Study of charge relaxation in poled silicate glasses

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Abstract. We have characterized relaxation peaks observed in the thermally stimulated relaxation current (TSDC) of thermally-poled soda-lime glass in 250-780°C temperature range. We relate the low-temperature (below glass transition) peak to chemical potential driven relaxation that is ionic diffusion. This peak tends to shift towards higher temperatures and to disappear in stronger-poled glasses. Two registered high-temperature (above glass transition, Tg) peaks are supposedly related to electric potential driven processes. Studies of the compositional profiles of poled glasses after secondary thermal processings allowed us concluding that the lower temperature peak found above Tg is supposedly related to the migration of univalent ions (sodium and potassium), while the higher-temperature one is because of the migration of bivalent calcium ions.

1. Introduction
Investigations dedicated to the study of the processes taking place in thermal poling of glasses are of great interest due to the possibility to use thermal poling for fabricating micro- and nanostructures for photonics, microfluidics, integrated optics and others. This is because the poling results in breaking central symmetry of initially isotropic glasses and in their structural and compositional modification. However today there is no full understanding of the mechanisms of these processes. It is known that glass polarization followed by the glass sample cooling under applied voltage results in the formation of “frozen” spatial charge under anodic surface of the poled glass [1] because of the redistribution of positive ions, the main charge carriers in glasses. At room temperature, uniform redistribution (in other terms, charge relaxation) of the frozen spatial charge is impossible due to kinetic restrictions (low mobility of the ions at room temperature), so that poled glasses stay in a thermodynamically non-equilibrium state. However, at elevated temperatures the mobility of the ions increases and, therefore, at certain increased temperatures, charge relaxation can take place. This results in the movement of poled glassy system towards thermodynamic equilibrium via frozen spatial charge redistribution that behaves in the appearance of depolarization currents. Temperature dependences of depolarization currents of poled glasses recorded at a constant heating rate are called TSDC spectra. The TSDC spectra of poled glasses provide useful information about the mechanisms of glass polarization and relaxation [2]. In particular, recently, on the base of TSDC spectra studies it has been found that the most part of the frozen in poling spatial charge proves to relax at temperatures above glass transition temperatures [3]. This has explained the problem related to the difference in the total charge passed through the glass sample in the polarization and depolarization processes [4]. In the present paper, we report our study on revealing the mechanisms of charge relaxation processes taking place in poled multicomponent silicate glasses.
2. Experimental
A soda-lime glass slides “Menzel” purchased from Agar Scientific was used in this study. The glass composition is presented in Table 1.

Table 1. Composition of Menzel glass in molar % of oxides [5].

|     | SiO₂  | Al₂O₃ | Na₂O | K₂O | MgO | CaO | others |
|-----|-------|-------|------|-----|-----|-----|--------|
|     | 72.2  | 1.2   | 14.3 | 1.2 | 4.3 | 6.4 | 0.33   |

The samples were slides 1 mm in thickness. Glass polarization was performed at 300°C for 30 min under DC electric voltage of 500 V. After the poling, the samples were cooled down to room temperature under the voltage applied and then voltage was off. The schematic of the poling experiment is shown in Figure 1a. We used stainless steel electrodes pressed to the glass surface with evaporated 5 nm chromium sublayer covered with 50 nm gold film on both surfaces of the slides. Step-like increasing of the poling voltage was used to prevent electric breakdown of the glass. Time dependences of the electrical current through the glass samples were recorded, which were used to calculate the electric charge passed through the glass slides in the course of the poling.

![Figure 1](image1.png)

**Figure 1.** Schematic of the glass polarization process (left) and a typical temporal dependence of the polarization current (right).

![Figure 2](image2.png)

**Figure 2.** Schematic of the TSDC measurements (left) and the TSDC spectrum of the poled Menzel glass slide which poling current temporal dependence is presented in Figure 1 (right).
The TSDC spectra of the poled samples were recorded at heating rate 5°C/min. The schematic of the TSDC measurements is shown in Figure 2. Above the glass transition temperature, which is \( \sim 530°C \), for the glass sample poled up to the almost complete disappearance of the polarization current, two depolarization current peaks were observed in the TSDC spectrum of poled glass that evidenced two different ions (with different mobilities) taking part in the charge relaxation processes.

![Figure 3](image-url)

**Figure 3.** Concentration profiles of the main charge carriers (Na, K and Ca) in the reference sample after the polarization (a) and in the samples which depolarization was interrupted at the temperatures \( T_1 \) (b), \( T_2 \) (c) and \( T_3 \) (d) as shown in Figure 2.

The TSDC spectra were taken from three samples poled at the same temperature, time and voltage, but their depolarization processes were interrupted at different temperatures \( T_1 \), \( T_2 \) and \( T_3 \) indicated in Figure 2. Concentration profiles of alkalis and alkaline-earth elements in these samples were measured with the secondary ion mass spectrometry (SIMS) – station CAMECA IMS7f. These profiles are presented in Figure 3.

The existence of a shoulder A at the left slope of the lower-temperature TSDC peak shown in Figure 1 allowed us supposing the existence of one more relaxation peak below the glass transition temperature. To reveal this we performed a set of glass poling experiments with varying density of the electric charge passed through the samples in the poling procedure. The results of the TSDC characterization of these samples in the temperature range 250-480°C are presented in Figure 4. Here one can see clear relaxation peak in the TSDC spectrum of the sample with the minimal charge density, and this peak shifts towards higher temperatures and degrades with increasing the density of the passed charge.
3. Discussion

The comparison of the SIMS-measured concentration profiles of the poled soda-lime glass samples, depolarization process of which was interrupted at different temperatures, leads to conclusion that the two TSDC peaks observed above the glass transition temperature should be associated with the relaxation (migration) of different types of charge carriers, namely: univalent alkali ions and bivalent alkali-earth ions. While the absence of essential changes in alkali and alkali-earth elements was registered at T₁ (below glass transition) temperature, the redistribution of the alkalis was seen at T₂, alkali-earth ions being at about the same positions. At T₃ temperature, both alkalis and alkali-earth ions shifted towards the anodic surface of the sample. It is worth to note that even at the highest, ~780°C, temperature the glass did not return in the initial state, and the concentrations of the glass modifiers stayed essentially below ones in the depth of the sample. This is probably related to the restructuring of the glass in poling, which behaves in the increase of bridging oxygen atoms and, respectively, the glass connectivity, followed by the formation of molecular oxygen in the poled glass [6].

The consideration of the relaxation peak (shoulder A on the left slope of the lower-temperature TSDC peak in Figure 2) observed below the glass transition temperature (q₁ in Figure 4) allows concluding that the TSDC peak position shifts towards higher temperatures and, in general, decreases in amplitude with increasing the charge passed through the samples in poling. Formally, this means that more severe poling condition degrades the low-temperature relaxation process. Since “frozen” spatial electric charge and, respectively, frozen electric field increases with the poling duration at initial stages of the poling [7], and, the same, with passed charge, one can conclude that drift mechanism of the relaxation starts prevailing when the “frozen” charge growth. Taking into account the temperature position of the q₁ peak and the start of the peak at 250°C we can relate it to the process driven by the gradient of chemical potential of ions, that is, sodium ions diffusion with the activation energy of ~0.8 eV [8], rather than the drift of these ions under the “frozen” electric field. The degradation and the shift of this peak to higher temperatures evidences decreasing in the number (or cross-section) of the channels related to diffusion transport (that is, gradient of chemical potential) with simultaneous increasing of the temperature at which the peak takes place. The latter indicates increasing the activation energy of this kind of relaxation, which could be because of the restructuring and compositional changes. Besides, the same behavior of TSDC spectra was observed in glasses differing in sodium-silicon relation [9,10]. In general, the behavior of the peak under discussion corresponds to

![Figure 4. TSDC spectra of glasses poled with different passed charge densities, q₁<q₂<q₃<q₄.](image-url)
the replacement of channels of diffusion-driven relaxation below the glass transition with electric drift driven relaxation channels above the glass transition.

4. Conclusion
Finally, we have proposed an explanation of the TSDC relaxation peaks observed in poled soda-lime glass below and above the glass transition temperature. Below the glass transition the diffusion-related TSDC peak exists, which degrades with the poling strength increase being replaced by two drift-related peaks. Lower temperature peak occurring at ~600 °C we associate with the drift of alkalis while the higher temperature peak at ~750 °C with alkaline-earth drift.

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