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Mixed-alkali effect in sodium–potassium glasses irradiated with electrons

Ondrej Gedeon [a,*], Karel Jurek [b], Ivo Drbohlav [b]

[a] Institute of Chemical Technology, Technicka 5, 166 28 Prague, Czech Republic
[b] Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 162 53 Prague 6, Czech Republic

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ABSTRACT

Mixed-alkali effect (MAE) was studied by irradiating $(15-x)Na_2O{\cdot}xK_2O{\cdot}85SiO_2$ glasses with electrons and observing the following glass response expressed through volume changes measured with AFM. Glasses were irradiated by 50 keV electrons with doses up to 191 kC/m^2. Low irradiation doses showed the volume compaction, extent of which was linearly dependent on potassium content. It was shown the compaction can be explained as the superposition of the relaxation around alkali ions and the silica network relaxation. At high doses most of glasses show volume expansions. High irradiation doses cause alkali depletion from the surface glass layer and reveal a typical MAE response in volume changes. It is explained in terms of negative correlation among the element specific migration paths. An alternative view of MAE is suggested: the coupling among moving ions is replaced by the correlation among migration paths that are predetermined in the structure of mixed glasses.

1. Introduction

Mixed-alkali effect (MAE) is experimentally well established phenomenon [1] that continuously challenges the glass scientists. MAE is a term that expresses a pronounced non-linearity of various physical and chemical properties when alkali ions of one type are continuously replaced with the unlike alkali ions. MAE can be observed by studying the dynamical properties as alkali diffusion [2,3], conductivity [4,5], but is also found for viscosity [6], chemical durability [7] and mechanical relaxation [8,9]. Hence, a strong correlation between unlike alkali ions must be present in alkali glass [10]. It is generally believed that MAE is of purely dynamic origin so that no coupling between silica sub-network and alkali ions is present. The essence of the correlation is, however, not clear up to now. The strong correlation between unlike alkali ions is mostly attributed to the existence of sites belonging to the particular type of alkali ion and to the existence of the separate migration paths for different alkali ions. However, recent works [11] indicate that the alkali conduction paths are not independent for unlike alkali ions and crossings of the paths can be responsible for the correlations. Such view fully suppresses the importance of the silicate sub-network and simply regards the silica network backbone just as a carrier of the sites for alkali ions.

Quantum mechanics simulation, however, shows an active role of the silica network at least for low alkali concentrations [12]. Revealed interchange transport includes bridging oxygen annihilation/creation or in other words demonstrates an importance of the local glass structure. Similar results were obtained within frames of classical molecular dynamics simulations [13] where activation energy for the hop from one site to another one was strongly determined by the alkali ion surrounding. For higher alkali concentrations Haven ratio, H_R, decreases to values 0.2–0.5 [14], indicating a strong correlation among like alkali ions and supporting the idea of the conduction paths. Nevertheless, the coupling of alkali ion paths with silica sub-network cannot be simply excluded even for high alkali concentrations and even the standard current model of Anderson and Stuart [15] works with a "doorway energy" needed for an ion to pass from one site to another one.

Electrons bombarding a solid introduce changes in the structure which has to be relaxed. Interaction of the electron beam with the solid includes atomic ionization, excitation of plasmons, and momentum transfer via Rutherford scattering, just to mention the most important contributions to the total cross section [16]. The electron irradiation also introduces disorder into the original structure and creates the electric field forcing alkali ions to migrate [17] toward bulk. The migration of alkali ions can be recorded by means of EPMA (Electron Probe Microanalysis) [18]. The so called decay curve (intensity of an X-ray signal coming from an alkali element versus time) reveals two strictly distinguished regimes. The linear-like curve abruptly changes into the exponential one after the time/dose, which is typical for the type of glass and experimental conditions and is called incubation time/dose. The second transport stage, spontaneous or fast migration, was explained within percolation theory [19] when the incubation time is the time needed for the formation of conductive paths. Molecular dynamics simulations showed that the release of alkali ions is elastic scattering assisted [20] so that the primary electrons play an active role in

* Corresponding author. Tel.: +420 220443695; fax: +420 224313200.
E-mail address: Ondrej.Gedeon@vscht.cz (O. Gedeon).

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the first, preparing stage of irradiation. Long enough irradiation then leaves the glass surface layer, approximately thick of half of the electron range, depleted from alkali ions. The transport properties in mixed sodium–potassium glasses under electron beam were also studied. Results for both medium irradiation energy of 50 keV [21] and high energy of 2.5 MeV [22] confirmed the influence of mixing of alkali ions.

Electron irradiation of vitreous silica generally causes the volume compaction [23,24], however, for OH-rich vitreous silica glass expansion was also reported [25]. In this case expansion precedes the compaction or in other words the expansion is observed for the low doses. The phenomenon was observed independently on the energy of the electron beam used. Recently, alkali glasses were irradiated [26] and the volume changes were also confirmed. Both the compaction and the following expansion were found. Extremely large doses then confirmed both alkali depletion in the surface layer of the irradiated glass and an expansion reaching up to 100% of the irradiation volume [27].

The aim of the paper is to study mixed sodium–potassium glasses of the composition of $(15-x)Na_2O{\cdot}xK_2O{\cdot}85SiO_2$ under the electron beam. During the irradiation alkali ions migrate out of the irradiated glass leaving the silica glass surface layer enriched with oxygen. The volume changes of irradiated glasses are measured with AFM. Assuming the conservation of conduction paths in the alkali depleted glasses the coupling of alkali ions transport with silica sub-network should be correlated with volume changes.

2. Experimental

The mixed alkali glasses were melted using high purity batches in Pt crucible and afterwards cast on a metal plate to prevent crystallization. The plate of each glass was annealed at 600 °C for 16 h. All glasses were transparent and contained no bubbles or cords. Glasses were cut and polished into prisms. After polishing, the specimens were immediately coated with a 30 nm carbon layer. The homogeneity of the samples were checked and confirmed with EPMA. The samples were spot by spot irradiated with the defocused electron beam of energy of 50 keV. The diameter of the beam was set to 60 μm, the absorbed current was 50 nA. The diameter was measured at the fluorescent screen using a built in optical microscope. At these irradiating conditions the increase of temperature is negligible [28]. Glass samples were irradiates with a series of electron doses 1.1–190 kC/m^2, each dose was continuous and independent, i.e. each experimental result was obtained from the continuous electron irradiation of the pristine glass and each irradiation spot was well separated from all others.

The volume changes were characterized by AFM through the highest points that were determined within each of the irradiated spots in a smart manner, i.e. the spikes or fluctuations on the scans were excluded [26]. An example of the approach is in Fig. 1. This scan reveals the volume change at the medium irradiation dose. Left- and right-hand sides of the scan are linear and enable to determine the profile of the original surface. All performed scans were performed through the center of the irradiated spot and hence each recorded profile can be considered a cylindrically symmetric.

During the electron irradiation, some surface contamination, dominantly at the irradiated spot, is expected. The contamination rate was calculated from the long-time electron irradiation of the K15 glass sample so that the thickness of the contamination layer could be measured by SEM. The rate of the contamination was then determined simply by the normalization to the dose. The same correction to the contamination was then used for all glass samples as no significant differences in surface reactivity among them are expected.

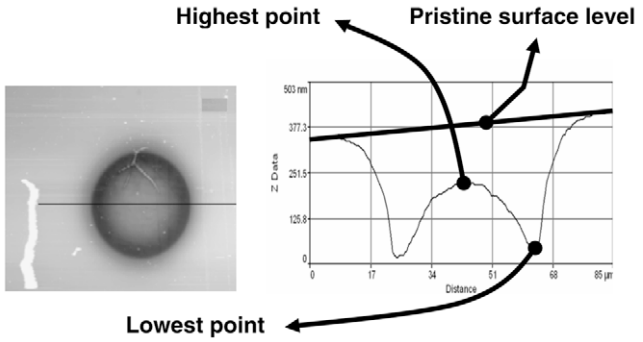

Fig. 1. A typical AFM picture of the irradiated glass surface spot (left). The line shows the track of the following scan, results of which are on right. The processing of scan is visualized (right); first the surface is levelled by the linear fitting of the unirradiated sides, then the lowest and highest points are determined.

The precise determination of a dose is mostly influenced by a beam fluctuation (around 1%) and by the electron backscattering coefficient that depends on the composition and the surface shape and roughness. The total uncertainness of dose can be estimated to be lower than 5%; values around 1% are expected for low doses and uncertainness increases with an increasing dose. Although AFM has an excellent vertical resolution a precise determination of contraction/expansion, as introduced in Fig. 1, depends on smoothness of the profiles. Here, uncertainness around 10% can be reasonable expected. Nevertheless, similar values of contraction/expansion suffer of the same uncertainness, nearly independently on the particular glass.

3. Results

The measured profiles are radial symmetric, except for the effect of the slightly declined surface. Although the source of the electron irradiation can be assumed nearly homogeneous the AFM profiles reveal a strong dependence on the distance from the center of the irradiation. The central part always determines the future behavior of its surrounding or in other words the outer part is delayed in its volume evolution. It is well demonstrated in Fig. 1 that catches the situation where the central part is in the dilatation stage, following the compressive one, while the outer parts are still in the compression stage. Such volume evolution can be explained by the interaction of the irradiated volume with the unirradiated one, surrounding the exposed area. The structural changes caused by the irradiation have to relax and the relaxation propagates out to beyond the irradiated volume. It was also confirmed by the long-time irradiations of $15K_2O{\cdot}85SiO_2$ glass where the volume changes propagated up to 88 μm from the center of the 60 μm beam [27]. Hence, the effect of the irradiation is much larger at the center than near the edge where most of the structural changes can be relaxed outside of the irradiated spot.

Results of the volume changes of the irradiated mixed alkali glasses together with vitreous SiO_2 are presented in Fig. 2. Clearly, the studied glasses can be divided into three groups according to their response to the medium and long irradiation doses. The first group consists of sodium and potassium binary glasses that reveal the same volume changes for the high doses. The dilatation for the largest dose reaches up to 1.4 μm. The second group consists of $10Na_2O{\cdot}5K_2O{\cdot}85SiO_2$, $7.5Na_2O{\cdot}7.5K_2O{\cdot}85SiO_2$, and SiO_2 glasses. Volume responses of the glasses to electron irradiation are in this group very similar; even for the longest doses only the surface depression is observed (reaching 0.7 μm). The last group is formed just by $5Na_2O{\cdot}10K_2O{\cdot}85SiO_2$ glass. This glass reveals dilatation for large doses similarly as the first group, but of the lower extent.