due to only negligible temperature increase during irradiation. The ID of K15 glass was evaluated to 4.8 kC/m^2 (see Fig. 1).

The doses are expressed in kC/m^2, in order to be consistent with our previous studies, so the presented results can be easily compared and discussed. However, many studies and reviews use the unit Gy, especially at high-energy irradiation experiments, therefore it is appropriate to find a relation between these two units. C/m^2 can be expressed by the following equation:

$$\frac{C}{m^2} = \frac{4It}{\pi d^2}$$

where I stands for current, t for time and d is the diameter of the irradiated area. Gy is defined as absorbed energy per weight of the absorbing material, which can be also expressed as:

$$Gy = \frac{4(1-R)IUt}{\rho \pi d^2 D}$$

where R stands for the backscattering coefficient (approximately 0.12 for silica glass at the used energy), U for the voltage, ρ for the density, and D for the electron range (approximately 20 μm). Hence, if we want to express Gy in C/m^2, we finally get the relation:

$$\tilde{\eta}[Gy] = \left(\frac{(1-R)U}{\rho D}\right) \cdot \eta\left[\frac{C}{m^2}\right]$$

where $\tilde{\eta}$ is the dose in Gy and η is the dose in C/m^2. So the expression in parantheses is the proportionality coefficient. Assuming the uncertainty of around 10% (in the determination of backscattering coefficient and of the electron range), the relation between Gy and kC/m^2 is for our experimental conditions as follows:

$$\frac{1kC}{m^2} \approx 2.510^9\ Gy = 2.5\ GGy$$

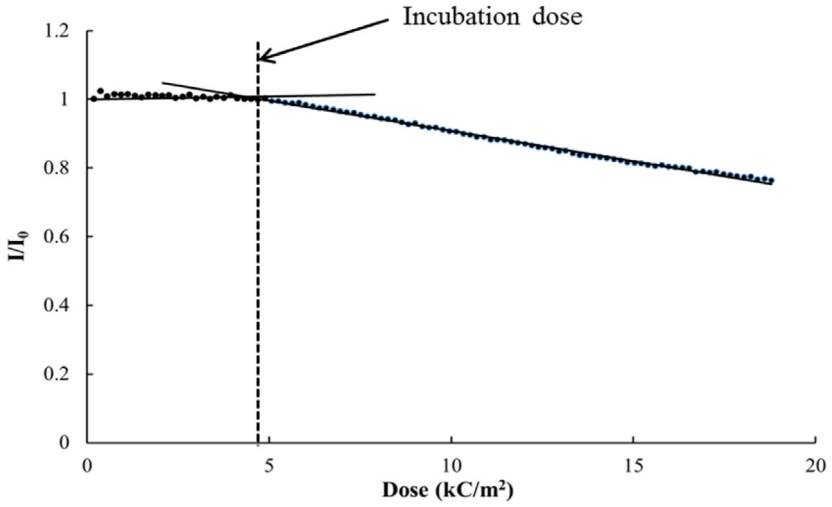

Fig. 1. The dependence of the potassium X-ray intensity on the dose. The curve was normalized to the intensity at the beginning of irradiation (I_0). ID is identified as the dose at which the slope of the intensity is changed.