Spatial charge relaxation in glasses poled in the air and argon atmospheres

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Abstract. Thermal poling of a multicomponent silicate glass was performed in air and in argon atmospheres at various voltages, and the temperature dependences of the depolarization currents (TSDC) in the poled glasses were studied. In addition, the concentration profiles of univalent and bivalent cations in subanodic regions of the poled glasses were measured with EDS and SIMS techniques. The difference in the displacements of bivalent ions at poling of the glasses in closed and open anode configurations allowed us to identify “frozen” spatial charge relaxation peaks observed in the TSDC measurements and to relate these peaks to hydrogen and bivalent metal ions relaxation.

1. Introduction

Thermal polarization (poling) of silicate glasses is known to lead to the significant modification of glass structure in such a way that the glasses after poling demonstrate properties of anisotropic optical media, in particular, second harmonic generation and linear electrooptic effect [1]. In perspective, periodical poling of glasses is of interest for efficient second harmonic generation [2]. The procedure of the poling consists in the heat treatment of a glass plate under DC voltage followed by the glass cooling down to room temperature under the applied voltage. The electric field applied to a multicomponent glass, similarly to the case of electrodiffusion or electron beam modification [3,4] shifts positive ions of alkaline and alkaline-earth metals from their initial position that results in changing composition and structure (therefore physical, including refractive index [5] and chemical properties) of the subanodic layer of the glass depleted with the positive charge carriers [6]. Negatively charged atoms of non-bridging oxygen remaining in the subanodic region and positive cations removed from this region create there an internal electric field [7], which, due to kinetic restrictions, proves to be “frozen” when the sample is cooled down to room temperature under the applied voltage. In addition, the spatial distribution of charges in glass is significantly affected by the H₂O⁺/H⁺ ion-compensators, which are formed when atmospheric water vapors dissociate at the anode and then penetrate into the subanodic region of the glass. Penetrating ion-compensators form chemical bonds with non-bridging negatively charged oxygen atoms, partially neutralizing the negative charge in the depleted region [8]. The results of glass polarization depend on the type of configuration of the electrodes used, that is, open electrodes (pressed conductive plates or corona electric discharge area in the atmosphere [9]) or closed electrodes (for example, deposited metal films), which prevent the atmosphere from influencing the polarization [10]. Different material science techniques can be applied to characterize glasses after the polarization [11]. Heating of the poled glasses leads to the volume relaxation [12], which allows for the formation of relief structures on glass surface [13], and...
spatial charge relaxation [14], the latter can be characterized via measurements of the thermally stimulated depolarization current (TSDC) [15]. In this paper, we compare charge relaxation in a soda-lime silicate glass poled with different anode configurations.

2. Experimental and discussion

In our study, we used plates of commercial silicate glass (Menzel glass [16]) with a thickness of 1 mm. The glass composition is given in table 1.

| Table 1. Composition of Menzel glass in wt % of oxides [16]. |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| SiO₂             | Al₂O₃            | Na₂O             | K₂O              | MgO              | CaO              | others           |
| 72.2             | 1.2              | 14.3             | 1.2              | 4.3              | 6.4              | 0.33             |

Glass sample 25 x 25 mm² was placed in a polarization cell and fixed from both sides with brushed stainless steel electrodes. The dimensions of the anodic and cathodic electrodes were 20 x 15 mm². The assembled cell was placed in a furnace heated to 300 °C. Then, the voltage was applied to the sample during 20 min. After this, the polarization cell was removed from the furnace and cooled for 3 minutes with the voltage source turned on. For different samples, the applied voltage was varied from 250 V to 1.25 kV with the step of 250 V.

Polarization was carried out both in air and in argon atmosphere. Polarization in argon atmosphere prevents the influence of atmospheric water vapors on the polarization process. In the case of polarization in argon, a flow system with the argon consumption of 4 l/min was used. Poling in argon appeared to be an analogous to the one with closed electrodes, for this mainly prevents the penetration of ion-compensators H₃O⁺/H into the glass. The dependencies of polarization current on time in the studied samples are presented in fig. 1.

![Figure. 1. Time dependences of polarization current at different applied voltages: a) in air; b) in Ar atmosphere.](image-url)

Note that ion-compensators neutralize a part of the negative charge in the depleted layer, reducing the internal “frozen” electric field, which affects the polarization current in the samples poled in air and in argon atmosphere. This difference in the values of polarization current for samples polarized...
under different conditions is demonstrated by Fig. 1. For samples polarized in air, the decrease in the polarization current is slower as compared to the samples polarized at the same voltage, but in an argon atmosphere. Respectively, the density of the electric charge passed through the samples (this charge is equal to the area under the curves in Fig. 1) is higher in the air-poled samples. We associate this primarily with the additional current of positive ions and the compensation of the negative space charge due to the penetration of hydrogen ions into the glass with the formation of silanol groups SiOH [17]. If glass polarization is performed in argon atmosphere, there is no source of hydrogen ions, and this explains the difference in the polarization time and in the passed charge. At high voltages (≥ 1 kV), it appears that there is an additional mechanism of the negative spatial charge compensation, which consists in the formation of molecular oxygen [1] (from two non-bridging oxygen bonds) and the generation of free electrons [18], which leave the glass for anode.

After the poling we characterized elemental concentration profiles in the subanodic region of the glasses poled in the open anode configuration with the EDS (Tescan SEM). Then we compared these with the profiles in the glasses poled in the closed anode configuration, which were measured earlier using the secondary ions mass spectrometry (SIMS, CAMECA IMS7f) [19, 20]. The concentration profiles of sodium and calcium in glasses poled in closed and open anode configuration are presented in fig. 2a and 2b, respectively.

Figure 2. Elemental profiles in subanodic regions of the glasses poled at 300 °C a) under 500 V DC in closed anode configuration and b) under 700 V in open anode configuration. Note: the maximum in sodium profile (in b) is due to non-sensitivity of EDS to hydrogen, which results in incorrect atomic percentage calculations.
Both profiles have a general tendency: sodium ions go deeper into the sample bulk than calcium ions, however, a particularity of polarization in air (open anode configuration) is a smaller displacement of calcium ions and a considerably larger displacement of sodium ions. The reason for this is the penetration into the glass of hydrogen ions, the mobility of which exceeds the mobility of calcium ions, but is significantly less than the mobility of sodium ions [8]. According to the existing modeling, this should result in the formation of a hydrogen-rich region just in the sodium-depleted region [21].

The results of our studies of spatial charge relaxation (TSDC measurements) in glasses polarized in air and in argon atmosphere at different voltages are shown in Fig. 3. TSDC spectra were measured from room temperature to 770 °C at the heating rate of 10 °C/min.

![TSDC spectra of the silicate glasses poled in air and in argon atmosphere under different voltages](image)

Figure. 3. TSDC spectra of the silicate glasses poled in air and in argon atmosphere under different voltages: (left) 250 V; (right) 500 V.

It is evident that the poling conditions significantly affect the shape of the TSDC spectra: 1) a perceptible increase in depolarization current in the glasses polarized in air is revealed at lower temperatures, 2) TSDC spectrum of the glasses polarized in air (unlike ones polarized in argon atmosphere), has an additional peak in the region of 680-690 °C. Presuming that during the polarization in argon atmosphere the cation-compensators weakly affect the polarization process because of their low concentration, a less pronounced peak (or its absence) responsible for the relaxation processes associated with the presence of hydrogen ions should be expected to appear in the TSDC spectra for the air-poled glasses. Analysis and comparison of the depolarization curves in Fig. 3 allows concluding that such a peak is a relaxation peak, the maximum of which is located in the temperature range of 680-690 °C.

According to [22], the relaxation peak located around 580 °C should be associated with the reverse drift of bivalent cations under the action of the internal (“frozen”) electric field. The TSDC spectra of the samples polarized in argon atmosphere at voltages of 250-1000 V are presented in Fig. 4. In Fig. 4, one can see that the magnitude of the depolarization peak with a maximum at ~ 570 °C increases with the applied voltage, and that its maximum exceeds the values of the corresponding peaks presented in the depolarization curves for the samples polarized at the same voltage, but in air. At the same time, from fig. 2 it follows that the polarization in closed anode configuration provides a greater displacement of bivalent cations as compared to the polarization in air. Thus, we can conclude that the relaxation peak with a maximum in the vicinity of 570 °C is most likely associated with the drift of bivalent cations, as it was supposed in [22]. The peculiarity of the spectrum corresponding to the 1 kV poled glass in the region 610-650 °C is, probably, due to switching on additional charge compensation mechanisms under the high electric field.
3. Conclusions
Different displacement of bivalent ions at poling of the silicate glasses in closed and open anode configuration allowed us the identification of the relaxation peaks of “frozen” spatial charge, which observed in thermally stimulated depolarization current. Thus, the peak in the range of 580°C is due to the motion of bivalent ions while the peak at 680-690°C should be related with hydrogenated ions.

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